ATMOSPHERIC REMOTE SENSING BY MICROWAVE RADIOMETRY

Edited by
Michael A. Janssen
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ATMOSPHERIC REMOTE SENSING BY MICROWAVE RADIOMETRY

Edited by

Michael A. Janssen

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*Ed R. Westwater*

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The Earth's atmosphere is a puzzle and a concern. Its unpredictable weather has always been a force to be reckoned with, but until recent times, our trust was implicit in the robustness of the atmospheric system as the foundation of our biosphere. Now we are not so sure. Far from being robust, this system is better described as a balance among a number of natural forces that we barely understand. Our concern is deepened when we consider the threat to this balance from our burgeoning civilization and its effluents. What, for example, are the chlorofluorocarbons doing to the ozone layer, and how significantly and on what time scales will the increasing CO₂ production change the climate? There will be no answers to such questions without a strong and steady program of research to understand fundamental atmospheric processes. Essential to this is the gathering of basic data such as temperature, pressure, wind, and the distribution of water vapor, clouds, and other active constituents. Such data enable us to test existing models for the atmosphere's energy balance, the depletion of the ozone layer, the hydrological cycle, climate trends, and other aspects of the atmospheric system that are of vital interest to us, and to formulate new and better models to guide us in the future. Remote sensing is central to this effort because it is the only way we can obtain the full spatial and temporal perspective needed to understand atmospheric processes. The strong conclusion is that the need for remote sensing will continue, and grow.

Microwaves, which we take as a generic term to include the centimeter, millimeter, and submillimeter regions of the spectrum, play a special role in the remote sensing of atmospheres. Microwave techniques bring a mixture of capabilities that complement remote-sensing methods used in other spectral regions. Microwaves penetrate clouds, for example, and provide an all-weather measurement capability as well as the only direct means for the determination of cloud water content. The coherent detection technique that characterizes microwave receivers allows the emission lines of atmospheric constituents to be examined with arbitrarily high-frequency resolution. Collision-broadened line shapes contain a wealth of information about atmospheric properties; furthermore, collisions are the dominant broadening mechanism to much higher altitudes in the microwave region than at shorter wavelengths. Because of such advantages, passive microwave remote sens-
1

AN INTRODUCTION TO THE PASSIVE MICROWAVE REMOTE SENSING OF ATMOSPHERES

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1.1 A GENERAL PERSPECTIVE

This volume treats a specific topic in remote sensing. First, we consider only the microwave region of the spectrum and the use of microwave instrumentation. Second, we are concerned exclusively with the interpretation of passive measurements, leaving active approaches in this spectral regime such as probing by radar and occultation of spacecraft radio signals by an atmosphere to other volumes in this series. Finally, we take the study of atmospheres as the ultimate objective of our remote sensing. The restriction to passive measurements and atmospheres means that we deal almost exclusively with the interpretation of atmospheric thermal emission. As we will see, this gives a sharp focus to the radiative transfer problem and the central issue of this volume, the determination of atmospheric parameters from observational data.

The microwave region along with its major atmospheric emission sources is shown in the context of the electromagnetic spectrum in Figure 1.1. The microwave region generally spans the range from about 3 GHz (1 gigahertz = 10⁹ Hz) to 300 GHz and above, although there is no wide acceptance of an exact range, or in particular, of an upper frequency limit. Terms that identify strictly spectral regimes are the centimeter, millimeter, and submillimeter regions. A useful criterion to identify the microwave region can be stated in terms of the technology

Atmospheric Remote Sensing by Microwave Radiometry, Edited by Michael A. Janssen
CHAPTER 1: INTRODUCTION TO PASSIVE REMOTE SENSING

Molecular Absorptions:

Venus

Earth

Mars

Major Planets

Titan

Io

Frequency: 3 GHz 30 GHz 300 GHz 3 THz
Wavelength: 10 cm 1 cm 1 mm 100 μm

Figure 1.1. The microwave region spans at least two, and arguably three, decades between the radio and infrared regions of the electromagnetic spectrum. Gases responsible for absorption in the atmospheres of the Earth and the planets are indicated. The shaded band for Venus depicts nonresonant collision-induced absorption by CO₂, which increases with frequency, and extreme pressure broadening of the 24-GHz NH₃ inversion band leads to significant absorption at all microwave frequencies in the atmospheres of the major planets. All features identified in the centimeter and millimeter ranges have been used for remote sensing and are the focus for the applications presented in this volume. Remote sensing in the submillimeter region is in its infancy and some of the molecular absorptions expected there are indicated.
and is consistent with its historical roots: it is the high-frequency extension of the radio range, with the upper end determined by the limits of the technology. The microwave approach is characterized in practical terms by the coherent detection of radiation, and this is generally the basis for the remote-sensing applications that are described in this volume.

Absorption of microwaves by atmospheric constituents provides the physical connection into an atmosphere that we exploit in various ways for remotely sensing its properties. Figure 1.1 shows the molecular absorptions that have proven useful for remote sensing in the centimeter and millimeter regions—these absorptions are described in detail in Chapters 2 and 8. The 22-GHz rotational line of water vapor and the spin-rotation band of oxygen centered around 60 GHz play dominant roles in the remote sensing of the Earth’s troposphere, along with strong absorption due to liquid water when present in clouds or as rain. Nonresonant pressure-induced absorption by CO$_2$ accounts for most absorption in the deep atmosphere of Venus, and the inversion band of NH$_3$ centered around 24 GHz is the major absorber in the deep atmospheres of the outer planets. Coherent detection, as achieved by heterodyne receivers (see Section 1.3), allows atmospheric emission lines to be examined at the highest possible spectral resolution. Unique studies of the upper atmospheres of the Earth, Venus, and the tenuous atmosphere of Mars have been possible using high-resolution measurements of the millimeter lines of the indicated minor constituents.

We can look forward to heterodyne applications at frequencies possibly as high as 10 THz (1 terahertz = $10^{12}$ Hz) in coming years. Whether we stretch to include these as "microwave" applications is not particularly important, although the remote-sensing applications developed for the millimeter region will apply directly to submillimeter lines, and in this sense we can consider the submillimeter region within the scope of this volume. Figure 1.1 indicates the variety of molecules that are accessible in this region, and the future possibilities for remote sensing of the Earth’s upper atmosphere using their submillimeter lines are explored in detail in Chapter 8. The development of the submillimeter region will eventually open up new vistas in planetary studies as well.

The remote-sensing applications that take advantage of these absorptions are bound by both a common foundation in radiative transfer theory and a common technology. With the specialization to the microwave region, it is expected that most readers will be unfamiliar with the long-wavelength versions of these topics, namely, the microwave radiative transfer equation and techniques of microwave radiometry. These are presented in the following two sections to provide a foundation for the rest of the volume.

### 1.2 THE MICROWAVE RADIATIVE TRANSFER EQUATION

The starting point for any passive remote-sensing application is the equation that describes the flow of radiant energy to be measured by a radiometer. The scalar form of this equation for atmospheric propagation is remarkably simple in the
Rayleigh–Jeans limit, and is sufficient to treat the large majority of microwave applications. We briefly outline the development of this equation on the assumption that the reader is familiar with basic concepts in radiative transfer, noting that more leisurely (and thorough) treatments can be found in several sources [1–5]. The emphasis in the following is to show where the standard approximations are made and what their implications are for our remote-sensing applications. A more general approach that includes scattering and polarization is outlined in Chapter 3 and also can be found in the sources referenced before.

1.2.1 Radiative Transfer in a Nonscattering Thermal Medium

The classical form of the radiative transfer theory was developed by Chandrasekhar [1]. The theory describes the intensity of radiation propagating in a general class of media that absorb, emit, and scatter the radiation. It is ideally suited for radiative transfer in media such as atmospheres in which the flow of energy plays the central role, and where such quantities as wave polarization or phase relationships play relatively minor roles or can be treated separately (for example, see Chapter 3 and Appendix 6A). The starting point of the theory is the description of the radiation field in terms of the specific intensity $I_v$, which is the instantaneous radiant power that flows at each point in the medium, per unit area, per unit-frequency interval at a specified frequency, and in a given direction per unit solid angle. As illustrated in Figure 1.2, its variation at a point $s$ along a line in the direction of propagation is obtained by considering the sources and sinks of the radiation in a volume element along that line. This leads to a differential form of the transfer equation,

$$\frac{dI_v}{ds} = - I_v \alpha + S$$

where $\alpha$ is an absorption coefficient, and $S$ is a source term, which respectively describe the loss and gain of energy into the given direction.

$$dP = I_v dA d\Omega dv \quad dl_v = - I_v \alpha ds + S ds$$

Figure 1.2. The specific intensity is the radiant energy flowing at each point in the medium per unit area normal to the flux, per unit solid angle, in the frequency range $\nu$ to $\nu + dv$. The variation of intensity with position is governed by an equation of transfer that takes into account the sinks and sources of radiation.
In the general theory, scattering into and from other directions can lead to both losses and gains to the intensity along a given direction and can be taken into account in the terms $S$ and $\alpha$. We will neglect scattering for the following, but will return later to the question of errors that this might introduce. Without scattering to consider, the source term $S$ needs to express only the locally generated contribution to the radiation, and the absorption coefficient $\alpha$ becomes a scalar characteristic of the medium that describes a true loss of energy from the radiation field into the medium. In particular, if we assume local thermodynamic equilibrium so that each point can be characterized by a temperature $T$, then the strict requirement of balance between the energy absorbed and emitted by any particular volume element leads to Kirchhoff’s law for the source term,

$$S = \alpha B_\nu(T)$$  

(1.2)

where $B_\nu(T)$ is the Planck function:

$$B_\nu(T) = \frac{2h\nu^3}{c^2} \frac{1}{e^{h\nu/kT} - 1}$$  

(1.3)

$h$ is Planck’s constant, $k$ is Boltzmann’s constant, $c$ is the speed of light, and $\nu$ is the frequency. The factor of 2 in the numerator accounts for both polarizations according to the usual convention. We note that $B_\nu$ is sometimes considered as a surface brightness, which is the flow of energy across a unit area, per unit frequency, from a source viewed through free space in an element of solid angle $d\Omega$. Brightness and intensity have the same units, and Figure 1.3 demonstrates that the two are equivalent in this case. This argument can be extended to show that the intensity is generally invariant along any direction in free space, or in any region in which there are no local sources or sinks of radiation [3].

With the assumptions leading to Eq. 1.2 and the corresponding neglect of scattering in the absorption coefficient $\alpha$, all terms of Eq. 1.1 depend only on the intensity along the path of propagation. Hence, the equation of transfer becomes a standard differential equation for which the complete solution is readily obtained. Substituting for $S$, we can write this solution as

$$I_\nu(0) = I_\nu(s_0) e^{-\tau(s_0)} + \int_0^{s_0} B_\nu(T) e^{-\tau(s)} \alpha \, ds$$  

(1.4)

**Figure 1.3.** The surface brightness $B_\nu(T)$ of a blackbody emitter as viewed through free space in the solid-angle element $d\Omega$ produces a flow of energy given by the specific intensity $I_\nu = B_\nu(T)$. 
where \( \tau \) is the optical depth and is defined as

\[
\tau(s) = \int_0^s \alpha(s') \, ds'
\]  

(1.5)

Anticipating the remote-sensing applications to follow, we have used the convention that the intensity is to be determined at the origin \( s = 0 \), where an instrument that measures the intensity is presumed to be located (see Figure 1.4). The integration then extends through the medium along the path of propagation and ends at some boundary \( s = s_0 \), where the condition is that the intensity has a starting value given by \( I_v(s_0) \).

1.2.2 Specializing to the Microwave Case

We introduce the microwave case by considering the low-frequency limit \( h\nu \ll kT \). This is known as the Rayleigh–Jeans limit and allows the Planck function to be approximated as

\[
B_\nu(T) \approx \frac{2\nu^2kT}{c^2} = \frac{2kT}{\lambda^2}
\]  

(1.6)

where \( \lambda \) is the wavelength. The significant feature of this limit is the linear relationship of the Planck function with physical temperature. This naturally suggests a scaling of the intensity as

\[
T_b(\nu) = \frac{\lambda^2}{2k} I_v
\]  

(1.7)

We will use this expression to define* the microwave brightness temperature \( T_b \), a quantity that will play the role of intensity in the radiative transfer equation but

*This is the Rayleigh–Jeans equivalent brightness temperature, and must be distinguished from the frequently-used thermodynamic definition—see Section 1.2.4 for further discussion. Also, this definition sometimes appears without the factor of 2 in the denominator, in which case, the intensity \( I_v \) refers to a single polarization of the radiation.
that has been dimensionally scaled to give units of degrees Kelvin. We emphasize
that this definition is not an approximation in itself, and the implications of the
departure of the Rayleigh–Jeans approximation from the Planck law are developed
later.

By using this definition, Eq. 1.4 can be rewritten as

$$T_b(v) = T_{b0}(v) e^{-\tau(s_0)} + \int_{s_0}^{s} \frac{T(s)}{\mathcal{R}(v, T(s))} e^{-\tau(s)} \alpha \, ds$$  \hspace{1cm} (1.8)

where the background brightness temperature $T_{b0}$ is derived from our general
boundary condition as

$$T_{b0} = \frac{\lambda^2}{2k} I_e(s_0)$$  \hspace{1cm} (1.9)

The factor

$$\mathcal{R}(v, T) = \frac{2kT}{\lambda^2} \frac{1}{B_v(T)} = \frac{kT}{h
u} \left( e^{\nu/kT} - 1 \right)$$  \hspace{1cm} (1.10)

and by using Eq. 1.7 in Eq. 1.3 can be seen to be just the ratio of the physical
temperature $T$ of a blackbody emitter to its brightness temperature $T_b$, namely,

$$\mathcal{R}(v, T) = \frac{T}{T_b}$$  \hspace{1cm} (1.11)

Expanding $\mathcal{R}(v, T)$ in terms of $\nu/kT$, we have

$$\mathcal{R}(v, T) = 1 + \frac{1}{2!} \left[ \frac{\nu}{kT} \right] + \frac{1}{3!} \left[ \frac{\nu}{kT} \right]^2 + \cdots$$  \hspace{1cm} (1.12)

where we see that $\mathcal{R}$ is always greater than unity, and approaches unity in the
Rayleigh–Jeans limit.

Equation 1.8 is exact as far as the Planck law is concerned. The Rayleigh–Jeans
approximation is incorporated by setting $\mathcal{R} = 1$, giving

$$T_b(v) = T_{b0} e^{-\tau(s_0)} + \int_{0}^{s_0} T(s) e^{-\tau(s)} \alpha \, ds$$  \hspace{1cm} (1.13)

This is the form of the radiative transfer equation commonly used in microwave
remote sensing. It is more accurate than one would expect at first glance; if one
assiduously holds to the Rayleigh–Jeans approximation to include the calibration
of a radiometer against blackbody targets, then this equation is actually correct to
the first order in $\nu/kT$ in spite of having neglecting this and all higher orders
when we chose $\mathcal{R} = 1$. The implications of the Rayleigh-Jeans approximation in this case and others are discussed further in Section 1.2.4.

### 1.2.3 Microwave Remote Sensing

The radiative transfer equation expressed in Eq. 1.13 is a simple weighted average over the physical temperature of an atmosphere. The emission $\alpha T \, ds$ from each element is attenuated by the factor $e^{-\tau}$ by the intervening medium as it travels toward the point of measurement. The sum of these contributions represents an average of temperature along the propagation path weighted at each point by $\alpha e^{-\tau}$.

The radiative transfer equation expresses the forward problem: if the absorption and temperature are known along the path of propagation, then the brightness temperature can be computed from this equation.

In remote-sensing applications, we are ultimately concerned with the inverse problem. In particular, we start with measurements of the brightness temperature with the objective of inferring the atmospheric properties that enter into the integrand of the radiative transfer equation. To illustrate the basic idea, let us consider two simple cases involving an atmosphere that we take to be isothermal at temperature $T$. From Eq. 1.13, we have

$$T_b = T \left[ 1 - e^{-\tau_a} \right]$$

where $\tau_a$ is the total optical depth through the atmosphere, and we have neglected the background term. If the optical depth is large, then we have for the first case

$$T_b = T \quad (\tau_a \gg 1, \text{ isothermal medium})$$

In this case, we can think of a radiometer as a remote thermometer because its output is proportional to the temperature of the atmosphere. If the optical depth is small, on the other hand, we can approximate the result to give the second case:

$$T_b = T \tau_a \quad (\tau_a \ll 1, \text{ isothermal medium})$$

If $T$ is known, then in this case the optical depth $\tau_a$ is determined. Hence, the concentration of a particular constituent of the atmosphere can be obtained if it is the source of opacity and its absorption coefficient is known.

In the general case, the temperature structure, the opacity, or both are unknown, and the inverse problem becomes more difficult. If we think of $T_b$ in a mathematical sense as a continuous function of the frequency, then we wish to solve the radiative transfer equation for an unknown function such as the temperature structure, $T(s)$, which appears in the integrand, and the inverse problem is seen to be that of an integral inversion. For example, if $T_b(\nu)$ and the opacity are known, then Eq. 1.13 is a linear integral equation—a Fredholm equation of the first kind—
that in principle can be inverted to obtain the temperature structure [6]. Realistically, the measurements of $T_b(\nu)$ are made in finite intervals of bandwidth centered on discrete points $\nu_i$. If the desired result is also allowed to be discrete (e.g., temperatures at intervals of altitude), then the problem can be rephrased as a matrix inversion. In either case, the uncertainties encountered in the inverse problem are much harder to trace. As is well known in remote sensing, deeply based indeterminacies are present in the inversion of integrals such as that in Eq. 1.13 or its matrix equivalent, and these can dominate even when measurement noise is vanishingly small. An excellent basic discussion of this point can be found, for example, in Twomey [7].

A more thorough discussion of the inverse problem in terms of the matrix formulation for the microwave case is given in Chapter 4. The practical approach to the inversion of Eq. 1.13 is usually unique to each application, however, and is a focus for the applications discussed in later chapters.

### 1.2.4 The Significance of the Approximations

The simple form of the radiative transfer equation given by Eq. 1.13 can be used for most applications without concern for the errors introduced by either the Rayleigh-Jeans approximation or the neglect of scattering. It is important to have a practical sense of where these errors arise and what they amount to, however, because these approximations are by no means universally valid in the microwave region. For example, deviations from the Rayleigh-Jeans approximation become more important as microwave remote sensing is extended to higher frequencies, and as applications at all frequencies become more exacting. Also, whereas typical cloud particles are not significant microwave scatterers, rain is, and is encountered frequently in tropospheric remote sensing.

#### The Rayleigh–Jeans Approximation

The definition of brightness temperature given by Eq. 1.7 is not unique. A quite different definition of brightness temperature is as the temperature of a blackbody radiator that produces the same intensity as the source being observed. The latter definition, which we will refer to as the *thermodynamic brightness temperature*, is given by the Institute of Electrical and Electronics Engineers [8], and is used in infrared work as well [9]. The first definition, which we will call the *Rayleigh–Jeans equivalent brightness temperature*, also appears in the literature [3, 10]. Unfortunately, many treatments avoid resolving this ambiguity by defining brightness temperature only after the Rayleigh–Jeans approximation has been introduced.

The relationship between the two definitions can be expressed for the emission from a blackbody radiator at temperature $T$ as

$$ R(\nu, T) = \frac{T_b \text{ (thermodynamic)}}{T_b \text{ (R–J equivalent)}} \quad (1.17) $$
This difference can be significant not only at high frequencies, but also when the surface brightness of the source is very low, as in the case of the cosmic background radiation. The Rayleigh–Jeans equivalent brightness temperature is particularly appropriate in a radiative transfer context because it is simply a scaling of intensity, and radiative transfer integrals are sums over intensity. The thermodynamic definition can lead to confusion in this context, although it has the advantage that the connection to physical temperature is strictly maintained.

Figure 1.5 shows how \( R \) depends on temperature and frequency. From this plot, we see that the fractional difference

\[
\frac{T - T_b}{T_b} = R(\nu, T) - 1
\]

is small for either low frequencies or high temperatures. Of more concern in many applications, however, is the absolute difference

\[
T - T_b = \frac{R(\nu, T) - 1}{R(\nu, T)} T
\]

which is plotted in Figure 6. This difference actually increases with temperature, and approaches the limit \((T - T_b) \to h\nu / 2k \approx 0.024\nu\) GHz. This difference can be significant throughout a large part of the microwave region.

Figure 1.6 demonstrates that the high-temperature asymptote of this difference is effectively reached at typical atmospheric temperatures, which is the main rea-
son that corrections to account for the Rayleigh–Jeans approximation are so often ignored in microwave remote sensing. To illustrate, if we add a step between the more general radiative transfer equation expressed by Eq. 1.8 and its approximation in Eq. 1.13 by expanding the former to the first order in $h\nu/kT$, then we arrive at the expression

$$T_b(\nu) + \frac{h\nu}{2k} = T_0 e^{-\tau(s_0)} + \int_0^{s_0} T(s) e^{-\tau(s)} \alpha ds \quad (1.20)$$

where $T_0$ is the physical temperature of a hypothetical blackbody at the boundary. Now, if we calibrate a radiometer against blackbody targets and ignore all departures from the Rayleigh–Jeans law, then we effectively redefine brightness temperature as $T_b(\nu) + h\nu/2k$, and thereby recover the simple form of Eq. 1.13. Hence, the naive application of Eq. 1.13 automatically accounts for the first-order correction, and a simple calculation shows that it can be used under normal circumstances to frequencies up to 300 GHz with errors less than $\sim 0.1$ K.

We caution that these approximations are no longer valid when the cosmic microwave background is present either as a cold-temperature reference or as the background term $T_{b0}$. For example, in the latter case, we can carry out the expansion leading to Eq. 1.20 for all but the background term, which we maintain exactly, and arrive at

$$T_{bc} = \frac{h\nu (e^{h\nu/kT_c} + 1)}{2k (e^{h\nu/kT_c} - 1)} \quad (1.21)$$
as the appropriate quantity to use for $T_0$ in Eq. 1.20 (or for $T_{b0}$ in Eq. 1.13), where $T_c = 2.736 \pm 0.017$ K is the cosmic background temperature [11]. $T_{bc}$ is also the appropriate value to use as the cold-sky-reference brightness temperature if the thermodynamic temperature of the hot target is taken to be its brightness temperature. Note that $T_{bc}$ is always greater than $T_c$, which is counterintuitive unless one remembers that we are only supplying the higher-order adjustments to the first-order correction already made in Eq. 1.20, and made implicitly in the naive application of Eq. 1.13.

The Neglect of Scattering

The question of scattering is more difficult to deal with in a quantitative way. This topic is thoroughly discussed in Chapter 3, and here we merely attempt to indicate a plausible limit inside of which scattering might be safely neglected. Let us take as a general criterion that the total power lost from the path of propagation due to scattering must be small compared to that involved in absorption or emission, keeping in mind that the notion of "small" ultimately depends on the experimenter and the case at hand. Specifically, let us consider scattering unimportant if the power lost from the beam due to scattering in each volume element is small compared to the power absorbed in that element, or, more conservatively, if the ratio of the scattering to absorption cross-section $Q_s / Q_a$ is small for the scattering particles involved. If we consider that the reemitted power will be comparable to that absorbed, then the net fraction of the total radiance due to scattering that is ultimately measured will then be less than or equal to this ratio. This is particularly true if there are other sources of absorption involved, and the condition can be overly conservative in some cases.

This condition is meaningful when considering liquid water, a strong microwave absorber that tends to dominate the radiative transfer process when it is present in even modest amounts in the form of clouds or rain. In Figure 1.7, we show the ratio $Q_s / Q_a$ for single spherical water droplets of radius $r$ that have been calculated using the frequency-dependent dielectric constant of water at a nominal temperature of 10°C [4]. The solid portions of the curves indicate the region where the Rayleigh scattering criterion $2\pi r \ll \lambda$ is valid, and the dashed upper region indicates the transition to the Mie scattering regime. The details of the Mie regime are not explicitly shown, but we note that the curves tend toward a value of order unity for $2\pi r \gg \lambda$.

The upper limit for cloud droplet radii in the Earth's atmosphere is around 0.1 mm [12]. Thus, at the frequencies commonly used for remote sensing of the troposphere—about 20 to 90 GHz—absorption in liquid water cloud regions exceeds scattering by at least two orders of magnitude, and we would expect errors to be comfortably less than 1% if we neglect scattering in the retrieval of temperatures in this frequency regime. The case becomes less clear for frequencies above 100 GHz, and scattering from cloud particles no longer can be ignored beyond 300 GHz. When cloud droplets coalesce to form rain, on the other hand, the resulting particle sizes approach the wavelength at all microwave frequencies. Drop-size distributions are highly variable, with the mean drop radius tending to increase...
with rain rate—from 0.5 to 1.5 mm for light to heavy rainfall [12]. As indicated in Figure 1.7, these dimensions put the scattering problem well into the Mie regime at all microwave remote-sensing frequencies. Consequently, the applicability of the nonscattering radiative transfer equation becomes highly questionable when observing through regions containing rain, and results obtained under such conditions require the special considerations discussed in Chapters 3 and 6.

1.3 MICROWAVE RADIOMETRY

The objectives of this section are to describe how microwave radiometers work and to present the basic concepts involved in making radiometric measurements. A full presentation of the techniques of microwave radiometry is well beyond the scope of this volume, and the interested reader can pursue this subject in more depth in several texts [2, 4, 13–15]. For our purposes, the function of a radiometer is to measure the radiant intensity \( I_v \) of the previous section, which, of course, is an idealized flow of power in infinitesimal elements of bandwidth and solid angle. In the following, we describe how the simplest radiometer—a total power radiometer—can be used to approximately measure the intensity over practical bandwidths and solid angles. This forms a basis for the topics of antennas, measurement uncertainty, and calibration. Finally, we describe the most common types of radiometers used in practice and discuss the current state of microwave technology.

Along the way, we introduce a working vocabulary so that the reader can follow discussions elsewhere that involve microwave radiometry. Italics identify the first use of each specialized microwave term, and a definition is given in context.
1.3.1 Fundamentals

A Simple Heterodyne Receiver

The typical microwave radiometer uses the so-called heterodyne* principle, where both the technique and the terminology date from the early days of radio. A heterodyne receiver is one in which the received signal, called the radio-frequency, or RF, signal, is translated to a different and usually lower frequency (the intermediate-frequency, or IF, signal) before it is detected. The simplest version of a heterodyne radiometer is shown in Figure 1.8. It is an example of a total power radiometer, and illustrates features common to most microwave radiometers. Although this circuit is rarely used as it stands, it provides a useful introduction to both the theory and practice of microwave radiometry.

First, imagine that we have a signal at some frequency incident on the antenna of this radiometer. The purpose of the antenna is to couple this RF signal into a transmission line (a waveguide, for example), the function of which is to carry the RF signal to and from the various elements of the circuit. In the example, this signal is introduced directly into a mixer, which is a nonlinear circuit element in which the RF signal is combined with a constant-frequency signal generated by a local oscillator, or LO [16]. Signals at various combination frequencies are produced at the output of this element because of its nonlinearity. These products include a signal whose frequency is the difference between the RF and LO frequencies, as shown schematically in Figure 1.9(a). This signal has the important property that its power is proportional to the power in the RF signal under the condition that the latter is much weaker than the LO signal. It is then filtered to exclude the unwanted products of the mixing, and amplified to produce the IF output signal.

Signals at microwave frequencies are often difficult or impossible to deal with directly, whereas a signal which has been downconverted to a sufficiently low IF frequency can be handled with a variety of techniques. After amplification and filtering, the power in the IF signal is measured with the use of a second nonlinear element, a square-law detector. This element is typically a diode that operates

*Also called superheterodyne, where the original distinction is now obsolete.
within its $i = \nu^2$ range and produces an output voltage that is proportional to the input power.

This example can be easily generalized to the case where broadband noise is received from a thermally emitting source. The mixer output then consists of a continuum of frequencies $|\nu_{LO} - \nu_{RF}|$ that corresponds to the frequencies $\nu_{RF}$ contained in the input noise signal. If the output is passed through a rectangular bandpass filter, the result will contain all frequencies originally present within two rectangular RF passbands that are images of the IF bandpass reflected around the LO frequency. This relationship is depicted in Figure 1.9(b). The two RF passbands are called the upper and lower sidebands of the receiver, which are effectively folded about the LO frequency by the mixer and translated into the IF band to create a double-sideband receiver. As before, the detector then converts the net power in this band into a linearly related voltage.

A variation on this circuit that is becoming increasingly important is the use of direct RF amplification as this capability continues to develop at centimeter and long millimeter wavelengths. An amplifier immediately following the antenna, as shown in Figure 1.10, can be used to raise the power of the incoming signal well above the thermally generated noise power in the mixer or other following components. This can improve the radiometer sensitivity without requiring high performance in the mixer and the remainder of the receiver. Also, RF amplification
followed by a filter can be used to create a single-sideband receiver if the RF power to appear in the desired sideband is amplified to a level well above that of its image band.

The Relationship of Received Power to Radiant Intensity

To account for the collection of thermal noise power by the antenna, we begin with Nyquist’s law [17] for the noise power available from a matched resistor that terminates a transmission line (a matched element is one that reflects no power incident upon it). Nyquist’s law is closely related to Planck’s law, but is derived for the specific case of radiation propagating within a terminated transmission line instead of a general cavity [5, 18]. If the temperature of the matched resistor is $T$, then the power per unit bandwidth propagating from the resistor is*

$$ P = kT $$

(1.22)

Let us now imagine that the transmission line is terminated by an antenna that is immersed in a uniform radiation field resulting from thermal blackbody emission at temperature $T$. For the moment, it is useful to think of an antenna as a matching device that couples the confined wave propagating inside the circuit to free space, and vice versa. The present case is then just a variation of Nyquist’s hypothetical circuit, and the power per unit bandwidth that is coupled into the circuit must be equal to that propagating back to free space from the resistor. This power is thus also given by Eq. 1.22.

Now, as with radiant intensity and the definition of brightness temperature in the previous section, we use the approximately linear relationship between power and temperature to define the antenna temperature:

$$ T_a = \frac{P}{k} $$

(1.23)

as an appropriately scaled measure of the thermal power introduced into the receiver.

*In the Rayleigh-Jeans limit. For simplification, we carry this approximation through the remainder of this chapter, noting that the more exact case is easily recovered by dividing the right side of Eq. 1.22 by $R(v, T)$. 
The Antenna

The purpose of an antenna, beyond its function as an impedance-matching device between free space and the receiver, is to provide selectivity in the measurement of the angular distribution of the radiation. For an arbitrary distribution of radiant intensity with angle, $I_v(\theta, \phi)$, the net noise power entering the receiver is determined by the antenna and its sensitivity to direction. Some very general relationships exist between this angular distribution and the received power. As a shortcut to get at these, let us make the plausible assumption that the antenna is a linear device that couples the radiant power from a particular element of solid angle $d\Omega = \sin \theta \, d\theta \, d\phi$ into the receiver by the relationship

$$dP = A_e(\theta, \phi)I_v(\theta, \phi) \, d\Omega \tag{1.24}$$

where $A_e$ is some linear coupling coefficient that depends only on the antenna and the direction of the incoming radiation. From the dimensions of this equation, $A_e$ has units of area, and can be thought of as the effective area of the aperture for radiation incident from the direction of the solid angle element $d\Omega$. If the radiation field is caused by an extended source of incoherent radiation, such as thermal emission from an atmosphere, then the total power introduced into the receiver is the direct sum over all directions, or

$$P = \int_{4\pi} A_e(\theta, \phi)I_v(\theta, \phi) \, d\Omega \tag{1.25}$$

If we translate our units for power and intensity into temperature using the definitions for antenna temperature and brightness temperature given in Eqs. 1.23 and 1.7, then we obtain

$$T_a = \int_{4\pi} \frac{A_e(\theta, \phi)}{\lambda^2} T_b(\theta, \phi) \, d\Omega \tag{1.26}$$

We identify the quantity that multiplies $T_b$ in the integrand as the antenna gain,*

$$g(\Omega) = \frac{A_e(\theta, \phi)}{\lambda^2} \tag{1.27}$$

This allows us to write a basic relationship between received power and the angular distribution of radiation as

$$T_a = \int_{4\pi} g(\theta, \phi)T_b(\theta, \phi) \, d\Omega \tag{1.28}$$

*The quantity that describes the antenna power pattern has several names and definitions that differ by a normalization constant, depending on the application. For example, the directivity of the antenna, or its directive gain, $G(\theta, \phi) = 4\pi g(\theta, \phi)$ is often used and gives the response of the antenna to radiation from a given direction relative to a hypothetical antenna with an isotropic power pattern.
We can interpret the antenna gain as the effective collecting area of the antenna, in units of wavelength squared, for radiation incident on it from the direction of the solid angle element $d\Omega$. Note that from the thermodynamic argument of the previous section, we must have

$$\int_{4\pi} g(\theta, \phi) \, d\Omega = 1 \quad (1.29)$$

To achieve selectivity in direction, a practical gain pattern will consist of a well-defined main beam with much lower gain away from the beam axis. A useful quantity to describe the angular resolution of such a pattern is the main-beam solid angle, which we define as

$$\Omega_a = \int_{4\pi} \frac{g(\Omega)}{g(0, 0)} \, d\Omega \quad (1.30)$$

where the angular coordinate system is assumed to be centered on the peak gain, $g(0, 0)$. For example, if the gain has a constant value over some solid angle and is zero outside, then the foregoing just returns that solid angle. An important relationship is obtained by using Eqs. 1.29 and 1.27 in Eq. 1.30

$$\Omega_a = \frac{\lambda^2}{A_e(0, 0)} \quad (1.31)$$

The effective area in the direction of maximum gain, $A_e(0, 0)$, is usually just called the effective aperture area, $A_e$. To the extent that area $A_e$ can be related to the size of a physical aperture, Eq. 1.31 characterizes a diffraction-limited optical system. For example, if we associate a diameter $D$ with the effective aperture $A_e$ such that $A_e = \pi D^2 / 4$ and a beam diameter $\theta_a$ such that $\Omega_a = \pi \theta_a^2 / 4$, then Eq. 1.31 reduces to

$$\theta_a = \frac{4 \lambda}{\pi D} \quad (1.32)$$

It is interesting that we can derive this relationship without recourse to wave-optics arguments or reference to a specific antenna geometry. The details of the gain pattern and its actual relationship to the physical aperture, of course, must be obtained using Maxwell's equations with the appropriate boundary conditions. A familiar point of reference for a diffraction-limited aperture is the diffraction pattern given by a uniformly illuminated circular aperture, for which the angular diameter of the first null of the interference pattern (the Rayleigh criterion) is approximately $1.22\lambda / D$. More generally, most microwave antennas can be approximated as a planar aperture with a spatially varying illumination, or field distribution. The angular distribution of outgoing power is then the Fourier transform of the autocorrelation of this aperture field distribution [2].
An important class of microwave antenna is the horn antenna, so-called because of its shape. In its simplest version, this need be little more than a section of waveguide with a uniformly expanding cross-section that is open at its wide end; the smooth taper of the walls minimizes reflection as an outgoing wave gradually expands to become a wave in free space. Horn exit apertures are rarely more than a few wavelengths in diameter, so their beamwidths typically exceed several degrees. The effective aperture illumination is not uniform, but is naturally tapered so that the field approaches zero at the horn rim. This has two consequences because of the Fourier relationship between aperture illumination and gain pattern: the main beam is broadened because the aperture illumination is effectively narrowed, and the interference fringes away from the main beam (or sidelobes) are reduced because of the lack of a sharp discontinuity in the illumination. With good design, it is possible to create an illumination across the horn exit aperture that is approximately Gaussian so that the sidelobes virtually disappear. More elaborate versions (scalar horns) are possible that ensure azimuthal symmetry of the resulting power pattern even though the input waveguide and its internal field distribution are not symmetric.

Horns can be used as feedhorns to illuminate large apertures, which give much higher angular resolution. Such antenna systems are often analogous to those familiar at optical and infrared wavelengths. For example, a parabolic reflector illuminated by a feedhorn is essentially a Newtonian telescope; Cassegrain and other multiple reflector systems are also common [2, 19–23]. These kinds of antennas provide resolutions from a few degrees down to a few arc minutes. Finally, aperture-synthesis techniques are possible in which large virtual apertures are created from assemblies of smaller real apertures [24]. This approach has made possible the study of distant radioastronomical sources at milliarcsecond resolution, and is important for the study of planetary atmospheres (see Section 1.3.3 and Chapters 9 and 10). Synthetic apertures have other implications for remote sensing [25, 26], and, for example, may eventually provide the large apertures needed for high-resolution Earth observations from geosynchronous orbit [27].

A somewhat arbitrary but standard measure of resolution for microwave antennas is the half-power beamwidth (HPBW), or the diameter of the gain pattern where its value is half that of the central peak (also used for the same purpose is the term Full Width at Half-Maximum, or FWHM). For example, the uniformly illuminated circular aperture of diameter $D$ has a HPBW of $1.02\lambda/D$. The typical tapering of the aperture illumination on a microwave aperture of diameter $D$ tends to increase the beamwidth and lower the sidelobes relative to this case. Microwave antennas used for remote sensing have half-power beamwidths in the range 1.3–1.7$\lambda/D$, depending on compromises made by the antenna designer. Hence an approximation that describes the beamwidths of most antennas to an accuracy of about 10% is

$$\theta_{\text{HPBW}} = \frac{1.5\lambda}{D}$$

(1.33)

Figure 1.11 shows a plot of this rule-of-thumb beamwidth versus aperture size for microwave frequencies. Antennas built for communications systems are usually
Figure 1.11. Relationship of aperture size $D$ to half-power beamwidth as a function of frequency for a nominally illuminated antenna (from the approximate relationship in Eq. 1.33). The lower horizontal axis gives aperture sizes typical of filled-aperture antennas. These provide angular resolutions read on the left-hand vertical axis. The upper horizontal scale gives aperture sizes in the domain of aperture-synthesis techniques and yield resolutions read on the right-hand vertical axis.

optimized for peak gain and tend to have narrower main beams for a given aperture diameter than this relationship implies because the increased sidelobes are of less concern in this application [23].

Because of wavelength, physical sizes of microwave antennas need to be much larger to achieve the same resolution as apertures at infrared or optical wavelengths. Antenna size is an important practical concern in many microwave applications as a result.

**Calibration**

The receiver output voltage must be calibrated in units of antenna temperature. This involves finding both a gain coefficient and an offset, where an offset is needed to account for power generated within the receiver itself. Received power is inevitably lost by absorption as it passes through successive stages of the receiver—the elements that are responsible for this loss reradiate power at their own physical temperature, and if this occurs before or within the mixer and the first stages of the amplifier, this power will be amplified along with the signal (in many radiometers, this internally generated power exceeds that of the signal). The net IF power reaching the square-law detector then consists of two components: (1) that which represents the amplified signal power and is proportional to the antenna temperature $T_a$, and (2) the internally generated power, which we identify as the receiver temperature $T_r$ with the understanding that it is to be calibrated on the same scale as the antenna temperature. The sum of these components is called the
system temperature,

\[ T_s = T_a + T_r \] (1.34)

As demonstrated in Figure 1.12, we can calibrate the radiometer and determine the offset at the same time by observing blackbody emitters at two different temperatures. For example, we can enclose the field of view of the antenna with a temperature-controlled microwave absorber (or load) at each of two temperatures, \( T_{\text{hot}} \) and \( T_{\text{cold}} \). If the radiometer is linear, which is usually well approximated in practice, then we can determine the antenna temperature \( T_a \) for a target at an unknown temperature as

\[ T_a = c(V - V_0) \] (1.35)

where \( V_0 \) is the voltage offset due to the receiver temperature (e.g., \( T_r = V_0/c \)), and the radiometer calibration constant \( c \) is determined as

\[ c = \frac{T_{\text{hot}} - T_{\text{cold}}}{V_{\text{hot}} - V_{\text{cold}}} \] (1.36)

where the voltages \( V_{\text{hot}} \) and \( V_{\text{cold}} \) are the measured output voltages for the respective \( T_{\text{hot}} \) and \( T_{\text{cold}} \) loads.

**The Radiometer Noise Formula**

Any measurement of noise power possesses an inherent statistical uncertainty that depends on the bandwidth \( B \) of the noise power and on the time \( t \) allowed for its

![Figure 1.12. Calibration of antenna temperature using a hot and cold load. The calibration coefficient is given by the measured slope, and the voltage intercept for zero antenna temperature determines the receiver temperature \( T_r \).](image-url)
measurement. A simple way to visualize this dependence is to consider the noise power as a time-varying voltage that corresponds to band-limited white noise (within a reasonably narrow bandpass, thermal noise contains approximately the same average power in every frequency interval; if the signal is passed through a rectangular bandpass filter, it will contain the same average power in every frequency interval within the bandpass and zero outside it). A typical measurement consists of the square-law detection of this signal followed by an averaging for time \( t \). The Fourier representation of a band-limited white-noise signal over time interval \( t \) consists of \( n = Bt \) components with coefficients whose absolute values are normally distributed with a uniform standard deviation. If we follow the detection and averaging process mathematically using the Fourier representation, then the measurement will be proportional to the sum of squares of the coefficients, and will be uncertain because of the uncertainty of the components that comprise it. The relative uncertainty \( \Delta P / P \) in the sum \( P \) can be shown to be inversely proportional to the square root of the number of coefficients [13, 28], or

\[
\frac{\Delta P}{P} = \frac{1}{\sqrt{n}} = \frac{1}{\sqrt{Bt}}
\]

(1.37)

Now, \( P \) and \( \Delta P \) are, respectively, proportional to the system temperature \( T_s \) and the uncertainty of the measurement \( \Delta T \), so that we readily obtain the noise formula

\[
\Delta T = \frac{T_s}{\sqrt{Bt}} \quad \text{(total power radiometer)}
\]

(1.38)

Figure 1.13 shows how the uncertainty of a 1-second measurement depends on system temperature and bandwidth for both this case and the Dicke-switched radiometer discussed in the next section.

### 1.3.2 Two Common Types of Radiometers

**The Dicke Radiometer**

The total power radiometer is not well suited for many applications because it is difficult to stabilize and calibrate. To appreciate the importance of gain fluctuations, consider as a typical case a total power radiometer with a system temperature of 500 K and a bandwidth of 100 kHz. According to the noise formula, the uncertainty of a 1-second measurement made with this radiometer would be 0.05 K, or one part in \( 10^4 \) of the total noise power. Because the gain acts on the total power, the stability of the radiometer would have to be held to one part in \( 10^4 \) so that gain fluctuations do not dominate the sensitivity of the instrument. Such stability is difficult to achieve. A general solution to this problem is the Dicke radiometer shown schematically in Figure 1.14. A switch follows the antenna in this circuit, which allows the receiver input to alternate between the antenna and a stable source of thermal-noise power provided by a reference load. A reference load can be an
Figure 1.13. Uncertainty (standard deviation) of a 1-second measurement as a function of system temperature and bandwidth. The values shown are from Eq. 1.38 for a total power radiometer and Eq. 1.39 for a Dicke-switched radiometer.

external load viewed by a second antenna or a load internal to the circuit, with the load maintained at a known temperature in either case. As the switch alternates position, the output voltage of the Dicke radiometer correspondingly alternates between the total powers from the antenna and the reference load. The receiver is followed by a synchronous detector, or lock-in amplifier, which rectifies the switched signal so that the output is proportional to the difference between antenna

Figure 1.14. Schematic of a Dicke radiometer.
and load temperatures. If the switching time is much shorter than the characteristic
period of the gain fluctuations, then the gain fluctuations cause only the measured
temperature difference to vary. Their effect is, therefore, reduced by the ratio of
the measured temperature difference to the total power, which can be made quite
small in many cases.

The measurement uncertainty for a Dicke radiometer that divides its time evenly
between the source and a reference of comparable temperature is

\[ \Delta T = \frac{2T}{\sqrt{Bt}} \]  

(Dicke radiometer) (1.39)

The factor-of-2 increase relative to the uncertainty of the total power radiometer
follows because the net integration time on the source is reduced by half, and
because two equally uncertain quantities are differenced to form the result, where
each consideration increases the uncertainty by a factor of root 2. The formula is
more complicated but easily derived if the source and reference temperatures are
significantly different [4].

The stable components and amplifiers of modern solid-state electronics have
reduced the need for rapidly switched Dicke radiometers, and have even made
total power radiometers practical in some applications. Nevertheless all radiome-
ters are designed to measure, in one way or another, the difference between the
desired antenna temperature and that of a reference source. For example, total
power radiometers with movable external targets or switched beams use the basic
principle of a Dicke radiometer and can achieve the same stability under some
circumstances. The term "Dicke radiometer" is usually reserved for radiometers
with an internal switch, however.

**The Microwave Spectrometer**

Many applications depend on the measurement of the spectral dependence of the
emission. A microwave spectrometer, or spectral line receiver, is obtained by sub-
dividing the IF passband of any of the prior radiometers and separately detecting
the output of each resulting segment. The heterodyne technique allows the spectral
region of interest to be placed at a convenient frequency for this analysis. The IF
passband can be subdivided as indicated in Figure 1.15 by using a bank of narrow-
band filters with the desired distribution of bandpass characteristics; alternatively,
digital sampling and autocorrelation or other techniques of spectral analysis can
be used. There is no effective upper limit to the resolution and number of frequency
elements that can be obtained. As an extreme case, for example, one spectrum
analyzer recently built for signal processing contains 8.4 million contiguous chan-
nels with 0.05-Hz resolution [29]. However, there is a practical limitation when
the spectral feature to be analyzed is so broad that it exceeds the practical IF
bandwidth of a radiometer. An example is the 22-GHz water-vapor line in the
Earth’s troposphere. Such a feature must be observed with the equivalent of a
single-frequency radiometer that can be tuned to a number of frequencies.
The accuracy of the frequency measurement also has no practical limit. Local oscillators at all microwave frequencies can be phase-locked to reference frequencies derived from time standards. Hence, it is possible to control the radiometer frequency to tolerances well below 1 Hz throughout the microwave range, which is far more accurate than needed for any remote-sensing application discussed in this volume. The ideality of microwave spectroscopy for both frequency accuracy and resolution makes this approach a very powerful tool for atmospheric remote sensing.

The simplest spectrometer system uses a double sideband receiver in which the spectral feature to be observed is folded into the IF passband with an image RF passband that contains no useful signal. In this case, the signal power is divided in half in the IF band relative to the net noise power and a single-sideband receiver temperature is conventionally defined to be twice as large as the system temperature $T_s$ of Eq. 1.34. The single-sideband temperature is the appropriate quantity to use in the noise formula of Eqs. 1.38 or 1.39 to determine the measurement uncertainty.

1.3.3 About Hardware

It is impossible to capture the state of microwave technology in a few pages, and the rapid development of this field would quickly date the attempt. However, we can introduce the main concepts and define terms likely to be encountered in the literature. We begin with the main building blocks that are available to the circuit designer, and follow with some examples of radiometer design.

**Circuit Elements**

**Waveguide.** The power radiated by an oscillating current increases as the square of the frequency, so that the usual view of a circuit as currents flowing in conduc-
tors becomes instead, at high frequencies, a radiation field controlled by appropriate boundary conditions. As a result, conventional circuits with wires are not feasible in the microwave region except when physical sizes are kept very small. Waveguide is commonly used as the basic signal-carrying medium at frequencies up to about 100 GHz, beyond which it becomes impractical for general use because of increasing attenuation and increasingly severe mechanical tolerances. Waveguides for passive systems are made in standard sizes for frequencies up to about 100 GHz, which are rectangular with a width-to-height ratio of 2:1. This geometry permits them to carry a single mode \( \text{TE}_{10} \) over a wide frequency range; multiple-mode transmission is undesirable because the performance of most circuit elements is rapidly degraded by mode mixing. The set of standard sizes gives overlapping single-mode transmission capability up to about 100 GHz. Table 1.1 lists the waveguide bands that are coordinated with these standard sizes. The band nomenclature is intentionally obscure because it is derived from code designations originating from classified radar development during World War II.

**Passive Components.** Many circuit elements can be constructed using waveguide geometries [30, 31]. Power dividers split the incoming power evenly into exit ports; the outputs can be in phase or out of phase according to the design. Directional couplers can transfer a desired amount of signal propagating in a given direction in one waveguide to another. A smoothly tapered resistive vane inserted into a waveguide parallel to the \( \text{TE}_{10} \) mode E-field can provide a nonreflecting attenuator, and a resisting material similarly tapered to eliminate reflections and placed to absorb all the entering power provides a matched load.

The novel properties of ferrites lead to a valuable class of microwave components. Ferrites comprise a class of nonconducting ceramiclike materials with the general composition \( \text{MO} \cdot \text{Fe}_2\text{O}_3 \), where M represents a divalent metal such as magnesium or iron. When a strong magnetic field is used to align the unpaired

<table>
<thead>
<tr>
<th>Band Designation</th>
<th>Nominal Frequency Range (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L )</td>
<td>1–2</td>
</tr>
<tr>
<td>( S )</td>
<td>2–4</td>
</tr>
<tr>
<td>( C )</td>
<td>4–8</td>
</tr>
<tr>
<td>( X )</td>
<td>8–12</td>
</tr>
<tr>
<td>( K_u )</td>
<td>12–18</td>
</tr>
<tr>
<td>( K )</td>
<td>18–27</td>
</tr>
<tr>
<td>( K_o )</td>
<td>27–40</td>
</tr>
<tr>
<td>( Q )</td>
<td>36–46</td>
</tr>
<tr>
<td>( V )</td>
<td>46–56</td>
</tr>
<tr>
<td>( W )</td>
<td>56–100</td>
</tr>
</tbody>
</table>
electrons in a ferrite, a wave propagating in this material experiences Faraday rotation; for example, the polarization of a linearly polarized wave traveling parallel to the magnetic field vector rotates in a sense determined by the direction of the magnetic field. The ferrite medium is nonreciprocal because the absolute sense of this rotation is the same for waves propagating either parallel or antiparallel to the magnetic field. This property has been exploited in waveguide geometries to produce nonreciprocal microwave components such as isolators, two-port devices in which a signal passes unimpeded in the forward direction, whereas a wave traveling in the reverse direction is rotated into an attenuator and absorbed. Isolators are used to ensure good matches in circuits that are especially sensitive to reflections. A three-port *circulator* is a device that passes a signal input to port 1 to port 2, port 2 to 3, and 3 to 1; circulators can be made with more than three ports. A *ferrite switch* can be made by controlling the direction of circulation in a three-port circulator with an externally applied magnetic field. A *latching* ferrite switch can be made by reversing the intrinsic magnetization of the ferrite with a pulsed current in an external coil; such switches routinely achieve microsecond switching times and are particularly valuable as the switching elements in Dicke radiometers.

**Mixers.** Waveguide techniques can be used to couple microwaves into and out of solid-state elements to produce a variety of active circuit components. Mixers are typically three-port devices that concentrate the microwave signal and local oscillator power entering through two ports as currents across a diode, while the IF power is drawn out through a third port. Considerations in the construction of a mixer include the matching of all three ports and the efficient conversion of the signal power to IF in the face of parasitic impedances that become prevalent at high frequencies. Smallness is a virtue in minimizing such impedances, and small area junctions such as are possible with Schottky-barrier diodes are important. The latter possess nearly ideal i–v curves and are extensively used in microwave applications. Other nonlinear elements such as Josephson junctions are finding increasing use at high frequencies.

**Sources.** The earlier generation of oscillators was based on properties of electron beams, which could be controlled to make devices such as klystrons and traveling-wave tubes. Such devices were intrinsically bulky, often short-lived, and required extensive supporting equipment such as high-current and high-voltage supplies. The discovery in 1963 of the oscillatory properties of bulk *n*-type GaAs and InP materials when subjected to a static voltage led to the *Gunn oscillator* [32], a solid-state device that has now almost universally replaced electron-beam devices as local oscillator sources in radiometers. Gunn oscillators have greatly simplified the practice of microwave radiometry. They can be phase-locked to standard frequencies and are readily available at frequencies up to 100 GHz, which appears to be a practical upper limit. LO signals are provided at higher frequencies by *frequency multipliers*, or devices that use the nonlinear properties of waveguide-mounted diodes to produce selectively enhanced harmonics from lower-frequency oscillators.
Waveguide-mounted avalanche diodes can be used to produce broad-band white noise with equivalent blackbody temperatures well in excess of their ambient temperatures (e.g., by factors of 100 or more). Such noise diodes provide a useful calibration signal when injected weakly into a radiometer through a directional coupler. The stability of such calibration signals can be much better than 1% when the diode voltages and physical temperatures are well-controlled.

RF Amplifiers. A number of approaches have been developed in recent years for direct amplification at microwave frequencies. Cryogenic amplifiers such as masers or cooled HEMTs (high-electron-mobility transistors) can produce significant gain with excellent efficiency so that very low system temperatures can be achieved. Maser amplifiers using pumped ruby have set the standard for low-noise communications in the centimeter wavelength range [33]. Development of solid-state amplifiers such as HEMTs has been relatively recent but rapid, and useful amplification has been achieved at frequencies as high as 100 GHz [34, 35].

Quasi-Optical Elements. Quasi-optical techniques are often used in the short-millimeter and submillimeter ranges where waveguides become impractical [36, 37]. Directed radiation in free space with a Gaussian intensity distribution perpendicular to the axis of propagation remains collimated over useful distances, and is easily formed by a scalar feed with a parabolic reflector. This beam-waveguide approach makes possible a variety of interesting circuit components such as frequency diplexers and filters. Gaussian beams are diffraction-limited and represent the long-wavelength limit of geometric optics; indeed, many quasi-optical devices such as Fabry–Perot diplexers are directly analogous to optical devices. Such techniques are fundamental to pioneering developments in terahertz receiver technology, which may someday extend the microwave approach to frequencies as high as 10 THz [37].

Radiometers
Microwave radiometers are as varied in their design as the applications for which they were developed. Considerations at a given frequency include performance factors such as sensitivity, accuracy, and spatial resolution (usually desired to be as high as possible), which must be balanced against opposing factors such as complexity, weight, size, and power (which ultimately determine the price to be paid). The receiver temperature \( T_r \) is a key performance factor in many applications, particularly in microwave spectroscopy and radio astronomy. Figure 1.16 shows single-sideband receiver temperatures that have been achieved to date as a function of frequency [38, 39]. The best performance at frequencies up to roughly 50 GHz is given by cryogenic systems using masers and cooled HEMTs for direct RF amplification, and by SIS (superconductor–insulator–superconductor) mixers farther into the millimeter and submillimeter regions. Such systems tend to be complex because of their cryogenic needs. Uncooled Schottky diode mixers are
adequate for most broadband applications at frequencies well into the millimeter region, because the signal is of the same approximate magnitude as the typical receiver temperature (for double-sideband applications, the receiver temperatures shown in Figure 1.16 should be divided in half). Uncooled HEMT amplifiers exhibit excellent performance to 100 GHz, and their full potential for radiometry is just beginning to be exploited.

Examples of the current generation of radiometers built for atmospheric remote sensing are shown in Figures 1.17 and 1.18. The first is a ground-based water-vapor radiometer built to measure the tropospheric water vapor and cloud liquid burden from atmospheric emission in the vicinity of the 22-GHz $H_2O$ line [40; see also Chapter 4]. This system was built to be portable and inexpensive while providing state-of-the-art accuracy in radiometry, and has been used in support of atmospheric radio-path-delay correction for geodesy (see Chapter 5). Figure 1.18 shows the most recent of the many radiometers that have been placed into Earth orbit to sense atmospheric temperature and water on global scales (see Chapter 6 and Table 6.1).

The study of the atmospheres of other planets requires a radioastronomical approach because the apparent disks of planets with major atmospheres range in diameter from about one arc-minute (Venus) to less than 3 arc-seconds (Neptune).
These cannot be resolved by even the largest single-antenna telescopes, even though much useful information can be gained by disk-averaged measurements (see Chapters 9 and 10). Arrays of antennas can be used to synthesize large virtual apertures. For example, the Very Large Array (VLA) in New Mexico (Figure 1.19) can achieve arc-second resolution or better at several centimeter wavelengths.

The microwave sections of radiometers currently used for remote sensing are constructed from discrete components plumbed together with waveguide. The physical bulk and complexity of microwave circuits built in this way have been limiting factors in the development of many applications. For example, it has been difficult to place microwave instruments on deep-space planetary missions because of the severe weight and power constraints associated with such missions. Also, practical applications such as the ground-based mapping of tropospheric temperature and water content for weather-related purposes require networks of sensors, and are limited by the presently large costs of individual units. However, the wave of miniaturization that began with the introduction of the transistor is just now
beginning to reach the centimeter to millimeter microwave region. The state of the art of radiometry at frequencies up to about 100 GHz is consequently entering a state of transition in which it can be expected that *monolithic microwave integrated circuit (MMIC)* components will replace many of those based on waveguide geometries. As an example, Figure 1.20 shows a prototype 30-GHz radiometer recently built at the Jet Propulsion Laboratory using only MMIC components and configured as a complete end-to-end system [41]. It is possible to construct such
Figure 1.19. A view of the Very Large Array on the Plains of San Augustin in New Mexico. The VLA was constructed by the National Radio Astronomical Observatory and consists of 27 antennas of 25-m diameter each, which are movable along three 20-km tracks arranged in a "Y" configuration. The array is capable of synthesizing a virtual aperture as large as 36 km in diameter. Each antenna contains receivers at discrete wavelengths in the range 1.35–20 cm.

Figure 1.20. A microwave radiometer built from MMIC components. The circuit is a total power heterodyne radiometer with RF preamplification, and includes a noise source for calibration and voltage-to-frequency conversion of the radiometer output. Thermoelectric junctions (not shown) are mounted to the base to provide temperature control.
a radiometer on a single substrate, which will lead to further miniaturization and cost reduction. When this technology matures, we can expect the costs of radiometers to fall dramatically at frequencies well into the millimeter region, and many of the applications described in this volume will open up for considerable future development.

REFERENCES


The transfer of electromagnetic radiation through an atmosphere is linked to its state (temperature, pressure, and composition) by the refractive index and by coefficients for absorption and scattering, if any. The purpose of this chapter is to introduce the physical basis of microwave absorption by atmospheric molecules. A comprehensive exposition of microwave spectroscopy would be beyond the scope of the chapter; instead, O₃, H₂O, CO, N₂O, ClO, O₂, NH₃, N₂ and CO₂ have been chosen as examples, and emphasis is placed on the features of their spectra that have been observed in the terrestrial and planetary atmospheres. (Line parameters are listed in the Appendix to Chapter 2.) However, this group of molecules is sufficiently diverse that some of the discussion here will apply to other molecules of interest. More extensive discussions of molecular spectroscopy can be found in References 1-6.

2.1 GENERAL EXPRESSION FOR ABSORPTION COEFFICIENT

The absorption coefficient in a medium is a macroscopic parameter that represents the interaction of incident electromagnetic energy with the constituent molecules. This interaction is governed by three general principles. First (Bohr's frequency
condition), the frequency $\nu$ of a photon emitted or absorbed by the gas is equal to the difference of two energy levels ($E_a - E_b$) of the gas, divided by Planck’s constant $\hbar$. Second (Einstein’s laws of emission and absorption), if $E_a$ is higher than $E_b$, the probability, given initial state $a$, of stimulated emission of a photon by a transition from state $a$ to state $b$ is equal to the probability, given initial state $b$, of absorption of a photon by a transition from $b$ to $a$. These two probabilities are both proportional to the incident energy at frequency $\nu$. Hence, net absorption (the difference between absorption and stimulated emission) is proportional to the difference in thermodynamic probabilities ($p_b - p_a$) of the two states. Third (Dirac’s perturbation theory), for the electromagnetic field to induce transitions between states $a$ and $b$, the operator with which the field interacts must have a non-zero matrix element linking the two states. For wavelengths that are very long compared to molecular dimensions, this operator is the dipole moment (either electric or magnetic).

In a diffuse isotropic medium, the power absorption coefficient at frequency $\nu$ is \[7, 8\]

\[
\alpha(\nu) = \frac{8\pi^3\nu}{3\hbar c V a,b} \sum \delta(\nu_{ab} - \nu)(p_b - p_a) \sum |\mathcal{M}_{ab}|^2
\] (2.1)

where $a$ and $b$ denote quantum states; $\mathcal{M}_\sigma$ is one of the three spatial components, denoted by the index $\sigma$, of the total dipole moment of the molecules within a volume $V$; $\mathcal{M}_{ab}$ is the matrix element of $\mathcal{M}_\sigma$ between $a$ and $b$; $p_a$ is the thermodynamic probability of state $a$; $h\nu_{ab} = E_a - E_b$ is the energy difference between states $a$ and $b$; $\delta$ is the Dirac delta function; $c$ is the speed of light. The small difference between the propagation speed in a gas and its value in vacuum is not important here.

Equation 2.1 is not in a form useful for actual computation because $a$ and $b$ are states of the entire system of interacting molecules, rather than of isolated molecules. The discussion in this chapter therefore begins in Section 2.2 with the line spectra of isolated molecules. Matrix elements are described at greater length in 2.2.4. The subject of line broadening due to molecular motion and collisions is introduced in Sections 2.3 and 2.4. Finally, Section 2.5 briefly describes absorption due to collision-induced dipole moments.

*Equations, such as Eq. 2.1, that involve a dipole moment assume use of the cgs system. In the SI system, $|\mathcal{M}_{ab}|^2$ would be replaced by $|\mathcal{M}_{ab}|^2/4\pi\epsilon_0$ for an electric dipole or $\mu_0|\mathcal{M}_{ab}|^2$ for a magnetic dipole.

†A molecule in free space has some nonzero probability per unit time of making a spontaneous transition to a lower energy state. This implies, because of Heisenberg’s uncertainty principle, that $\delta(\nu_{ab} - \nu)$ should be replaced by a function having unit area but nonzero width. However, this natural line width is negligible for microwave lines, in comparison with the broadening due to other mechanisms to be discussed in this chapter [3, p. 44].
2.2 ENERGY LEVELS AND LINE SPECTRA OF ISOLATED MOLECULES

2.2.1 Born–Oppenheimer Approximation

The motion of the particles—nuclei and electrons—constituting a molecule can be described by a wave function $\Psi$ that depends on the coordinates of all the particles. In the absence of external perturbations, $\Psi$ is expressed as a function of time $t$ by

$$\Psi = \psi e^{-iEt/h} \quad (2.2)$$

where $h$ is $h/2\pi$, and $E$ is the energy of the state represented by a wave function $\psi$ that obeys the time-independent Schrödinger equation [9, p. 53],

$$H\psi = E\psi \quad (2.3)$$

where $H$ is the Hamiltonian operator. Thus, the problem of determining the energy levels of the molecule is one of finding the eigenvalues of the operator $H$.

Because the electrons in the molecule are very much lighter than the nuclei, and move in fields of roughly the same strength, the electronic motion is more rapid than the motion of the nuclei. In quantum-mechanical terms, the electronic energy levels are generally much more widely spaced than the energies of vibration and rotation of the nuclei. It is possible, therefore, to treat the electronic motion with internuclear distances as parameters, and to treat the motion of the nuclei with the electronic state prespecified. This, the Born–Oppenheimer approximation [9, p. 259], is implemented by separating the wave function into an electronic part and a part for vibration, rotation, and nuclear spin:* $\psi = \psi_{\text{elec}}\psi_{\text{vib-rot-nuc}}$. The eigenvalue problem for electronic motion relative to the nuclei can be solved with a Hamiltonian that includes only electronic kinetic energy and the Coulomb energy of attractions and repulsions among the electrons and nuclei, considering the latter to be fixed. This Hamiltonian, therefore, acts only on $\psi_{\text{elec}}$. The electronic energy, thus calculated as a function of the internuclear distances for each electronic state, then constitutes an effective potential energy for vibrational motion of the nuclei.

In simple molecules such as those that constitute the atmosphere, the vibrational energy levels are generally more widely spaced than the rotational energies, and separation of $\psi_{\text{vib}}$ from $\psi_{\text{rot}}$ and $\psi_{\text{nuc}}$ is appropriate. Then the rotational energy eigenvalue problem can be solved for a prespecified vibrational state, and vice versa. Typically, transitions between electronic states occur in the ultraviolet, vibrational transitions occur in the infrared, and rotational transitions are responsible for microwave, submillimeter, or long infrared lines. Energies associated with interactions involving nuclear spins (hyperfine splitting) are usually equivalent to a few MHz or less.

*For the present, we ignore the translational motion of the molecule, but it will be discussed in Section 2.3.
Pure rotational transitions account for the microwave spectra of $\text{H}_2\text{O}$, $\text{O}_3$, $\text{CO}$, and $\text{N}_2\text{O}$. The microwave spectra of $\text{ClO}$, $\text{O}_2$ and $\text{NH}_3$ involve some additional interactions, which are discussed in Sections 2.2.10–2.2.12.

### 2.2.2 Energy Levels and Wave Functions of a Rigid Rotor

Let us consider the rotational Hamiltonian [1, p. 48]:

$$H_{\text{rot}} = \frac{P_x^2}{2I_x} + \frac{P_y^2}{2I_y} + \frac{P_z^2}{2I_z}$$

in which $I_x$, $I_y$, and $I_z$ are the moments of inertia along the directions of the principal axes of the body (i.e., the principal axes of the ellipsoid of inertia), and $P_x$, $P_y$, and $P_z$ are the corresponding components of the angular-momentum operator. The operator representing the square of the total angular momentum has eigenvalues $J(J + 1)\hbar^2$, where $J$ is a nonnegative integer. The component of the angular-momentum operator along a direction fixed in space has eigenvalues $M\hbar$, with $M$ an integer such that $-J \leq M \leq J$ [10, p. 10].

As simple as Eq. 2.4 appears, the solution of Schrödinger's equation with $H = H_{\text{rot}}$ is possible in closed form only for the special case where two of the principal moments of inertia are equal. These solutions are the symmetric-top wave functions. Their importance lies not in being exact wave functions for any particular molecule, but rather because they provide a basis in terms of which the rotational wave functions of any molecule can be expanded. The symmetric-top wave functions are distinguished by the quantum numbers $J$, $M$, and a third quantum number $K$, where $K\hbar$ is the projection of the angular momentum on the axis of symmetry. $K$ must be an integer satisfying $-J \leq K \leq J$. The wave functions are of the form [5, p. 120; 9, p. 275].

$$\psi_{JKM} = \Theta_{JKM}(\theta)e^{iM\phi}e^{iKx}$$

where the functions $\Theta_{JKM}$ are related to the hypergeometric function; $\theta$ and $\phi$ are the polar and azimuthal angles, respectively, which specify the orientation of the axis of symmetry with respect to a set of space-fixed axes; and $\chi$ measures the angle of rotation of the top about its axis of symmetry; $\theta$, $\phi$, and $\chi$ are known as the Euler angles [10, p. 6].

If $z$ is the symmetry axis, then $I_x = I_y$ and $H_{\text{rot}}$ can be written as $(P^2 - P_z^2)/2I_x + P_z^2/2I_z$, where $P^2$ is the square of the total angular momentum. The eigenvalues of $H_{\text{rot}}$ for the symmetric top are, therefore,

$$E_{\text{rot}} = \hbar[BJ(J + 1) + (A - B)K^2]$$

where

$$A = \frac{\hbar}{8\pi^2I_z}$$

(2.7a)
are rotational constants with dimensions of frequency. In the absence of any interaction (as with a magnetic field) that would establish a preferred direction in space, the energy levels do not depend on \( M \). Furthermore, \( E_\text{rot} \) is unaltered by reversing the sign of \( K \); thus, each energy level with \( K \neq 0 \) has a degeneracy factor of \( 2(2J + 1) \), and the \( K = 0 \) levels are \( (2J + 1) \)-fold degenerate.

When \( I_z \) is smaller than \( I_x \) and \( I_y \), the symmetric top is described as prolate; when \( I_z \) is larger, it is oblate. The extreme case of a prolate top is a linear molecule, for which the third principal moment of inertia approaches zero. Then \( A \) approaches infinity, with the consequence that linear molecules must have \( K = 0 \). Prolate and oblate symmetric tops share the same set of wave functions, but differ in the coefficient of the \( K^2 \) term in Eq. 2.6 and, therefore, in their energy-level structure. For a given \( J \), the general prolate top has energies increasing with \( |K| \); for oblate tops, the \( |K| \) dependence is reversed.

The planar molecules \( \text{H}_2\text{O} \) and \( \text{O}_3 \) are asymmetric rotors in the sense of having no two principal moments of inertia equal. The rotational constant \( C = \hbar / 8\pi^2 I_y \) is defined along with those in Eqs. 2.7a and b, and the axes are conventionally chosen so that \( A > B > C \). The degree of asymmetry can be characterized by Ray's parameter,

\[
\kappa = \frac{2B - A - C}{A - C}
\]  

which ranges from \(-1\) for prolate symmetry to \(+1\) for oblate symmetry. For water, \( \kappa = -0.49 \); ozone, only slightly asymmetric, has \( \kappa = -0.97 \).

If one imagines a prolate top being slowly deformed into an oblate top so that \( \kappa \) varies continuously from \(-1\) to \(1\), the energies of the quantum states also vary in a continuous manner, as illustrated in Fig. 2.1[11]. However, the projection of angular momentum on the \( z \)-axis (or any molecule-fixed axis) is not a constant of the motion for an asymmetric rotor and \( K \), therefore, is no longer a good quantum number. The energy levels nevertheless can be labeled by \( J \) and the two values of \( |K| \) to which they connect in the limiting cases: these are designated \( K_-1 \) and \( K_1 \).

Figure 2.1 shows the energy levels of different values of \( J \) as separated, for the sake of clarity. However, the level spacing depends on the rotational constants of the molecule, and levels with different \( J \)'s will be interleaved as \( J \) increases. This situation gives rise to the rich and complicated rotational spectra of asymmetric molecules.

The rotational wave function for an asymmetric rotor can be expanded in terms

\*Another method of labeling the levels is \( J_\tau \), where the subscript is an integer, \(-J \leq \tau \leq J\), increasing with energy. The two types of subscripts are related by \( \tau = K_-1 - K_1 \).
Figure 2.1. The energy levels of a rigid rotor for $J = 0$ to 3, as a function of Ray's asymmetry parameter $\kappa$. The vertical spacing of levels depends on the rotational constants.

of symmetric-top wave functions:

$$\psi_{\text{rot}} = \sum_{K} a_{JK} \psi_{JKM}$$  \hspace{1cm} (2.9)$$

where the coefficients $a_{JK}$ depend on which axis of the molecule is defined to be the $z$-axis [1, p. 95]. If the axis having the least moment of inertia is chosen, the expansion is termed prolate; if the axis with the greatest moment of inertia is chosen, it is oblate. A rotation by $180^\circ$ about the $z$-axis changes $\psi_{JKM}$, Eq. 2.5, by the factor $\exp(i\pi K) = (-1)^K$; thus, it is symmetric or antisymmetric as $K$ has even or odd parity, respectively.

Even for an asymmetric rotor, the ellipsoid of inertia is invariant under a $180^\circ$ rotation about any of the three principal axes. The rotational Hamiltonian given
by Eq. 2.4 is specified by the principal moments of inertia, so the effect of this rotation on \( \psi_{\text{rot}} \) can be only to multiply it by a constant factor \( c \). Two 180° rotations about the same axis are equivalent to no rotation. Thus, \( c^2 = 1 \) and \( c = \pm 1 \); that is, \( \psi_{\text{rot}} \) must be either a symmetric or antisymmetric wave function. Hence, the expansion (Eq. 2.9) will contain terms of only even \( K \) or only odd \( K \), and their parity will be the same as \( K_{-1} \) if the expansion is prolate, or the same as \( K_1 \) if it is oblate. Consequently, \( \psi_{\text{rot}} \) is multiplied by \((-1)^{K_{-1}}\) for a 180° rotation about the axis of least moment of inertia, and by \((-1)^{K_1}\) for a 180° rotation about the axis of greatest moment of inertia. The symmetry of \( \psi_{\text{rot}} \) under a 180° rotation about the intermediate axis must then be the same as for a combination of rotations about the other two, because successive 180° rotations about three orthogonal axes return an object to its original position. These symmetry properties are summarized in Table 2.1; they will be used in the discussion of statistical weights and selection rules.

The symmetry properties of linear rotor wave functions can be inferred from Figure 2.1 and Table 2.1 if we recall that a linear molecule is a prolate rotor having \( K_{-1} = 0 \). Inspection of Figure 2.1 shows that in the \( J_{K_{-1}K_1} \) designation system, the linear rotor wave functions are \( J_0 \); thus, they are symmetric in a 180° rotation about either the \( b \)- or \( c \)-axis (i.e., an end-for-end interchange) if \( J \) is even, and antisymmetric if \( J \) is odd.

This section has described rotating rigid bodies. Real molecules are not rigid, and their moments of inertia depend on their rotational and vibrational states. Accurate calculation of line frequencies generally requires the inclusion of terms in the Hamiltonian to account for centrifugal stretching [12–15]. Vibrational and centrifugal distortion of symmetric-top molecules lowers their symmetry and tends to remove the twofold degeneracy associated with the quantum number \( |K| \) for a rigid symmetric top. Section 2.2.12 discusses vibration in connection with the microwave spectrum of \( \text{NH}_3 \).

### Table 2.1 Symmetry Properties and Nuclear Spin Degeneracies of Rotational Levels

<table>
<thead>
<tr>
<th>Parity of ( K_{-1} )</th>
<th>Symmetry of Rotational Wave Function with Respect to 180° Rotation about Axis*</th>
<th>Statistical Weight due to Nuclear Spin</th>
</tr>
</thead>
<tbody>
<tr>
<td>( e^b )</td>
<td>( e )</td>
<td>( 1 )</td>
</tr>
<tr>
<td>( o^b )</td>
<td>( o )</td>
<td>( -1 )</td>
</tr>
<tr>
<td>( e )</td>
<td>( o )</td>
<td>( 1 )</td>
</tr>
<tr>
<td>( o )</td>
<td>( e )</td>
<td>( -1 )</td>
</tr>
</tbody>
</table>

*Axis \( a \) has the least moment, axis \( b \) the intermediate, moment, and axis \( c \) the greatest moment of inertia.

*\( e \), even; \( o \), odd.
2.2.3 Degeneracies Due to Nuclear Spin

In molecules whose nuclei have nonzero spin, coupling of the spin with the rotational or electronic angular momentum leads to hyperfine splitting of the rotational energy levels. In the approximation that hyperfine splitting is negligible, the resulting degeneracy becomes a factor in the statistical weight of each level, and also in the associated line intensities.

If there are two or more equivalent nuclei (i.e., nuclei of the same isotope and situated in equivalent positions) in a molecule, the quantum statistics of these nuclei produce consequences for its line spectrum. Nuclei of even mass number, and consequently having integer spin, obey Bose–Einstein statistics, which means that the total wave function $\psi = \psi_{\text{elec}}\psi_{\text{vib}}\psi_{\text{rot}}\psi_{\text{nuc}}$ must be symmetric with respect to an operation that interchanges two equivalent nuclei. Nuclei of odd mass number (thus having half-integer spin) obey Fermi-Dirac statistics, which require that $\psi$ be antisymmetric in the same type of operation [9, p. 402]. Rotational wave functions of different symmetries, therefore, must be combined with nuclear-spin wave functions of the appropriate symmetry to make the total wave function either symmetric or antisymmetric, as required. The details of how this occurs depend on the molecule and are therefore deferred to the sections describing individual molecules (e.g., 2.2.6, 2.2.7, 2.2.11, and 2.2.12). However, the result is that rotational states of different symmetry will have unequal statistical weights in molecules with equivalent nuclei.

2.2.4 Selection Rules for Rotational Transitions

If there is no interaction between molecules, the quantum states in Eq. 2.1 become products of states of isolated molecules. The dipole moments of different molecules are then uncorrelated, so

$$|\mathcal{M}_{ab}|^2 = nV|\mu_{ab}|^2$$

(2.10)

where $n$ is the number density of molecules, and $\mu$ is the dipole moment of a single molecule, resulting from the nuclear and electronic charge distributions.

Let us consider the case where $a$ and $b$ denote different rotational states. The orientation of a molecule with respect to a set of space-fixed axes can be specified by the three Euler angles, $\theta$, $\phi$, and $\chi$. The component of $\mu$ along any space-fixed axis, for example, $\mu_Z$, is determined by the cosine of an appropriate angle, so it is an operator on the rotational wave functions, and $\mu$ is, therefore, a vector operator. The matrix element of $\mu^Z$ linking states $a$ and $b$ can be equated to an integral of the form

$$\mu_{ab} = \mu \int \int \psi_a^*(\theta, \phi, \chi) \cos \beta \psi_b(\theta, \phi, \chi) d(\cos \theta) d\phi d\chi$$

(2.11)

where $\beta$ is the angle between the dipole moment and the space-fixed Z-axis (if the dipole moment is used to define the molecule's z-axis, then $\beta = \theta$), and $\mu$ is the magnitude of the dipole moment.
The function $\cos \beta$ is antisymmetric under an operation that reverses the direction of the dipole moment. For example, if $\mathbf{\mu}$ is parallel to the $b$-axis of the molecule, as is the case for $\text{H}_2\text{O}$ and $\text{O}_3$, then rotation by $180^\circ$ about either the $a$- or $c$-axes is such an operation. However, we have already seen that the rotational wave functions are either symmetric or antisymmetric for a $180^\circ$ rotation about a principal axis of the molecule. If $\psi_a$ and $\psi_b$ both have the same symmetry, then the integral in Eq. 2.11 will yield zero. The same statement evidently applies to all three components $\mu_{ab}^\alpha$ because the definition of the $Z$-direction in space is arbitrary. In order to have a nonzero matrix element, $\psi_a$ and $\psi_b$ must have opposite symmetry for rotation about either of the two axes perpendicular to the dipole moment, if it is parallel to one of the principal axes. If this is the $b$-axis, then Table 2.1 shows that the dipole-moment matrix element linking two states will be nonzero only for transitions of the types $ee \leftrightarrow oo$ or $eo \leftrightarrow oe$. Selection rules for dipole moments parallel to the $a$- or $c$-axis can be obtained from the table in the same way.

If a $180^\circ$ rotation about one of the principal axes of a molecule has the sole effect of interchanging two equivalent nuclei, then that axis must contain the electric dipole moment (if the molecule has one). Inspection of Table 2.1 shows that the symmetry properties of any two wave functions are the same with respect to rotation about the axis containing the dipole moment if they are simultaneously opposite with respect to rotations about the other two axes. Hence, the statistical weights due to nuclear spin of the two states in a radiating transition are equal. This statement is true in general of molecules containing equivalent nuclei [5, p. 138; 6, p. 55].

The $\theta$ variation of a symmetric-top wave function, where $\theta$ is the angle between the molecule’s $z$-axis and the space-fixed $Z$-axis, is given by a function $\Theta_{JKM}(\theta)$. The orthogonality properties of these functions, when combined in integrals such as Eq. 2.11, are such that any dipole-moment matrix element can be nonzero only if $|J_a - J_b| \leq 1 \leq J_a + J_b$ [3, p. 29], where $J_a$ and $J_b$ are the quantum numbers for total angular momentum of the two states. Because asymmetric rotor wave functions can be expressed by Eq. 2.9, where the sum involves $\psi_{JKM}$ all with the same $J$, this selection rule applies to rotational wave functions for all molecular shapes.

### 2.2.5 Line Intensities

For computational purposes, it is generally useful to rewrite Eq. 2.1 in the form

$$\alpha(\nu) = n \sum_{f,i} S_{fi}(T) F(\nu, \nu_{fi})$$

(2.12)

where $\alpha(\nu)$ is the power-absorption coefficient due to a specified molecular species, $n$ is the number of molecules of this species per unit volume, $f$ and $i$ denote energy levels of an isolated molecule, $S_{fi}(T)$ is the intensity at temperature $T$ of a single line for a single molecule, and $F(\nu, \nu_{fi})$ is a line-shape function normalized in such a way that $F(\nu, \nu_{fi}) \to \delta(\nu - \nu_{fi})$ for isolated molecules. (Line shapes are
discussed in Sections 2.3 and 2.4.) As written, the summation in Eq. 2.12 extends over all combinations of \( f \) and \( i \), thus including line frequencies \( \nu_f = (E_f - E_i) / h \) that are negative as well as positive; but more often, one would restrict the summation to positive line frequencies and include the negative-resonant term in \( F(\nu, \nu_f) \) (if necessary, in the pressure range of interest). The summation then need include only those lines that contribute to the frequency range of interest.

Making use of the ideal gas law, one has

\[
n = \frac{aP}{kT}
\]

where \( P \) is the partial pressure of the absorbing gas, and \( a \) is the fractional abundance of the specified isotopic variant of the molecule. Isotopic substitutions in a molecule alter the transition frequencies because of the different masses of the nuclei. When more than one absorbing species is present, the total absorption coefficient is given by the sum of absorption coefficients for each species.

The line intensity consistent with Eqs. 2.1, 2.10, and 2.12 is

\[
S_{\nu_f}(T) = \frac{8\pi^3 \nu_f^2 (\mu_{\nu_f})^2}{3hcQ(T)} g_i \left( e^{-E_i/kT} - e^{-E_f/kT} \right)
\]

\[
= \frac{16\pi^3 \nu_f^2 (\mu_{\nu_f})^2}{3hcQ(T)} g_i \sinh \left( \frac{h\nu_f}{kT} \right) e^{-\frac{(E_f + E_i)}{2kT}}
\]

in which a Maxwell-Boltzmann distribution of state occupation probabilities (implying local thermodynamic equilibrium) has been used; \( g_i \) is the statistical weight due to nuclear spin for level \( i \),

\[
Q(T) = \sum_i g_i (2J_i + 1) e^{-E_i/kT}
\]

is the internal partition function; and \( \mu_{\nu_f} \) is the reduced (meaning that it does not depend on the orientational quantum numbers \( M \)) matrix element, between levels \( f \) and \( i \), of the molecular dipole moment, measured in esu·cm for an electric dipole or erg/gauss for a magnetic dipole. \((\mu_{\nu_f})^2 \) is equal to the sum of the squared magnitudes of matrix elements over the degenerate orientational states of levels \( f \) and \( i \) and also over the three spatial components \( \sigma \) [10, p. 76]. We note that \( |\mu_{\nu_f}| = |\mu_f| \) and \( g_i = g_f \) (see Section 2.2.4).

When \( \nu_f \) (GHz) < 10\( T \) (Kelvin), Eq. 2.14 is approximated within 1\% by

\[
S_{\nu_f}(T) = \frac{8\pi^3 \nu_f^2 (\mu_{\nu_f})^2}{3ckTQ(T)} e^{-\frac{(E_f + E_i)}{2kT}}
\]

If one has a table (as in the Appendix to Chapter 2) of line intensities at a specified temperature \( T_0 \) along with the associated energy levels, then \( S_{\nu_f}(T) \) can be com-
2.2 ENERGY LEVELS AND LINE SPECTRA OF ISOLATED MOLECULES

puted as

\[ S_f(T) = S_f(T_0) \frac{T_0 Q(T_0)}{T Q(T)} \exp \left[ \frac{E_f + E_i}{2kT_0} \left( 1 - \frac{T_0}{T} \right) \right] \]  \hspace{1cm} (2.17)

provided that one knows the temperature dependence of \( Q \). Generally, \( Q(T) \) can be separated as [6, p. 503]

\[ Q(T) = Q_{\text{elec}}(T) Q_{\text{vib}}(T) Q_{\text{rot}}(T) \]  \hspace{1cm} (2.18)

For asymmetric (\( \text{H}_2\text{O}, \text{O}_3 \)) or symmetric-top molecules (\( \text{NH}_3 \)), a good approximation to the temperature dependence of \( Q_{\text{rot}} \) is [6, p. 505]

\[ \frac{Q_{\text{rot}}(T)}{Q_{\text{rot}}(T_0)} = (T/T_0)^{3/2} \]  \hspace{1cm} (2.19)

Linear molecules (\( \text{O}_2, \text{N}_2\text{O}, \text{CO}, \text{ClO} \)) have fewer rotational states, and in this case [6, p. 505],

\[ \frac{Q_{\text{rot}}(T)}{Q_{\text{rot}}(T_0)} = \frac{T}{T_0} \]  \hspace{1cm} (2.20)

For most molecules, the excited electronic states lie so high in energy that \( Q_{\text{elec}} \) is very nearly unity. The only exception among the molecules treated here is \( \text{ClO} \), for which

\[ Q_{\text{elec}}(T) = 1 + \exp \left( -\frac{E_e}{kT} \right) \]  \hspace{1cm} (2.21)

with \( E_e/k = 458 \text{ K} \) [16].

Using a harmonic oscillator model [6, p. 503],

\[ Q_{\text{vib}}(T) = \prod_v \left[ 1 - \exp \left( -\hbar \omega_v/kT \right) \right]^{-d_v} \]  \hspace{1cm} (2.22)

where \( \omega_v \) is the fundamental frequency of the \( v \)th mode of vibration (e.g., a diatomic molecule has one mode of vibration), and \( d_v \) is usually 1 but may be 2 if a vibrational mode is degenerate, as is the bending mode of \( \text{N}_2\text{O} \). (Temperature equivalents of the vibrational frequencies are listed in footnotes to the line tables in the Appendix to this chapter.) In \( \text{O}_2, \text{CO}, \text{ClO}, \text{H}_2\text{O}, \) and \( \text{NH}_3 \), \( Q_{\text{vib}} \) can be well approximated by unity at temperatures encountered in the terrestrial atmosphere. In \( \text{O}_3 \) and \( \text{N}_2\text{O} \), only the lowest-energy mode of vibration, the bending mode, need be included in Eq. 2.22 at temperatures up to \( \sim 300 \text{ K} \).

2.2.6 Rotational Spectrum of Ozone

The three nuclei in \( ^{16}\text{O}_3 \) form an angle of 117°. The two outer nuclei are in equivalent positions. These nuclei obey Bose–Einstein statistics, so the total wave func-
tion must be symmetric with respect to an operation that interchanges the outer nuclei. This operation can be represented as the product of two rotations. The first is a rotation of the entire molecule by 180° about the axis passing through the central nucleus and equidistant from the two outer nuclei, in the plane of the molecule. (This axis is the one having an intermediate moment of inertia.) The second rotation, of the electrons with respect to the nuclei, returns the electrons to their original positions. $\psi_{\text{elec}}$ is a function of the coordinates of the electrons relative to the nuclei, so it is uninfluenced by the first rotation. The ground state $\psi_{\text{elec}}$ is symmetric with respect to the second rotation. $\psi_{\text{vib}}$ is a function of the relative coordinates of the nuclei and, therefore, is unchanged by either rotation. The $^{16}\text{O}$ nuclei have zero spin, so there is only one possible $\psi_{\text{nuc}}$, and it is symmetric. Thus, $\psi_{\text{rot}}$ must also be symmetric with respect to rotation by 180° about the $b$-axis.

Table 2.1 shows that this condition is satisfied only in states where $K$ and $K_1$ have the same parity; these are the only possible rotational states for the ground electronic state of $^{16}\text{O}_3$. Numerous microwave transitions occur between these states.

We note in passing that the foregoing statements also apply to $^{32}\text{S}_2$, in which sulfur is substituted for the central atom.

### 2.2.7 Rotational Spectrum of Water Vapor

In $\text{H}_2\text{O}$, the oxygen nucleus lies at the vertex of a 105° angle formed with the hydrogen nuclei, which thus are in equivalent positions. Protons obey Fermi-Dirac statistics, so the total wave function $\psi$ must be antisymmetric with respect to the interchange of the hydrogen nuclei. As in the previous section, this operation involves a 180° rotation about the axis with intermediate moment of inertia. The ground-state electronic wave function is symmetric, so the antisymmetry of $\psi$ depends on $\psi_{\text{rot}}$ and $\psi_{\text{nuc}}$.

Let us consider the symmetry properties of $\psi_{\text{nuc}}$ for $\text{H}_2^{16}\text{O}$. The $^{16}\text{O}$ nucleus has zero spin. Each hydrogen nucleus has spin quantum number $= \frac{1}{2}$, and the component of the spin operator along an axis fixed in space has eigenvalue $\pm \frac{1}{2}h$. The wave functions associated with these two eigenvalues will be denoted by $\sigma^+\text{ and } \sigma^-\text{, and the nucleus to which the wave function pertains will be indicated by a subscript 1 or 2. The space of possible wave functions for }\psi_{\text{nuc}}\text{ thus has four dimensions. The subspace of symmetric spin wave functions is three-dimensional and is spanned by the three wave functions }$

$$
\psi_{\text{nuc}} = \begin{cases} 
\sigma_1^+ \sigma_2^+ \\
\sigma_1^+ \sigma_2^+ \text{ or } \\
2^{-1/2}(\sigma_1^+ \sigma_2^- + \sigma_1^- \sigma_2^+) 
\end{cases} 
$$

The subspace of antisymmetric spin wave functions is one-dimensional, with

$$
\psi_{\text{nuc}} = 2^{-1/2}(\sigma_1^+ \sigma_2^- - \sigma_1^- \sigma_2^+) 
$$

(2.24)
To obtain a total wave function $\psi$ that is antisymmetric with respect to the interchange of the hydrogen nuclei, the symmetric $\psi_{\text{nuc}}$ (Eq. 2.23) must combine with the $\psi_{\text{rot}}$ that are antisymmetric about the axis with an intermediate moment of inertia ($b$-axis); as shown in Table 2.1, these are the rotational states for which $K_{-1}$ and $K_1$ are of opposite parity. The antisymmetric $\psi_{\text{nuc}}$ (Eq. 2.24) combines with the rotational states that are symmetric about the $b$-axis: $K_{-1}$ and $K_1$ having the same parity.

Because of the small moments of inertia of water vapor, most of its strong rotational transitions lie at submillimeter and infrared wavelengths. The two important microwave transitions are at 22.235 and 183.310 GHz. The first of these occurs between nuclear spin triplets of the type (Eq. 2.23) and its splitting is approximately 400 kHz [16a]; the second is between singlet spin states of the type (Eq. 2.24).

Water vapor also has a continuum absorption, which will be described in Section 2.4.3.

### 2.2.8 Rotational Spectrum of Carbon Monoxide

Carbon monoxide (CO) is a linear molecule, so its rotational energy levels are specified by the first term on the right side of Eq. 2.6. The frequency of a transition from $J$ to $J + 1$ is $2B(J + 1)$, which produces a spectrum of lines at integer multiples of 115.3 GHz.

### 2.2.9 Rotational Spectrum of Nitrous Oxide

Nitrous oxide has the linear structure N-N-O. The two nitrogen nuclei are not in equivalent positions, so rotation of the molecule does not interchange them. Hence, all rotational levels have the same statistical weight due to nuclear spin.

Rotational transitions lie at integer multiples of $2B = 25.1$ GHz, in the ground vibrational state. In excited vibrational states, interaction between vibrational and rotational motion produces a splitting of levels that is called $l$-type doubling [3, p. 128]; however, the weaker microwave lines associated with excited states have not yet been observed in the atmosphere.

### 2.2.10 Rotational Spectrum of Chlorine Monoxide

The electronic state of lowest energy for most molecules is one in which the electrons are paired (the two electrons of a pair have the same quantum numbers except for opposite spins) and in which their orbital angular momenta sum to zero. However, the ClO radical possesses an odd number of electrons and thus has a net electronic-spin angular momentum with quantum number of $\frac{1}{2}$. Furthermore, the ground electronic state is one with orbital angular momentum. In a diatomic molecule, the electrons move in an axially symmetric potential, so they encounter no torque about the internuclear axis. The projection of the orbital angular momentum on that axis is, therefore, a constant of their motion and is characterized by a
quantum number $\Lambda$. In the ground state of ClO, $\Lambda = 1$. The electronic orbital angular momentum perpendicular to the axis is not constant.

The electronic spin and orbital motion, and the rotation of the molecule as a whole, generate magnetic fields. Interactions between these fields couple the various angular momenta and separate the energies of states that would otherwise be degenerate. Hund classified the possible types of coupling into five cases, according to the predominant interactions [1, p. 177]. The wave functions and associated quantum numbers apply to a given molecule to the extent that it approximates one of these pure cases.

In ClO, the strongest coupling is that of the electronic spin to the orbital angular momentum along the internuclear axis. This is Hund’s case (a). The component of electronic spin along the axis has the possible values $\pm \frac{1}{2} \hbar$. The sum of orbital and spin angular momenta along the axis is given the quantum number $Q$. The ground state has $Q = \frac{1}{2}$; the $Q = \frac{3}{2}$ state is slightly higher in energy and, therefore, is included in the electronic partition function, Eq. 2.21.

The electronic angular momentum then adds vectorially to the rotational angular momentum of the molecule, forming a resultant with quantum number $J$. The relation between this resultant angular momentum and its projection $Q\hbar$ on the internuclear axis is the same as in a symmetric top, so an expression of the form given by Eq. 2.6, with $Q$ replacing $K$, is valid for the associated rotational energy. However, $Q$ is constant in a given electronic state, so it is more appropriate to regard the second term of this expression as part of the electronic energy and to write

$$E_{\text{rot}} = \hbar BJ(J + 1)$$

(2.25)

as usual for a linear molecule. Because $J$ cannot be smaller than its projection on the internuclear axis, it has the possible values $\frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \ldots$, in the ground state of ClO. Transitions between levels $J$ and $J + 1$ then give rise to lines at frequencies

$$\nu_{J + 1, J} = 2B(J + 1)$$

(2.26)

which are spaced at intervals of $2B = 37.2$ GHz [13].

The preceding discussion gives an approximate description of the rotational spectrum of ClO. A more precise description must include the interaction between the magnetic moment associated with the spin of the chlorine nucleus and the magnetic fields generated by the electrons [13]. The nuclear electric quadrupole moment also interacts with the electric-field gradient at the nucleus [13]. These weaker interactions cause the hyperfine splitting of energy levels, which in ClO is $\ll 100$ MHz. The levels are distinguished by different values of the total angular momentum, which is the resultant of $J$ and the chlorine nuclear spin. This total angular momentum has quantum number $F$, with $J - \frac{3}{2} \leq F \leq J + \frac{3}{2}$. (Both $^{35}$Cl and $^{37}$Cl have nuclear spin of $\frac{3}{2}$.) Hence, for each value of $J$, there are four levels, each with a different $F$ value. Transitions between different levels have the usual
2.2 ENERGY LEVELS AND LINE SPECTRA OF ISOLATED MOLECULES

Figure 2.2. Energy-level diagram and hyperfine structure of the \( J = \frac{3}{2} \) to \( J = \frac{5}{2} \) rotational transition in the ground state of \( ^3\text{Cl}^{16}\text{O} \) [14].

dipole-moment selection rules: \( \Delta F = 0, \pm 1 \). Thus, each of the lines corresponding to Eq. 2.26 is split into nine components, as shown in Figure 2.2 for the \( J = \frac{3}{2} \) and \( \frac{5}{2} \) levels.

Although the component of electronic orbital angular momentum perpendicular to the internuclear axis is not constant, its magnetic interaction with the rotational angular momentum causes a further splitting of the energy levels known as \( \Lambda \)-type doubling [5, p. 226]. In the ground state of ClO, this splitting is \( \leq 1 \) MHz [17]. The electronic angular momentum will interact with an external magnetic field, producing Zeeman splitting [18]. In the Earth's magnetic field, this effect is \( \sim 1 \) MHz for the \( J = \frac{3}{2} \) to \( \frac{5}{2} \) transitions, and it decreases with increasing \( J \). These line splittings do not appear to be significant in the context of observations of ClO in the terrestrial atmosphere.
2.2.11 Spin-Rotation Spectrum of Oxygen

The ground electronic state of \( \text{O}_2 \) is one in which the orbital angular momentum averages to zero, but there are two unpaired electron spins [19]. The magnetic fields associated with the electron spins interact with each other and with the magnetic field generated by rotation of the molecule. The total spin angular momentum, with a quantum number of 1, adds vectorially to the rotational angular momentum, which is given the quantum number \( N \), to form a resultant angular momentum with quantum number \( J \), where \( J = N - 1 \), \( N \), or \( N + 1 \). This is Hund’s coupling case (b) [1, p. 178].* The energies of the states with \( J = N \) are given in the rigid rotor approximation by

\[
E_{J=N} = hBN(N + 1)
\]

(2.27)

with \( B = 43.1 \) GHz [15]. The states with \( J = N - 1 \) and \( J = N + 1 \) are lower in energy by amounts that, with one exception (at 118.75 GHz), are on the order of \( h \cdot 60 \) GHz. Because the coupling between spin and rotational angular momentum is rather weak, both \( N \) and \( J \) are needed to specify an energy level. For example, the state with \( J = 2 \), \( N = 1 \) differs in energy from the state with \( J = 2 \), \( N = 3 \) by \( h \cdot 425 \) GHz.

The ground-state electronic wave function of \( ^{16}\text{O}_2 \) is antisymmetric with respect to the interchange of the nuclei. This antisymmetry is not affected by the electron-spin orientation in a Hund’s case (b) molecule [5, p. 238]. The nuclear spin is zero, and thus the Bose–Einstein requirement for symmetry of the total wave function is met only by antisymmetric rotational wave functions, which are those with odd values of the rotational quantum number \( N \) (see Section 2.2.2).

The magnetic moment associated with each of the unpaired electrons has a magnitude slightly greater than one Bohr magneton \( \mu_B \) and is antiparallel to the spin. The total magnetic moment \( \mu \) of \( \text{O}_2 \) (which is essentially due to the electron spins) will interact with an external magnetic field \( \mathbf{B} \) and split the energies of states with different values of the quantum number \( M \), which would otherwise be degenerate. This is the Zeeman effect. The term of the Hamiltonian corresponding to this interaction is [1, p. 284; 21]

\[
H_{\text{mag}} = -\mu \cdot \mathbf{B} = 2.00229\mu_B S \cdot \mathbf{B}
\]

(2.28)

where \( S \) is the spin operator measured in units of \( h \). We shall consider the case in which \( \mathbf{B} \) is less than a few hundred gauss, so that \( H_{\text{mag}} \) represents a small perturbation of the Hamiltonian. Then a good approximation to the energy levels can be obtained by adding the diagonal matrix elements of \( H_{\text{mag}} \) to the energy levels of the Hamiltonian without magnetic field. A diagonal element of \( H_{\text{mag}} \) is equivalent to the time average of the interaction energy (which is proportional to the electron spin) in one of the states described by a Hund’s case (b) wave function. The cou-

*The eigenfunctions for oxygen differ slightly from the ideal case (b), with a resulting modification in the microwave line strengths of \( \leq 2\% \) [20].
pling between spin and rotational angular momentum in Hund's case (b) forces the spin vector to precess about the total angular-momentum vector, which then precesses much more slowly about the external magnetic field. The interaction energy Eq. 2.28 is therefore obtained by first projecting the spin onto the total angular momentum and then taking the component of this projection along the external magnetic field [1, p. 286]. Figure 2.3 shows the energy levels for the states with $N = 3$ and $J = 3, 4$. When $J = N$, the rotational angular momentum, the spin, and their resultant form an isosceles triangle, so that the projection of the spin on the total angular momentum is smaller than for the states with $J = N \pm 1$, though not zero.

Oxygen has no permanent electric dipole moment, but it will interact with an electromagnetic wave by means of its magnetic dipole. This interaction is much weaker than that of a typical molecular electric dipole, but the great abundance of oxygen in the atmosphere compensates for the intrinsic weakness of its absorption. Selection rules for magnetic-dipole matrix elements differ in one respect from those for electric dipoles, which were described in Section 2.2.4. Because of its association with angular momentum, a magnetic-dipole moment is an even operator, in contrast to an electric-dipole moment, which is fixed in the molecule and is therefore an odd operator [22]. The magnetic-dipole moment has a nonzero matrix element only between two oxygen wave functions that are both symmetric or both antisymmetric.

![Figure 2.3](image-url)

Figure 2.3. Energy-level diagram for the $N = 3, J = 3, 4$ states of $O_2$ [23].
The selection rules with respect to angular momentum quantum numbers are

\[ |\Delta J| \leq 1 \leq J + J' \]  

(2.29a)

and

\[ |\Delta M| \leq 1 \]  

(2.29b)

(The latter rule is of observational consequence only in the Zeeman effect.) These selection rules permit transitions between the levels \( J = N \) and \( J = N + 1 \) (which, conventionally, are designated as \( N^+ \) lines), between \( J = N \) and \( J = N - 1 \) (designated \( N^- \)), or within a given \((J, N)\) level (except the \( J = 0, N = 1 \) level). Transitions between levels \( J = N - 1 \) and \( J = N + 1 \) are prohibited. Transitions between levels with different \( N \) and \(|\Delta J| \leq 1 \) are possible, but these produce lines at submillimeter wavelengths \([20, 23]\).

Transitions with \( \Delta J = \pm 1 \) for which \( \Delta M = 0 \) are known as \( \pi \) components and those for which \( \Delta M = \pm 1 \) are \( \sigma^\pm \) components. Table 2.2 gives the frequency displacements, with respect to the unsplit resonant frequency, for the possible Zeeman components as a function of \( N \) and \( M \), the quantum numbers for the upper \((J = N)\) levels of the oxygen lines. The limits on possible values of \( M \) are set by the smaller of the two values of \( J \) involved in a transition; hence, the different limits for \( N^- \) lines. Table 2.3 gives the intensities of each component, referenced to the unsplit oxygen line intensities listed in Appendix 2A. Figure 2.4 shows the spectrum of Zeeman components for the \( 3^+ \) line in a field of 0.5 gauss (typical for midlatitudes). Lines with higher \( N \) have more components, but they are more closely spaced, giving approximately the same maximum splitting.

If the observation frequency is displaced from a line center by more than \( \sim 6 \) MHz, or if the entire propagation path lies at pressures of more than a few millibars, the Zeeman splitting of an oxygen line can safely be ignored in a radiative transfer calculation for the terrestrial atmosphere. If the observation includes the core of a line formed at low pressures, however, it is necessary to consider the Zeeman effect. In this case, absorption and emission depend on the angle between

| TABLE 2.2 Frequency Shifts of \( \text{O}_2 \) Zeeman Components from Line Center \([23]^a\) |
|-----------------|-----------------|
| \( \Delta M \)   | \( N^+ \) lines   | \( N^- \) lines   |
| 0               | \(-a\Delta C \frac{M(N - 1)}{N(N + 1)},\) for \(|M| \leq N\) | \(a\Delta C \frac{M(N + 2)}{N(N + 1)},\) for \(|M| \leq N - 1\) |
| \( \pm 1 \)      | \(-a\Delta C \frac{M(N - 1) \pm N}{N(N + 1)},\) for \(|M| \leq N\) | \(a\Delta C \frac{M(N + 2) \pm (N + 1)}{N(N + 1)},\) for \(|M \pm 1| \leq N - 1\) |

\(^a a = 2.8026 \text{ MHz/gauss}. \Delta C = \text{external magnetic field strength}. M = \text{orientational quantum number for the } J = N \text{ level}.\)
2.2 ENERGY LEVELS AND LINE SPECTRA OF ISOLATED MOLECULES

<table>
<thead>
<tr>
<th>ΔM</th>
<th>( N+ ) lines</th>
<th>( N- ) lines</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \frac{3[(N+1)^2 - M^2]}{(N+1)(2N+1)(2N+3)} )</td>
<td>( \frac{3(N^2 - M^2)}{N(2N-1)(2N+1)} )</td>
</tr>
<tr>
<td>±1</td>
<td>( \frac{3(N \pm M + 1)(N \pm M + 2)}{4(N+1)(2N+1)(2N+3)} )</td>
<td>( \frac{3(N \mp M)(N \mp M - 1)}{4N(2N-1)(2N+1)} )</td>
</tr>
</tbody>
</table>

Table 2.3: Intensities of O₂ Zeeman Components, Relative to Unsplit Lines [23]

the terrestrial magnetic field and the direction of propagation of the electromagnetic wave, and on its polarization [24, 24a]. Furthermore, different polarizations in general will be partially coherent, so the coherency-matrix formulation of the radiative transfer equation should be used to calculate brightness temperatures [24, 24a, 25].

However, there are two special cases in which the scalar form of the radiative transfer equation, described in Chapter 1, can be used for Zeeman-split lines. These cases occur when the coherency matrix is diagonal in a fixed polarization basis. If the direction of propagation is perpendicular to the constant magnetic field \( \mathbf{J}_0 \), the characteristic polarizations (which diagonalize the coherency matrix) are linear and either parallel or perpendicular to \( \mathbf{J}_0 \). For the electric field \( \mathbf{E}_RF \) perpendicular, the microwave magnetic field \( \mathbf{J}_RF \) is parallel or antiparallel to \( \mathbf{J}_0 \) and it therefore interacts with the Z-component of the oxygen magnetic moment, where the Z-direction is defined by \( \mathbf{J}_0 \). There is no dependence of this interaction on the azimuthal angle \( \phi \). The dependence of the rotational wave functions on azimuth is given by a factor of the form \( \exp(iM\phi) \), so the matrix element between two rotational states (as in Eq. 2.11) can be nonzero only if \( \Delta M = 0 \). Thus, the absorption for each line is contributed solely by the \( \pi \) components (dependence on \( N \) is omitted for clarity):

\[
\alpha(\mathbf{J}_RF//\mathbf{J}_0) = n \sum_M S_{M,M}(T) F(\nu, \nu_{M,M})
\]  

(2.30)

Figure 2.4. Zeeman components of the 3+ oxygen line.
The line-shape function $F$ is discussed in Sections 2.3 and 2.4. For the orthogonal polarization, the interaction between $\mathbf{\mu}$ and $\mathbf{C}_{RF}$ has a $\cos \phi$ dependence, and it therefore excites only the $\sigma$ components:

$$\alpha(\varepsilon_{RF} / \mathbf{C}) = n \sum_{M} [S_{M,M+1}(T)F(\nu, \nu_{M,M+1}) + S_{M,M-1}(T)F(\nu, \nu_{M,M-1})].$$

(2.31)

The second special case occurs when the direction of propagation is along the magnetic field $\mathbf{C}$. The characteristic polarizations are then right-circular and left-circular. A right-circular wave is absorbed by the $\sigma^+$ components:

$$\alpha_{RC} = 2n \sum_{M} S_{M,M+1}(T)F(\nu, \nu_{M,M+1})$$

(2.32)

and a left-circular wave by the $\sigma^-$ components:

$$\alpha_{LC} = 2n \sum_{M} S_{M,M-1}(T)F(\nu, \nu_{M,M-1})$$

(2.33)

If the direction of propagation is antiparallel to $\mathbf{C}$, $\sigma^+$ and $\sigma^-$ are interchanged in Eqs. 2.32 and 2.33.

We note that the intensities of the Zeeman components are defined such that

$$\sum_{M} S_{M,M}(T) = 2 \sum_{M} S_{M,M+1}(T) = 2 \sum_{M} S_{M,M-1}(T) = S(T)$$

(2.34)

where $S(T)$ is the intensity of the unsplit line. Thus, the absorption by oxygen becomes unpolarized and isotropic when the observation frequency is displaced from the line center by an amount large compared to the Zeeman splitting.

In the Earth’s magnetic field, the resonant frequencies of the $\Delta J = 0$ transitions are $\lesssim 1$ MHz (0 MHz for $\Delta M = 0$). Considering that the line intensity, Eq. 2.16, contains the factor $\nu_0^2$, one might suppose these transitions to be entirely negligible. This would be the case were it not for the effect of collisions between molecules. Equation 2.1 shows that the relevant energy difference is really between two states of the system of interacting molecules. At pressures near 1 atmosphere, the $\Delta J = 0$ matrix elements of oxygen produce a detectable, unpolarized absorption in the GHz range of frequencies. This nonresonant absorption will be discussed further in Section 2.4.

2.2.12 Inversion Spectrum of Ammonia

Ammonia (NH$_3$) has a tetrahedral structure, with the potential function shown in Figure 2.5 for motion of the nitrogen nucleus perpendicular to the plane of the hydrogen nuclei. The first two wave functions for this mode of motion are also shown. The height of the central barrier in the potential exceeds the kinetic energy
Figure 2.5. Potential-energy function and two lowest-energy wave functions for the position of the nitrogen nucleus relative to the plane of the hydrogen nuclei in NH₃.

associated with each of these two wave functions by more than a factor of 2. Nevertheless, the wave functions have nonzero values inside the barrier; this is an example of the quantum-mechanical tunneling effect. The shape of the potential function depends somewhat on the rotational quantum numbers of the molecule, and the difference in energy between \( \psi_0(z_N) \) and \( \psi_1(z_N) \) varies inversely with the height of the potential barrier [1, p. 302]. The strongest of the transitions between \( \psi_0(z_N) \) and \( \psi_1(z_N) \) lies in the 20–30-GHz range [26]. Strictly speaking, these are vibrational transitions, although they often are not classified as such. They are called inversion lines, because the passing of the nitrogen nucleus through the plane of the hydrogens turns the molecule inside out. Transition frequencies for other vibrational modes and for \( \psi_1(z_N) \) to \( \psi_2(z_N) \) lie in the infrared. Pure rotational transitions of NH₃ produce submillimeter-wavelength lines [27].

The statistical weights of NH₃ rotational levels due to nuclear spin can be deduced from consideration of a rotation by 120° about the axis of symmetry. This
rotation is equivalent to two interchanges of hydrogen nuclei.* Therefore, the total wave function must be symmetric with respect to this operation. In the ground state, \( \psi_\text{elec} \) is symmetric (i.e., with respect to the inverse rotation of the electrons, which returns them to their original position) and \( \psi_\text{vib} \) is unaffected. \( \psi_{JKM} \) changes by the factor \( \exp(i2\pi K/3) \), which makes it symmetric if \( K \) is divisible by 3. If \( K \) is not a multiple of 3, we can construct the nuclear spin wave functions

\[
\psi^K_{\text{nuc}} = \begin{cases} 
3^{-1/2} (\sigma_1^1 \sigma_2^1 \sigma_3^1 + e^{i2\pi K/3} \sigma_1^1 \sigma_2^1 \sigma_3^1 + e^{i4\pi K/3} \sigma_1^1 \sigma_2^1 \sigma_3^1) \\
3^{-1/2} (\sigma_1^1 \sigma_2^1 \sigma_3^1 + e^{i2\pi K/3} \sigma_1^1 \sigma_2^1 \sigma_3^1 + e^{i4\pi K/3} \sigma_1^1 \sigma_2^1 \sigma_3^1)
\end{cases}
\]  
(2.35a)

for which the product \( \psi_{JKM} \psi^K_{\text{nuc}} \) has the required threefold symmetry. When \( K \) is divisible by 3, Eqs. 2.35a and 2.35b reduce to

\[
\psi_{\text{nuc}} = \begin{cases} 
3^{-1/2} (\sigma_1^1 \sigma_2^1 \sigma_3^1 + \sigma_1^1 \sigma_2^1 \sigma_3^1 + \sigma_1^1 \sigma_2^1 \sigma_3^1) \\
3^{-1/2} (\sigma_1^1 \sigma_2^1 \sigma_3^1 + \sigma_1^1 \sigma_2^1 \sigma_3^1 + \sigma_1^1 \sigma_2^1 \sigma_3^1)
\end{cases}
\]  
(2.36a)

Also,

\[
\psi_{\text{nuc}} = \begin{cases} 
\sigma_1^1 \sigma_2^1 \sigma_3^1 \\
\sigma_1^1 \sigma_2^1 \sigma_3^1
\end{cases}
\]  
(2.36c)

have the correct symmetry for \( K \) divisible by 3. Thus, the statistical weight due to nuclear spin is twice as large for states with \( K \) divisible by 3 as for the other states.†

Let us now consider the operation of a 180° rotation about an axis in the plane of the hydrogen nuclei and passing through one of them, equidistant from the other two. This rotation has the same result as the transformation \( z_N \rightarrow -z_N \), except that the two off-axis hydrogen nuclei are interchanged. The total wave function must be antisymmetric with respect to the product of these two operations, because the hydrogen nuclei follow Fermi–Dirac statistics. With the nuclei in their equilibrium positions, \( \text{NH}_3 \) is an oblate symmetric top. Figure 2.1 shows that the energy levels of an asymmetric rotor merge into those of a symmetric top as \( \kappa \rightarrow 1 \) or \( -1 \). The wave functions, however, do not go over into \( \psi_{JKM} \) or \( \psi_{J - KM} \) when \( K \neq 0 \), but rather into linear combinations of the form \( 2^{-1/2} (\psi_{JKM} \pm \psi_{J - KM}) \). These are

*If the hydrogen nuclei are numbered 1, 2, and 3, then the permutation 3, 1, and 2 is equivalent to the interchange of 1 with 2 followed by the interchange of 2 with 3.

†To be precise, each of the wave functions in Eqs. 2.35 and 2.36 could be multiplied by one of three possible wave functions for the spin of the \( ^{14}\text{N} \) nucleus. However, because there is no other nucleus equivalent to the \( ^{14}\text{N} \), its spin degeneracy factor has no effect on the spectrum in the approximation that interactions involving spins are neglected.
equally good eigenfunctions for the rigid symmetric top, and are known as Wang symmetric rotor functions. Wave functions antisymmetric to exchange of two hydrogen nuclei can be written as*

\[
\psi_{\text{vib-rot-nuc}} = 2^{-1/2} \psi_n(z_N)(\psi_{JKM}^{K} \psi_{\text{nuc}}^{K} \pm \psi_{J-KM}^{K} \psi_{\text{nuc}}^{-K}).
\] (2.37)

The choice of a plus or minus sign depends on \( n, J, \) and \( K \) [1, p. 71]; thus, the antisymmetry requirement removes the twofold degeneracy associated with the quantum numbers \( \pm K \). However, if \( K = 0 \), it would be necessary to choose the minus sign when \( n + J \) has even parity, and this choice reduces the expression Eq. 2.37 to zero. Hence, alternating energy levels are prohibited; there are no microwave inversion lines associated with \( K = 0 \).

Hyperfine splitting of the NH\(_3\) inversion lines is \( \approx 2.5 \text{ MHz} \) [28–30]. This splitting can be ignored at the high pressures encountered in the atmospheres of the major planets.

### 2.3. THERMAL (DOPPLER) BROADENING

Up to this point, the discussion has ignored the translational motion of the molecules. In the absence of collisions, the translational part of the molecular wave function is simply a plane wave, which is separable from the rest of the wave function. The motion of each molecule about its center of mass can then be described as in Section 2.2, except that the line frequencies are Doppler-shifted by a factor proportional to the projection of the molecular velocity along the direction of propagation of the electromagnetic wave. A well-known result of the kinetic theory of gases is that the distribution of velocity components along any fixed direction is Gaussian. Thermally broadened lines, therefore, have the Doppler shape factor,

\[
F(\nu, \nu_\beta) = \pi^{-1/2} \beta_D^{-1} \exp \left[-\left(\frac{\nu - \nu_\beta}{\beta_D}\right)^2\right]
\] (2.38)

where the parameter \( \beta_D \) is given by [64a]

\[
\beta_D = \left(\frac{2kT}{mc^2}\right)^{1/2} \nu_\beta = 4.30 \cdot 10^{-7}\left(\frac{T}{M_m}\right)^{1/2} \nu_\beta
\] (2.39)

in which \( m \) is the mass of the molecule, and \( M_m \) is its molecular weight in g/mole.

The width of the line at half-maximum is \( 2(\ln 2)^{1/2} \beta_D \). The thermal broadening of typical atmospheric lines is \( \sim 10^{-6} \) times the line frequency, and for microwave

*The neglected modes of vibration are assumed to be in their ground states.*
lines, it is surpassed by pressure broadening in the stratosphere and troposphere. Section 2.4.2 discusses the case in which both types of broadening are significant.

2.4 PRESSURE BROADENING

2.4.1 General Discussion

Pressure broadening is the perturbation of an absorbing molecule’s line spectrum by collisions with other molecules. (The Doppler effect will be ignored until Section 2.4.2.) In a gas of interacting molecules, a potential energy that depends on the relative positions and orientations of the molecules is added to the Hamiltonians for the separate molecules. The result of this alteration to the Hamiltonian is that the gas is able to absorb photons at frequencies well removed from the resonances. In fact, it will be seen that at sufficiently high pressure, even the wings of negative-frequency resonances (which nominally represent emission transitions because $E_f < E_i$) contribute to absorption.

To discuss the effect of collisions, it is helpful to rewrite Eq. 2.1 in a form that emphasizes molecular dynamics. This can be done by introducing the Fourier expansion of the Dirac delta function,

\[ \delta(\nu) = \int_{-\infty}^{\infty} e^{i2\pi \nu t} \, dt \]  

(2.40)

which will enable us to write the absorption spectrum in terms of the Fourier transform of a correlation function. After describing the form of the correlation function in the “impact” approximation, we will obtain the spectrum by taking the transform. Further approximations may be valid in various pressure regimes; Sections 2.4.2 to 2.4.4 consider them in increasing order of pressure.

With the use of Eq. 2.40, and assuming local thermodynamic equilibrium [which implies that $p_a = p_b \exp (-\hbar \nu / kT)$], and also assuming that $\hbar \nu \ll kT$, Eq. 2.1 becomes

\[ \alpha(\nu) = \frac{8\pi^3 \nu^2}{3ckTV} \int_{-\infty}^{\infty} e^{-i2\pi \nu t} \Phi(t) \, dt \]  

(2.41)

where $\Phi(t)$ is the correlation function of the total dipole moment $\mathcal{M}$ in the volume $V$:

\[ \Phi(t) = \sum_{a,b,\sigma} p_b \mathcal{M}_{ba}^\sigma e^{iE_{a\sigma}/\hbar} / \mathcal{M}_{\sigma a}^\sigma e^{-iE_{a\sigma}/\hbar} \]

\[ = \sum_{a,b,\sigma} p_b \mathcal{M}_{ab}^\sigma (0) \mathcal{M}_{\sigma a}^\sigma (t) \]  

(2.42)

Each matrix element $\mathcal{M}_{\sigma a}^\sigma (t)$ is equal to an integral similar in form to Eq. 2.11, but with $\psi$ replaced by the time-dependent wave function $\Psi = \psi \exp (-iEt/\hbar)$. 

2.4 PRESSURE BROADENING

Because $\mathcal{M}$ is a Hermitian operator and the statistics of the system are assumed to be stationary, $\Phi(t)$ satisfies the relation

$$\Phi(-t) = \Phi^*(t) \tag{2.43}$$

The product of matrix elements in Eq. 2.42 is weighted by the probability $p_b$ of finding the system in state $b$, so the sum over all states represents the expected value of the product of matrix elements; hence, a correlation function evaluated for the time delay $t$. However, Eq. 2.42 is still expressed in terms of states $(a, b)$ of the entire gas within the volume $V$, whereas we desire a formulation that will yield line shapes associated with transitions between the states of an isolated absorbing molecule. To obtain such a formulation, it is necessary to make some simplifying assumptions concerning collisions.

One very powerful assumption is that of binary collisions: when the density of molecules in the gas is sufficiently low, an absorbing molecule can be considered to interact with one perturbing molecule at a time. Calculations employing the binary-collision approximation have successfully reproduced measured absorption coefficients at pressures as high as 6 atmospheres in NH$_3$ [31] and 51 atmospheres in O$_2$ [32]. The first implication of this assumption is that cross-correlations between different absorbing molecules are negligible, so that $\Phi(t)$ can be related to the correlation function $\Phi_1(t)$ for a single absorbing molecule by

$$\Phi(t) = nV\Phi_1(t) \tag{2.44}$$

where $n$ is the number density of the absorbing species. Second, the binary-collision approximation implies that $\Phi_1(t)$ can be evaluated by averaging over all possible collision trajectories, over the distribution of relative speeds between absorbing and perturbing molecules, and over the distribution of initial states of the perturbers.

A further approximation that is widely applied in microwave spectroscopy is the impact approximation, in which $\Phi_1(t)$ is determined by considering only the effects of completed collisions. Hence, it is valid for time intervals $t \gg t_c = 10^{-12}$ s, where $t_c$ is the typical length of time during which molecules interact strongly.

In place of the eigenstates $(a, b)$ of the entire gas, a complete basis in which to represent the Hamiltonian for the two-molecule collision is the product space of states of the isolated molecules. The Hamiltonian can be written as $H_1 + H_2 + V(t)$, where $H_1$ and $H_2$ are Hamiltonians for the isolated absorber and perturber, respectively, and $V(t)$ is the potential energy of the interaction between the two molecules. This potential is due to the dipole, quadrupole, and higher-order moments of the molecules, whether permanent or induced in the collision [33, Chapter 13; 34].

$V(t)$ depends on time $t$ through the collision trajectory, which implicitly introduces the "classical-path approximation": that the molecules follow predeter-
dined trajectories (often taken to be straight lines for ease of calculation) instead
of being represented by traveling-wave solutions of the time-dependent Schrödinguer equation. From a wave-mechanical viewpoint, the classical path is a geometric-optics approximation, and is therefore valid when the de Broglie wavelength of the perturber is small compared to the size of the intermolecular potential well. At translational energies typical of atmospheric temperatures, this is true for all but the lightest molecules, hydrogen and helium [35]. Furthermore, if the translational motion of the molecules is treated quantum-mechanically [36], the functional form of the line shape is the same as that obtained by use of the classical path.

As a simple example of the effect of collisions on the correlation function, let us consider the system whose energy-level diagram is shown in Figure 2.6. The absorbing molecule has nonzero dipole-moment matrix elements between a lowest state, which is taken as the zero of the energy scale, and several states of higher energy $E_f$. The dipole-moment matrix elements between states $f$ and $f'$ are zero, but $\nabla(t)$ has nonzero matrix elements linking these states; thus, the interactions occurring in collisions permit transitions between these states. The transitions due to collisions constitute a Markov random process with constant rates. (A transition rate is the conditional probability per unit time of a transition from one state to another, given that the absorbing molecule is in the former state.) Collisions do not, however, cause interactions involving the lowest state in this example. This is Baranger's [37] 'one-state' case. It does not correspond to any situation arising in microwave spectroscopy, but it contains most of the features of the general problem. We consider only positive resonance frequencies for the moment. The dipole-moment correlation function has an exponential form for $t >> t_c$ [7, 31, 37, 38]:

$$
\Phi_1(t) = p_0 \sum_{f,j',a} \mu_{0j}^a (e^{i\Omega_{jj'}} t)^{\frac{1}{2}} \mu_{f0}^a
$$

in which the complex matrix $\Omega$ has elements

$$
\Omega_{ff'} = 2\pi (\delta_{ff'} E_f/\hbar + iR_{ff'})
$$

Figure 2.6. The one-state example of pressure broadening.
where \( \delta_{ff'} \) is the Kronecker delta. The relaxation matrix \( R \) is calculable from the intermolecular potential [37, 38]. In the binary-collision approximation, \( R \) is proportional to the number density of perturbing molecules. It also depends on temperature through the average over perturber states and speeds. If more than one species of perturber is present in the gas, \( R \) is the sum of contributions from each species.

For \( R = 0 \) (no collisions), Eq. 2.45 is a sum of complex exponential functions of time (cosines, if negative resonant frequencies are included) with frequencies \( E_j/\hbar \) corresponding to the free motion of the dipole and with amplitudes corresponding to the line intensities. The effect of collisions, expressed by the \( R \) matrix, is to damp out the correlation as \( t \to \infty \). This loss of correlation is caused in three ways: a collision can cause a transition to a different energy level, it can temporarily perturb the energy of a state and cause a random change in phase, which is the integral of frequency over time, or it can reorient the rotational motion of the dipole. Collisions of the first type are termed inelastic; the others are elastic collisions. A diagonal element \( R_{jj} \) (multiplied by \( 2\pi \)) defines the reciprocal of the mean time interval between `strong' collisions, whether elastic or inelastic, for the state \( f \). An off-diagonal element \( 2\pi R_{jj'} \) is equal to minus the rate of transitions from \( j' \) to \( j \) due to inelastic collisions [7]. Both diagonal and off-diagonal elements can be different for different states of the molecule, as can the intermolecular potential.

We now consider the general case in which both upper and lower energy levels of each line are perturbed by collisions and the negative resonant frequencies are included.\(^*\) To reduce the notational burden, a single index \( j \), which can be positive or negative, will replace in order of frequency the line designation \((f, i)\). A vector \( \mathbf{D} \) containing the reduced dipole-moment matrix elements is defined as

\[
D_j = \mu_{fi} \quad (2.47a)
\]

\[
D_{-j} = \mu_{jf} \quad (2.47b)
\]

In the same vector space, termed the `line space' [37], a diagonal matrix \( \mathbf{v}_L \) of line frequencies is defined with

\[
(v_L)_{ji} = v_j = v_{fi} \quad (2.48a)
\]

\[
(v_L)_{-j, -j} = v_{-j} = v_{jf} = -v_{fi} \quad (2.48b)
\]

The diagonal matrix \( \mathbf{p} \) of occupation probabilities for microwave lines in local thermodynamic equilibrium has \( j, j' \)th element

\[
p_j = g_i \exp \left[ -\left( E_f + E_i \right)/2kT \right]/Q(T) \quad (2.49a)
\]

*Regarding the negative-frequency resonances, we note that the absorption coefficient \( \alpha(v) \) must be an even function of \( v \) because a real electromagnetic wave varying as \( \cos(2\pi vt) \) can be represented by two complex exponentials, \( \exp(i2\pi vt) \) and \( \exp(-i2\pi vt) \). If \( \alpha(v) \) were not even, a real wave would turn into a complex wave as it propagated through the atmosphere.
The correlation function for $t \gg t_c$ can then be expressed as [7, 37, 38]

$$\Phi_1(t) = D^T \exp \left[ 2\pi t (i\nu_L - R) \right] pD$$ \hspace{1cm} (2.50)

where $R$ is the relaxation matrix in line space. The elements of $R$ now contain the influence of perturber interactions with both the upper and lower levels of the lines. As in the one-state case, the correlation function for the free motion of the molecule without collisions ($R = 0$) is a sum of cosine functions, and $R$ embodies the effect of the collisions, which damp out the correlation as $t \to \infty$.

To evaluate the Fourier transform in Eq. 2.41 in the impact approximation, one assumes the range of Eq. 2.50 to be $t \geq 0$ and uses Eq. 2.43 and 2.44 to define the correlation function for $t < 0$. The result is [37-39]

$$\alpha(\nu) = \frac{8\pi^2 \nu^2 n}{3ckT} \text{Im} \left[ D^T (\nu I - \nu_L - iR)^{-1} pD \right]$$ \hspace{1cm} (2.51)

where $I$ is the identity matrix. The matrix $\nu_L + iR$ can be diagonalized by a transformation of the form $X^{-1}(\nu_L + iR)X = \Lambda$ [37, 38]; thus

$$\alpha(\nu) = \frac{8\pi^2 \nu^2 n}{3ckT} \sum_j \frac{\text{Im} \Lambda_j \Re G_{jj} + (\nu - \Re \Lambda_j) \Im G_{jj}}{(\nu - \Re \Lambda_j)^2 + (\Im \Lambda_j)^2}$$ \hspace{1cm} (2.52)

in which $G = X^{-1}pDD^TX$.

In the binary-collision approximation, the effect of collisions is a modulation of the free dipole motion. Hence the line shape obtained in the impact approximation is valid for frequencies that are displaced from resonance by less than $(2\pi t_c)^{-1} \approx 100$ GHz. Thus, it can also be used for submillimeter and infrared lines near resonance, but it is not applicable to the microwave tails of those lines. This point will be discussed further in Section 2.4.3 with respect to the spectrum of water vapor.

$X, \Lambda$, and $G$ depend on the perturber number density (i.e., on pressure) through $R$. A significant simplification results if we restrict consideration to pressures sufficiently low that only terms up to first order in $R$ need be retained in $\Lambda$ and $G$ [40]:

$$\Lambda_j = \nu_j + iR_{jj} + \cdots$$ \hspace{1cm} (2.53)

$$G_{jj} = D_j^2 p_j + i2D_j p_j \sum_{j' \neq j} \frac{D_{j'}R_{jj'}}{\nu_j - \nu_{j'}} + \cdots$$ \hspace{1cm} (2.54)

*At a given frequency, some of the terms in Eq. 2.52 may be negative because of the $(\nu - \Re \Lambda_j)$ factors in their numerators. However, the negative terms will be balanced by corresponding positive contributions in other terms. The overall absorption coefficient for a gas in thermodynamic equilibrium must be positive.
This first-order expansion is applicable for pressures at which the absolute values of the parameters

\[ Y_j = \text{Im} \left( \frac{G_{jj}}{\text{Re} \ G_{jj}} \right) \]  

are smaller than unity. There is a partial cancellation of higher-order terms [41]. Now, using the line intensity \( S_j(T) \) given by Eq. 2.16, we can write Eq. 2.52 as

\[ \alpha(v) = \frac{n}{\pi} \sum_{j \geq 0} S_j(T) \left( \frac{v}{\nu_j} \right)^2 \left[ \frac{R_{jj} + (v - \nu_j) Y_j}{(v - \nu_j)^2 + R_{jj}^2} + \frac{R_{jj} - (v + \nu_j) Y_j}{(v + \nu_j)^2 + R_{jj}^2} \right] \]  

The sum in Eq. 2.56 is taken over \( j \geq 0 \) because negative-frequency resonances are included in the shape factor. If nonresonant absorption \( \nu = 0 \) is present, its line intensity is not defined, but \( S_0(T)/\nu_0^2 \) has a finite nonzero value as \( \nu_0 \to 0 \).

For small \( R \), Eq. 2.56 approaches the line spectrum of the isolated molecule. The lines have half-widths equal to the diagonal elements of \( R \). It has been assumed here that the elements of \( R \) are purely real. In general, \( R \) can be complex, although for microwave spectra, the imaginary parts of the elements of \( R \), as defined here, are usually much smaller than the real parts. If present, the imaginary parts of the diagonal elements \( R_{jj} \) shift the resonant frequencies, as one can see from Eq. 2.53.

The effect of the off-diagonal elements of \( R \), which enter Eq. 2.56 through the \( Y_j \), is called line interference, coupling, mixing, blending, or merging. The terms containing \( Y_j \) will be significant in Eq. 2.56 only if all of the following conditions are satisfied: (1) At least some of the off-diagonal elements of \( R \) are comparable in order of magnitude to the diagonal elements. (2) The summation in the imaginary part of Eq. 2.54, in which some of the terms can have opposite sign, does not yield a null result. (3) More than one line contributes significantly to \( \alpha(v) \).

### 2.4.2 Low Pressures (Mesosphere and Stratosphere)

If there is no overlap of other lines from the same molecule, including negative-frequency resonances, then the shape factor in Eq. 2.56 can be approximated by the Lorentz shape factor for an isolated line near resonance:

\[ F(v, \nu_\text{fi}) = \pi^{-1} (v/\nu_\text{fi})^2 \frac{\gamma_c}{(v - \nu_\text{fi})^2 + \gamma_c^2} \]  

where \( \gamma_c = R_{jj} \) is the collisional half-width for the line. If the line is very narrow compared to its resonant frequency, so that \( v \approx \nu_\text{fi} \), then the factor \( (v/\nu_\text{fi})^2 \) can be omitted. In the stratosphere and mesosphere, pressure broadening is due overwhelmingly to collisions with molecules of the two major constituents, nitrogen and oxygen, which are uniformly mixed. Therefore, the line widths are proportional to the total pressure. From Eqs. 2.12 and 2.57, the absorption coefficient at
the line center is $n_0 S / \pi \gamma_c$, which is proportional to the mixing ratio of the absorbing gas.

At some pressure level in the mesosphere, the collisional width of a given line decreases to the point that thermal broadening is significant. An assumption that the two broadening processes act independently leads to the Voigt shape factor [42, p. 218]:

$$F(\nu, \nu_f) = \int_{-\infty}^{\infty} F_L(\nu, \nu') F_D(\nu', \nu_f) \, d\nu'$$

This is the convolution of the Lorentz shape factor $F_L$ given by Eq. 2.57 without the $(\nu / \nu_f)^2$ factor, with the Doppler shape factor $F_D$ given by Eq. 2.38. Equation 2.58 neglects the dependence of collisional broadening on the relative speed of the molecules and also neglects the fact that thermal broadening becomes less effective with increasing density* [43, 44; 45, Chapter 7]. However, deviations from the Voigt line shape exceed a few percent only when the perturbing molecule’s mass is more than five times the absorber’s mass [44, 46].

The half-width at half-maximum of the Voigt function is approximately given by [47]

$$\gamma_v = 0.5346 \gamma_c + (0.2166 \gamma_c^2 + 0.6931 \beta_D^2)^{1/2}$$

where $\beta_D$ is the thermal broadening parameter given by Eq. 2.39. Figure 2.7 plots $\gamma_v$ versus altitude for two microwave lines of H$_2$O in the terrestrial atmosphere.

For some purposes, it may be adequate to approximate the combined effect of pressure and thermal broadening by using the collisional line shape, Eq. 2.56 or 2.57, with $\gamma_c$ replaced by $\gamma_v$. However, the collisional shape factors yield higher absorption in the line wings than the Voigt shape factor when $\gamma_c < \beta_D$.

When the detailed shape of a mesospheric line is to be interpreted, the Voigt function can be accurately evaluated by the polynomial expression [48]

$$F(\nu, \nu_f) = \pi^{-1/2} \beta_D^{-1} \text{Re} \left[ \sum_{j=0}^{6} \frac{a_j \xi^j}{\sum_{j=0}^{7} b_j \xi^j} \right]$$

where

$$\xi = \gamma_c / \beta_D + i(\nu - \nu_f) / \beta_D$$

and the $a$ and $b$ coefficients are listed in Table 2.4. (The imaginary part of this polynomial expression is the dispersion shape factor.)

*The second of these effects is known as collisional narrowing, but actual narrowing of the line would occur only in the absence of pressure broadening (e.g., in nuclear magnetic-resonance spectra).
Figure 2.7. Half-widths $\gamma_v$ of two H$_2$O lines in the 1976 U.S. Standard Atmosphere. The transition from predominant thermal broadening to predominant pressure broadening occurs at higher pressure for the higher-frequency line.

Figure 2.8 is an example of a stratospheric oxygen line observed from the ground [49]. Because Zeeman splitting of the line is significant here, the polarization-coherency matrix equation of radiative transfer was used to compute the theoretical curves [24a]. Overlapping oxygen lines in the troposphere attenuate the stratospheric emission (by $\sim 6$ db), so the full collisional band shape, Eq. 2.56, was used in the calculations. Equation 2.59 was used for the line-width parameter.

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Figure 2.8. Emission from the 27 line of stratospheric O₂, observed from the ground at Haystack Observatory. The brightness temperature is the average of two orthogonal polarizations, and the scale has an arbitrary zero. Error brackets on the measured points show the rms noise level; the calibration accuracy was estimated to be ±10% [49].

Very little of the emitted energy from this line originates in parts of the atmosphere where thermal broadening predominates; thus, the more precise Voigt function is not required. The curves in Figure 2.8 are calculated for a magnetic field of 0.56 gauss at 18° to the direction of propagation, which was vertical. The two atmospheric models differ by 5 to 10 K at the 30- to 60-km altitudes where the line is formed. This line is very sensitive to stratospheric temperature because of the exponential factor in the line intensity, Eq. 2.16.

2.4.3 Moderate Pressures (Troposphere)

Absorption by tropospheric gases has two consequences for atmospheric remote sensing: it makes possible the sensing of tropospheric temperature and composition, and it attenuates emission from the upper atmosphere when the observer is on the ground. In both respects, tropospheric absorption is dominated by oxygen and water vapor.

At tropospheric pressures, the oxygen lines between roughly 50 and 70 GHz overlap to form an absorption band. Equation 2.56 describes the shape of this band. The nonresonant terms (with \( v_j = 0 \)) reduce to the following expression, which has the Debye shape factor:

\[
\alpha_0(\nu) = \frac{Cn_0\gamma_0\nu^2}{T(\nu^2 + \gamma_0^2)}
\]  (2.62)
where $C = 1.53 \times 10^{-24}$ cm$^2$GHz$^{-1}$K (theoretical value), and $\gamma_0$ is the nonresonant broadening parameter (see Table 2A.1 in the Appendix to Chapter 2). This component contributes a small amount of absorption throughout the microwave spectrum. It accounts for almost all of the absorption by oxygen below 10 GHz, which allows experimental determination of $\gamma_0$ [50].

Width parameters for the resonant oxygen lines can be determined from measurements at low pressures, where the line shape near resonance is approximated by Eq. 2.57 [51]. The interference effect, which becomes measurable as the lines begin to overlap, is a linear combination of the $Y_j$ in Eq. 2.56. Measurements at different frequencies reflect different combinations of the $Y_j$. If the other line parameters are known, determination of the interference parameters is a linear inversion problem [52]; it can be solved by methods similar to those used to infer an atmospheric temperature profile from brightness temperature measurements, given the weighting functions.

Figure 2.9 shows some measurements of absorption and dispersion in the ox-

---

**Figure 2.9.** Dispersion and absorption in dry air. The difference between the solid and dashed curves is the effect of line coupling in the oxygen band [52].
ygen band [51]. The solid curves are calculated with interference parameters adjusted to fit dispersion, which was measured with greater precision than absorption. Interference parameters on the low side of the band are positive, whereas those on the high side are negative; therefore, the interference effect lowers absorption on the wings and raises it in the middle of the band.

For water vapor, a calculation of the $R$ matrix for nine microwave and submillimeter lines yielded off-diagonal elements approximately two orders of magnitude smaller than the diagonal elements [53]. Hence, with $Y = 0$, the frequency dependence of each term in Eq. 2.56 reduces to the shape factor of Van Vleck and Weisskopf [54]:

$$F(\nu, \nu_f) = \pi^{-1}(\nu/\nu_f)^2 \left[ \frac{\gamma_c}{(\nu - \nu_f)^2 + \gamma_c^2} + \frac{\gamma_c}{(\nu + \nu_f)^2 + \gamma_c^2} \right]$$  \hspace{1cm} (2.63)

Experimental confirmation of Eq. 2.63 has been obtained for the 22-GHz line [55, 56].

However, measurements in both pure water vapor and moist air show more absorption than is contributed by the microwave and submillimeter resonances [55, 57–62]. Along with absorption from the lines listed in the Appendix, it is necessary to add a so-called “continuum” term [62, 63]:

$$\alpha_c(\nu) = (C_s P_{H_2O}^2 \theta^{10.5} + C_f P_{H_2O} P_{dry} \theta^3) \nu^2,$$  \hspace{1cm} (2.64)

where $C_s = 1.50 \times 10^{-7} \text{ cm}^{-1}\text{ bar}^{-2}\text{ GHz}^{-2}$, $C_f = 4.74 \times 10^{-9} \text{ cm}^{-1}\text{ bar}^{-2}\text{ GHz}^{-2}$, $\theta = 300K/T$, $P_{H_2O}$ is the partial pressure of water vapor, and $P_{dry}$ is the partial pressure of the dry-air components. The coefficients $C_s$ and $C_f$ and the pressure and temperature dependence in Eq. 2.64 were adjusted to fit measurements at 138 GHz, at which frequency the uncertainties in $C_s$ and $C_f$ were estimated as approximately 3% and 1%, respectively [62]. The frequency dependence is based on other measurements [55, 64, 64a]. Of course, the values of these coefficients depend to some extent on the number of lines that are treated as separate contributions and on their assumed shape. The following three paragraphs discuss some of the hypotheses that have been proposed regarding the origin of the absorption represented by Eq. 2.64. (Also see the discussion in Deepak et al. [65a].)

1. Wings of Infrared Lines [55]. Because of the microwave region’s large displacement in frequency from these resonances, the impact approximation is not valid. However, without using the impact approximation, it is possible to derive an expression having the form of Eq. 2.51 but with $R$ depending on $\nu$ [66]. Over the microwave spectrum, the frequency dependence of absorption from distant resonances is mostly due to the $\nu^2$ factor in Eq. 2.51. As long as the binary collision approximation is applicable, the pressure dependence of absorption in the

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*One set of atmospheric measurements [65] was interpreted as indicating absorption proportional to $P_{H_2O} P_{dry}$; however, these measurements can be accounted for by Eq. 2.64 [61].
wings of lines comes from the abundance $n$ of absorbing molecules multiplied by
the appropriate elements of $R$, which are proportional to the number density of
perturbing molecules. Hence, self-broadening of $H_2O$ produces a $P_{H_2O}^2$ term and
foreign-gas broadening produces a $P_{H_2O}P_{dry}$ term. Calculations of pressure
broadening for the distant wings of water-vapor lines have been done only with a
simplified intermolecular potential, but they yield good agreement with both the
magnitude and temperature dependence of Eq. 2.64 [66a].

2. Collision-induced Absorption [67, 68]. During close collisions, the inter­
molecular potential is a large perturbation to the molecular Hamiltonians, and the
wave functions are highly distorted in comparison to the isolated molecular wave
functions. Hence, the normal selection rules do not hold precisely, and transitions
not considered in the previous paragraph may contribute to absorption. This effect
has not been calculated rigorously for any molecule of the asymmetric-rotor type.

3. Water Dimers [69]. Microwave lines of $(H_2O)_2$ have been detected by mo­
lecular-beam techniques [70–71a]. On the basis of these experiments and theoretical
calculations, the dimer is believed to have the structure $H_2O-\text{HOH}$, with a
hydrogen bond joining the two water molecules. It is a nearly prolate rotor with the
energy levels split by several different tunneling motions, giving a complicated
microwave spectrum [72]. At atmospheric temperatures several vibrational levels
would be excited, and the dimer’s molecular parameters are not yet sufficiently
well known to calculate its absorption spectrum in the atmosphere. However, nu­
merous overlapping resonances would yield absorption proportional to the dimer
abundance, which in thermodynamic equilibrium varies in proportion to the square
of the number density of monomers [73]. Hence, it could contribute to the first
term in Eq. 2.64. In contradiction to earlier reports of an atmospheric dimer line
near 225 GHz [e.g., 73], high-resolution measurements at atmospheric tempera­
tures show no resonant features that can be attributed to dimers [74, 75]. If dimers
at atmospheric pressures and temperatures have an unstructured absorption spec­
trum varying as $\nu^2$, the frequency dependence is accidental.

The common element among these explanations of the water vapor continuum
is that the first term in Eq. 2.64 results from the interaction between two water
molecules, and the second term is due to the interaction of a water molecule with
a nitrogen or oxygen molecule. The explanations differ with regard to the states
(bound or free) that are involved in the transitions, and in their wave functions.
Thus, the issue is: which states are the most important to consider in a calculation?
This is still fertile ground for theorists [76], but for the purpose of calculating
atmospheric absorption, one would probably find a parametric approximation such
as Eq. 2.64 to be the most convenient model.

Figure 2.10 shows the calculated zenith opacity of the troposphere as a function
of frequency for three values of precipitable water content. The water vapor was
distributed vertically with constant relative humidity (0%, 17%, 87% for the U.S.
Standard Atmosphere). Some measurements corresponding to the highest humidity
are plotted by open circles. For the values of $H_2O$ partial pressure in this figure,
most of the absorption between lines is due to the second term in Eq. 2.64. Hence,
the variation of opacity with water vapor is roughly linear; by means of this relation, the opacity for zero water vapor was estimated (filled circles).

At relative humidity \( \geq 98\% \), some of the moisture in air is converted to hydrosols (haze, fog or cloud). This source of absorption is outside the subject of this chapter, but is discussed in References 62, 63, 65a, and in Chapter 3.

2.4.4 High Pressures (Deep Planetary Atmospheres)

When pressure broadening causes the lines of a band to overlap so much that structure due to individual resonances is lost, the band can be replaced by one resonance with an average frequency \( \bar{v} \). If (as for NH₃) there are no other nearby bands and no zero-frequency transitions, line-space vectors then have two elements, corresponding to \(-\bar{v}\) and \(+\bar{v}\). Moreover, Ben-Reuven [39] argues that for ammonia, the elements of the relaxation matrix \( R \) coupling different inversion transitions are much smaller than the diagonal elements.* In this case, \( R \) reduces to the direct sum of \( 2 \times 2 \) matrices (with index values corresponding to \(-\nu fi\) and \(+\nu fi\)) of the form

\[
\begin{bmatrix}
\gamma_c & -\xi \\
-\xi & \gamma_c
\end{bmatrix}
\]

*The cumulative effect of the former elements at high pressures in pure NH₃ is equivalent to a reduction of \( \gamma_c \) by 6% [77].

Figure 2.10. Tropospheric (0–11 km) zenith attenuation in the U.S. Standard Atmosphere for three values of precipitable water vapor. Measurements are from References 65 and 75a–75d. The calculated curves include absorption by water vapor, oxygen, and nitrogen. The narrow lines of stratospheric attenuation are not represented here.
for each inversion transition. The off-diagonal elements $-\zeta$ are due to transitions between levels $f$ and $i$ caused by collisions (rather than radiation). By evaluating the matrix inverse in Eq. 2.51, Ben-Reuven obtained the line-shape factor [39, 77]

$$F(\nu, \nu_\beta) = \left(\frac{2}{\pi}\right)\left(\frac{\nu}{\nu_\beta}\right)^2 \frac{(\gamma_c - \zeta)\nu^2 + (\gamma_c + \zeta)(\nu_\beta^2 + \gamma_c^2 - \zeta^2)}{(\nu^2 - \nu_\beta^2 - \gamma_c^2 + \zeta^2)^2 + 4\nu^2\gamma_c^2}$$ (2.65)

This line shape has been used to calculate absorption by NH$_3$ in the atmosphere of Jupiter [78]. The relationship between Eqs. 2.65 and 2.56 can be seen if $\zeta$ is taken to be negligible compared with $\nu_\beta^2 + \gamma_c^2$. Then $Y = -\zeta/\nu_\beta$, which is consistent with Eqs. 2.54 and 2.55 in a system having two energy levels.

In the two special cases when $\zeta = 0$ or $\zeta = \gamma_c$, Eq. 2.65 reduces to the shape factors obtained by Van Vleck and Weisskopf [54] and Gross [79], respectively, using classical reasoning. However, the relative sizes of off-diagonal elements of $R$ vary with the absorbing and perturbing molecules and are not susceptible to blanket generalizations.

If transitions occur at both zero and nonzero frequencies (as for O$_2$), $R$ can be treated as a 3 × 3 matrix with indices corresponding to ($-\nu_\beta$, 0, $+\nu_\beta$) at high pressures or when the observed frequency is far from the resonant band [80, 81].

When a band of merged lines is considered as a single resonance, the ratio $\gamma_c/P$ is typically smaller than for the individual lines when they are resolved at lower pressures [80, 81]. For example, if in Figure 2.6 the energies $E_1, \cdots, E_4$ were equal, to within the width of the lines, then collisions would reduce the correlation function by virtue of their effect on the phase or spatial orientation of the radiation, but not by transfers from one state to another. This effect can be seen in Figure 2.9, where line interference acts to make the resonance narrower than would be predicted by consideration only of the diagonal elements of $R$.

At gas densities so high that $\gamma_c$ approaches $(2\pi r_c)^{-1} = 100$ GHz, both the impact approximation and the binary-collision approximation are no longer valid, and the relaxation matrix is not simply proportional to density. Theoretical investigations are more difficult in this pressure regime, but at least in principle, the problem can be approached through use of techniques such as cumulant expansions [82].

### 2.5 COLLISION-INDUCED ABSORPTION BY NITROGEN AND CARBON DIOXIDE

N$_2$ and CO$_2$ have no permanent dipole moments, and, therefore, isolated molecules of these gases do not exhibit pure rotational spectra. (CO$_2$ does have an infrared vibration–rotation spectrum.) However, these molecules possess electric quadrupole moments, and during collisions, the quadrupole moment of one molecule interacts with the polarizability of its partner to induce a dipole moment in the partner molecule. The matrix elements of an induced dipole do not follow the
CHAPTER 2: ABSORPTION OF MICROWAVES BY ATMOSPHERIC GASES

selection rules applicable to a dipole moment fixed in the molecule. The selection rules for an induced dipole are those of the inducing multipole moment [83]; in the case of a quadrupole, $|\Delta f| = 0$ or 2.

The correlation function for the induced dipole consists of a short pulse, whose length is determined by the collision duration, modulating the transition frequency. The width of a collision-induced resonance (which is the Fourier transform of the correlation function) is, therefore, on the order of 300 to 1000 GHz or more, and it is independent of the gas density. In the microwave part of the spectrum, the frequency dependence of absorption comes from the $\nu^2$ factor in Eq. 2.41.

The number of binary collisions per unit time in a given volume is one-half the number of molecules divided by the mean time between collisions for each molecule. This mean time varies inversely with number density $n$, so collision-induced absorption varies as $n^2$ for identical molecules or $n_1 n_2$ for unlike molecules.

In a mixture of $N_2$ and $CO_2$, collision-induced absorption can be calculated by the empirical expression [84, 85]

$$\alpha(\nu) = (C_{N_2} P_{N_2}^2 \theta^{3.55} + C_{N_2 - CO_2} P_{N_2} P_{CO_2} \theta^{4.7} + C_{CO_2} P_{CO_2}^2 \theta^{5.08}) \nu^2 \quad (2.66)$$

where

$$C_{N_2} = 1.05 \times 10^{-12} \text{ cm}^{-1} \text{bar}^{-2} \text{GHz}^{-2} \quad [85]$$

$$C_{N_2 - CO_2} = 2.71 \times 10^{-11} \text{ cm}^{-1} \text{bar}^{-2} \text{GHz}^{-2} \quad [84]$$

$$C_{CO_2} = 7.43 \times 10^{-11} \text{ cm}^{-1} \text{bar}^{-2} \text{GHz}^{-2} \quad [85]$$

$\theta = 300/T$, and $P_{N_2}$ and $P_{CO_2}$ are the partial pressures of the two gases. The ideal-gas law has been used here to substitute pressure for density.

In the terrestrial atmosphere, the second and third terms in Eq. 2.66 are negligible. The first term contributes a small amount of absorption that may be noticeable in a dry atmosphere for $\nu \gtrsim 150$ GHz. It is responsible for the high-frequency upturn of the 0-mm H$_2$O curve in Figure 2.10. One could add a contribution from induced absorption in $N_2$-$O_2$ collisions, but this would be a minor correction.

In the atmosphere of Venus, $CO_2$ is a major contributor to microwave opacity. Equation 2.66 is probably accurate to $\sim 20\%$ for conditions on Venus. It can be improved by corrections for departures from the ideal-gas law and from the $\nu^2$ dependence at high frequencies, and by corrections for three-body collisions [85, 86].

Acknowledgments

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REFERENCES


76. E. Hudis, Y. Ben-Aryeh, and U. P. Oppenheim, The contribution of third order linear


where $P_{H_2}$, $P_{He}$, and $P_{NH_3}$ are the partial pressures of hydrogen, helium, and ammonia, respectively, in bars, and $w$ is the self-broadened line half-width coefficient [14] listed in Table 2A.6. The coefficients in Eq. 2A.7 and 2A.8 are appropriate for pressures at which the inversion lines overlap; the fact that the coefficient of $P_{NH_3}$ is 0.6 times the individual resolved line half-widths is possibly due to coupling of lines. It suggests that, over a pressure range including both resolved and overlapped lines, Eq. 2.51 or 2.52 would be required to describe the ammonia band in a predominantly hydrogen atmosphere.

Uncertainties in the line frequencies are less than 0.5 MHz in all cases, and 0.01 MHz is not uncommon. Line intensities are considered to have uncertainties of at most a few percent. Where available, measured width parameters have been used in preference to theoretical calculations; the estimated uncertainties range from 1% to 20%. Sometimes relative values of a parameter for different lines of a molecule are calculable with greater precision than absolute values, or a weighted sum of certain parameters (e.g., the oxygen interference coefficients) is measurable with more precision than individual values; for these reasons, the number of digits given in the tables sometimes exceeds the absolute accuracy of the parameters.

REFERENCES

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*aNonresonant $w = 0.56$ GHz/bar [1]; $x = 0.8$ [1]; line-intensity cutoff = $0.8E-17$; $^{16}$O₂ constitutes 0.2085 of the molecules in dry air; vibrational mode: $T_v = 2239$ K.

Relative abundance $a = 0.9865$; vibrational mode: $T_v = 3084$ K.
### TABLE 2A.2 Line Parameters for H$_2^{16}$O [4–7]a

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aLine-intensity cutoff = 0.2E-21 (frequency); relative abundance $a = 0.9973$; vibrational modes: $T_v = 2294$ K, 5262 K, 5404 K.

### TABLE 2A.3 Line Parameters for $^{12}$C$^{16}$O [4, 8, 9]a

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aRelative abundance $a = 0.9865$; vibrational mode: $T_v = 3084$ K.

### TABLE 2A.4 Line Parameters for $^{14}$N$_2^{16}$O [4, 10]a

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aRelative abundance $a = 0.9904$; Vibrational modes: $T_v = 847$ K (doubly degenerate), 1849 K, 3200 K.
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*Line-intensity cutoff = 0.5E-13; Widths from Rothman et al. [11] were multiplied by 1.1, following the discussion in Connor and Radford [13]; relative abundance $a = 0.9928$; vibrational modes: $T_{V} = 1008$ K, 1499 K, 1587 K.*
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*Line intensity cutoff $= 0.3E-13$; $w$ is for self-broadening of resolved lines (also see Eqs. A7 and A8); relative abundance $a = 0.9960$; vibrational modes: $T_v = 1367$ K, 2345 K (doubly degenerate), 4798 K, 4912 K (doubly degenerate).
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</table>

$^a_w = 3.49$ GHz/bar, $x = 0.75$ [15]; relative abundance $a = 0.7559$; vibrational mode; $T_v = 1212$ K.
Hydrometeors (liquid or frozen water particles either suspended or falling in the atmosphere) affect the propagation of microwaves within the troposphere and lower stratosphere by both absorbing and scattering radiation. Due to local thermodynamic equilibrium between these particles and the surrounding atmosphere, absorbing hydrometeors also cause emission of microwaves. The absorption, emission, and scattering by liquid and frozen hydrometeors can cause detectable changes in the microwave brightness temperature. Consequently, cloud and precipitation properties can be remotely sensed from brightness measurements made at appropriate frequencies and locations. In addition, hydrometeors attenuate radio signals and radar pulses, cause multipath interference, and increase antenna noise temperatures. All of these effects can seriously degrade the performance of terrestrial and satellite radio communication links and radar systems.

The general problem of radiative transfer in an absorbing and scattering medium has been addressed by a number of investigators [1–7]. In this chapter, we discuss the physics of microwave radiative transfer within terrestrial clouds and precipitation, and describe an iterative numerical model for computing the vertical temperature-weighting functions and corresponding microwave brightness temperatures for a hydrometeor-laden atmosphere. The radiative transfer model is useful for interpreting satellite-, aircraft-, and ground-based brightness temperature measurements of clouds and precipitation and predicting the effects of hydrometeors on antenna temperature and propagation loss.
CHAPTER 3: MICROWAVE RADIATIVE TRANSFER IN HYDROMETEORS

3.1 DIFFERENTIAL RADIATIVE TRANSFER EQUATION

In general, the second-order statistics of an arbitrarily polarized electromagnetic radiation field can be described by a four-component modified Stokes’ vector:

\[ \vec{I}(\vec{r}, \hat{s}) = \begin{pmatrix} I_v \\ I_h \\ U \\ V \end{pmatrix} \text{W/(m}^2\text{-sr-Hz)} \]  

(3.1)

where \( I_v \) and \( I_h \) are the spectral intensities of the vertically and horizontally polarized field components, respectively; \( U \) and \( V \) are the in-phase and quadrature covariances, respectively, between the vertical and horizontal field components; \( \vec{r} \) is a position vector; and \( \hat{s} \) is a unit vector in the direction of intensity propagation. By assuming local thermodynamic equilibrium, \( \vec{I} \) obeys the differential radiative transfer equation (DRTE):

\[
\vec{s} \cdot \nabla \vec{I}(\vec{r}, \hat{s}, \nu) = -\vec{\alpha}_e(\vec{r}, \hat{s}, \nu) \cdot \vec{I}(\vec{r}, \hat{s}, \nu) + \vec{\alpha}_a(\vec{r}, -\hat{s}, \nu) B(T(\vec{r}), \nu) \\
+ \int_{4\pi} \vec{P}(\vec{r}, \hat{s}, \hat{s}', \nu) \cdot \vec{I}(\vec{r}, \hat{s}', \nu) d\Omega'
\]  

(3.2)

where \( \vec{\alpha}_e \) is the extinction matrix, \( \vec{\alpha}_a \) is the absorption vector, \( \vec{P} \) is the phase matrix, \( \nu \) is the frequency, and \( T(\vec{r}) \) is the thermodynamic temperature. The extinction matrix, absorption vector, and phase matrix describe the macroscopic interaction of the radiation field with absorbing and scattering gases and particles.

The spectral intensity function \( B(T, \nu) \) is the energy density emitted by a blackbody (for one of two orthogonal modes) at thermodynamic temperature \( T \). For frequencies up to \( \sim 300 \text{ GHz} \) and terrestrial temperatures, the spectral intensity can be linearized with respect to temperature:

\[
B(T, \nu) \approx \frac{kT}{\lambda^2}
\]  

(3.3)

where \( \lambda \) is the wavelength, and \( k \) is Boltzmann’s constant. This is the Rayleigh–Jeans approximation. Because of this nearly linear relationship, it is convenient to scale the spectral intensity vector \( \vec{I} \) to an equivalent “brightness” temperature vector \( T_B \):

\[
T_B = \frac{\lambda^2}{k} \vec{I} = \begin{pmatrix} T_{Bv} \\ T_{Bh} \\ T_U \\ T_V \end{pmatrix} \text{(K)}
\]  

(3.4)
Unique solutions to Eq. 3.2 can be found by specifying boundary conditions describing the reflection (both specular and diffuse) and emission of the radiation field at all medium discontinuities.

As formulated, the DRTE is a phenomenological relation based on the detailed balancing of energy flux at each point in space and each frequency, and assumes that all scattered fields are incoherent. Macroscopic wave-interference phenomena, such as propagation-path bending in an atmosphere with an inhomogeneous refractive index, coherent superposition of scattered waves near medium discontinuities, or multiple-coherent scattering (e.g., backscatter enhancement [8]) are not modeled.

3.2 SCATTERING AND ABSORPTION BY HYDROMETEORS

The interaction of the radiation field with hydrometeors is based on the scattering and absorption of coherent electromagnetic waves propagating in a polydispersion of liquid and ice dielectric particles [9]. The size distribution and phase of hydrometeors vary widely, depending on the particular cloud type or precipitation event (e.g., cumulus cloud, cumulus-, mature-, or dissipating-stage rain cell, cirrus anvil, or stratiform cirrus) as well as the ambient temperature, geographical location, and time of year. The average fractional volume of liquid or frozen precipitation usually does not exceed ~5 × 10⁻⁶; hence, the distribution is sparse. For purposes of microwave radiative transfer modeling, hydrometeors can be classified into a few distinct categories:

1. Small liquid droplets of radius less than ~50 μm, typical of nonprecipitating cumulus and stratus clouds, fog, and haze [10–12].
2. Liquid precipitation, of radius between 50 μm and ~5 mm. Due to viscous forces, these hydrometeors are slightly oblate in shape.
3. Frozen particles of dimensions less than ~1 mm. These hydrometeors, of which cirrus anvil particles would be an example, are needle-, plate-, or dendrite-shaped.
4. Frozen particles (snow, hail, or graupel) of size between 1 mm and ~10 mm. These hydrometeors generally consist of a combination of liquid and ice phases and entrained regions of air.

Liquid hydrometeors of radius less than ~50 μm absorb microwave radiation appreciably, but scatter very little. The absorption coefficient \( \alpha_{a, \text{CLOUD}} \) for a distribution of such cloud particles can be calculated using the optical extinction theorem [6], and is proportional to the cloud liquid density \( M \) [13]:

\[
\alpha_{a, \text{CLOUD}} = 6\pi \times 10^{-2} \mu M \frac{\text{Im} \{\epsilon\}}{\epsilon + 2} (\text{N/km})
\]  

(3.5)
where \( \nu \) is in GHz, \( M \) is in g/m\(^3\), and \( \epsilon \) is the relative dielectric constant of cloud liquid water. Hence, radiative transfer through small cloud droplets can be analyzed in the same manner as through a hydrometeor-free atmosphere. That is to say, only absorption and emission occur.

For larger liquid hydrometeors (e.g., rain) or most frozen hydrometeors (e.g., snow, hail, and cirrus ice), microwave scattering can be significant, particularly at high frequencies. Moreover, the absorption and scattering are dependent on particle-size distribution and shape parameters, in addition to total water density. Examples where the approximation in Eq. 3.5 is not applicable are stratiform and convective precipitation cells, particularly at frequencies above 30 GHz (\( \lambda < 1 \) cm). Such cells can be modeled by sparse distributions of electrically large liquid-, ice-, or mixed-phase spheres. For these precipitation events, typical hydrometeor separation distances are \( \sim 1 \) cm for a large cloud drop of radius \( \sim 50 \) \( \mu \)m, and \( \sim 10 \) cm for a raindrop of radius \( \sim 1 \) mm [10]. Hence, at wavelengths shorter than 1 cm, hydrometeors can be considered to scatter and absorb independently, due to the electrically large interseparation distances.

Due to viscous forces, raindrops assume a slightly oblate shape as they fall, with the minor axis in the direction of relative airflow. However, the ratio of the semiminor axis \( a \) relative to the semimajor axis \( b \) depends on the drop equivolumetric diameter \( D \) (in mm) according to [14]:

\[
a/b = 1 - 0.048D
\]

(3.6) For small drops (\( \sim 1 \) mm in diameter or less), surface tension dominates over hydrodynamic forces, and the drop shapes are nearly spherical. Drops as large as 4 mm in diameter exhibit axial ratios of \( \sim 0.8 \). Those larger than \( \sim 8 \) mm in diameter are hydrodynamically unstable, and tend to break up into smaller drops [9]. Thus, the spherical-drop assumption is increasingly accurate in the limit of small drop diameters, but will be somewhat compromised by drop-shape variations for diameters larger than a few millimeters.

Ice particles exhibit a wide range of habits [15], for which there is relatively little reliable statistical data. For reasons of simplicity and lack of more suitable models, a spherical ice shape is often used in radiative transfer models. Upon melting, large ice particles often consist of frozen water and entrained air mixed with liquid.*

In cases where depolarization of waves by scattering raindrops and oriented ice particles is of interest, the spherical-particle assumption is too simplistic. In these cases, hydrometeors can be modeled by either prolate spheroids (e.g., for ice needles) or oblate spheroids (e.g., for large raindrops or ice plates) [16–17]. During thunderstorm electrification, spheroid-shaped hydrometeors will preferentially align themselves with their longest axis parallel to the local electric field [18, 19].

*Because the microwave radar reflectivity of liquid is approximately 4.47 times (6.5 dB) greater than ice [15a], the melting, air-entrained ice particles exhibit substantially larger radar echoes than the same quantities of either pure liquid or ice. In radar meteorology, this causes the so-called "bright band" near the melting layer.
The percentage of hydrometeors in the liquid phase (relative to the ice phase) decreases approximately linearly with temperature from 100% at 0°C to 0% at the temperature of ice nucleation, which is generally between −20 to −40°C [10, 20]. The homogeneous nucleation temperature for pure supercooled liquid water depends on the drop size: smaller drops tend to require lower temperatures [21], although at −40°C, almost all drops are frozen. Heterogeneous nucleation by atmospheric aerosols can raise the ice nucleation temperature to approximately −20°C. Temperature differences between hydrometeors and the ambient air outside a convective cell are less than +4°C in regions of updraft and greater than −3°C in regions of downdraft [22]. Because these are relatively small uncertainties compared to typical observed brightness perturbations over convective cells, the hydrometeor temperature at a given altitude can be taken to be the same as the ambient temperature.

The microwave dielectric constant $\varepsilon_w$ of pure liquid water arises from the electrically polar nature of the $\text{H}_2\text{O}$ molecule and the Debye relaxation of the field-aligned solution of molecules. Saxton and Lane [23], Ray [24], and, more recently, Klein and Swift [25] have developed expressions for the dielectric constant of liquid water. Ray’s results are more applicable for pure water at microwave frequencies and atmospheric temperatures within clouds and rain cells, hence are favored.

The dielectric constant $\varepsilon_i$ of hexagonal (Ih) phase ice* at microwave frequencies arises via a mechanism similar to that of liquid water, except that the polarization and relaxation time constants are approximately seven orders of magnitude longer. Warren [27] has compiled several investigators’ results on the dielectric constant of ice from 0.1 to 1000 GHz in tabular form. However, Warren notes that there have been no reliable measurements of the refractive index of ice between 1.25 and 12.5 mm wavelength.

### 3.2.1 Scattering and Absorption by Sparse Distributions of Particles

Scattering and absorption by sparse particle distributions is based on the field radiated by a single particle excited by an incident plane wave of a given amplitude and polarization. The scattering function matrix $\bar{F}(\theta_s, \phi_s, \theta_i, \phi_i)$ describes the amplitude and polarization of the scattered wave along any direction at a distance $r$ far from the scatterer:

$$\bar{E}_s(r, \theta_s, \phi_s) = \frac{e^{-jkr}}{r} \bar{F}(\theta_s, \phi_s, \theta_i, \phi_i) \cdot \bar{E}_i(0, \theta_i, \phi_i) \tag{3.7}$$

where $\bar{E}_i$ and $\bar{E}_s$ are the complex electric fields of the incident and scattered waves, respectively, and $k = 2\pi/\lambda$ is the wave number. A spherical coordinate system

*Ice phases other than hexagonal (Ih) require highly unnatural conditions of temperature and pressure for formation [26].
with the origin at the center of the scatterer and with the z-axis in the vertical direction is assumed in Eq. 3.7. By using the vertical and horizontal polarization basis:

\[
\overline{F} = \begin{bmatrix}
    f_{vv}(\theta_s, \phi_s, \theta_i, \phi_i) & f_{vh}(\theta_s, \phi_s, \theta_i, \phi_i) \\
    f_{hv}(\theta_s, \phi_s, \theta_i, \phi_i) & f_{hh}(\theta_s, \phi_s, \theta_i, \phi_i)
\end{bmatrix}
\]  

(3.8)

In principle, the scattering function matrix \( \overline{F} \) for any object can be determined analytically from its \( T \)-matrix coefficients using the vector spherical-mode field expansion [6, 28].

The Stokes' vectors of the incident and scattered radiation fields (\( \bar{I}_i \) and \( \bar{I}_s \), respectively) can be found from the electric fields \( \bar{E}_i \) and \( \bar{E}_s \). The Stokes' matrix \( \bar{\sigma} \) describes the resulting relationship between the incident and scattered Stokes' vectors, where

\[
\bar{I}_s = \frac{1}{r^2} \bar{\sigma} \cdot \bar{I}_i
\]  

(3.9)

and

\[
\bar{\sigma}(\theta_s, \phi_s, \theta_i, \phi_i) = \begin{bmatrix}
    |f_{vv}|^2 & |f_{vh}|^2 \\
    |f_{hv}|^2 & |f_{hh}|^2 \\
    2\text{Re}\{f_{vv}f_{hv}^*\} & 2\text{Re}\{f_{vh}f_{hh}^*\} \\
    2\text{Im}\{f_{vv}f_{hv}^*\} & 2\text{Im}\{f_{vh}f_{hh}^*\} \\
    \text{Re}\{f_{vh}f_{vv}^*\} & \text{Im}\{f_{vh}f_{vv}^*\} \\
    \text{Re}\{f_{hh}f_{hv}^*\} & \text{Im}\{f_{hh}f_{hv}^*\} \\
    \text{Re}\{f_{vv}f_{hh}^* + f_{vh}f_{hv}^*\} & -\text{Im}\{f_{vv}f_{hh}^* - f_{vh}f_{hv}^*\} \\
    \text{Im}\{f_{vv}f_{hh}^* + f_{vh}f_{hv}^*\} & \text{Re}\{f_{vv}f_{hh}^* - f_{vh}f_{hv}^*\}
\end{bmatrix}
\]  

(3.10)

The phase matrix is subsequently computed by averaging over an ensemble of particles of varying geometry, orientation, and dielectric constitution:

\[
\bar{P}(\theta_s, \phi_s, \theta_i, \phi_i) = n_0 \langle \bar{\sigma}(\theta_s, \phi_s, \theta_i, \phi_i) \rangle
\]  

(3.11)

where \( n_0 \) is the total particle density, \( \langle \cdot \rangle \) is the configurational expectation operator, and each particle is assumed to scatter incoherently.

From the scattering function, the extinction matrix \( \overline{\sigma}_e \) can be calculated under Foldy's effective field approximation [4, 29]:
3.2 SCATTERING AND ABSORPTION BY HYDROMETEORS

\[
\begin{aligned}
\frac{1}{\alpha_e(\delta)} &= \begin{bmatrix}
-2\text{Re}\{M_{vv}\} & 0 \\
0 & -2\text{Re}\{M_{hh}\} \\
-2\text{Re}\{M_{hv}\} & -2\text{Re}\{M_{vh}\} \\
2\text{Im}\{M_{hv}\} & -2\text{Im}\{M_{vh}\}
\end{bmatrix} \\
&+ \alpha_{ag} \hat{I} \\
\text{Re}\{M_{sv}\} & -\text{Im}\{M_{vh}\} \\
-\text{Re}\{M_{hv}\} & \text{Im}\{M_{hv}\} \\
-(\text{Re}\{M_{ev}\} + \text{Re}\{M_{hh}\}) & \left(\text{Im}\{M_{ev}\} - \text{Im}\{M_{hh}\}\right) \\
-(\text{Im}\{M_{ev}\} - \text{Im}\{M_{hh}\}) & -(\text{Re}\{M_{ev}\} + \text{Re}\{M_{hh}\})
\end{aligned}
\]

(3.12)

where \(M_{ab} = (j2\pi n_0/k) \left\langle f_{a\beta}(\delta, \delta') \right\rangle\), the total gaseous absorption coefficient \(\alpha_{ag}\) is a sum of the background absorption due to all of the constituent molecules \(\alpha_{ag} = \sum_i \alpha_{agi}\), and \(\hat{I}\) is the identity matrix. The diagonal elements of \(\frac{1}{\alpha_e}\) are the attenuation rates of the coherent part of the wave, and are consistent with the optical extinction theorem.

From the phase matrix and extinction matrix, the absorption vector \(\alpha_a\) for the particles is computed:

\[
\begin{aligned}
\alpha_a(\delta) &= \begin{bmatrix}
\alpha_{e11}(\delta) - \int_{4\pi} \left[P_{11}(\delta', \delta) + P_{21}(\delta', \delta)\right] d\Omega' \\
\alpha_{e22}(\delta) - \int_{4\pi} \left[P_{12}(\delta', \delta) + P_{22}(\delta', \delta)\right] d\Omega' \\
2\alpha_{e13}(\delta) + 2\alpha_{e23}(\delta) - 2 \int_{4\pi} \left[P_{13}(\delta', \delta) + P_{23}(\delta', \delta)\right] d\Omega' \\
-2\alpha_{e14}(\delta) - 2\alpha_{e24}(\delta) + 2 \int_{4\pi} \left[P_{14}(\delta', \delta) + P_{24}(\delta', \delta)\right] d\Omega'
\end{bmatrix}
\end{aligned}
\]

(3.13)

Tsang et al. [6] discuss energy conservation and reciprocity within the framework of Eqs. 3.11–3.13.

3.2.2 Gaseous Absorption in the Troposphere and Lower Stratosphere

The primary gaseous absorbers in the troposphere and lower stratosphere for frequencies below 300 GHz are diatomic oxygen (O\(_2\)) and water vapor (H\(_2\)O) (Figure 3.1). Carbon dioxide (CO\(_2\)), carbon monoxide (CO), nitrous oxide (N\(_2\)O), and ozone (O\(_3\)) exhibit resonant absorptions, and nitrogen (N\(_2\)) exhibits a weak non-resonant absorption [30] at microwave frequencies. However, these trace species can be neglected for altitudes and frequencies of concern in this chapter.
The microwave absorption spectrum of the linear molecule $^{16}\text{O}_2$ in the electronic ground ($^3\Sigma$) state arises from a fine-structure transition caused by the interaction of the molecule’s permanent magnetic dipole with the magnetic field produced by the rotor’s orbital angular momentum [31, 32]. Approximately 33 transitions of significant strength in the atmosphere are located between 50 and 70 GHz and a single isolated transition is located at 118.750 GHz. A satisfactory absorption model has been formulated by Rosenkranz (see Chapter 2; [33–35]) using a first-order approximation to the impact theory of overlapping spectral lines [36]. Zeeman splitting of microwave $\text{O}_2$ lines by the Earth’s magnetic field is important at altitudes starting in the upper stratosphere [37, 38], and hence is neglected. Absorption by the isotopic species $^{16}\text{O}^{18}\text{O}$ is also negligible for purposes of passive tropospheric and lower-stratospheric remote sensing [39].

The microwave absorption spectrum of the asymmetric top $^1\text{H}_2^{16}\text{O}$ is due to rotational transitions induced by the interaction of external fields with the molecule’s permanent electric-dipole moment. Water vapor resonances at microwave frequencies are modeled by the VVW line-shape function [40–42]. An additional absorption contribution by water vapor takes the form of a “continuum” that varies slowly with frequency [41]. Empirical characterization of both $\text{H}_2\text{O}$ continuum and resonant absorption has been done by Liebe [42–44].

Figure 3.1. Clear-air absorption $\alpha_{\text{ag}}$ at selected altitudes and relative humidities.
3.2.3 Planar-Stratified Atmosphere Approximation

Although clouds and rain cells can be horizontally small (a few kilometers or less) relative to their vertical extent (often several kilometers), a horizontally stratified (or planar-stratified) model of sparse dielectric spheres is often useful for predicting cloud and rain-cell brightness temperatures,* particularly for nadiral observations at the cell or cloud center. Due to the azimuthal symmetry of the planar-stratified approximation, only the vertically and horizontally polarized Stokes' parameters are required to describe the brightness temperature field, where $\theta$ is the angle of propagation measured with respect to the zenith direction. The two polarization components are uncoupled except through either the phase matrix or the surface bistatic scattering coefficient, and follow

$$
\cos \theta \frac{dT_b(h, \theta, \nu)}{dh} = -\bar{\alpha}_e(h, \theta) \cdot T_b(h, \theta, \nu) + \bar{\alpha}_s(h, \theta) T(h)
+ \int_0^{\pi} \bar{P}'(h, \theta, \theta', \nu) \cdot T_b(h, \pi - \theta', \nu) \sin \theta' \, d\theta'
$$

(3.14)

where $h$ is the height, $\theta$ is the angle of the direction of propagation measured from the vertical (the polar angle), and $\bar{P}'$ is the reduced ($2 \times 2$) phase matrix:

$$
\bar{P}'(h, \theta, \theta', \nu) = \int_0^{2\pi} \bar{P}(h, \theta, \phi, \theta', \phi', \nu) \, d\phi'
$$

(3.15)

The dimensional reduction of the phase matrix from the general $4 \times 4$ case is a consequence of azimuthal symmetry. The matrix elements $P'_{\alpha\beta}(\theta, \theta')$ are proportional to the angular distributions (in the variable $\theta$) of $\alpha$-polarized scattered radiation ($\alpha = \nu, h$) due to $\beta$-polarized radiation ($\beta = \nu, h$) incident from the direction $\theta'$. The reduced phase matrix describes the fraction of radiation scattered along the wall of a cone of half-angle $\theta$ and thickness $d\theta$ due to radiation incident along another cone wall of half-angle $\theta'$ and thickness $d\theta'$ (Figure 3.2).

In the planar-stratified case, the extinction matrix and absorption vector in Eq. 3.15 can be reduced to the simplified forms:

$$
\bar{\alpha}_e(h, \nu) = \alpha_e \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}
$$

(3.16)

*Methods of solution of the DRTE for horizontally inhomogeneous scattering atmospheres are described elsewhere [1, 16, 45].
where $\alpha_s$ is the scattering coefficient, and gaseous absorption is included. For the spherical-particle case, it is convenient to define the normalized phase matrix:

$$\overline{p}'(\theta, \theta') = \frac{P'(h, \theta \theta')}{\alpha_s}$$

(3.20)

where $\int_0^\pi \overline{p}' \sin \theta' \, d\theta' = 1$. 
3.2.4 Monodispersed Spherical Hydrometeor Scattering and Extinction

The scattering function matrix $\overline{F}$ for a sphere is calculated using the Mie vector spherical-mode expansion [19, 46]. The phase matrix and extinction and scattering coefficients for a monodispersion of spherical particles are subsequently determined from $\overline{F}$. The extinction and scattering coefficients are

$$
\alpha_e = n_0 \pi a^2 \eta_e(x, m)
$$
$$
\alpha_s = n_0 \pi a^2 \eta_s(x, m)
$$

where $x = 2\pi a/\lambda$ is the "size parameter," which is the ratio of the particle circumference to the wavelength and $m = \sqrt{\epsilon}$ is the complex index of refraction of the sphere of radius $a$. The efficiencies $\eta_e$ and $\eta_s$ are the ratios of the extinction and scattering cross-sections, respectively, to the particle's geometric cross-section $\pi a^2$:

$$
\eta_e(x, m) = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n + 1) \Re \{a_n + b_n\}
$$
$$
\eta_s(x, m) = \frac{2}{x^2} \sum_{n=1}^{\infty} (2n + 1) (|a_n|^2 + |b_n|^2)
$$

The Mie coefficients are

$$
a_n = \frac{j_n(mx) [xj_n(x)]' - j_n(x) [mxj_n(mx)]'}{j_n(mx) [xh_n(x)]' - h_n(x) [mxj_n(mx)]'}
$$
$$
b_n = \frac{-j_n(x) [mxj_n(mx)]' - m^2 j_n(mx) [xj_n(x)]'}{h_n(x) [mxj_n(mx)]' - m^2 j_n(mx) [xh_n(x)]'}
$$

where $j_n(\cdot)$ and $h_n(\cdot)$ are the spherical Bessel and Hankel functions, respectively, of the first kind.

The fraction of power $G$ scattered in the forward direction is

$$
G(x, m) = \int_{4\pi} \left[ P_{11}(\hat{s}', \hat{s}) + P_{21}(\hat{s}', \hat{s}) \right] (\hat{s}' \cdot \hat{s}) \, d\Omega'
$$
$$
= \int_{4\pi} \left[ P_{12}(\hat{s}', \hat{s}) + P_{22}(\hat{s}', \hat{s}) \right] (\hat{s}' \cdot \hat{s}) \, d\Omega'
$$

This is the phase matrix asymmetry parameter. For particles scattering only in the forward direction $G = 1$; in the backward direction $G = -1$; for isotropic scat-
tering $G = 0$. For a sphere [47]:

$$
G = \frac{1}{\eta_s(x, m)} \frac{4}{x^2} \sum_{n=1}^{\infty} \left[ \frac{n(n + 2)}{n + 1} \text{Re} \{a_n^* a_{n+1} + b_n^* b_{n+1}\} + \frac{2n + 1}{n(n + 1)} \text{Re} \{a_n^* b_n\} \right] (3.25)
$$

which was first derived by Debye [48] to describe the pressure of light on a sphere.

Monodispersive Mie calculations of $\alpha_e$, $\alpha_s$, and $G$ for liquid and frozen spheres are shown in Figures 3.3 and 3.4 for particle radii of 0.01, 0.1, 1.0, and 10.0 mm at a temperature of 0°C. The computations use upward recursion [2] for large-size parameters and a polynomial approximation [49] for small-size parameters. These algorithms are numerically stable for values of $m$ and $x$ encountered in realistic precipitation models at frequencies below $\sim 1000 \text{ GHz}$. The monodisperse parameters typically exhibit resonances for size parameters greater than or near unity. The asymmetry $G$ is positive (indicating predominantly forward scattering) for ice, and negative over only a small range of frequencies for liquid. Series expressions for the reduced monodispersive Mie phase matrix $\bar{\rho}'(\theta, \theta')$ are given by Tsang et al. [6]. The monodispersed Mie phase matrix exhibits an increasing number of lobes for size parameters exceeding unity.

For spheres satisfying $ka < 0.1$, the Rayleigh approximations for the extinction and scattering coefficients are applicable:

$$
\begin{align*}
\alpha_e & \approx 3kf \left( \text{Im} \{y\} + \frac{3}{5}(ka)^2 \text{Re} \{y^2\} \right) \\
\alpha_s & \approx 2kf(ka)^3 |y|^2 \\
\alpha_e - \alpha_s & = 3kf \left( \text{Im} \{y\} - \frac{4}{5}(ka)^3(\text{Im} \{y\})^2 \right)
\end{align*} (3.26)
$$

where $y = (\epsilon - 1)/(\epsilon + 2)$, $f = n_0(\frac{4}{3}\pi a^3)$ is the fractional volume of scatterers, and accuracy to order $(ka)^3$ has been retained. (Equation 3.5 follows from Eq. 3.26 by neglecting all terms of order $(ka)^3$.) The reduced Rayleigh phase matrix is [1]

$$
\bar{\rho}'(\theta, \theta') = \frac{1}{8} \begin{bmatrix}
2 \sin^2 \theta \sin^2 \theta' + \cos^2 \theta \cos^2 \theta' \cos^2 \theta \\
\cos^2 \theta' & 1
\end{bmatrix} (3.27)
$$

In the Rayleigh limit, the asymmetry $G = 0$ and the scattered energy is distributed equally in the forward and backward directions.
3.2 SCATTERING AND ABSORPTION BY HYDROMETEORS

Figure 3.3. Monodispersive Mie hydrometeor absorption and scattering for 1 g/m³ of (a) liquid and (b) ice. Calculations are shown for radii of 0.01, 0.1, 1.0, and 10.0 mm at 0°C.
Figure 3.4. Monodispersive Mie hydrometeor asymmetry parameter $G$ for (a) liquid, and (b) ice.
### 3.2.5 Polydispersed Spherical Hydrometeor Scattering and Extinction

The resonances in the Mie quantities for monodispersed hydrometeors are smoothed for realistic cases of polydispersed hydrometeors. The size spectra of hydrometeors can be modeled by a modified gamma distribution [2]:

$$n(D) = N_0(A D)^P e^{-(A D)^Q}$$  \hspace{1cm} (3.28)

where $n(D)$ (m$^{-3}$mm$^{-1}$) is the number of particles with equivalent liquid-sphere diameters between $D$ and $D + dD$ (mm), and $N_0$ (m$^{-3}$mm$^{-1}$), $A$ (mm$^{-1}$), $P$, and $Q$ are parameters. The mean diameter $\langle D \rangle$, diameter variance $\sigma_D$, mode diameter $D_M$, total number density of particles $n_0$, fractional volume $f$, water (liquid or ice) density $M$, and reflectivity $Z = n_0 \langle D^6 \rangle$ follow from Eq. 3.28:

$$\langle D \rangle = \frac{1}{A} \frac{\Gamma(P + 2)}{\Gamma(P + 1)}$$  \hspace{1cm} (mm)

$$\sigma_D = \frac{1}{A} \sqrt{\frac{\Gamma(P + 3/Q)}{\Gamma(P + 1/Q)}} - \frac{\Gamma^2(P + 2/Q)}{\Gamma^2(P + 1/Q)}$$  \hspace{1cm} (mm)

$$D_M = \frac{1}{A} \left( \frac{P}{Q} \right)^{1/Q}$$  \hspace{1cm} (mm)

$$n_0 = \frac{N_0}{AQ} \Gamma\left( \frac{P + 1}{Q} \right)$$  \hspace{1cm} (m$^{-3}$)

$$f = \pi \times 10^{-9} \frac{N_0}{6A^2Q} \Gamma\left( \frac{P + 4}{Q} \right)$$

$$M = 10^6 f \text{ (g/m}^3\text{)}$$

$$Z = \frac{N_0}{A^7Q} \Gamma\left( \frac{P + 7}{Q} \right)$$  \hspace{1cm} (mm$^6$m$^{-3}$)  \hspace{1cm} (3.29)

where $\Gamma(n + 1) = n!$ is the gamma function. The parameter $P$ describes the rate of increase of particle concentration at small diameters, and the parameter $Q$ describes the falloff in particle concentration at large diameters.

Aggregate hydrometeor extinction and scattering coefficients and phase function asymmetry $g$ are computed by integration over the distribution of particle sizes:

$$\alpha_e = \frac{\pi}{4} \int_0^\infty \eta_e \left( \frac{\pi D}{\lambda}, m \right) D^2 n(D) \, dD$$
When computing these parameters using numerical quadrature, care must be taken so that the Mie resonances are adequately sampled within the region of support of the particle-size spectrum, and that contributions up to several mean particle diameters are included. Indeed, a maximum natural hydrometeor size limit is imposed by hydrodynamic stability for rain and by growth and accretion time for snow, hail, and graupel.

Polydispersive absorption and scattering by liquid and frozen spherical hydrometeors are shown in Figure 3.5 for mean particle radii of $0.01$, $0.1$, $1.0$, and $10.0$ mm. The calculations assume $M = 1$ g/m$^3$ density and an exponential size distribution ($P = 0$ and $Q = 1$), for which $\langle D \rangle = \Lambda^{-1}$. Several trends are suggested in Figure 3.5a. For the exponential case, the peaks of the scattering curves indicate the transition from the Rayleigh to the Mie region. The wavelength at these peaks follows the approximate relation

$$\frac{\pi}{\lambda \Lambda} = \frac{\pi \langle D \rangle}{\lambda} \approx 0.8 \quad (3.31)$$

In the Rayleigh region, liquid scattering $\alpha_{s,\text{LIQUID}} \sim \nu^4 M \langle D \rangle^3$, whereas in the Mie region, both liquid scattering and absorption are nearly frequency-independent, and follow $\alpha_{s,\text{LIQUID}} \sim M/\langle D \rangle$. For frequencies from $10$–$300$ GHz, liquid scattering is greater than absorption for average diameters $\langle D \rangle$ greater than $\sim 0.5$ mm (corresponding to MP rain rates greater than $\sim 30$ mm/h). At all microwave frequencies, ice scattering is dominant over ice absorption, with Rayleigh ice scattering following $\alpha_{s,\text{ICE}} \sim \nu^4 M \langle D \rangle^3$, and Mie ice scattering following $\alpha_{s,\text{ICE}} \sim M/\langle D \rangle$.

The natural distribution of raindrop size has been determined by Marshall and Palmer (MP) [50] to approximately follow a simple exponential law over a wide range of meteorological conditions and precipitation rates:

$$n(D) = N_0 e^{-\Lambda D}, \text{ where } \begin{cases} N_0 = 8 \times 10^3 \text{ (m}^{-3} \cdot \text{mm}^{-1}) \\ \Lambda = 4.1 R^{-0.21} \text{ (mm}^{-1}) \end{cases} \quad (3.32)$$

where $R$ is the rain rate in mm/h. Similar exponential distributions were measured by Laws and Parson [51], and by Joss et al. [52], who classified the size spectra according to the type of precipitation: drizzle, widespread, or thunderstorm [9, 53].
Figure 3.5. Polydisperse Mie hydrometeor absorption and scattering for 1 g/m³ of (a) liquid and (b) ice, assuming an exponential size distribution. Calculations are shown for mean particle radii of 0.01, 0.1, 1.0, and 10.0 mm at 0°C.
Sekhon and Srivastava (SS) [54] have derived an exponential relationship for the equivalent liquid-sphere size distribution of snowflakes near the ground:

\[ n(D) = N_0 e^{-\Lambda D}, \text{ where } \left\{ \begin{array}{l} N_0 = (2.50 \times 10^3)R^{-0.94} \text{ (m}^{-3} \cdot \text{ mm}^{-1}) \\ \Lambda = 2.29R^{-0.45} \text{ (mm}^{-1}) \end{array} \right. \] (3.33)

where \( R \) is the equivalent liquid-water precipitation rate in mm/h. The SS distribution is a modification of one derived earlier by Gunn and Marshall [55]. However, the SS relations are based on additional data, and have been formulated to yield precipitation rates consistent with measured snowflake terminal velocities [56]. For densities greater than 0.1 g/m\(^3\), the mean particle size for the SS distribution is larger (by up to ~ four times) than the MP mean size. In contrast to rain, where the drops' shape and maximum size are determined by hydrodynamic processes, the sizes and shapes of frozen hydrometeors are determined largely by growth and accretion processes [10, 20]. Thus, the equivalent melted-sphere size distribution of frozen precipitation is more dependent on the specific meteorological conditions than for rain.* In addition, entrained air or dendritic habits increase the effective ice-particle size relative to the melted-sphere size, and require the use of appropriate air–ice dielectric mixing formulas [59].

Theoretical calculations of spherical hydrometeor absorption and scattering coefficients using the MP size distribution for liquid and the SS size distribution for ice are shown for various precipitation rates at 0°C in Figure 3.6. The liquid calculations compare favorably with independent calculations by Savage [60], as indicated by specific points in Figure 3.6(a). The polydispersive asymmetry \( g \) for MP liquid-sphere distributions varies from slightly negative (~ -0.1) for frequencies near 10 GHz and rain rates greater than a few millimeters per hour to ~0.8 for frequencies between 300 and 1000 GHz; see Figure 3.7(a). For SS ice-sphere distributions, \( g \) is always positive over the frequency range 1 to 1000 GHz, and does not exceed 0.9. In both liquid and ice cases forward scattering is dominant from ~30–1000 GHz.

### 3.2.6 Phase-Matrix Approximations

Exact Mie calculations of the polydispersive phase matrix \( \bar{p} \) \((\theta, \theta')\) are more computationally burdensome than calculations of \( \alpha_e \) or \( \alpha_s \), and may not be warranted due to other model uncertainties. Hence, approximations to the Mie phase matrix are often desirable. For instance, for planar-stratified spherical hydrometeors satisfying \( ka_{\text{max}} < 0.1 \), where \( a_{\text{max}} \) is the maximum hydrometeor radius, the reduced Rayleigh phase-matrix approximation (Eq. 3.27) is applicable. At microwave frequencies, nonprecipitating liquid clouds, fog, and haze usually meet this condition.

*Indeed, in situ anvil ice measurements by Heymsfield and Palmer [57] have suggested particle sizes two to three times smaller than the SS distribution, and simultaneous radar and radiometer observations by Gasiewski and Staelin [58] have suggested that thunderstorm anvils may contain larger ice particles than predicted by the SS distribution.
Figure 3.6. Polydispersive Mie hydrometeor absorption and scattering. (a) Liquid, assuming a Marshall-Palmer drop-size distribution. Computations from Savage for absorption (●) and scattering (×) are plotted for comparison. (b) Ice, assuming a Sekhon-Srivastava distribution. Calculations are shown for precipitation rates of 1, 10, and 40 mm/h for both phases and 100 mm/h for liquid.
Figure 3.7. Polydispersive Mie hydrometeor asymmetry parameter g. (a) Liquid, assuming a Marshall-Palmer (1948) drop-size distribution. (b) Ice, assuming a Sekhon-Srivastava (1970) distribution. Calculations are shown for precipitation rates of 1, 10, and 40 mm/h for both phases and 100 mm/h for liquid.
3.2 SCATTERING AND ABSORPTION BY HYDROMETEORS

For cases where the polarization of the scattered fields can be neglected, only one Stokes’ parameter is necessary to describe the radiation field. In this case, the scattered radiation can be described by an appropriate scalar Stokes’ function $\sigma$:

$$I_{\beta s} = \frac{1}{r^2} \sigma (\cos \Theta) I_{\beta i}$$  \hspace{1cm} (3.34)

where $\Theta$ is the scattering angle relative to the forward direction, and $\beta = \nu$ or $h$. The normalized phase function $p(\cos \Theta)$ follows from ensemble averaging:

$$p(\cos \Theta) \equiv \frac{\langle \sigma (\cos \Theta) \rangle}{\frac{1}{2} \int_0^{\pi} \langle \sigma (\cos \Theta) \rangle \sin \Theta \, d\Theta}$$  \hspace{1cm} (3.35)

where $\int_0^{4\pi} p(\cos \Theta) \, d\Omega / 4\pi = 1$. The reduced phase matrix for the planar-stratified problem with two Stokes’ parameters is subsequently approximated as

$$\bar{p}'(\theta, \theta') \approx \frac{1}{4\pi} \int_0^{2\pi} p(-\cos \theta \cos \theta' - \sin \theta \sin \theta' \cos [\phi - \phi']) \, d[\phi - \phi'] \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$  \hspace{1cm} (3.36)

where the vertical and horizontal polarizations are uncoupled, and treated identically.

The phase function should be chosen to fit (albeit somewhat arbitrarily) the shape and asymmetry of the actual phase matrix. Some commonly used phase functions, along with the corresponding reduced normalized phase matrices, are [7]:

1. Isotropic phase function [1]:

$$p(\cos \Theta) = 1$$

$$\bar{p}'(\theta, \theta') = \frac{1}{2} \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$  \hspace{1cm} (3.37)

The scattered power is distributed uniformly in all directions. This approximation is not applicable for hydrometeor distributions with $g \neq 0$.

2. Sobolev, or two-term [16, 61]:

$$p(\cos \Theta) = 1 + 3g \cos \Theta$$

$$\bar{p}'(\theta, \theta') = \frac{1}{2} (1 - 3g \cos \theta \cos \theta') \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$  \hspace{1cm} (3.38)
The scattering asymmetry is correctly described, although the phase function is not positive definite for $|g| > \frac{1}{3}$. For such cases, the Sobolev phase function has no physical interpretation.

3. Rayleigh phase function [1]:

$$ p(\cos \Theta) = \frac{1}{4}(1 + \cos^2 \Theta) $$

$$ \overline{p}'(\theta, \theta') = \frac{1}{8}(1 + \frac{1}{2} \sin^2 \theta \sin^2 \theta' + \cos^2 \theta \cos^2 \theta') \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} $$  (3.39)

This approximation is adequate for small particle distributions where $ka_{\text{max}} < 0.1$, and $g = 0$.

4. Henyey-Greenstein (HG) [62]:

$$ p(\cos \Theta) = \frac{1 - g^2}{(1 + g^2 - 2g \cos \Theta)^{3/2}} $$

$$ \overline{p}'(\theta, \theta') = \frac{1 - g^2}{2\pi} \int_0^\pi \frac{d(\phi - \phi')}{[1 + g^2 + 2g \cos \theta \cos \theta' + 2g \sin \theta \sin \theta' \cos(\phi - \phi')]^{3/2}} 
\cdot \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} $$  (3.40)

The HG phase function models anisotropic hydrometeor scattering, is positive definite, and possesses the desirable property of being able to model forward-, isotropic-, and backward-scattering, (as well as degrees in between these extremes) by continuously varying the asymmetry $g$.

5. Two-stream:

$$ p(\Theta) = \left[ \frac{1 - g}{2} \frac{\delta(\Theta - \pi)}{\sin(\Theta - \pi)} - \frac{1 + g}{2} \frac{\delta(\Theta)}{\sin \Theta} \right] $$

$$ \overline{p}'(\theta, \theta') = \left[ \frac{1 - g}{2} \frac{\delta(\theta - \theta')}{\sin(\theta - \theta')} - \frac{1 + g}{2} \frac{\delta(\theta + \pi - \theta')}{\sin(\theta + \pi - \theta')} \right] 
\cdot \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} $$  (3.41)

where $\delta(\Theta)$ is the Dirac delta function. Scattering occurs only in the forward and backward directions; the fraction of back-scattered power is $(1 - g)/2$. 

Although the computation of the reduced phase matrix is simplified by neglecting polarization, the resulting model only approximately describes the actual angular distribution of scattered radiation. Better approximations can be made using multiple-parameter phase functions [63]. However, phase-matrix approximation errors are generally of lesser importance than errors in the computation of the scattering, extinction, and asymmetry coefficients $\alpha_s$, $\alpha_e$, and $g$. These coefficients, which describe the amount of redirected radiation, determine the behavior of the DRTE solution.

3.3 DRTE SOLUTIONS: THE FORWARD-TRANSFER PROBLEM

The solution to the DRTE (Eq. 3.2) for a given atmospheric profile and surface specification is termed the forward-transfer problem.\* The forward-transfer problem for the nonscattering case is considerably simpler than for the scattering case, and is considered first.

3.3.1 Nonscattering Solution

For a nonscattering planar-stratified atmosphere, $\bar{P} = 0$, and the DRTE (Eq. 3.14) reduces to

\[
\cos \theta \frac{dT_B(h, \theta, \nu)}{dh} = -\alpha_a(h) T_B(h, \theta, \nu) + \alpha_a(h) T(h)
\]

(3.42)

where $\alpha_a = \alpha_e$ is the total absorption coefficient. Coupling between the different directions of propagation occurs only by reflection at the surface. For a specularly reflecting surface, Eq. 3.42 can be integrated for $\theta \leq \pi/2$ to yield the upwelling brightness:

\[
T_B(h, \theta, \nu) = \int_0^h T(h') \alpha_a(h', \nu) \sec \theta \\
\cdot \exp \left[ -\int_{h'}^h \alpha_a(h'', \nu) \sec \theta \, dh'' \right] dh' \\
+ \exp \left[ -\int_0^h \alpha_a(h', \nu) \sec \theta \, dh' \right] \left\{ T_S[1 - r_B(\theta)] \\
+ r_B(\theta) \left( \int_0^\infty T(h') \alpha_a(h', \nu) \sec \theta \\
\cdot \exp \left[ -\int_0^{h'} \alpha_a(h'', \nu) \sec \theta \, dh'' \right] dh' \\
+ T_{CB} \exp \left[ -\int_0^\infty \alpha_a(h', \nu) \sec \theta \, dh' \right] \right\}
\]

(3.43)

\*This is in contrast to the inverse, or retrieval, problem in remote sensing.
where the polarization index $\beta$ is either $\nu$ or $h$, $r_\beta(\theta)$ is the surface reflectivity, $T_s$ is the surface temperature, and $T_{CB}$ is the cosmic background temperature (2.7 K).

Over land, the microwave surface reflectivity is typically 5%, although this can vary by up to several percent, depending on the vegetation coverage and type, soil moisture, thickness, and age of snow and ice cover, frequency $\nu$, and angle $\theta$. Over smooth water surfaces, the reflectivity is calculated from the Fresnel relations:

$$r_\nu = \frac{-\epsilon_\nu \cos \theta + \sqrt{\epsilon_\nu - \sin^2 \theta}}{\epsilon_\nu \cos \theta + \sqrt{\epsilon_\nu - \sin^2 \theta}}$$
$$r_h = \frac{\cos \theta - \sqrt{\epsilon_\nu - \sin^2 \theta}}{\cos \theta + \sqrt{\epsilon_\nu - \sin^2 \theta}}$$

(3.44)

where the complex relative dielectric constant $\epsilon_\nu$ is derived from the pure-water model given by Ray [24], using the conductivity expressions of Klein and Swift [25]. A salinity fraction of 3.5% is typical for open ocean; this figure would be smaller for bays and estuaries, and negligible for fresh-water bodies. A commonly used linear approximation to the nadiral ocean surface reflectivity is

$$r_\beta = 0.638 - 0.00272\nu$$

(3.45)

where $\nu$ is in GHz. Ocean foam, which usually is present for wind speeds $w$ greater than \(-7\) m/s,* is modeled as a perfect blackbody, with a frequency-dependent effective fractional surface coverage $f_s$ [64]:

$$f_s = \begin{cases} 
0.006(1 - e^{-\nu/w}) (w - 7) & w \geq 7 \text{ m/s} \\
0 & w < 7 \text{ m/s} 
\end{cases}$$

(3.46)

where $\nu_0 = 7.5$ GHz, and $w$ is in m/s. For a nonspecular surface, the reflected brightness term in Eq. 3.43 will contain contributions from all downwelling angles weighted by the bistatic scattering coefficient of the surface [6, 64–66].

For $\theta \geq \pi/2$, the brightness consists of only downwelling and cosmic background contributions:

$$T_{B\beta}(h, \theta, \nu) = \int_{0}^{\infty} T(h') \alpha_\beta(h', \nu) (\sec \theta)$$
$$\cdot \exp \left[ -\int_{h'}^{h} \alpha_\beta(h'', \nu) (\sec \theta) \, dh'' \right] \, dh'$$
$$+ T_{CB} \exp \left[ -\int_{0}^{\infty} \alpha_\beta(h', \nu) (\sec \theta) \, dh' \right]$$

(3.47)

*Wind speeds are measured at a height of 20 m above the ocean surface.
For absorbing (but non-scattering) clouds, Eqs. 3.43 or 3.47 is valid provided that the cloud absorption is included in $\alpha_a$.

Equations 3.43 and 3.47 can be recast in the form of an integral over height of any atmospheric profile parameter (e.g., water vapor) multiplied by a suitable weighting function, which displays the vertical sensitivity of the brightness temperature to the particular parameter. Thus, the temperature weighting function set \{ $W(h', h, \theta)$, $\bar{W}_S(h, \theta)$, $\bar{W}_{CB}(h, \theta)$ \} gives the relationship between the brightness temperature vector $\bar{T}_B(h, \theta)$ and the atmospheric temperature profile $T(h)$, the surface temperature $T_S$, and the cosmic background temperature $T_{CB}$ [67]:

$$\bar{T}_B(h, \theta) = \int_0^\infty T(h') W(h', h, \theta) \, dh' + T_S \bar{W}_S(h, \theta) T_S + T_{CB} \bar{W}_{CB}(h, \theta) T_{CB}$$

(3.48)

The function $W$ represents the relative contribution to the two polarizations of the brightness temperature from any atmospheric level. For microwave frequencies and temperature excursions typical of the atmosphere, the weighting function is nearly independent of temperature [68]; hence, the relationship between brightness temperature and thermodynamic temperature is practically linear.

For water vapor or cloud water density, a relation similar to Eq. 3.48 can be formulated. However, the relation would be nonlinear, because fluctuations in water vapor and cloud water strongly perturb the total absorption coefficient, and hence the weighting function.

### 3.3.2 Numerical Quadrature: Nonscattering Solution

In practice, Eq. 3.48 is implemented by discretization at a suitable set of pressure levels \{ $P_n$ \}, $n = 1, \cdots, N$, in which case, $W(h', h, \theta)$ becomes a discrete set of quadrature weights \{ $W_{n\beta}$ \}:

$$T_{B\beta}(h, \theta, \nu) = \sum_{n=1}^M T_n W_{n\beta}(h, \theta, \nu) + T_S \bar{W}_{S\beta}(h, \theta, \nu) + T_{CB} \bar{W}_{CB\beta}(h, \theta, \nu)$$

(3.49)

where $T_n$ is the corresponding atmospheric temperature at the $n$th level. The quadrature weights can be computed by casting the solution for $T_{B\beta}$ (Eqs. 3.43 and 3.47) into an integral over the transmissivity $\tau$:

$$T_{B\beta}(h, \theta) = \int_0^1 T(t) \, dt$$

(3.50)

where $\tau(h', h, \theta) = e^{-r(h', h, \theta)}$, and

$$\tau(h', h, \theta) = \int_{h'}^h \alpha_a(h'') \sec \theta \, dh''$$

(3.51)
is the integrated opacity from the observer to altitude $h'$ along the radio path.* In Eq. 3.51, the radio path was assumed to be direct (i.e., no reflection from the surface was assumed). For surface-reflected radio paths, two additional terms are needed to describe the opacity upon reflection:

$$\tau(h', h, \theta) = \int_0^{h'} \alpha_a(h'') \sec \theta \, dh'' + u_{-1}(h') \left[ 1 - r_{\beta}(\theta) \right] + r_{\beta}(\theta) \int_0^{h'} \alpha_a(h'') \sec \theta \, dh''$$  \hspace{1cm} (3.52)

where $u_{-1}$ is the unit step function. Let $\tau_{n+1}$, $\tau_n$, $\tau_{n-1}$ and $t_{n+1}$, $t_n$, $t_{n-1}$ be the opacity and transmissivity, respectively, from the observer to the $(n+1)$th, $n$th, $(n-1)$th level, and let $\Delta \tau^+_n \equiv \tau_{n+1} - \tau_n$; $\Delta \tau^-_n \equiv \tau_n - \tau_{n-1}$ (see Figure 3.8). Then for trapezoidal rule quadrature, the $n$th level weight becomes

$$W_{n\beta} = \frac{1}{2} (t_{n+1} - t_n) + \frac{1}{2} (t_n - t_{n-1})$$

$$= \frac{1}{2} e^{-\tau^+_n} \left[ 1 - e^{-\Delta \tau^-_n + \Delta \tau^+_n} \right]$$  \hspace{1cm} (3.53)

where

$$\Delta \tau^+_n = \left( \frac{\alpha_{an+1} T_{n+1}}{P_{n+1}} + \frac{\alpha_{an} T_n}{P_n} \right) \left( \frac{P_n - P_{n+1}}{2} \right)$$

$$\cdot \left( \frac{R \sec \theta}{G_0 \sum_i m_i X_i} \right) \left( 1 + \frac{h_{n+1} + h_n}{R_c} \right)$$

$$\Delta \tau^-_n = \left( \frac{\alpha_{an} T_n}{P_n} + \frac{\alpha_{an-1} T_{n-1}}{P_{n-1}} \right) \left( \frac{P_{n-1} - P_n}{2} \right)$$

$$\cdot \left( \frac{R \sec \theta}{G_0 \sum_i m_i X_i} \right) \left( 1 + \frac{h_n + h_{n-1}}{R_c} \right)$$  \hspace{1cm} (3.54)

and $\alpha_{an}$ is the power-absorption coefficient evaluated at the $n$th level. The differential hydrostatic equation [69]:

$$\frac{dP}{P} = \frac{G_0 \sum_i m_i X_i}{(1 + 2h/R_c)RT} \, dh$$  \hspace{1cm} (3.55)

*The radio path may be curved by refraction, particularly for $\theta$ near 90°.
3.3 DRTE SOLUTIONS: THE FORWARD-TRANSFER PROBLEM

Figure 3.8. Quadrature geometry for the numerical integration of the radiative transfer equation.

relates the altitude levels \( h_n \) to the pressure levels, where \( G_0 \) is the gravitational acceleration at sea level, \( R \) is the gas constant, and \( R_e \) is the Earth’s radius. The quantity \( \Sigma_i m_i X_i = 28.96 \, \text{g/mol} \) is the average molecular weight of the atmosphere, valid for altitudes below \( \sim 100 \) km. A first-order correction to account for gravitational weakening with increasing altitude is included.

For the purpose of displaying the continuous weighting function \( W_\beta(h', h, \theta) \), the quadrature weights \( W_{n0} \) can be upsampled by linearly interpolation:

\[
W_\beta(h_n, h, \theta) = \frac{W_{n0}}{(h_{n+1} - h_{n-1})/2} \tag{3.56}
\]

However, for irregularly spaced altitude levels, this produces discontinuities in the upsampled \( W_\beta \), particularly at cloud boundaries, where the absorption changes abruptly.* For upwelling brightness from the hydrometeor-free troposphere and stratosphere, atmospheric temperature and absorption vary slowly enough that discretization at pressure levels spaced \( \sim 1 \) km apart from the surface to an altitude \( \sim \) two times the weighting-function peak altitude \( a_p \) is sufficient to reduce the quadrature error to less than 0.1 K. The peak altitude \( a_p \) is defined as the altitude at which the weighting function is maximized. This altitude is approximately the level at which the opacity from the observer equals unity [41].

The calculated nadiral temperature weighting functions for a hypothetical seven-channel satellite-based 118-GHz radiometer over land are plotted in Figure 3.9 for a hydrometeor-free atmosphere. The mean annual U.S. standard atmosphere [70] is used for the temperature profile; 20% surface relative humidity and an expo-

*In order to properly upsample the quadrature weights, additional information on the smoothness of \( W(h', h, \theta) \) is required.
CHAPTER 3: MICROWAVE RADIATIVE TRANSFER IN HYDROMETEORS

Figure 3.9. Computed hydrometeor free temperature weighting functions for nadiral observations over land using a satellite-based radiometer with seven channels located around the 118.75-GHz $\text{O}_2$ resonance. The IF center frequencies (in MHz) for each double-sideband channel are indicated. The symbols (●) indicate the surface weights (unitless, ranging from 0–1). Over a highly emissive surface such as land or new sea ice, absorbing hydrometeors increase $a_p$ relative to the clear-air value. If the weighting function peaks below the tropopause, the brightness temperatures will decrease by $\sim \Gamma \Delta a_p$, where $\Gamma \approx 7 \text{ K/km}$ is the atmospheric lapse rate, and $\Delta a_p$ is the increase in the weighting-function peak altitude. Over a moderately reflective surface, such as the ocean, the weighting function’s peak altitude can increase or decrease, depending on the reflectivity, atmospheric opacity, and cloud opacity [73]. In this case, the corre-
sponding brightness temperature perturbations due to absorbing clouds over ocean can be positive or negative. Temperature weighting functions with peak altitudes \( a_p \) at least one radiometrical depth above the cloud layer will not be appreciably affected. Thus, a set of channels such as those in Figure 3.9 can provide information on the altitude of scattering and absorbing hydrometeor layers [74].

### 3.3.3 Iterative Solution for a Scattering Atmosphere

In a scattering atmosphere, each direction of propagation is coupled to all other directions at each level through the phase matrix. A closed-form analytic solution comparable to Eqs. 3.43 and 3.47 is possible only for special cases, for example, when particles scatter only in the forward or backward directions [75].

In this section, an iterative technique based on perturbation theory* is formulated to solve Eq. 3.14 for the temperature weighting functions and polarized brightness temperatures for a planar-stratified scattering atmosphere. The scattering term

\[
\sigma_c(h) \int_0^\pi \bar{p}'(h, \theta, \theta', \nu) \cdot \bar{T}_B(h, \pi - \theta', \nu) \sin \theta' \, d\theta'
\]

(3.57)

is interpreted as a perturbation to the radiative transfer equation. The perturbation series expansion for the brightness temperature becomes

\[
\bar{T}_B(h, \theta, \nu) = \sum_{n=0}^{\infty} \bar{T}_B^{(n)}(h, \theta, \nu)
\]

(3.58)

where the unperturbed brightness vector \( \bar{T}_B^{(0)} \) satisfies the nonscattering DRTE:

\[
\cos \theta \frac{dT_B^{(0)}(h, \theta, \nu)}{dh} = -\sigma_c(h, \theta) \cdot \bar{T}_B^{(0)}(h, \theta, \nu) + \sigma_a(h, \theta) \begin{pmatrix} T(h) \\ T(h) \end{pmatrix}
\]

(3.59)

and the \( n \)th-order correction to the brightness vector satisfies

\[
\cos \theta \frac{dT_B^{(n)}(h, \theta, \nu)}{dh} = -\sigma_c(h, \theta) \cdot \bar{T}_B^{(n)}(h, \theta, \nu)
\]

\[
+ \sigma_a(h) \int_0^\pi \bar{p}'(h, \theta, \theta', \nu) \cdot \bar{T}_B^{(n-1)}(h, \pi - \theta', \nu) \sin \theta' \, d\theta'
\]

(3.60)

*The iterative method has also been referred to as the method of "successive orders of scattering" [45].
The iterative solution for the brightness temperature becomes

\[
\overline{T_B^{(0)}}(h, \theta, \nu) = \int_0^\infty T(h') \left[ 1 - \overline{\omega}(h') \right] \overline{W^{(e)}}(h, h', \theta, \nu) \, dh' + T_S \overline{W_S^{(e)}}(h, \theta, \nu) + T_{CB} \overline{W_{CB}^{(e)}}(h, \theta, \nu)
\]

\[
\overline{T_B^{(n+1)}}(h, \theta, \nu) = \int_0^\infty \left[ \overline{\omega}(h') \int_0^\pi \overline{p'}(h', \theta, \theta', \nu) \cdot \overline{T_B^{(n)}}(h', \pi - \theta', \nu) \, d\theta' \right] \cdot \overline{W^{(e)}}(h', h, \theta, \nu) \, dh'
\]  

(3.61)

where \( \overline{\omega} = \alpha_s / \alpha_e \) is the total single-scattering albedo and the superscript \( (e) \) indicates that the weighting function \( \overline{W^{(e)}} \) is calculated using the extinction (rather than absorption) coefficient as the measure of differential opacity:

\[
\overline{W^{(e)}}(h', h, \theta) = \begin{cases} 
\kappa_v(h') \sec \theta \left[ \left( \frac{1}{1} \right) \exp \left[ - \int_{h'}^h \alpha_e(h'') \sec \theta \, dh'' \right] 
+ \left( \frac{r_v(\theta)}{r_h(\theta)} \right) \exp \left[ - \int_0^{h'} \alpha_e(h'') \sec \theta \, dh'' \right] \right] & 0 \leq \theta \leq \pi/2 \\
\alpha_e(h') \sec \theta \left( \frac{1}{1} \right) \exp \left[ - \int_{h'}^h \alpha_e(h'') \sec \theta \, dh'' \right] & \pi/2 < \theta \leq \pi \\
\left( 1 - r_v(\theta) \right) \left( 1 - r_h(\theta) \right) \exp \left[ - \int_0^{h'} \alpha_e(h'') \sec \theta \, dh'' \right] & 0 \leq \theta \leq \pi/2 \\
\left( 0 \right) & \pi/2 < \theta \leq \pi \\
\left( r_v(\theta) \right) \exp \left[ - \int_0^{h} \alpha_e(h'') \sec \theta \, dh'' \right] & \pi/2 < \theta \leq \pi \\
\end{cases}
\]

\[
\overline{W_S^{(e)}}(h, \theta) = \begin{cases} 
\left( 0 \right) & 0 \leq \theta \leq \pi/2 \\
\left( 0 \right) & \pi/2 < \theta \leq \pi \\
\left( r_v(\theta) \right) \exp \left[ - \int_0^{h} \alpha_e(h'') \sec \theta \, dh'' \right] & \pi/2 < \theta \leq \pi \\
\end{cases}
\]

\[
\overline{W_{CB}^{(e)}}(h, 0) = \begin{cases} 
\left( 1 \right) \exp \left[ - \int_0^{\infty} \alpha_e(h'') \sec \theta \, dh'' \right] & 0 \leq \theta \leq \pi/2 \\
\left( 1 \right) \exp \left[ - \int_0^{\infty} \alpha_e(h'') \sec \theta \, dh'' \right] & \pi/2 < \theta \leq \pi \\
\end{cases}
\]  

(3.62)
In Eq. 3.62, the quantities \( r_v(\theta) \) and \( r_h(\theta) \) are the vertical and horizontal specular surface reflectivities, respectively.

By implicitly defining the \( n \)th-order temperature weighting function correction set \( \{ \overline{W}^{(n)}(h', h, \theta), \overline{W}_S^{(n)}(h, \theta), \overline{W}_{CB}^{(n)}(h, \theta) \} \) to be

\[
\overline{T}^{(n)}_B(h, \theta) = \int_0^\infty T(h') \overline{W}^{(n)}(h', h, \theta) \, dh' + T_3 \overline{W}_S^{(n)}(h, \theta) + T_{CB} \overline{W}_{CB}^{(n)}(h, \theta)
\]

(3.63)

an iterative procedure to compute the weighting function corrections can be written

\[
\begin{align*}
\overline{W}^{(0)}(h', h, \theta) &= [1 - \overline{\omega}(h)] \overline{W}^{(e)}(h', h, \theta) \\
\overline{W}_S^{(0)}(h, \theta) &= \overline{W}_S^{(e)}(h, \theta) \\
\overline{W}_{CB}^{(0)}(h, \theta) &= \overline{W}_{CB}^{(e)}(h, \theta)
\end{align*}
\]

(3.64)

\[
\begin{align*}
\overline{W}^{(n+1)}(h', h, \theta) &= \int_0^\infty \overline{\omega}(h'') \left[ \int_0^\pi \overline{P}'(h'', \theta, \theta') \cdot \overline{W}^{(n)}(h', h'', \pi - \theta') \right. \\
&\quad \cdot \sin \theta' \, d\theta' \overline{W}^{(e)}(h'', h, \theta) \, dh'' \\
\overline{W}_S^{(n+1)}(h, \theta) &= \int_0^\infty \overline{\omega}(h'') \left[ \int_0^\pi \overline{P}'(h'', \theta, \theta') \cdot \overline{W}_S^{(n)}(h'', \pi - \theta') \right. \\
&\quad \cdot \sin \theta' \, d\theta' \overline{W}^{(e)}(h'', h, \theta) \, dh'' \\
\overline{W}_{CB}^{(n+1)}(h, \theta) &= \int_0^\infty \overline{\omega}(h'') \left[ \int_0^\pi \overline{P}'(h'', \theta, \theta') \cdot \overline{W}_{CB}^{(n)}(h'', \pi - \theta') \right. \\
&\quad \cdot \sin \theta' \, d\theta' \overline{W}^{(e)}(h'', h, \theta) \, dh''
\end{align*}
\]

(3.65)

In Eqs. 3.61 and 3.65, the product of two column vectors

\[
\overline{A} = \begin{pmatrix} A_1 \\ A_2 \end{pmatrix} \quad \text{and} \quad \overline{B} = \begin{pmatrix} B_1 \\ B_2 \end{pmatrix}
\]

is interpreted as

\[
\overline{A}\overline{B} = \begin{pmatrix} A_1 B_1 \\ A_2 B_2 \end{pmatrix}
\]

The temperature weighting function set becomes:
\( \overline{W}(h', h, \theta) = \sum_{n=0}^{\infty} \overline{W}^{(n)}(h', h, \theta) \)

\( \overline{W}_S(h, \theta) = \sum_{n=0}^{\infty} \overline{W}_S^{(n)}(h, \theta) \)

\( \overline{W}_{CB}(h, \theta) = \sum_{n=0}^{\infty} \overline{W}_{CB}^{(n)}(h, \theta) \) (3.66)

The effects of diffuse surface reflection can be included by modifying the weighting function set \( \{ \overline{W}^{(e)}, \overline{W}_S^{(e)}, \overline{W}_{CB}^{(e)} \} \).

### 3.3.4 Numerical Quadrature: Scattering Solution

Convergence of the perturbation series in Eqs. 3.58 and 3.66 is monotonically increasing. For a maximum brightness error of \( \Delta T_B \), the required number of terms \( N_{\text{iter}} \) is related to the maximum value of the total single-scattering albedo \( \bar{\omega}_{\text{max}} = \max_h \bar{\omega}(h) \) by

\[
N_{\text{iter}} \geq \frac{\ln \left( \frac{\Delta T_B}{T_{\text{max}}} (1 - \bar{\omega}_{\text{max}}) \right)}{\ln \bar{\omega}_{\text{max}}}
\]

(3.67)

where \( T_{\text{max}} \) is the maximum profile temperature (typically, 300 K). In practice, the number of iterations required for convergence to within an accuracy of \( \sim 1\% \) is usually much smaller than \( N_{\text{iter}} \) because the maximum albedo occurs only over relatively thin precipitation layers. This is the number of "significant" photon-scattering events encountered prior to absorption, or the order of the scattering. The complexity of the computation increases as:

\[
(\text{No. of iterations}) \times (\text{No. of angles})^2 \times (\text{No. of levels})^3
\]

(3.68)

By reinterpreting the scattering-induced perturbation term to be

\[
\alpha_s(h) \int_0^\pi \left( \tilde{p}'(h, \theta, \theta', \nu) - \bar{\omega}'(\theta - \theta') \right) \frac{\delta(\theta - \theta')}{\sin(\theta - \theta')} \cdot \overline{T}_B(h, \pi - \theta', \nu) \, d\theta'
\]

(3.69)

an iterative solution that converges in an oscillatory, rather than monotonic, fashion can be constructed. For highly forward-peaked phase matrices (i.e., \( g \) near unity), this method will converge faster than the method defined by Eqs. 3.64–3.66, because the effective scattering albedo is reduced by treating the forward-scattered radiation as unscattered.

The forward-transfer computation defined by Eqs. 3.64–3.66 has been carried
out by trapezoidal quadrature over typically 40 to 50 levels in height, and Gaussian-Legendre quadrature over six to eight angles in the polar coordinate. This degree of discretization is sufficient in view of the smoothness of the phase matrix $\mathbf{P}(\theta, \theta')$ and the atmospheric constituent profiles, and the desired accuracy of 1% in the brightness-temperature calculation. In the case of a simulated rain cell of 1 g/m$^3$ density from 1 to 10 km, increasing the number of angles from 8 to 16 changed the computed brightness temperature at 120.66 GHz by typically less than 1 K.

### 3.3.5 Eigenanalysis

For cases where $\omega_{\text{max}}$ approaches unity, the slow rate of convergence of the iterative method can prove computationally prohibitive. For such cases, the analysis of a horizontally stratified atmosphere modeled by homogeneous slabs of arbitrary albedo is facilitated by eigenanalysis techniques. The radiation field is described by a complete set of eigenmodes, each of which is characterized by an angular intensity distribution that remains unchanged as the mode propagates through the slab [6]:

$$
\mathbf{T}_{B}(h, \theta) = \sum_{i} a_{i} \mathbf{t}_{Bi}(\theta) e^{\kappa h} 
$$

(3.70)

where the $a_{i}$ are the expansion coefficients of the radiation field in the eigenfunction basis $\{\mathbf{t}_{Bi}(\theta)\}$, which follow the orthogonality relation

$$
\int_{0}^{\pi} \mathbf{t}_{Bi}(\theta) \cdot \mathbf{t}_{Bj}(\theta) \sin \theta \, d\theta = \delta_{ij} 
$$

(3.71)

This is recognized as a separation-of-variables approach. The vertical attenuation coefficient $\kappa_{i}$ of the $i$th mode is the root of the characteristic equation

$$
(k_{i} \cos \theta + \alpha_{e}) \mathbf{t}_{Bi}(\theta) = \alpha_{s} \int_{0}^{\pi} \mathbf{P}(\theta, \theta') \cdot \mathbf{t}_{Bi}(\pi - \theta') \sin \theta' \, d\theta' 
$$

(3.72)

The phase-matrix and single-scattering albedo determine the angular distribution $\mathbf{t}_{Bi}(\theta)$ for each mode through Eq. 3.72. A closed-form solution for the eigenmodes of the reduced Rayleigh phase matrix under the planar-stratified assumption was formulated by Siewert [76]. The solution was extended to include a generalized phase matrix by Benassi et al. [77].

A particularly useful case arises when the phase matrix is approximated to have only forward- and back-scattering components, as in Eq. 3.41. A result is that fluxes in all propagation directions are decoupled except for the forward and backward directions. The radiative transfer problem reduces to one-dimensional scattering of two coupled fluxes [4, 78], which admits to an analytical solution for the
two eigenmodes:

\[
T_{B_\beta}(h, \theta = 0) = a_{\beta_+} e^{-\kappa h} + a_{\beta_-} \left(1 - \frac{\sqrt{1 - \bar{\omega}^2}}{\bar{\omega}}\right) e^{\kappa h}
\]

\[
T_{B_\beta}(h, \theta = \pi) = a_{\beta_+} \left(1 - \frac{\sqrt{1 - \bar{\omega}^2}}{\bar{\omega}}\right) e^{\kappa h} + a_{\beta_-} e^{\kappa h}
\]

where \(\kappa\) is the mode power attenuation coefficient, \(\alpha_{sb} = \alpha_i (1 - g)/2\) is the back-scattering coefficient, \(\bar{\omega} = \alpha_{sb}/(\alpha_{sb} + \alpha_a)\) is the back-scattering albedo, and \(\alpha_a\) is the total absorption coefficient. In this two-stream (or two-flux) model, forward-scattered energy can be treated as having not interacted with the scatterers; hence, only back-scattered energy is significant. Only the vertically propagating modes are presented in Eq. 3.73. The normal reflectivity \(r_c\) and transmissivity \(t_c\) of a homogeneous scattering layer of thickness \(\Delta h\) for the two-stream model are

\[
r_c = \frac{\bar{\omega}}{1 + \sqrt{1 - \bar{\omega}^2} \coth (\kappa \Delta h)}
\]

\[
t_c = \frac{\sqrt{1 - \bar{\omega}^2} \csch (\kappa \Delta h)}{1 + \sqrt{1 - \bar{\omega}^2} \coth (\kappa \Delta h)}
\]

The two-stream model is exact for the analysis of scattering on an inhomogeneous single-mode transmission line. However, for a planar-stratified atmosphere, the two-stream model yields a value for the mode attenuation coefficient \(\kappa\) that is unrealistically low, because the meandering of photons in directions away from the mode propagation direction is not considered.

The two-stream approximation is generalized to an arbitrary number \(M\) of streams in the discrete-ordinate eigenanalysis method [6, 79]. Consider a thin homogeneous atmospheric layer extending from height \(h_n\) to \(h_{n+1}\). Equation 3.72 can be solved numerically using \(M\)-point Gauss-Legendre quadrature, yielding a set of \(M\) stream angles \(\theta_m\), along with a corresponding set of attenuation rates \(\kappa_i\) for each discretized mode and a set of \(M\) discrete-angle eigenmodes \(i_{Bim}\) for the angular intensity distribution:

\[
\{i_{Bim}, \kappa_i, \theta_m\} \quad i = 1, \ldots, M; \quad m = 1, \ldots, M
\]

The radiation field within the layer is approximated by a sum of eigenmodes:

\[
\bar{T}_B(h, \theta_m) = \sum_{i=1}^{M} a_i \bar{i}_{Bim} e^{-\kappa_i h}
\]
The discretized radiation field at the slab top \( h_{n+1} \) is computed in terms of the field at the bottom \( h_n \):

\[
\overline{T}_B(h_{n+1}, \theta_m) = \sum_{i=1}^{M} i_{Bin} \left[ e^{-\kappa_i(h_{n+1} - h_n)} \sum_{p=1}^{M} i_{Bip} \cdot \overline{T}_B(h_n, \theta_p) \right]
\]  

(3.77)

Fluxes in all discrete propagation directions are mutually coupled through the phase matrix. The number of streams \( M \) must be large enough to adequately sample angular variations in the incident radiation fields and phase matrices.

The solution to the forward-transfer problem requires combining the individual reflection and transmission properties of adjacent slabs. This can be done using invariant imbedding [75], Amburtsumian's method [7] (the method of adding) or slab doubling [16a]. To account for the radiation emitted within each slab, the source term \( \overline{\alpha}_a(h, \theta) T(h) \) in the DRTE (Eq. 3.14) must be included. This can be done using the method of invariant imbedding [74]. Equivalently, the DRTE is of the form

\[
\mathcal{L} \overline{T}_B(h, \theta) = \overline{\alpha}_a(h, \theta) T(h)
\]  

(3.78)

where \( \mathcal{L} \) is a linear integrodifferential operator. Hence, the particular solution can be obtained by convolution of the source term with the appropriate Green's function for the operator [80], where the Green's function is constructed from the eigenmodes and eigenvalues of \( \mathcal{L} \).

### 3.4 NUMERICAL MODEL APPLICATIONS AND LIMITATIONS

Some applications and limitations of the aforementioned numerical radiative transfer model are described in this section. The validity of the model has been checked using airborne passive microwave observations at 53 and 118 GHz. Although the spherical-hydrometeor assumption yields good agreement with observations over cumulus and mature convective precipitation, the scattering and absorption properties of hydrometeors within dissipating convection (e.g., cirrus anvils) require a more detailed model. The precise form of the phase function used is relatively unimportant, provided that the hydrometeor-scattering asymmetry is accurately modeled.

The numerical radiative transfer model has applications in analysis and design of passive remote-sensing systems and development of precipitation-parameter-retrieval algorithms using passive microwave data. These applications are illustrated in the following investigations of (1) coincident 53- and 118-GHz passive \( O_2 \) observations over precipitation, (2) the retrieval of precipitation cell-top altitude using passive 118-GHz brightness spectra, and (3) the sensitivity of passive microwave window-channel observations to clouds and precipitation.
3.4.1 Comparison of Observed and Computed Brightnesses

Coincident observations of brightness temperatures over mature convection have been favorably compared to computations using the iterative planar-stratified model (Section 3.3.3). The summertime convective cell couplet was located ~100 km southwest of Huntsville, Alabama. The observations were made at three frequencies near the 118.75-GHz O₂ resonance using Massachusetts Institute of Technology’s Millimeter-wave Temperature Sounder (MTS) aboard the NASA ER-2 high-altitude aircraft on July 11, 1986, during the Cooperative Huntsville Meteorological Experiment (COHMEX) [58]. Computations were performed using hydrometeor-size distribution and phase profiles derived from coincident equivalent reflectivity (Zₑ) measurements obtained using a weather radar at Huntsville.

A vertical reflectivity cross-section of the couplet coincided with the ER-2 flight track within ~2-km spatial and ~4-minute temporal separation. Depending on the air temperature, the hydrometeor phase at each level was classified as either liquid, ice, or a mixture of liquid and ice [81]. For temperatures above freezing (0°C), MP-distributed rain with Z = Zₑ was assumed. For temperatures below that of ice nucleation (−35°C), SS-distributed ice was assumed, with Z = 4.47Zₑ to correct for the lower refractive index of ice relative to water [15a]. The relationships between the equivalent reflectivity Zₑ and the density M, size parameter Λ, and density parameter N₀ for the pure liquid and ice phases follow from Eqs. 3.29, 3.32, and 3.33 (Table 3.1). For temperatures between the freezing and ice nucleation extremes, the ice-to-liquid mixing ratio was assumed to increase linearly with height from 0% at 0°C at 100% at −35°C, with the total equivalent reflectivity fixed by Zₑ. Radar-estimated hydrometeor density profiles are shown in Figure 3.10 for selected spots in the anvil region, main cumulus cell core, and an adjacent mature-cell core.

Nadiral 118-GHz brightness spectra were computed at 14 locations along the flight track. Computations used temperature profiles measured by a near-coincident radiosonde. Relative humidity is 100% within the cell and the surface reflectivity is 5%. The atmosphere is vertically discretized into layers of approximately 1/₂-km thickness. The observed and computed brightnesses are shown in Figure 3.11 for the extreme and intermediate opacity MTS channels. The discrepancies over the convective region fall within 10% of the observed perturbation amplitudes, and can be ascribed to hydrometeor model, radar, and registration errors. However, discrepancies in the anvil region (A) suggest that significantly less scattering oc-

### TABLE 3.1 Relationships Between the Equivalent Radar Reflectivity Zₑ (mm⁶/m³) and Precipitation Rate R, Density M, Size Parameter Λ, and Distribution Parameter N₀ for the Marshall–Palmer Liquid, Sekhon–Srivastava Ice Distributions

<table>
<thead>
<tr>
<th>Distribution</th>
<th>R (mm/hr)</th>
<th>M (g/m³)</th>
<th>Λ (mm⁻¹)</th>
<th>N₀ (m⁻²mm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>(3.65 × 10⁻²)Zₑ⁰.⁶₂⁵</td>
<td>(5.51 × 10⁻³)Zₑ⁰.₅₂⁴</td>
<td>8.22Zₑ⁻⁰.₁₃₁</td>
<td>8.0 × 10¹</td>
</tr>
<tr>
<td>SS</td>
<td>(6.66 × 10⁻²)Zₑ⁰.₄₅¹</td>
<td>(2.78 × 10⁻²)Zₑ⁻₀.₃₈⁹</td>
<td>7.75Zₑ⁻₀.₂₀₄</td>
<td>(3.19 × 10⁴)Zₑ⁻₀.₄₂₆</td>
</tr>
</tbody>
</table>
3.4 NUMERICAL MODEL APPLICATIONS AND LIMITATIONS

Figure 3.10. Estimates of liquid and ice hydrometeor density for three representative storm cell regions as derived from radar reflectivity: (a) anvil, assuming an SS ice distribution, (b) adjacent cell core, and (c) main cell core.

curred than computed using the planar-stratified model (see Figure 3.11, region A). This discrepancy is attributed to a larger variability in the ice-particle shape and size distributions within cirrus anvils than over convective regions [58]. The comparison suggests that the scattering and absorption properties of hydrometeors within dissipating convection (e.g., cirrus anvils) require a more accurate description than the exponentially distributed sphere model can provide. However, over cumulus and mature precipitation, the MP liquid/SS ice/HG hydrometeor model adequately explains the observed data.

3.4.2 Effects of Phase-Matrix Approximations

The sensitivity of the numerical model to the aforementioned phase-matrix approximations (see Section 3.2.6) is shown using computations for a representative rain cell. The computed weighting functions sets for nadiral 118.75 ± 1.91-GHz precipitation observations at 20-km altitude over land are shown in Figure 3.12. In all calculations, the MP and SS size distributions are used for liquid and ice, respectively, and the temperature of ice nucleation is −30°C. Hydrometeor density is 1 g/m³ from 1 to 10 km altitude, corresponding to a MP rain rate of 18 mm/h. The temperature profile is an interpolation from the U.S. standard atmosphere for June at 35° north latitude, and the surface reflectivity is 5%. Discretization is over 8 angles and 37 levels, with 40 iterations typically required for convergence.
Figure 3.11. Comparison of computed versus observed brightness temperatures over a storm-cell couplet for two extreme and one intermediate opacity channel near the 118.75-GHz O$_2$ resonance.

Figure 3.12(a) shows nonscattering calculations (Eq. 3.43) using extinction and absorption, respectively, as measures of the differential opacity. These are to be compared with solutions using three symmetric phase matrix approximations [Rayleigh phase function, Rayleigh and isotropic phase matrices; Figure 3.12(b)], two asymmetric phase-matrix approximations [Sobolev and HG phase functions; Figure 3.12(c)], and the two-stream invariant imbedding model [Figure 3.12(d)]. (The hydrometeor-free weighting-function set is shown in each plot for reference.)

In all cases, the calculated surface weights $W_s$ are negligible, indicating that the cell is radiometrically opaque. When scattering is modeled, the cosmic background weights $W_{CB}$ are nonzero, indicating reflection from the glaciated cell top. All of the symmetric phase-matrix approximations yield nearly identical weighting-functions sets, as do both of the asymmetric phase functions. However, the $W_{CB}$ for the asymmetric phase functions are smaller than for the symmetric functions. This is expected because the Mie hydrometeor asymmetry parameter $g \approx 0.55$, causing the majority of power to be scattered in the forward direction. Because this fraction of power can be considered to have not interacted with the precipitation at all, the asymmetric phase functions will cause less cell-top reflection than the symmetric ones. It is concluded that the weighting functions for a scattering atmosphere are relatively insensitive to the precise angular dependence of the phase matrix, but quite sensitive to the scattering asymmetry. Thus, if polarization is not important,
Figure 3.12. Computed temperature-weighting functions for a hydrometeor-free atmosphere (clear-air) and a representative 1 g/m³ 1-10-km cell: (a) neglecting scattering; (b) iterative, using the isotropic and Rayleigh phase functions and the Rayleigh phase matrix; (c) iterative, using the anisotropic Heney-Greenstein and Sobolev phase functions; and (d) using the two-stream model. Symbols near 0- and 25-km altitude indicate the surface and cosmic background weights, respectively.
a phase-function approximation to the exact Mie phase matrix is acceptable provided that the scattering asymmetry is accurately modeled.

Because two- and multiple-stream eigenanalysis, [Figure 3.12(d)] does not require iteration, it is computationally preferable to the perturbation method, especially for albedos near unity. However, the two-stream model does not consider scattering in directions other than $\theta$ or $\pi - \theta$, and, hence, underestimates the absorption of photons scattered out of the direction of observation. This causes a deeper penetration of the computed weighting function into the cell top compared to the Sobolev or HG case, Figure 3.12(c).

### 3.4.3 Frequency Dependence of Brightness Temperatures Over Clouds

Comparisons of computed and observed brightness temperatures over convective precipitation cells using "similar weighting function" (SWF) O$_2$ channels within the 60-GHz (5-mm wavelength) and 118-GHz absorption bands have been used to investigate whether additional meteorological information can be obtained from coincident multiband passive observations. In the context of passive atmospheric remote sensing, SWF channels have nearly identical clear-air temperature weighting functions. Radiometric channels at 53.65 GHz and at 118.75 ± 1.45 GHz satisfy this criterion. Indeed, both nonscattering weighting functions peak at $\sim 5$-km altitude (see Figure 3.13, 0 g/m$^3$ density), and the channels exhibit nearly identical brightness temperatures ($\sim 260$ K) over hydrometeor-free regions.

However, due to the frequency dependence of hydrometeor scattering and absorption, the response of these SWF channels to liquid and frozen precipitation is markedly different. A scatter plot of the brightness temperatures for the two SWF channels is shown in Figure 3.14 for nadiral MTS observations during two passes over strong convection on June 29, 1986, during COHMEX [58]. The convection was observed over land $\sim 100$ km southwest of Norfolk, Virginia. The crosshairs (lower left) are an offset added to the observations for agreement with computations over hydrometeor-free regions. The observed data show that for weak brightness perturbations, the 118-GHz brightness is more strongly affected than the 53-GHz brightness. However, for strong perturbations, the 53- and 118-GHz brightnesses are comparably affected.

For comparison, brightness temperatures computed using the iterative method for cells of varying top altitude and water density are overlayed. The computations assume MP liquid spheres, SS ice spheres, and HG phase functions. Cell-top altitudes range from 2 to 16 km, and the cell-bottom altitudes are at 1 km. The hydrometeor densities are uniform in the vertical direction, ranging from 0 to 10 g/m$^3$. This domain covers typically encountered altitude and density values for midlatitude convective precipitation cells. The U.S. standard atmosphere interpolated to July at 35° north latitude is used for the temperature profile; the temperature of ice nucleation is $-$30°C. An exponential water-vapor decay with a 2.5-km scale height and 60% surface relative humidity is assumed, except in re-
Figure 3.13. Computed weighting functions for similar weighting-function O$_2$ channels at (a) 53.65 GHz and (b) 118.75 ± 1.45 GHz for hydrometeor-free (●) and 10-km-top model precipitation cells with uniform densities of 0.01 (○), 0.1 (□), 1.0 (△), and 10.0 (◇) g/m$^3$. 
CHAPTER 3: MICROWAVE RADIATIVE TRANSFER IN HYDROMETEORS

Figure 3.14. Brightness temperatures over precipitation for similar weighting-function O\textsubscript{2} channels at 53.65 GHz and 118.75 ± 1.45 GHz. The points are data observed over strong convection. The solid lines are computed constant-altitude curves, parametrized by cell density. A Marshall–Palmer liquid-size distribution and a Sekhon–Srivastava (solid) or Marshall–Palmer (dashed) ice-size distribution were assumed.

regions of nonzero hydrometeor density, where the relative humidity is 100%. A specular land background with 5% reflectivity is assumed.

The computations verify that small negative perturbations (of amplitude ≤35 K) in the 118-GHz brightness are two to three times as large as coincident SWF 53-GHz perturbations. This can be explained by the small electrical size of the hydrometeors in tenuous radiometrically transparent clouds. For such cases, water densities are generally less than 0.1 g/m\textsuperscript{3}, in which case, the mean hydrometeor diameter (\lambda\textsuperscript{-1}) is less than ~0.25 mm for both liquid and ice. Thus, the mean-size parameter \langle x \rangle = \pi / \lambda \Lambda \approx 0.3 is less than unity, resulting in a strong Rayleigh frequency dependence that varies from \nu\textsuperscript{1.2} to \nu\textsuperscript{1.3} and from \nu\textsuperscript{1.5} to \nu\textsuperscript{2.1} for liquid and ice absorption, respectively, and from \nu\textsuperscript{2} to \nu\textsuperscript{4} for either liquid or ice scattering (Figure 3.5). Accordingly, we expect ~2.2–2.8 and ~3.3–5.4 times as much absorption at 118 GHz (relative to 53 GHz) for liquid and ice, respectively, and ~5–25 times as much scattering. The resulting frequency dependence in the nadiral weighting functions for 10 km top-altitude cells is illustrated in Figure 3.13 (0.01 and 0.1 g/m\textsuperscript{3} density). The functions show a larger cell-top reflectivity (indicated by a larger cosmic background weight), a larger cell opacity (indicated by a lower relative surface weight), and a higher weighting-function peak altitude at 118 GHz than at 53 GHz.

Over heavier cumulonimbus clouds and convective precipitation, negative 118-GHz perturbations of amplitude larger than 35 K track the 53-GHz perturba-
tions more closely. Over such regions, perturbation ratios $\Delta T_{118}/\Delta T_{33}$ as low as unity are observed. The similarity of the perturbations can be explained by the mean hydrometeor size for water densities greater than 0.1 g/m$^3$. For these densities, the mean-size parameter $\langle x \rangle$ approaches or exceeds unity, resulting in Mie-frequency behavior. Because the Mie scattering and absorption efficiencies are nearly constant with frequency, $\alpha_s$ and $\alpha_a$ are nearly frequency-independent from 53 to 118 GHz. The result is that the weighting functions for 53- and 118-GHz SWF channels over heavy clouds and precipitation are comparable, as in the hydrometeor-free case (see Figure 3.13, 1.0 and 10.0 g/m$^3$ density).

Brightness temperatures computed assuming an MP (rather than SS) ice-size distribution, illustrate the sensitivity of the 53/118 SWF observations to ice-particle size. Because the MP mean size is smaller than the SS mean size for most heavy radiometrically opaque cells, the frequency dependence of the ice scattering and absorption is stronger for MP- than for SS-distributed ice particles. Thus, when a MP ice-size distribution is assumed, the perturbation ratios $\Delta T_{118}/\Delta T_{33}$ tend to increase (Figure 3.14, dashed curve).

### 3.4.4 Retrieval of Precipitation Parameters

The calculations illustrated in Figure 3.14 can be used to determine the precipitation-parameter-retrieval capability of satellite-based SWF $O_2$ channels. The curves of constant altitude and density in the 53/118-GHz SWF brightness plots form a curvilinear coordinate system over a large portion of cell altitude and density space, particularly over the radiometrically opaque range from 0.5 to 10.0 g/m$^3$ in water density and for cell-top altitudes above 7 km. This suggests that SWF $O_2$ channels might be used to retrieve cell-top density for radiometrically opaque cells. However, variations in the hydrometeor ice-size distribution significantly shift and distort the curvilinear grid. This is illustrated by the dashed curves for 10- and 16-km altitudes, which were computed using an MP ice-size distribution. It is concluded that an additional degree of freedom is available from coincident 53- and 118-GHz SWF precipitation cell observations, and is related to ice-particle size and density. However, this additional degree is alone insufficient to estimate either ice size or density unambiguously.

The potential to retrieve rain-cell parameters from 118-GHz spectra alone was investigated by analyzing the sensitivity of the nonlinear numerical map from cell-top altitude and density to the radiometrically observable space. The numerical model computations used the same constant-density cell model as described in the preceding 53/118-GHz analysis. Nadiral 118-GHz brightness spectra were computed for a set of cell-top altitudes ranging from 2 to 16 km (in 2-km increments) and for total water densities from 0.01 to 10.0 g/m$^3$ (two values per decade). A composite plot of the computed brightness-temperature spectral perturbations is given in Figure 3.15.

The two largest principal-mode (or Karhunen–Loève, KL) coefficients in the 118-GHz rain-cell brightness perturbation spectra are significantly larger than the sensitivity of practical Earth-observing spectrometers ($\sim 0.5$ K rms). These spec-
Figure 3.15. Composite plot of computed 118-GHz brightness-temperature perturbation spectra for uniform-density precipitation cells over land. Cell-top altitudes range from 2 to 16 km and water densities range from 0.01 to 10.0 g/m$^3$.

...
Figure 3.16. Computed map from cell-top altitude and density to the principal mode amplitudes $k_1$ and $k_2$. (a) Constant-altitude curves for 8-, 10-, 12-, 14-, and 16-km cell tops assuming a Sekhon-Srivastava ice-size distribution (solid) and a Marshall-Palmer ice size distribution (short dashed, 16 km only). The long dashes define the observed range of $k_1$ and $k_2$ values. (b) Enlargement of (a) near the origin for the SS ice-size distribution, including constant-altitude curves for 2-, 4-, and 6-km cell tops and constant-density curves (dashed) for 0.01, 0.03, and 0.1 g/m$^3$ total water (liquid and ice). The bold lines define decision region boundaries for purely liquid and glaciated precipitation.
highly absorbing surface backgrounds such as land [Figure 3.16(b)]. The computations suggest that cell-top altitude for radiometrically opaque liquid precipitation cells over land can be retrieved using 118-GHz spectra. Such cells are characterized by water densities of $\sim 0.5$ g/m$^3$, corresponding to rain rates of at least 8 mm/h under the MP distribution. The expected retrieval accuracy is less than a kilometer. The altitude retrieval capability is a consequence of the physical temperature of the absorbing blackbody, which nominally decreases at the lapse rate of 7 K/km. The numerical model calculations further suggest that the presence of a glaciated cell top is unambiguously detectable by comparing $k_1$ with a threshold value of $-20$ to $-25$ K. For values of $k_1$ lower than this threshold, the presence of ice is ascertained. For values of $k_1$ greater than this threshold, the existence of high-altitude radiometrically transparent ice cover can be ascertained by testing for unusually high values of $k_2$. Approximate decision regions for ascertaining the presence of ice are shown in Figure 3.16(b). High-altitude radiometrically transparent clouds (e.g., thin cirrus) might also be detected by virtue of their unusually high values of both $k_1$ ($\geq -70$) and $k_2$ ($\geq -3$).

The sensitivities of the amplitudes $k_1$ and $k_2$ to cell-top altitude for radiometrically opaque cells (i.e., cells with densities greater than $\sim 0.5$ g/m$^3$) provide a physical justification for statistical 118-GHz cell-top altitude retrieval [74]. For a given cell-top altitude, $k_1$ varies by less than 20% for over radiometrically opaque cells, with $k_2$ varying only slightly more. The dependence of $k_1$ on altitude is monotonic, with the altitude sensitivity of $k_1$ also increasing monotonically above 10-km altitude. The dependence of $k_2$ on altitude arises from the progressively higher peaking altitudes of the clear-air 118-GHz weighting functions. Although the dependence of $k_2$ on cell-top altitude is multiple-valued, this ambiguity can be resolved through $k_1$. For cell-top altitudes greater than $\sim 12$ km (which can be determined using $k_1$), the altitude sensitivity of $k_2$ increases monotonically.

The separation of the hooked regions of the constant-altitude curves in Figure 3.16 suggests that the minimum attainable rms error from 118-GHz retrievals of radiometrically opaque cell-top altitudes will be 1–1.5 km. This is consistent with 118-GHz statistical retrievals of cell-top altitude, which have exhibited rms errors of $\sim 1.5$ km [74]. Variations in the hydrometeor-size distribution have little effect on the retrieved cell-top altitude [see short dashed curve, Figure 3.16(b)], although variations in the altitudes of freezing and ice nucleation will shift the computed curves slightly, particularly for radiometrically thin ice canopies.

### 3.4.5 Sensitivity of Microwave Window Channels to Hydrometeors

To further illustrate the sensitivity of passive microwave observations to hydrometeors, the computed nadiral temperature-weighting functions for several uniform-density clouds and rain cells are shown in Figure 3.17 for the tropospheric window frequencies 6, 10, 18, 37, 90, 166, 220, and 340 GHz [82]. The computations used the iterative method (described in Section 3.3.3), assuming MP liquid spheres, SS ice spheres, and HG phase functions. Hydrometeor density
Figure 3.17. Computed nadiral weighting functions for the tropospheric window frequencies 6, 10, 18, 37, 90, 166, 220, and 340 GHz over uniform-density rain cells. The short dashed lines indicate the cell bottom and top altitudes (1 and 10 km, respectively). The long-dashed line indicates the altitude of ice nucleation (~7 km). The surface and cosmic background weights (W_s and W_{CB}) are shown above each plot.
ranges from 0 to 3 g/m³, and is uniform in altitude from 1 to 10 km. The mean-annual U.S. standard atmosphere is used for the temperature profile; the temperature of ice nucleation is −30°C. An exponential water-vapor decay with a 2-km scale height and 80% surface relative humidity is assumed, except in regions of nonzero hydrometeor density, where the relative humidity is 100%. The atmosphere is vertically discretized into layers of approximately ½-km thickness. A land background with 5% reflectivity is assumed.

From 6 to 220 GHz, the absorption due to liquid water and water vapor in the lower portion of the cell increases with frequency, as indicated by the relative amount of lifting in the weighting function peak altitudes below 7 km. Thus, the higher-frequency channels are progressively more sensitive to low-level liquid over land. At 340 GHz, a slight reduction in liquid scattering and absorption [see Figure 3.6(a)] somewhat reduces this sensitivity relative to 220 GHz.

The nonzero cosmic background weights $W_{CB}$ are due essentially to cell-top reflection, with the exception of minor contributions from surface reflection in the channels below 100 GHz. Depending on the ice density in the cell top (and, hence, the single-scattering albedo), the cell-top reflectivity can exceed 60%. Because water-vapor absorption decreases the ice single-scattering albedo at the higher frequencies (166, 220, and 340 GHz), the maximum cell-top reflectivities occur at somewhat lower frequencies (37 and 90 GHz). For typical ice densities, the cell-top reflectivities at 6 and 18 GHz always remain small (<20%). The reduction in the surface weights $W_S$ (relative to the hydrometeor-free cases) with increasing cell density is a consequence of increasing cell opacity and reflectivity. Although little absorption occurs in the ice layer at 6, 10, and 18 GHz, this becomes progressively stronger at higher frequencies.

For radiometrically opaque cells (i.e., $W_S \approx 0$), the cell-probing depth is the distance down into the cell over which most emission occurs. This defines a region that bounds most of the weighting function’s area below the cell top. Below this region, no direct radiometric observations of hydrometeor parameters can be made. However, indirect information on low-level hydrometeors might be inferred from correlations with direct radiometric observations of hydrometeors at higher levels in the cell. For a given cell density, the cell-probing depth decreases monotonically with increasing frequency. This suggests that hydrometeor-parameter profiling might be possible using microwave channels spaced widely apart in frequency [83].

The cell-probing depth can also be used to determine the applicability of the planar-stratified model for horizontally inhomogeneous precipitation cells. If the cell-probing depth is considerably smaller than the horizontal-scale size of dominant inhomogeneities in the cell’s hydrometeor distribution, then the planar-stratified model is applicable. In the case of a horizontally homogeneous precipitation cell, the scale size is the minimum horizontal extent of the cell. If the probing depth is comparable to or larger than the scale size, then the applicability of the planar-stratified model will depend on the particular amount of photon scattering from the line of sight into the horizontal directions (determined by the phase matrix), the coherent-wave attenuation in the horizontal direction (determined by the extinction matrix), and the scale size and magnitude of the cell inhomogeneities.
Figure 3.18. Computed nadiral brightness temperature (K) for a uniform density 1–10-km cell over land. Cell densities are 0, 0.03, 0.3, and 3.0 g/m³. The model assumed Marshall–Palmer liquid and Sekhon–Srivastava ice spheres, with Henyey–Greenstein phase functions.

The applicability of the planar-stratified model for horizontally finite cells has been investigated [84].

Brightness temperatures for the microwave window channels (Figure 3.18) illustrate the nonlinear dependence of the microwave spectrum to hydrometeor density. The higher frequencies (166, 220, and 340 GHz) are particularly sensitive to low water densities, but their sensitivities decrease at densities typical of light to moderate precipitation (~5–10 mm/h). In general, the wideband microwave spectrum is sensitive to several other meteorological parameters, including the cell top and bottom altitudes, the temperature of ice nucleation, the ice-size distribution, and the surface reflectivity. Off-nadir observations can also exhibit polarization sensitivity to hydrometeors, particularly over nearly specular surfaces such as the ocean [85].

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REFERENCES


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Ground-based radiometric measurements of atmospheric thermal emission have proven useful in a variety of applications, including meteorological observations and forecasting, communications, geodesy and long-baseline interferometry, satellite validation, climate, and fundamental molecular physics. One reason for the utility of these measurements is that, with careful design, radiometers can be operated in a long-term unattended mode under almost all weather conditions [1]. Another reason is the long-term development of theory and laboratory measurements that has led to a fundamental understanding of microwave radiative transfer (see Chapter 2).

In this chapter, we first provide a summary of methods used in deriving profiles from radiometric measurements. We then present applications of radiometric measurements that were made primarily by the Wave Propagation Laboratory (WPL) of the National Oceanic and Atmospheric Administration (NOAA). These observations were made by multichannel radiometers that operate from 20 to 90 GHz (15 to 3.3 mm). We confine our attention to tropospheric absorption and emission from water vapor, oxygen, and cloud liquid.

### 4.1 PROFILE INVERSION THEORY

The utility of ground-based microwave techniques to geophysics depends on the accuracy to which meteorologically significant parameters can be extracted from...
brightness-temperature observations. A necessary condition for parameter retrieval is that the direct problem of radiative transfer be solved (see Chapter 1). In the direct problem, from the spatial distributions of all relevant absorbers, scatterers, and emitters, we calculate the brightness temperatures resulting from these distributions. A more difficult task is to solve the inverse problem: given the measurements, what are the parameters (or profiles) that gave rise to them?

Inverse problems are common not only to geophysics, but to a large number of other disciplines, such as medicine, nuclear physics, and optics. From a mathematical point of view, many of the inverse problems can be reduced to solving a Fredholm first-kind integral equation. Properties of these equations (mainly undesirable) and techniques for their solution have been extensively studied in the past 30 years, both by mathematicians [2] and by scientists involved in atmospheric remote sensing [3–5]. In this section, after showing how the radiative transfer equation can be linearized and reduced to a Fredholm first-kind equation, we outline some of the commonly used techniques for solving this equation.

### 4.1.1 Linearization of the Radiative Transfer Equation

We linearize the radiative transfer equation (RTE), Eq. 1.8, by first expressing the integral as sums over small homogeneous layers \( i \) and then considering the effect on the brightness temperature \( T_b \) of small perturbations in temperature \( \delta T \), and in the absorption coefficient \( \delta \alpha \). Here we will not linearize the transfer equation for downlooking systems, but our results are easily generalized to this case. We first rewrite Eq. 1.8 in a slightly different form, and neglect subscripts indicating frequency:

\[
T_b = \int_0^\infty T'(s)\alpha(s)e^{-\tau(0,s)}ds + T_{b0}e^{-\tau(0,\infty)} \tag{4.1}
\]

where

\[
T'(s) = \frac{T(s)}{\Re[T(s)]}
\]

and

\[
\Re(T) = \frac{kT}{h\nu}(e^{h\nu/kT} - 1)
\]

As discussed in Chapter 1, the Rayleigh–Jeans approximation can be made by setting \( \Re(T) \approx 1 \), or, equivalently, by setting \( T'(s) \approx T(s) \). For generality, we will use the exact expression using \( T' \). The background brightness temperature \( T_{b0} \) is defined by Eq. 1.9.

We have changed the equation defining optical depth, Eq. 1.5, to a slightly more general form:

\[
\tau(s_1, s_2) = \int_{s_1}^{s_2} \alpha(s')ds' \tag{4.2}
\]
If we explicitly separate the contributions to $T_b$ from a layer $i$ extending between $s_{i-1}$ and $s_i$ (see Figure 4.1), we get

$$T_b = \int_0^{s_i} T'\alpha e^{-\tau(0,s)} \, ds + \int_{s_{i-1}}^{s_i} T'\alpha e^{-\tau(s_{i-1},s)} \, ds + e^{-\tau(0,s_i)} \int_s^{s_i} T'\alpha e^{-\tau(s_i,s')} \, ds' + e^{-\tau(0,s)} \int_0^{s_i} T'\alpha e^{-\tau(s_i,s)} \, ds + T_{bo} e^{-\tau(0,\infty)}$$

(4.3)

We consider changes in $T_b$, $(\delta T_b)_i$, due to changes in temperature, $\delta T_i$, and absorption, $\delta \alpha_i$, that occur only within layer $i$, and neglect second-order terms in $\delta T_i \cdot \delta \alpha_i$ to get

$$(\delta T_b)_i = e^{-\tau(0,s_{i-1})} [1 - e^{-\tau(s_{i-1},s_i)}] \frac{dT'_i}{dT_i} \delta T_i$$

$$+ \left[ T'_i e^{-\tau(0,s_i)} - e^{-\tau(0,s_i)} \int_{s_i}^{\infty} T'\alpha e^{-\tau(s_i,s')} \, ds' - T_{bo} e^{-\tau(0,\infty)} \right] \delta \tau_i$$

(4.4)

where

$$\delta \tau_i = \int_{s_{i-1}}^{s_i} \delta \alpha(s') \, ds'$$
and $\bar{T}_i^*$ is related to the average temperature of layer $i$. If we consider only the major constituents of the troposphere, $\alpha$ is a function of temperature $T$, dry density $\rho$, water vapor density $\rho_V$, and cloud liquid density $\rho_C$: $\alpha = \alpha (T, \rho, \rho_V, \rho_C)$. Thus,

$$\delta T_i = \int_{s_{i-1}}^{s_i} \left( \frac{\partial \alpha}{\partial T} \delta T + \frac{\partial \alpha}{\partial \rho} \delta \rho + \frac{\partial \alpha}{\partial \rho_V} \delta \rho_V + \frac{\partial \alpha}{\partial \rho_C} \delta \rho_C \right) ds \quad (4.5)$$

As we pass to the limit, the layer $(s_{i-1}, s_i)$, centered at $s$, approaches $\delta s$, and we get

$$(\delta T_b)_s = W_T(s) \delta T(s) \delta s$$

$$+ W_\rho(s) \delta \rho(s) \delta s + W_\rho_V(s) \delta \rho_V(s) \delta s + W_\rho_C(s) \delta \rho_C(s) \delta s \quad (4.6)$$

where

$$W_T(s) = \frac{dT'}{dT} (s) \alpha(s) e^{-\tau(0, s)}$$

$$+ e^{-\tau(0, s)} \frac{\partial \alpha(s)}{\partial T} \left[ T'(s) - T_{b0} e^{-\tau(s, \infty)} - \int_s^\infty T' e^{-\tau(s, s')} ds' \right] \quad (4.7)$$

and

$$W_\rho(x) = e^{-\tau(0, s)} \frac{\partial \alpha(s)}{\partial \rho_x} \left[ T'(s) - T_{b0} e^{-\tau(s, \infty)} - \int_s^\infty T' e^{-\tau(s, s')} ds' \right] \quad (4.8)$$

The quantity $W_T(s)$, called the temperature weighting function, is a measure of the brightness temperature response to a change in temperature at level $s$. Although it is common in the remote-sensing community to call $\alpha(s) \cdot \exp \left[ -\tau(0, s) \right]$ the temperature-weighting function, this is strictly correct in the Rayleigh-Jeans approximation only when $\partial \alpha / \partial T = 0$. The weighting function for the generic density variable $\rho_x$ is given by Eq. 4.8. Here, $x$ can represent dry density, water-vapor density, or cloud-liquid density. The total change in brightness temperature $\delta T_b$ from changes in all of the variables along the profile from 0 to $\infty$ is given by

$$\delta T_b = \int_0^\infty W_T(s) \delta T(s) ds + \int_0^\infty W_\rho(s) \delta \rho(s) ds$$

$$+ \int_0^\infty W_\rho_V(s) \delta \rho_V(s) ds + \int_0^\infty W_\rho_C(s) \delta \rho_C(s) ds \quad (4.9)$$

Equation 4.9 is called the linearized radiative transfer equation, or the perturbation form of the radiative transfer equation [6]. The weighting functions defined by Eqs. 4.7 and 4.8, and entering in Eq. 4.9, assume fundamental importance in profile-inversion theory. It should be emphasized that these functions are relative
to some initial background (or first-guess) profiles of all the variables contributing to the brightness temperature; for example, temperature, dry-air density, water-vapor density, and cloud-liquid density. Examples of weighting functions for various types of ground-based and satellite microwave remote-sensing problems will be given in Sections 4.2 and 4.3.

4.1.2 Use of the Linearized Radiative Transfer Equation in Profile Retrieval

In general, one starts with a set of brightness temperature measurements $T_{b,\text{meas}}$ from which profiles are to be derived. The idea behind linearized inversion is to start with some initial-guess profile and, using the set of measurements at hand, derive corrections to the initial guess. If the set of measurement ordinates, usually spectral channels, has been well chosen, the sensitivity of $T_b$ to the desired profile will be maximized, and the corresponding influence of unwanted emission will be minimized. However, in most practical problems, some contamination will occur. For example, in temperature sounding (see Section 4.3), there is usually some influence on the set of $T_b$'s from both water vapor and clouds. In such cases, the simultaneous use of temperature-, water vapor- and cloud-sensing channels is desirable. Consequently, this requires a first-guess profile for all of these variables. For simplicity of notation, let $f_o(s)$ represent this initial state of temperature, density, and moisture. By means of Eq. 4.1, we calculate $(T_b)_0$ for this function:

$$ (T_b)_0 = T_b[f_o(s)] $$

Next, using both $T_{b,\text{meas}}$ and $(T_b)_0$, we form

$$ \delta T_b = T_{b,\text{meas}} - (T_b)_0 $$

and solve Eq. 4.9 for the perturbation profiles of temperature and density. For moderate to highly nonlinear problems, the process can be iterated by recalculating $(T_b)_0$ and the weighting functions from a previous solution, and then repeating the solution process.

Two features of radiometric measurements of $T_b$ are generally true: the first is that only a finite number of measurements are available; second, the measurements are imperfect and always contain errors. We indicate this explicitly when we relate Eq. 4.9 to a Fredholm integral equation of the first kind:

$$ g_i + \epsilon_i = \int_a^b W_i(s)f(s)\, ds + \epsilon_i, \quad i = 1, 2, \cdots, n $$

where $g_i$ is the $i$th "perfect" measurement that is contaminated by an unknown error $\epsilon_i$, $W_i(s)$ is the known weighting function, and the unknown function $f(s)$ is defined in the interval $a \leq s \leq b$. We use standard mathematical notation in Eq.
4.12; the correspondence with Eqs. 4.9–4.11 requires regarding \( f(s) \) as a composite of unknown temperature and density profiles, and \( W_i(s) \) as a composite of their corresponding weighting functions.

In most practical and numerical problems, rather than considering the case of inferring functions defined on a continuous interval, \( a \leq s \leq b \), one considers only functions defined on a discrete set of points \( s_i, i = 1, 2, \cdots, m \). For computer implementation, integrals are replaced by their quadrature approximation, and integral equations are replaced by matrix equations. Thus, the discrete analog of Eq. 4.12 is

\[
\mathbf{g}_e = \mathbf{g} + \mathbf{\varepsilon} = \mathbf{A}\mathbf{f} + \mathbf{\varepsilon}
\]

(4.13)

where \( A_{ij} = w_j W_i(s_j), \ i = 1, 2, \cdots, n; j = 1, 2, \cdots, m \)

\[
\mathbf{f} = \begin{bmatrix} f(s_1), & f(s_2), & \cdots, & f(s_m) \end{bmatrix}^T
\]

\[
\mathbf{g}_e = \begin{bmatrix} g_{e_1}, & g_{e_2}, & \cdots, & g_{e_m} \end{bmatrix}^T
\]

and \( w_j \) is quadrature weight associated with the \( j \)th point. The superscript \( T \) means matrix transposition. The measurement vector \( g_e \) is the sum of the perfect measurement vector \( g \) and the noise vector \( \varepsilon \).

In radiometric sensing, the error terms \( \varepsilon_i \) can arise from several different causes:

1. **Experimental** noise. This noise consists of both a random component and a bias. The random noise is usually Gaussian in character and has known statistics. Bias terms are particularly troublesome, and must be reduced to tolerable levels by careful calibration and by comparison of derived products with ground truth.

2. **Linearization** errors. If the errors from linearizing Eq. 4.1 are not some reasonable factor less than the experimental noise level, iterative methods are necessary.

3. Errors from unknown parameters. Such errors include emission from the Earth’s surface when its emissivity or its temperature are not exactly known, and atmospheric emission from contaminating species, for example, emission from water vapor or ozone in a temperature-sounding problem. These errors can frequently be reduced by taking additional measurements at appropriate frequencies. If supplementary measurements are not available, the errors can be modeled as random variables with estimated statistics.

4. Errors in the weighting functions. If, given the complete state of the atmosphere, it is impossible to calculate the brightness temperatures with an accuracy better than the experimental noise level, the inverse problem cannot be solved by physical retrieval methods. Fortunately, in the microwave sounding problem, a wealth of experimental and theoretical information exists on the relevant variables of radiative transfer [7–9] and the direct problem seems well understood.
4.1.3 Description of Commonly Used Inversion Techniques

We have discussed how the RTE can be linearized in terms of a suitable initial-guess profile, and also how the RTE can be discretized and placed in a form suitable for computer implementation. In the following portions of this section, we will describe some commonly used techniques for profile reconstruction. Which of these techniques is appropriate for a particular problem depends on the amount of information available for a first-guess profile, the accuracy of the first guess, the amount of *a priori* information, and the computer resources available.

**Regularization Techniques**

Regularization of the quadrature approximation to the first-kind Eq. 4.12 was developed in the early 1960s [2, 5] and was first applied to the thermal-sounding problem by Wark and Fleming [10]. This process introduces controlled smoothing of solutions by deriving a compromise between a weighted least-squares solution to Eq. 4.13 and a least-squares departure from an *a priori* guess. Mathematically, this smoothing is achieved by minimizing a quadratic form that is the sum of two positive terms—one measuring the fit to the measurements $g_e$ and the other measuring the fit to the *a priori* guess $f_0$. Thus, the quadratic form $Q(f)$:

\[
Q(f) = (Af - g_e)^T (Af - g_e) + \gamma (f - f_0)^T (f - f_0)
\]

is minimized with respect to $f$ to yield

\[
\hat{f} = f_0 + A^T [AA^T + \gamma I]^{-1} [g_e - Af_0]
\]

where $\hat{f}$ is the solution derived from an initial guess $f_0$, $\gamma$ is a strictly positive smoothing parameter, and $I$ is the identity matrix. A thorough discussion of the choice of $\gamma$ is given in [5]; its relationship to inverse signal-to-noise ratio is discussed in Westwater and Strand [11].

The accuracy of the solution, Eq. 4.15, depends on the first guess of $f_0$. Thus, problems can arise either from an unreasonably smooth $f_0$; for example, $f_0 = \text{constant}$, or from an $f_0$ that has too much structure; for example, $f_0$ contains either too sharp a change of gradient or even the correct gradient change at the wrong location. At the present time, thermal soundings are derived using an $f_0$ based either on climatology or on a meteorological forecast [6]. As might be expected, rms retrieval errors, evaluated over an ensemble of profiles, are generally smaller when a forecast, rather than a climatological, $f_0$ is used [12]. However, when a forecast initial guess is used, the resultant retrieval is not independent of the forecast, and it is not always apparent if the structure in a solution is from measurements or from the forecast. Thus, it is frequently useful to compare the solution of the inverse problem with the initial guess. In any event, it is evident that the choice of $f_0$ depends on many factors, including the use to which the retrieval $\hat{f}$ is applied.

To illustrate the dependence of the temperature retrieval on the initial guess, in Figure 4.2, we show rms errors in deriving temperature as a function of pressure.
CHAPTER 4: REMOTE SENSING OF METEOROLOGICAL VARIABLES

Figure 4.2. Profiles of the rms temperature differences between 139 radiosonde profiles and regularization solutions when forecasts and climatology are used as initial profiles. After Fleming [12].

from satellite measurements of upwelling radiance. The retrievals were derived by the regularization method from computer-simulated radiances contaminated by noise [12]. In general, the accuracy of the solution reflects the accuracy of the initial guess.

Iterative Techniques

Iterative techniques, in which a solution \( f \) is approached by successive approximations, have been developed and applied to thermal sounding [13, 14]. The general form of linear iterative algorithms is

\[
\hat{f}_k = \hat{f}_{k-1} + D A^T (g_r - A \hat{f}_{k-1}) \quad k = 1, 2, \ldots \tag{4.16}
\]

where \( D \) is a specified matrix. The effect of various choices of \( D \) was investigated by Strand [15]. In particular, he showed that

\[
D = (A^T A + \gamma I)^{-1} \tag{4.17}
\]
with starting vector $f_0$ gives in the first iteration exactly the same solution as Eq. 4.15. Strand’s work was especially important in showing the close correspondence between iterative and smoothing methods. If the number of iterations, $k$, is allowed to become arbitrarily large, driving the residuals to zero, the solution becomes unstable. This is precisely what happens in the regularization method when the smoothing parameter $\gamma$ is allowed to approach zero. In his application of iterative methods to quasi-operational soundings, Smith [14] iterates until the residuals are close to the experimental noise levels.

**A Priori Linear Statistical Method**

The *a priori* linear statistical method [3, 11] has been applied to both ground-based and satellite thermal sounding for several years. This method requires knowledge of the average and covariance of both the unknown function $f$ and the error $\varepsilon$. We define $\langle f \rangle$, $\langle \varepsilon \rangle$ as the ensemble average of $f$, $\varepsilon$:

$$\langle f \rangle = \mathbb{E}(f) \quad (4.18)$$

and

$$\langle \varepsilon \rangle = \mathbb{E}(\varepsilon) \equiv 0 \quad (4.19)$$

The covariance matrices of $f$ and $\varepsilon$ are given by

$$S_f = \mathbb{E}(f - \langle f \rangle)(f - \langle f \rangle)^T \quad (4.20)$$

and

$$S_\varepsilon = \mathbb{E}(\varepsilon\varepsilon^T) \quad (4.21)$$

The expectation value $\mathbb{E}$ is taken over a joint probability distribution of $f$ and $\varepsilon$, and the superscript $T$ refers to matrix transposition. In practice, an *a priori* ensemble of representative radiosonde profiles is used to determine $\langle f \rangle$ and $S_f$, and $S_\varepsilon$ is determined experimentally.

At least three separate derivations of statistical inversion equations have been presented: (1) maximum likelihood, assuming Gaussian statistics [16]; (2) minimum variance [17, 18]; and (3) maximum probability, using Bayes theorem [19]. To emphasize the obvious correspondence with the regularization method given by Eqs. 4.14 and 4.15, we present the maximum likelihood method. A general reference text for maximum likelihood estimation is Morrison [20]. We assume (a) that both $f$ and $\varepsilon$ obey Gaussian statistics and (b) that $f$ and $\varepsilon$ are uncorrelated. The assumptions (a) imply that

$$p_r(f) = \frac{1}{(2\pi)^n/2 |S_f|^1} \exp \left[-\frac{1}{2}(f - \langle f \rangle)^T S_f^{-1}(f - \langle f \rangle)\right] \quad (4.22)$$
and

\[ p_\varepsilon(\varepsilon) = \frac{1}{(2\pi)^{n/2} |S_\varepsilon|} \exp \left( - \frac{1}{2} \varepsilon^T S_\varepsilon^{-1} \varepsilon \right) \]  

(4.23)

where \( |S_f| \) and \( |S_\varepsilon| \) are the determinants of \( S_f \) and \( S_\varepsilon \), respectively. The assumption that \( f \) and \( \varepsilon \) are uncorrelated leads to

\[ p_{f,\varepsilon}(f, \varepsilon) = p_f(f) p_\varepsilon(\varepsilon) \]  

(4.24)

In Eqs. 4.22-4.24, \( p_f(f) \) and \( p_\varepsilon(\varepsilon) \) are the probability densities of \( f \) and \( \varepsilon \), respectively, and \( p_{f,\varepsilon}(f, \varepsilon) \) is the joint density of \( f \) and \( \varepsilon \). The likelihood function of \( f \) is \( p_{f,\varepsilon}(f, \varepsilon) \)

\[ L(f) = p_f(f) p_\varepsilon(g_e - Af) \]  

(4.25)

where Eq. 4.13 has been used to express \( \varepsilon \) in terms of \( g_e \) and \( f \). Because \( L(f) \) is maximized when its logarithm is maximized, the maximum likelihood estimate of \( f \) is found by solving

\[ \frac{\partial \ln L(f)}{\partial f} = 0 \]  

(4.26)

This is equivalent to minimizing the quadratic form \( Q(f) \):

\[ Q(f) = (Af - g_e)^T S_e^{-1} (Af - g_e) + (f - \langle f \rangle)^T S_f^{-1} (f - \langle f \rangle) \]  

(4.27)

The two terms in Eq. 4.27 represent the weighted least-squares fit to the measurements \( g_e \) and the weighted least-squares fit to the climatological mean \( \langle f \rangle \). An intuitive way of interpreting the estimation process is that two sets of measurements are available to estimate \( f \): the first is \( g_e \), the second is \( \langle f \rangle \).

Minimizing Eq. 4.27 with respect to \( f \) yields

\[ \hat{f} = \langle f \rangle + S_f A^T (AS_f A^T + S_e)^{-1} (g_e - A \langle f \rangle) \]  

(4.28)

A slightly more general form of Eq. 4.28 is written as

\[ \hat{f}' = E(f' g_e'^T) E(g_e' g_e'^T)^{-1} g_e' \]  

(4.29)

where the primed quantities refer to departures from the mean; for example, \( f' = f - \langle f \rangle \), etc. The covariance matrix of the error in the estimation of \( f \), \( S_{f-\hat{f}} \), is given by

\[ S_{f-\hat{f}} = S_f - S_{f,g_e} S_{g_e}^{-1} S_{g_e,f} \]  

(4.30)
where

$$S_{r,g_e} = E(f - \langle f \rangle)(g_e - \langle g_e \rangle)^T$$  \hspace{1cm} (4.31)

Equations 4.29 and 4.30 have a variety of practical uses in atmospheric remote sensing. We mention the following:

1. Direct retrieval of a profile and its linear functionals. Examples of retrievals of temperature and water-vapor profiles will be given in Sections 4.3, 4.4 and 4.5.

2. An \textit{a priori} estimate of system achievability. We illustrate in Figure 4.3 [20a] the use of Eq. 4.30 in predicting accuracy in remote sensing of vertical temperature profiles. The curve labeled "Climatology" shows the square roots of the diagonal elements of $S_f$, and each point represents the rms variation of temperature over a 3-month period. The curve labeled "Predicted Error" is the square root of the diagonal elements of $S_{f-f}$ and represents the predicted rms error from retrievals using noise-contaminated brightness temperature measurements. As shown, experimentally achieved accuracies are in close correspondence with \textit{a priori} predictions.

3. A criterion for optimum measurement ordinates. For a fixed number of measurement ordinates, the optimum location of measurements is the one that

![Figure 4.3. Predicted radiometer errors and climatological variations (solid curves), observed differences between (mean and rms) radiometer and radiosonde (dashed curves), and rms differences of mean temperature for 100-mbar layers (circles). After Decker [20a].](image-url)
gives the minimum expected mean square error, that is, the set that minimizes Eq. 4.30 [11].

4. Imposition of constraints. Exact constraints, such as the knowledge of surface temperatures, can be imposed by applying LaGrange multiplier techniques to the minimization of Eq. 4.27. More subtle constraints, such as the location of sharp spatial gradients in \( f \), or the knowledge that \( f \) is a particular climatological type, can be imposed by placing the appropriate restrictions on the \( a priori \) ensemble used to derive \( S_f \) [21].

**Regression Methods**

In some satellite applications, radiances calculated from radiosondes do not satisfactorily agree with measured radiances. This can occur for a variety of causes, such as improper atmospheric transmission models, uncertainties in the frequency response of bandpass filters, and spatial and temporal differences between radiosondes and satellites. To circumvent these problems, several groups used regression methods to process soundings. In these methods, the cross-covariance matrix \( S_{f,g_e} \) and the covariance matrix \( S_{g_e} \) in Eq. 4.29 are determined from a representative ensemble of realizations of \( f \) and \( g_e \). This set of realizations is derived from collocated (in space and time) radiosonde and radiometric observations. The matrix product \( S_{f,g_e} S_{g_e}^{-1} \) forms a set of regression coefficients that does not require an algorithm to calculate \( g_e \) from \( f \). For operational temperature and moisture soundings provided by NOAA/NESDIS (National Environmental Satellite, Data and Information Service), these coefficients were computed for five separate latitude zones and updated weekly using collocated radiosonde and satellite data uniformly distributed over the previous 2 weeks [22].

**Inverse Covariance Weighting**

In applications that require the combination of distinct systems, it is sometimes desirable to merge profile retrievals that were obtained separately and independently. For example, ground-based retrievals obtained by \( a priori \) statistical methods can be combined with operational satellite retrievals derived by regression techniques. Thus, if \( f_i, i = 1, 2, \) is the unbiased retrieval derived from the \( i \)th system and \( S_i \) is its known covariance matrix, then the unbiased combined retrieval is given by [3]

\[
\hat{f} = (S_1^{-1} + S_2^{-1})^{-1} (S_1^{-1}\hat{f}_1 + S_2^{-1}\hat{f}_2)
\]  

(4.32)

The method is readily generalized to three or more independent systems.

**Concluding Remarks**

In this section, we have summarized techniques that we apply later to solve inverse problems in radiometric remote sensing. However, there are other techniques that are still being developed and applied, but are beyond the scope of the work reported here. Among these techniques are the following.
1. Kalman filtering [23–25]. Kalman filtering is a generalization of the statistical estimation procedure presented here. In the Kalman technique, a state vector is estimated as it evolves according to a known model with known uncertainties from both current and past measurements.

2. Pattern classification [26–28]. A generic ensemble of measurements and profiles is decomposed into specific classes or subensembles, each of which contains profiles of similar shape. Subensemble-specific expansion functions are then used in profile retrieval. The decomposition can be achieved from radiances alone, but an improvement in classification can be obtained if synoptic meteorological information is also used.

3. Multidimensional retrievals [29]. This technique is particularly appropriate for satellite retrievals and introduces horizontal and vertical correlations into the retrieval process. If this approach were implemented for a surface-based application, then temporal and vertical correlations would be used.

4. Variations of the Backus–Gilbert technique [30, 31]. This technique constructs "averaging kernels" from a linear combination of weighting functions. For a particular height level, the coefficients in the averaging kernel selection allow a compromise between spatial resolution and variance from instrumental noise.

4.2 Radiometric Systems Operated by the WPL

In most of this chapter, data from WPL radiometers are used to illustrate the concepts and capabilities of current ground-based systems. Although we do show data taken with other radiometers, the WPL radiometers typify the state of the art for ground-based remote sensing and we will briefly describe both zenith-viewing and scannable systems. Table 4.1 shows a description of the current WPL radiometric facilities.

4.2.1 The Six-Channel Radiometer

Since 1982, WPL has operated a fully automatic ground-based remote-sensing system called the Profiler [1]. This system, designed to measure tropospheric meteorological variables, uses both UHF and VHF radars to measure winds, and microwave radiometers to derive temperature and moisture. For convenience, the radiometric portion of the system described here will be referred to as the Profiler. All electronics, computers, and antennas are housed in a trailer whose temperature is strictly controlled. The antennas view zenith radiation incident on a flat plate reflector that is external to the trailer. Radiation from the zenith direction is redirected by the reflector oriented at 45° through a Teflon/Styrofoam window onto an offset parabolic antenna. At one focus of the parabola is a hybrid-mode feed that is constructed to give equal beamwidths of 2.5° to the frequency pairs that share the antenna.
CHAPTER 4: REMOTE SENSING OF METEOROLOGICAL VARIABLES

TABLE 4.1  WPL Radiometer Facilities

<table>
<thead>
<tr>
<th>Location</th>
<th>Equipment</th>
<th>Viewing</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Stapleton Airport, Denver, Colorado</td>
<td>Six-channel radiometer</td>
<td>Zenith equal</td>
<td>Currently operating</td>
</tr>
<tr>
<td></td>
<td>(20.6, 31.65, 52.85,</td>
<td>beamwidths at all</td>
<td></td>
</tr>
<tr>
<td></td>
<td>54.85, 55.45, and 58.8 GHz)</td>
<td>channels (2.5°)</td>
<td></td>
</tr>
<tr>
<td>2. Platteville, Colorado</td>
<td>Two-channel radiometer</td>
<td>Zenith, equal</td>
<td>Currently operating</td>
</tr>
<tr>
<td></td>
<td>(20.6 and 31.65 GHz)</td>
<td>beamwidths (5.0°)</td>
<td></td>
</tr>
<tr>
<td>3. Fleming, Colorado</td>
<td>Two-channel radiometer</td>
<td>Zenith, equal</td>
<td>Discontinued October 1, 1988</td>
</tr>
<tr>
<td></td>
<td>(20.6 and 31.65 GHz)</td>
<td>beamwidths (5.0°)</td>
<td></td>
</tr>
<tr>
<td>4. Flagler, Colorado</td>
<td>Two-channel radiometer</td>
<td>Zenith, equal</td>
<td>Discontinued October 1, 1988</td>
</tr>
<tr>
<td></td>
<td>(20.6 and 31.65 GHz)</td>
<td>beamwidths (5.0°)</td>
<td></td>
</tr>
<tr>
<td>5. Transportable</td>
<td>Three-channel radiometer</td>
<td>Steerable full-sky</td>
<td>Currently operating</td>
</tr>
<tr>
<td></td>
<td>(20.6, 31.65, and 90.0 GHz)</td>
<td>coverage, equal</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>beamwidths (2.5°)</td>
<td></td>
</tr>
<tr>
<td>6. Transportable</td>
<td>Two infrared radiometers</td>
<td>Steerable (5.0°)</td>
<td>Currently operating</td>
</tr>
<tr>
<td></td>
<td>(10.6-μm wavelength)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Stapleton Airport, Denver, Colorado</td>
<td>Two-channel radiometer</td>
<td>Zenith, equal</td>
<td>Under construction</td>
</tr>
<tr>
<td></td>
<td>(23.9 and 31.65 GHz)</td>
<td>beamwidths (2.5°)</td>
<td></td>
</tr>
</tbody>
</table>

WPL currently operates a 6-channel microwave instrument with moisture-sensing channels at 20.6 and 31.65 GHz, and temperature-sensing channels at 52.85, 53.85, 55.45, and 58.80 GHz. The channel at 20.6 is near the 22.235-GHz water-vapor absorption line and the 31-GHz channel is in a clear-air "window." The upper four channels are in the 60-GHz oxygen absorption band. For this instrument, three parabolas are required for the six frequencies. The receivers are of the Hach [9] type and use automatic gain control (AGC) with triple switching between the antenna, a reference blackbody at 45°C, and a second blackbody at a temperature 100°C above the first. In addition to the six radiometric measurements, surface meteorological observations of pressure, temperature, and relative humidity are also taken. All data are averaged on a 2-min time interval and provided to various users. The system operates next to the National Weather Service (NWS) Forecast Office at Stapleton International Airport, Denver, Colorado. A radiosonde launch facility is located about 10 m from the radiometer, and, consequently, ground truth is available at least twice daily from balloon soundings of
4.2 RADIOMETRIC SYSTEMS OPERATED BY THE WPL

Temperature, water vapor, and winds. External calibration of the system uses: (a) calculations of brightness temperature from radiosondes and (b) the “tip cal” method [31a].

The response of a radiometer channel to atmospheric variables is described quantitatively by the weighting functions (see Eqs. 4.7 and 4.8) for temperature, water vapor density, dry-air density, and cloud liquid density. Another commonly used choice of variables would replace vapor and dry-air densities by vapor partial pressure and total pressure. The weighting functions depend on (a) the absorption characteristics of the 22.235-GHz water-vapor line and the vapor continuum, (b) the 60-GHz oxygen-absorption band, and (c) the Debye absorption of cloud liquid particles. The pressure, temperature, and density dependencies of all of the absorbers are required to evaluate Eqs. 4.7 and 4.8. A representative set of weighting functions is shown in Figure 4.4[31b]. For these calculations, the absorption coefficients for H$_2$O and O$_2$ were taken from Liebe [7] and those for cloud liquid from Westwater [32]. The channel responses can be summarized as follows:

Temperature. Because of strong O$_2$ absorption near 60 GHz, the primary response to temperature is from the three highest-frequency channels, with a much smaller response from the lower three. Thus, for example, in measuring water vapor from 20.6- and 31.65-GHz channels, the effects of temperature are usually of second order.

Dry Density. The contribution of dry density or total pressure fluctuations to brightness-temperature fluctuations is generally negligible, or can be very well estimated from surface meteorological observations.

Water Vapor Density. Because of its nearness to the 22.235-GHz H$_2$O line, the greatest response to vapor is exhibited by the 20.6-GHz channel, and, in the region where most of the water vapor is concentrated, its weighting function is almost independent of height, that is, precipitable water will have the strongest influence on clear-air variations. The plots also show that the vapor influence on the “temperature-sensing” channel at 53.85 GHz must be taken into account.

Cloud Liquid Density. The lower four channels are all influenced by clouds, and cloud effects must be accounted for in both temperature and water-vapor retrievals. As illustrated in Sections 4.4 and 4.5, the data from channels at 20.6 and 31.65 GHz are sufficient to determine the total amounts of cloud liquid water and precipitable liquid water.

4.2.2 The Colorado Research Network of Dual-Channel Radiometers

A limited network of dual-channel radiometers, operating at 20.6 and 31.65 GHz, was operated in the front range of eastern Colorado from 1985 to 1988 [32a]. The receiver designs were identical and the antenna designs were similar to the lower-frequency pair of the six-channel system, except that the beamwidths were 5.0°.
Figure 4.4. Weighting functions for temperature, water vapor, liquid-water density, and dry-air density, for the six-channel radiometer. These functions were generated from a 10-year climatological mean for the months of December, January, and February at Denver, Colorado. After Canavero et al. [31b].
In addition, no radiosonde information was routinely available for ground truth at the outlying sites. Consequently, all external calibration was done by the "tip cal" method. The location of the Colorado Research Network is shown in Figure 4.5. The stations at Denver and Platteville are still operating; a third radiometer has been operated at various locations within Colorado. Derived products from the radiometers are distributed in real time to local research and operational meteorologists. In addition, archives of the data are maintained and used for several geophysical research purposes.

4.2.3 The Steerable Three-Channel Radiometer

In a parallel development to the six-channel radiometer, in 1980, a steerable and transportable two-frequency radiometer was also designed and constructed [33]. This instrument, with channels at 20.6 and 31.65 GHz, was used in a variety of activities: weather modification, clouds and climate, and satellite communication. It also was operated beside each of the network radiometers for calibration and data intercomparison experiments [34]. Finally, in 1987, a third channel was added to the steerable radiometer. This channel, operating at 90.0 GHz (3.3 mm), is proving to be of value in several new applications, as we describe in Section 4.6. The steerable radiometer has many common design features with the zenith-viewing instruments described before. The receiver design for each channel is identical, and offset parabolic reflectors are used. The beamwidths of all three channels are the same, 2.5°. However, the design of the flat reflectors is different, with two,
rather than one, reflecting plates being used. A side view of the system, drawn to include the 90.0-GHz channel, is shown in Figure 4.6.

Weighting functions for this system are shown in Figure 4.7. The channel responses can be summarized as follows:

*Temperature.* The temperature response at 90 GHz is a factor of 3 to 4 greater than either that of 20.6 or 31.65 GHz, but, in general, is small. For example, a $10^\circ$C increase in temperature of the first kilometer would change the 90-GHz $T_b$ by $-0.6$ K.

*Pressure.* The response to pressure fluctuations is negligible.

*Water Vapor Density.* Near the surface, the response at 90 GHz is about a factor of 2 stronger than that at 20.6. The response also decays approximately linearly with height, which is in sharp contrast to the behavior at 20.6 GHz.

*Cloud Liquid Density.* Notice in particular that the 90.0-GHz channel responds to changes in liquid by a factor of about 5 relative to the cloud-sensitive 31.65-GHz channel. This increased sensitivity to liquid can be important when determining if small amounts of liquid are present in supercooled clouds. On the negative side, the 90.0-GHz channel will saturate for liquid amounts on the order of 1 to 2 mm. Thus, this channel may only be useful in clear or in winter cloud studies.

![Diagram](image-url)  
**Figure 4.6.** Side view of a steerable three-channel radiometer, showing the mechanical layout; central rays from the zenith are shown as dashed lines with arrows. After Westwater and Snider [32a].
As discussed in Chapter 2, microwave thermal radiation from the atmosphere originates primarily from oxygen, water vapor, and liquid water, and depends on their temperature and concentration. For a well-mixed gas such as oxygen, whose fractional concentration is independent of altitude below 80 km, the radiation contains information primarily on atmospheric temperature. It is thus possible to infer temperature structure from both satellite-based (see Chapter 6) [5] and ground-based [1, 35, 36] radiation measurements in the 60-GHz (wavelength = 0.5 cm) oxygen-absorption complex.

Temperature profiles are measured by radiosonde balloons, or RAOBs, every 12 hours at numerous locations on the continents. Numerical weather forecasts, based on dynamical models and these radiosonde observations, have a certain degree of accuracy. To be useful, indirect soundings must provide information that is not predictable from the forecasts. Because radiometric retrievals of temperature and humidity profiles are limited in vertical resolution, the unique information that can be provided is from the extensive horizontal coverage supplied by satellites and from the temporal continuity provided by surface-based radiometers. Because
clouds are present roughly 50% of the time, this extended spatial and temporal coverage can be achieved only if the remote sounders can produce accurate profiles in the presence of cloud.

For the benefit of the reader not accustomed to seeing vertical temperature profiles, a few representative radiosonde soundings of this variable are shown in Figure 4.8. The two ordinate scales, height in km and pressure in mbar, are used commonly in atmospheric science. The convective profile on the left is common during summertime days; the surface-based (nocturnal) inversion is common to winter and to nighttime conditions; finally, the elevated inversion occurs both at the interface of two different air masses and when subsidence is present. The upper level, called the tropopause (the boundary between the troposphere and the stratosphere), is usually characterized by an abrupt change in the rate of decrease of temperature with height. The height and temperature at the base of the surface-based inversion, at the base of the elevated inversion, and at the tropopause are all important meteorological parameters, and the ability to measure them remotely is desirable.

Before presenting retrieval results for either ground-based, satellite-based, or combined temperature soundings, some qualitative remarks about temperature-weighting functions are appropriate. If we neglect the (usually) weak temperature

![Typical Atmospheric Vertical Temperature Profiles](image)

**Figure 4.8.** Typical atmospheric-temperature profiles from radiosondes (Pt. Mugu, California, March 1976).
dependence of the transmission in Eq. 4.6, and, in addition, make the Rayleigh–Jeans approximation, then $\partial \alpha / \partial T \sim 0$ and the weighting function is approximately given by

$$W_T(s) \sim \alpha(s) \cdot \exp \left[ - \int_0^s \alpha(s') ds' \right].$$

The weighting functions for satellite remote sensing are qualitatively described as follows, where we interpret $s$ as the depth into the atmosphere. At the top of the atmosphere where $s = 0$, the density of oxygen, and hence $\alpha(0)$ and $W_T(0)$ are 0. Because of competition between increasing emission and decreasing transmission, the satellite weighting functions increase smoothly with $s$ from a zero value to a single maximum and then smoothly decay to small values. The peak of the function is determined by the strength of the absorption $\alpha(s)$: weighting functions corresponding to strong lines peak high in the atmosphere and lower regions are probed.

Figure 4.9. Temperature-weighting functions, in relative units, for various channels of the ground-based radiometric Profiler and the satellite-based Microwave Sounding Unit (MSU). The three upper curves are for the MSU; the four lower curves are for the Profiler. After Westwater et al. [37].
using weaker, more transparent lines. For the ground-based case, the shapes of the weighting functions are completely different. Here, as we interpret \( s \) as the height above the surface, the absorption \( \alpha(s) \) has its maximum at the surface and decays approximately exponentially with height. Hence, \( W_T(s) \) has its maximum at the surface, but decays with a rate that depends on the strength of \( \alpha(s) \): for strong absorption, \( W_T(s) \) decays quickly and only the lower atmosphere is seen; at weaker absorption, the higher levels are probed. Typical weighting functions, plotted relative to their maxima, for satellite- and ground-based systems are shown in Figure 4.9 [37].

4.3.1 Ground-Based Temperature Sensing

Microwave temperature-profiling radiometers have been designed primarily for downward viewing from a satellite. However, upward-looking instruments can provide useful high-temporal-resolution information about low-altitude temperature structure [1, 35, 36, 38]. In this section, we present examples of ground-based retrievals, and comment on the advantages and limitations of the technique. Weighting functions for temperature sensing can be generated by frequency variation, by angular variation, or by a combination of both [38a]. Here, we will discuss only multifrequency techniques at a fixed zenith. Typical weighting functions for the WPL six-channel upward-looking radiometer were shown in Figure 4.4.

We use the \textit{a priori} statistical inversion Eq. 4.29 to derive temperature profiles at the Denver location of the six-channel radiometer. The measurement vector \( \mathbf{g}_e \) is composed of nine components: \( \tau \)'s at 20.6 and 31.65 GHz; \( T_b \)'s at 52.85, 53.85, 55.45, and 58.8 GHz; and surface meteorological measurements of temperature, pressure, and relative humidity. Our \textit{a priori} ensembles of meteorological variables that are required for the statistical averaging in Eq. 4.29 were taken from a 10-year climatology of radiosondes at Denver. "Pseudo-measurements" of \( \mathbf{g}_e \) were simulated by calculation of \( T_b \)'s from the radiosondes and then contaminating them with 0.5 K Gaussian noise. Clouds were simulated by the techniques described in Decker et al. [39]. Finally, retrieval coefficients are constructed from 3-month averages centered on the month in operation; for example, for the month of July, we use coefficients from \textit{a priori} data of June, July, and August.

A time sequence of temperature retrievals, extending over 14 hours, is shown in Figure 4.10. Although some of the sharp profile structure is smoothed, a reasonable representation is obtained of the decay and reestablishment of the nocturnal thermal inversion.

A variety of temperature and humidity retrievals (see Section 4.4) are compared with radiosondes in Figure 4.11. In general, fine details of the profile are smoothed out, but the overall features of the profiles are well represented up to tropopause altitudes. An undesirable feature of these retrievals is the smoothing of elevated inversions.

A statistical comparison of Profiler temperature retrievals versus radiosondes was given in Figure 4.3. Note that in the first \( \sim 500 \) mbars of the atmosphere, the
Figure 4.10. Time sequence of lower atmospheric-temperature profiles at 2-h intervals showing the decay and reformation of a ground-based temperature inversion. Successive profiles are displaced by 5°C to the right of the preceding profile. The profiles are derived from radiometric measurements. Dashed lines are radiosonde profiles at 0400 and 1600 MST. After Hogg et al. [1].

Figure 4.11. Retrievals of temperature and humidity profiles at Pt. Mugu, California; solid lines, radiosonde measurements; dashed lines, radiometer retrievals. After Decker et al. [39].
rms accuracy is less than 2 K rms, but that above this level, the accuracy degrades rapidly. To improve the accuracy above 500 mbars, the combination of the ground-based radiometer with (a) satellite observations and (b) Radio Acoustic Sounding System (RASS) measurements has been investigated.

Various quantities of interest can be derived from basic meteorological profiles of temperature and humidity. Although radiometric profile retrievals lack the vertical resolution that is required for some applications, integrated quantities derived from these profiles may be perfectly adequate for other purposes. Such is the case for both geopotential heights and thicknesses, variables that are useful in numerical forecasting. As we show, pressure thickness is related to the average (virtual) temperature between pressure levels. From the hydrostatic equation, Eq. 4.33, and the general gas law equation, Eq. 4.34, we get

\[ dP = -\rho gdz \]  

and

\[ P = \rho (R/M) T_v \]  

where

- \( P \) = pressure
- \( \rho \) = density
- \( g \) = acceleration of gravity
- \( z \) = altitude
- \( R \) = general gas constant
- \( M \) = molecular weight of dry air
- \( T_v \) = virtual temperature

Substituting \( \rho \) from Eq. 4.34 into Eq. 4.33, we get

\[ dz = -(R/Mg) T_v \ln P \]  

or

\[ z_2 - z_1 = -(R/Mg) \int_{\ln P_1}^{\ln P_2} T_v d \ln P \]  

that is, the thickness \( \Delta z = z_2 - z_1 \) between pressure levels \( P_1 \) and \( P_2 \) is proportional to the average temperature with respect to \( \ln P \). When \( z_1 \) and \( P_1 \) are surface values, then the height corresponding to \( P, h(P) \), is called the geopotential height. Figure 4.12 shows thicknesses of four layers that were obtained from data taken at both Pt. Mugu and the Gulf of Alaska using a five-channel radiometer [39]. The thickness intervals range from 1000–850 mbars to 500–300 mbars. The agreement is excellent for the lowest interval, rms difference = 5 m, but degrades to 41 m at the 500–300-mbar level. An example of a time-series comparison of geopotential heights measured by a radiometer and by RAOBs is shown in Figure 4.13. Generally, the determination of integrated quantities by radiometers is much more
4.3 INDIRECT TEMPERATURE SENSING

4.3.2 Combined Ground- and Satellite-Based Temperature Sensing

Remote sensing of temperature profiles using a combination of passive microwave radiometric observations from surface- and satellite-based platforms was suggested by Westwater and Grody [40]. Their computer simulations showed that over the pressure interval 1000–300 mbars, rms retrieval accuracies of 1 to 2°K were achievable with current radiometric technology. Such simulations show the utility of Eq. 4.30 in predicting the performance of different combinations of remote-sensing systems. Figure 4.14 shows the predicted performance of (a) a six-channel surface-based radiometric system, (b) a four-channel satellite-based system, and
Figure 4.13. Time series of geopotential heights \( (Z) \) in km at 700, 500, and 300 mbars as derived from the six-channel radiometer. (Denver, Colorado, December 21, 1983.) Dots represent NWS radiosondes.

(c) the combination of (a) and (b). For all three of the climatologies illustrated in Figure 4.14, the surface-based radiometers yield significantly better accuracy than the satellite in the first 300 mbars above the surface, the satellite is the more accurate of the two above this level, and the combination of the two is a significant improvement over either separate system.

Currently available experimental systems allowed the combination of ground- and satellite-based observations. The ground-based Profiler [1] and the orbiting satellite-based Microwave Sounding Unit (MSU) were used for this combination [37]. Profiler and MSU temperature-weighting functions were shown in Figure 4.9. Note how the Profiler capabilities, which are exponentially reduced above 500 mbars, are complemented by the MSU; conversely, note how the relatively high vertical resolution at lower altitudes of the Profiler complements the MSU below 500 mbars.

Data from the Profiler and the MSU were collected over Denver, Colorado, for about a year [37]. For ground truth, NWS RAOBs were also obtained. Due to differences in sampling volumes and observations times, RAOBs are not always satisfactory for comparisons with the satellite overpasses. For this study, satellite data were restricted to ±3 h and about ±1° from the Profiler location in Denver.
Figure 4.14. Computer-simulated estimates of temperature-profile retrieval accuracy using dependent sample linear regression analysis. After Westwater and Grody [40].
The retrieval method used was Eq. 4.29 with a 12-channel data vector composed of the nine-component Profiler data and the upper three channels of the MSU. The rms differences of the separate systems and their combination are shown in Figure 4.15. These experimentally-achieved accuracies are in general agreement with the theoretical predictions for Denver shown in Figure 4.14.

In addition to temperature retrievals, geopotential heights and thicknesses (see Eq. 4.36) were also derived from these data for various combinations of measurements. The results of comparing retrievals and RAOBs, shown in Tables 4.2 and 4.3, clearly show the advantages of combining the two sets of observations. Note Table 4.2 The rms Differences Relative to RAOBs in Determination of Geopotential Height (m) for Various Combinations of Remote-Sensing Systems

<table>
<thead>
<tr>
<th>Pressure Level (mbar)</th>
<th>Climatology (Monthly Means)</th>
<th>Surface Meteorology</th>
<th>MSU</th>
<th>MSU + Surface</th>
<th>Profiler</th>
<th>MSU + Profiler</th>
<th>Functional Precision of Radiosondes [41]</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 (N = 458)</td>
<td>32.2</td>
<td>18.7</td>
<td>17.2</td>
<td>13.5</td>
<td>3.8</td>
<td>3.8</td>
<td>5.1</td>
</tr>
<tr>
<td>500 (N = 458)</td>
<td>71.3</td>
<td>49.6</td>
<td>32.2</td>
<td>31.2</td>
<td>13.1</td>
<td>12.4</td>
<td>12.7</td>
</tr>
<tr>
<td>300 (N = 456)</td>
<td>117.9</td>
<td>89.5</td>
<td>57.3</td>
<td>56.9</td>
<td>33.0</td>
<td>31.1</td>
<td>20.3</td>
</tr>
<tr>
<td>100 (N = 446)</td>
<td>93.1</td>
<td>74.3</td>
<td>60.6</td>
<td>51.7</td>
<td>67.6</td>
<td>46.0</td>
<td>27.9</td>
</tr>
</tbody>
</table>

Source: After Westwater et al. [37].
that the accuracy of geopotential heights, as derived from the MSU plus Profiler, is comparable with the functional precision of RAOBs, as determined by Hoehne [41].

### 4.3.3 Use of Radar Measurements of Tropopause Height to Improve Radiometric Temperature Retrievals

Using a VHF radar operating at the 6-m wavelength, Gage and Green [42] showed that it is possible to measure the altitude of the tropopause. Shortly after, Westwater and Grody [40] showed that measurements of this height could increase the accuracy of radiometric retrievals in the vicinity of the tropopause by as much as 1 K rms. In this section, we summarize the work [37, 43] on combining tropopause height and radiometric observations. The retrieval technique is a variation of Eq. 4.29: instead of using a statistical ensemble composed of all radiosondes within a given 3-month interval, only those radiosondes that had their tropopause height within a narrow pressure interval were used in the ensemble. Note that tropopause height was not used as a component of the data vector $g_e$, but was used as a statistical classifier.

In March 1980, an experiment was conducted in which VHF radar measurements of tropopause height, Profiler and MSU radiometric observations, and RAOB observations were all available simultaneously. Figure 4.16 shows a comparison of radar- and RAOB-measured tropopause heights. The rms differences of the heights were calculated as 0.65 km. When these heights were combined with Profiler radiometric observations, noticeable improvements in retrieval accuracy were obtained at tropopause altitudes [37]. The rms retrieval accuracies, both with and without radar information, for the Profiler (a), MSU (b), and Profiler plus MSU (c) are shown in Figure 4.17. It is seen that the tropopause height information substantially improves the retrieval accuracy of all three systems.
4.3.4 Temperature Retrieval from Combined Winds and Radiometers

Currently, a 30-station network of wind-profiling radars is scheduled for deployment in the central United States in the 1990s [44]. These instruments will measure winds on an hourly basis at altitudes ranging from 500 m AGL to 16.25 km AGL. Temperature profiles can be derived [45] from these wind profiles alone by using an equation of motion called the diagnostic divergence equation. Derived profiles have more structure in the middle troposphere than those derived from either ground- or satellite-based thermal soundings. However, in the lower troposphere, radiometric retrievals are generally more accurate, and in the upper troposphere, satellite retrievals are better. WPL and Dr. Y. H. Kuo of the National Center for Atmospheric Research (NCAR) are jointly developing methods for combining wind and radiometer data; similar work is being done by Gal-Chen [46]. Because the Wind Profiler network is not yet in place, only simulation studies are available to analyze the technique. Kuo and WPL simulated a Wind Profiler network using data from an atmospheric variability experiment. Here, profiles of wind, temperature, and humidity were measured every 3 h at stations that were 150 km apart. From the array of winds, first-guess temperature profiles were derived using the Kuo algorithm [45]. Next, from the actual profiles of temperature and humidity, brightness-temperature measurements were simulated using the radiative transfer equation (RTE). Finally, starting with the wind-derived first guess, derived profiles were adjusted interactively using Eq. 4.16 until the RTE was satisfied to
Figure 4.17. Rms differences between radiosonde-measured temperatures and radiometric retrievals. Curves labeled "combined" refer to radiometer plus radar data. (a) Profiler plus VHF radar, (b) MSU plus VHF radar, and (c) Profiler plus MSU plus VHF radar. After Westwater et al. [37].
within the assumed noise levels of 0.5 K. An example of an iterative retrieval is shown in Figure 4.18. Typical statistical comparisons of actual and derived profiles are shown in Figure 4.19 [46a]. As was true in the combination of ground- and satellite-based thermal soundings, the blending of information from two sources produces a better product than could either source alone.

Figure 4.18. Temperature retrieval using a profile derived from a simulated Wind Profiler network as an initial guess for the six-channel radiometer. The curve "without radiometers" is from [45].

Figure 4.19. Rms errors for temperature profiles derived from a network of wind observations (without radiometers) and from a network combined with simulated six-channel brightness observations. After Westwater [46a]. The curve "without radiometers" is from [45].
4.3.5 Combined Radiometer and RASS Temperature Soundings

A new development in remote temperature sensing occurred with the development of the Radio Acoustic Sounding System (RASS) [47]. In this technique, an acoustic source, placed beside a wind-profiling radar, transmits an acoustic wave into the volume of air sensed by the radar. The radar obtains a sound-speed profile from the Doppler-shifted frequency of the electromagnetic energy backscattered from the acoustic wave. A simple relationship between sound speed and virtual temperature \((T_v)\) yields a \(T_v\) profile whose vertical resolution is defined by the radar range resolution (typically 150 to 450 m). The technique provides excellent temperature profiles over a height range that is determined by (a) acoustic attenuation, which is a strong function of frequency, and (b) horizontal wind, which can blow the acoustic pulse out of the volume sensed by the radar. For the 915-MHz radar operating beside the six-channel radiometer in Denver, Colorado, the upper height range of RASS varied from 1.0 to 2.9 km. Thus, a portion of a profile can be determined by RASS and blended with other sources of information to provide an entire profile [48]. We show in Figure 4.20 both separate and blended

![Figure 4.20](image)

**Figure 4.20.** Temperature profiles determined from radiosonde, RASS, six-channel radiometer (Profiler), and Profiler–RASS combination (March 2, 1988). After Westwater [46a].
portions of radiometric and RASS profiles. In this case, the RASS used an electromagnetic frequency of 915 MHz and an acoustic frequency of about 2 kHz. Because of the large acoustic attenuation at 2 kHz, the altitude range of the technique was limited to 2 km. As is obvious from the figure, the range of accurate profiling from the combined technique is considerably higher than 2 km.

By using the statistical inversion method, Eq. 4.29, the RASS measurements can also be used to estimate the temperature profile above the last range gate. Schroeder [48], using data from the six-channel radiometer, from RASS and from their combination, evaluated the accuracy of each. Her results, shown in Figure 4.21, indicate that the combined system generally produces the superior results. In the winter statistics, Figure 4.21(b), even with the combined system, there is a sharp increase in error in the pressure difference region 100 to 150 mbars. The use of a 405-MHz RASS system will probably correct this error. WPL is investigating combined surface- and satellite-based data to improve mid- and upper-tropospheric temperature retrievals [49].

Figure 4.21. Rms differences between rawinsonde-measured temperatures and temperatures retrieved from RASS (dashed), radiometer (dotted), and combined RASS/radiometer (dot-dashed) systems for (a) summer and (b) winter data sets. Dots on the vertical axis represent every fourth retrieved sounding level. After Schroeder [48].
4.4 MICROWAVE RADIOMETRIC MEASUREMENTS OF WATER VAPOR

Measurements of water vapor are needed in a wide variety of geophysical problems, both in research and applications. Examples of applications of such data are encountered in determining heat balance in climatology, in weather-modification experiments, and in mesoscale forecasting. Other applications require removing the "contaminating" effects of water vapor in radio interferometry, in geodetic meteorology, and in remote sensing of temperature and surface parameters.

In contrast to absolute temperature, whose percentage variability is only 10 to 20%, water vapor exhibits a large variability in space and in time. There is a huge difference in total water content between the equator and the poles, and, for a fixed location, the total content can vary by a factor of 30 during a year. In the troposphere, where most of the vapor is present, vapor concentration generally decreases with altitude, but a high degree of spatial structure is frequently evident. Typical radiosonde soundings of humidity are shown in Figure 4.22. Given the high degree of vertical structure of water vapor and the smooth water-vapor weighting functions shown in Figures 4.4 and 4.7, it is apparent that microwave radiometry alone will not resolve this structure. Consequently, most of the work in the field has concentrated on providing accurate measurements of integrated quantities, such as precipitable water vapor and electrical path length.

![Typical Profiles of Absolute Humidity](image)

Figure 4.22. Typical atmospheric profiles of absolute humidity (Pt. Mugu, California, March 1976).
4.4.1 Measurements of Precipitable Water Vapor

Precipitable water vapor is an important component of many moisture-related processes in the atmosphere. For example, the occurrence of convective clouds and precipitation is closely related to the amount of water vapor in the layer from the surface to 400 mbars [50]. Consequently, measurements of integrated vapor have been used in the design of cloud-seeding experiments [51]. Continuous observations of this quantity may also be useful in operational precipitation forecasting using a mesoscale numerical forecast model [51a], and in meteorological research applications such as the estimation of water-vapor flux into convective cells [52]. Other problems that require integrated water vapor, although not necessarily in the zenith direction, include electrical path length correction (see Chapter 5) and real-time prediction of transmission for both infrared and millimeter wave propagation.

Measurements of microwave thermal emission and its variation with atmospheric moisture were first reported in Dicke et al. [53]. Although most of their measurements were taken during clear conditions, they mentioned that some cumulus clouds were quite absorbing at centimeter wavelengths. Subsequently, Barrett and Chung [54] and Staelin [55] discussed the determination of profile information from multispectral emission or extinction observations. In addition, Staelin [55] discussed the possibilities of simultaneous vapor and cloud liquid determination. These possibilities were experimentally demonstrated in Toong and Staelin [56], where vapor and cloud liquid were derived from emission observations at five frequencies. In addition, the Russian literature contains many descriptions of experimental determinations of vapor and liquid [57–59]. For down-looking systems, Rosenkranz et al. [60] gave accuracy estimates for radiometric moisture determination.

These initial results were sufficiently promising that researchers from many countries constructed and operated ground-based water-vapor radiometers [1, 33, 35, 36, 61–64]. In this section, we summarize results obtained since 1980 with these instruments.

The total amount of water vapor in a vertical column through the atmosphere per unit cross-section, the precipitable water vapor \( V \), is given by

\[
V = \int_0^\infty \rho_V(h) \, dh
\]  

(4.37)

where \( \rho_V = \) density of water vapor \((\text{g/cm}^3)\)  
\( h = \) height above the surface \((\text{cm})\)

Because the density of liquid water is approximately 1 \( \text{g/cm}^3 \), the units of \( V \) in \( \text{g/cm}^2 \) or in \( \text{cm} \) are practically interchangeable. As another practical comment on units, we note that

\[
V \, (\text{mm}) = \rho_V \, (\text{g/m}^3) \cdot h \, (\text{km})
\]

From polar regions to the tropics, \( V \) can vary from 0.1 to 75 mm.
In the clear air, it is possible to derive \( V \) from a single emission measurement. However, during cloudy conditions, cloud liquid emits microwave energy, so that its effect must be taken into account. We designate integrated cloud liquid by \( L \), and discuss its determination in Section 4.5. A large body of experimental evidence now exists showing that with two well-chosen frequencies, both \( L \) and \( V \) can be measured simultaneously [1, 3, 35, 61].

Although \( V \) and \( L \) can be estimated directly from \( T_b \) measurements, using Eq. 4.24, it is useful first to derive total absorption \( \tau(0, \infty) \) (opacity) from \( T_b \) and then to derive \( V \) and \( L \) from absorption [65]. We first define a mean radiating temperature \( T_{mr} \) as

\[
T'_{mr} = \int_0^\infty T' e^{-\tau(0, S)} ds \frac{1}{1 - e^{-\tau(0, \infty)}} (4.38)
\]

In terms of \( T'_{mr} \), the transfer equation, Eq. 1.8, can be written

\[
T_b = T_b0 e^{-\tau(0, \infty)} + T'_{mr}(1 - e^{-\tau(0, \infty)}) (4.39)
\]

where the cosmic background term \( T_b0 \) is \(-2.735 \) K (see Chapter 1). Solving Eq. 4.39 for \( \tau(0, \infty) \) yields

\[
\tau(0, \infty) = -\ln \left( \frac{T_{mr} - T_b}{T'_{mr} - T_b0} \right) (4.40)
\]

In practice, \( T'_{mr} \) can be estimated from climatology with sufficient accuracy to allow accurate determinations of \( \tau(0, \infty) \). The accuracy in deriving absorption from emission degrades as the absorption increases and also degrades for increasing error in the determination of \( T'_{mr} \) [65]. If we now have brightness-temperature measurements at two frequencies for which the contributions from \( V \) and \( L \) differ substantially with frequency, then values of \( \tau(0, \infty) \), derived from Eq. 4.40, can be inserted into Eq. 4.29 to derive both \( V \) and \( L \): If \( \tau_1 \) and \( \tau_2 \) denote the two optical depths, then from Eq. 4.29, we get

\[
(\dot{V}, \dot{L}) = (\langle V \rangle, \langle L \rangle) + \begin{pmatrix} S_{V, \tau_1} & S_{V, \tau_2} \\ S_{L, \tau_1} & S_{L, \tau_2} \end{pmatrix} \begin{pmatrix} S_{\tau_1} & S_{\tau_1, \tau_2} \\ S_{\tau_1, \tau_2} & S_{\tau_2} \end{pmatrix}^{-1} \begin{pmatrix} \tau_1 - \langle \tau_1 \rangle \\ \tau_2 - \langle \tau_2 \rangle \end{pmatrix} (4.41)
\]

Equation 4.41, when evaluated, yields very simple expressions for \( \dot{V} \) and \( \dot{L} \):

\[
\dot{V} = a_0 + a_1 \tau_1 + a_2 \tau_2 (4.42)
\]

and

\[
\dot{L} = b_0 + b_1 \tau_1 + b_2 \tau_2 (4.43)
\]
Other refinements of the technique include (a) using different coefficients for clear and cloudy conditions and (b) using an adaptive technique in which the coefficients $a$ and $b$ are a function of inferred $\tilde{V}$ and $\tilde{L}$ [66].

Currently, dual-channel radiometric measurements of $V$ are routinely obtained at Denver and Platteville, Colorado. To reduce the amount of data required for processing and archiving, 2-min averages were chosen. The 2-min data are first edited to remove strong cloud effects on vapor retrievals by rejecting data for which the 31-GHz $T_l > 100$ K. The data are then sent to local meteorologists, including those of NOAA and NCAR. A 4-day time series of these data, twice-daily radiosondes (RAOBs) released by the NWS, and special launches of research radiosondes (CLASS) are shown in Figure 4.23 [66a]. We note the excellent agreement with both kinds of radiosonde systems. The accuracy of the radiometric measurements has been estimated by comparison with NWS RAOBs. Figure 4.24 shows

![Figure 4.23. Time series of precipitable water vapor $V$ (cm) derived by WPL's dual-channel radiometer. Circles with dots represent CLASS radiosonde determinations of $V$; circles with crosses represent NWS soundings. Data were taken during GAPEX [66a].](image-url)
Figure 4.24. Scatter plot of $V$ (mm) determined by radiometer (Profiler) and by NWS radiosondes.

A scatter plot of dual-channel versus RAOB measurements of $V$ obtained over a 1-year period in Denver. The rms difference between the two is 0.17 cm. However, given that the RAOB itself has been evaluated to have an accuracy of $\sim 1.1$ mm [41], the true accuracy of the radiometric measurement of $V$ is probably as good as or better than that of RAOBs.

An important feature of dual-channel ground-based radiometers is their ability to measure rapidly moving features of moisture flow. An example of this is seen in Figure 4.25, in which a variation in $V$ from 4 to 1 cm occurred within a time interval of about 30 min. This extreme variation is common in the Texas-Oklahoma region during the passage of the so-called "dry line." Given that variations of moisture occur this rapidly, it is not difficult to understand why forecasting of precipitation is so difficult, especially when the forecasts are based on twice-daily radiosonde observations.

4.4.2 Spectra of Precipitable Water Vapor

In addition to time series, it is also possible to study water-vapor fluctuations and their associated periods by spectral analysis. Periodicities on the synoptic scale are
frequently captured by radiosondes released every 12 hours. Observations of more rapidly varying phenomena ideally are done with high-response in-situ sensors or with remote sensors. The first spectra of fluctuations of $V$ were given in Hogg et al. [67]. Figure 4.26 shows spectra obtained from three hours of 2-min data as well as spectra computed from the radiometer's internal noise. The observed fluctuations are at least a factor of 100 above the noise level. Note the broad spectral peak at around 5 cycles/hour as well as one at about 12 cycles/hour. In addition to peaks, there is also the effect of turbulent fluctuations. As is well known [67a], in the inertial subrange, such fluctuations decay with frequency according to a $-5/3$ power law. We show for comparison, a line representing a $-5/3$ spectral decay.

Spectral peaks as observed by radiometers are frequently caused by the passage of gravity waves. Ciotti et al. [68] reported on radiometric observations of periodicities in water-vapor fluctuations. One particular event occurred during an extensive experiment designed to study waves. Periodicities derived from spectral analysis showed spectral peaks that agreed quite well with features derived from special rapid-scan satellite data, and from analysis of surface-pressure fluctuations. The analysis was further extended to show that the disturbance in question was generated by an internal gravity wave generated by wind shear in the jet aloft [31b].

4.4.3 Observations of Precipitable Water Vapor from the Colorado Research Network

As discussed in Section 4.3, in addition to radiometer measurements in Denver, from 1985 to 1988, a research network of two-frequency radiometers was operated in the plains of eastern Colorado (see Figure 4.5). A typical set of simultaneous observations of $V$ from all four stations is shown in Figure 4.27. We note the
Figure 4.26. Spectra of $V$ (cm) as determined from dual-channel radiometer measurements. AR refers to autoregressive spectral method; FT refers to Fourier-transform spectral method. Details of spectral methods used are given by Ciotti et al. [68].

coherent features of the movement of water vapor that are evident at the times indicated on the figure.

The continuous water-vapor data from the Colorado Research Network are also useful for satellite validation and calibration. Infrared radiance observations, taken by an instrument known as the Visible and Infrared Spin Scan Radiometer (VISSR) Atmospheric Sounder (VAS) mounted on a Geostationary Operational Environmental Satellite (GOES) [69] have been used to derive images of $V$ [70, 71]. Recently, a NOAA organization known as Prototype Regional Observing and Forecasting Service (PROFS) has generated quantitative imagery over a multistate region centered over Colorado [72]. The quantitative imagery was generated by a linear regression of VAS brightness temperatures against $V$'s derived from NWS
RAOBs. To improve the accuracy of this product on a smaller spatial domain, namely, that of multicounty scale, PROFS used $V$ data from the Colorado Research Network to provide hourly calibration points for the VAS data \cite{72}. A typical result showing contours of $V$ is shown in Figure 4.28 \cite{73}. This type of contour display is now produced routinely by PROFS. Other applications of the network data are discussed in Sections 4.4 and 4.6.

### 4.4.4 Measurements of Water Vapor Profiles

The dual-channel water vapor weighting functions shown in Figure 4.4 are quite smooth, exhibiting a roughly linear dependence on height. Consequently, it is not at all obvious that profiles can be retrieved from such measurements. However, several researchers \cite{39, 61, 74} have derived low-resolution profiles from ground-based $T_b$ measurements, supplemented with surface meteorological measurements of temperature, humidity, and pressure. If $\rho_V(h)$ is determined by a priori statistical inversion, then an adequate supply of a priori RAOBs is also necessary.
4.4 MICROWAVE RADIOMETRIC MEASUREMENTS OF WATER VAPOR

Water vapor profiles can also be determined using Eq. 4.15 or 4.16 if a first-guess profile \((\rho_v)_0\) is available from the output of a forecast model. Current research is focused on assimilating a field of precipitable water-vapor observations, such as would be available from a network of radiometers, with a mesoscale numerical model [51a]. All work reported in this section used the statistical retrieval method expressed in Equation 4.29.

In the work of Westwater et al. [74a], both two- and six-channel radiometers were used in the vapor-profile recovery; weighting functions for this instrument were shown in Figure 4.4. The derived humidity profiles, as shown in Figure 4.29 [74a], followed gross changes in the profile structure. Low-resolution profiles such as the ones shown in this section are clearly not adequate for some applications.
Figure 4.29. Examples of water-vapor-profile retrievals from the six-channel profiler, the dual-channel radiometer, and radiosondes. After Westwater et al. [74a].
Figure 4.30. Time-height cross-sections of vapor density ($\rho_v$), $U$ component ($U$), and vapor flux ($\rho_v U$) from a radar-radiometer remote-sensing system (top) and from rawinsondes (bottom). The dots on the lower time axis indicate the times of rawinsonde launches. After Uttal et al. [75].
However, in determining integrated quantities, such as pressure heights, phase-delay corrections, etc., such profiles are of benefit.

A new and promising method of measuring water vapor fluxes was recently published [75]. This method used the combination of $\rho_v(h)$ measured by a dual-channel microwave radiometer and wind profiles, measured by a 8.6-mm Doppler radar, to derive the fluxes. Their method was applied to the study of vapor fluxes across a mountain barrier during two wintertime storms. Figure 4.30 shows flux determined by the remote-sensing technique and by a series of 3-h radiosonde launches. The radiometer–radar method yields significant small-scale structure in the moisture-flux field that was smoothed by the radiosonde measurements. For both of the winter storms that were observed, short-lived vapor pulses, on the order of 2–5-h duration, were important in determining precipitation, liquid water, and riming. The authors’ conclusions, quoted in what follows, represent many of the advantages of remote sensors over radiosonde (or rawinsonde) sampling:

1) *The profiles from the radar and the radiometer are instantaneous.* In comparison, the rawinsonde ascent time is significant on the time of storm evolution, and the physical properties of the air mass can change significantly as the rawinsonde travels between the surface and the top of the measurement layer.

2) *The remote sensing profile is a true vertical measurement.* In contrast the rawinsonde drifts horizontally as it rises and it is impossible to establish how much of the measured variation is due to vertical atmospheric structure and how much is due to horizontal atmospheric structure.

3) *The remote sensing method can sample the air mass quasi-continuously whereas rawinsondes can obtain only one sample per launch.*

### 4.5 MICROWAVE RADIOMETRIC MEASUREMENTS OF CLOUD LIQUID

#### 4.5.1 Technique and Examples of Data

In a sense, cloud liquid is a contaminant on the microwave radiometric determination of temperature and water vapor. However, measurements of liquid are valuable in their own right. Important applications that are discussed later in this section are aircraft-icing detection, weather modification, and climate. For non-precipitating clouds, microwave emission and absorption come principally from cloud liquid, with contributions from ice being negligibly small [9]. However, scattering from ice during precipitation has been observed at 37 and 92 GHz [75a].

One technique used to determine integrated cloud liquid $L$ as well as precipitable vapor $V$ was given in Eqs. 4.40–4.43. First, attenuation is derived from $T_b$ by Eq. 4.40. Then, $L$ is derived using Eq. 4.43. Because neither $L$ nor profiles of liquid density are measured by RAOBs, modeling must be done to develop satisfactory *a priori* data, if statistical inversion is to be used [39]. A nonstatistical inversion algorithm is given in Westwater [65].
Another consequence of RAOBs not measuring $L$ is that ground-truth measurements to verify the accuracy of the radiometric determination are very difficult to obtain. Probably the best comparison to date is that of Snider et al. [76]. They compared liquid, determined from the absorption of a microwave satellite signal, with radiometrically-measured liquid, and found rms differences of 0.28 mm. Theoretical predictions, valid for nonprecipitating clouds, indicate that about 10% accuracy in the determination of $L$ can be achieved.

As an example of the kind of liquid data produced routinely by a dual-channel system, Figure 4.31 [76a] shows a time series of data measured during periods of intermittent rain. As might be expected, a high degree of temporal variability is present in the behavior of $L$. In this time series, the liquid amounts greater than about 2 mm were generally associated with rain.

A two-frequency microwave radiometer with a fully steerable antenna has also shown some interesting angular variations in both integrated vapor $V$ and liquid $L$. Figure 4.32 shows data obtained by scanning a dual-channel system at a constant elevation angle of 15° [77]. Such data may be useful for determining departures from stratification of $V$ on radio-phase measuring systems [78] and in determining concentrations of liquid in visually homogeneous clouds.

![Figure 4.31](image-url)

*Figure 4.31.* Total integrated liquid measured by the radiometric system on March 3, 1980, and rainfall data were measured at the radiometer site using a weighting bucket raingage. After Snider and Rottner [76a].
CONTINUOUS 360 DEG AZIMUTH SCAN DATA  
STEAMBOAT SPRGS, CO ELEV ANGLE = 15.0 DEG.  
DAY NO. 355  
21 DEC 1981

Figure 4.32. Radiometer output during a series of azimuth scans at 15° elevation angle. After Snider [77].

4.5.2 Applications of Radiometers to Winter Snowpack Augmentation

Cloud seeding to increase winter snowpacks over mountainous regions of the western United States has been investigated for almost 40 years [79]. However, the development of scientific methods for weather modification depends on understanding the physical processes associated with the formation and evolution of supercooled liquid water (SLW). To aid in this understanding, a strong requirement exists to measure the temporal and spatial distribution of SLW within clouds, both before and after seeding. Measurements of SLW by scannable water vapor radiometers have been done in several major field programs [79, 80] and such radiometers are now considered to be essential for such programs.
Because the radiometers measure the integrated liquid in a given direction, additional information is required to determine if the liquid is supercooled. In modification experiments, it is common to deploy the radiometer at an altitude whose temperature is below freezing. Thus, assuming the absence of strong temperature inversions, any liquid observed is supercooled. Frequently, liquid water is produced by uplifting of water vapor when winds are deflected by mountain barriers. Measurements of SLW in radial directions have been valuable in relating amounts of liquid to such terrain features. An example of several azimuth scans made consecutively over a period of about 1.5 h is shown in Figure 4.33. Statistical examination of scans made during about 15 storms observed in the Tushar Mountains of southwestern Utah showed that, on average, maximum liquid is situated above the lift regions of the upwind mountain barrier [81]. Steerable-beam radiometer observations at Steamboat Springs, Colorado, showed a similar consistent maximum above the upwind slopes of a mountain barrier [80, 82]. Clearly, orographic forcing has an important effect upon formation of SLW in mountainous regions.

An example of the temporal and spatial behavior of SLW during a winter storm is presented in Figure 4.34 [83]. This display, referred to as an “azimuth–time” diagram, is constructed from azimuth scans recorded continuously during storms. It offers a convenient means of presenting the time history and spatial distribution over periods of several hours. The example clearly shows the passage of SLW in two separate events as well as the directional distribution of SLW during the entire storm. Continuous observations such as these have allowed scientists to relate the behavior of liquid water during storms to synoptic conditions, local convective activity, the occurrence of precipitation, and other meteorological factors.

### 4.5.3 Remote Detection of Aircraft-Icing Conditions

In many ways, the same type of conditions that allow for augmentation of snowfall by seeding can also cause ice to form on aircraft. This formation of ice continues to be a significant hazard to lower-atmospheric flight. For example, during the 5½-year period beginning in January 1978, 280 icing-related accidents resulting in 364 fatalities were reported in the United States [84]. SLW along the flight path causes ice to accumulate on aircraft and that results in such accidents. Instruments that could be deployed at airports to measure SLW would be of great value. Because radiometers can detect liquid water in the atmosphere, and because they can be operated automatically and continuously, they are currently being investigated as icing-detection and -warning devices.

The first paper reporting microwave radiometric observations of SLW that were simultaneously accompanied by aircraft reports of icing conditions was by Hogg et al. [85]. This initial result was followed by an in-depth study of 2 years of zenith-viewing radiometer data taken at Stapleton International Airport, Denver, Colorado [86]. By correlating radiometer measurements and sky cover observations with pilot reports of icing conditions, an icing index was derived that identified 90% of reported icing conditions within 18.5 km of the observing site. Figure 4.35 shows a time series of this index over a month’s time as well as a comparison
Figure 4.33. Consecutive azimuth scans at 22.5° elevation showing the highly variable spatial distribution of liquid water over a mountain barrier near Beaver, Utah. After Snider et al. [81].
4.5 MICROWAVE RADIOMETRIC MEASUREMENTS OF CLOUD LIQUID

Figure 4.34. Azimuth-time diagram showing contours of constant SLW during a winter storm. After Snider et al. [81].

Figure 4.35. Aircraft-icing index: X’s are from pilot reports, the dashed line is from seven surface measurements, and the solid line is from radiometric liquid measurement only. After Popa Fotino et al. [86].

showing the excellent agreement with pilot reports. From this figure, it is also evident that the liquid measurement is the dominant variable in the icing index. A zenith-viewing radiometer measures the integrated amount of cloud liquid overhead. To determine if the liquid is supercooled, additional information is necessary. If, for example, the cloud-base temperature were known to be 0°C or
lower, then, assuming the temperature within the cloud decreased with height, the observed liquid would be supercooled. In recent experiments, WPL used combined remote sensors to solve partially the SLW identification problem. First, an operational NWS lidar ceilometer provided measurements of the base height of a cloud. Next, a RASS [47] provided high vertical-resolution measurements of virtual temperature. Finally, if the lidar indicated that the cloud-base height was above the freezing level as determined by RASS, then any observed liquid was supercooled. During a recently conducted aircraft-icing experiment, these measurements gave useful information in identifying SLW [87]. Figure 4.36 shows results from the experiment in addition to pilot reports of icing.

In another application of combined measurement techniques, data from a lidar ceilometer, a RASS, and a microwave radiometer were used to derive the height of the liquid-bearing portion of a cloud. If the temperature profile is given and the base and top of a cloud are known, then under the adiabatic approximation [87a], the amount of liquid in a cloud can be estimated. Conversely, if the base height, temperature profile, and cloud liquid are given, the top height of the cloud can be estimated [87]. An example of this kind of determination of cloud parameters is also shown in Figure 4.36. In addition, we show cloud-base temperatures as mea-

![Figure 4.36](image-url)

**Figure 4.36.** Time series for 1200 UTC February 12 to 0000 UTC February 16: (a) Denver lidar ceilometer cloud-base height measurement, cloud-top height computed using moist adiabatic approximation and aircraft-icing severity at the height of PIREP, where 1 = light, 2 = light to moderate, 3 = moderate, 4 = moderate to severe, and 5 = severe. (b) Cloud-base height measured by ceilometer at Denver. Shaded area is the cloud depth as measured by the ceilometer. (c) Infrared radiometer measurement of the cloud-base temperature at Denver. (d) Infrared radiometer measurement at Elbert.
sured by an infrared radiometer. The assumption that limits the general applica-
bility of the technique is the adiabatic approximation, which can fail due to en-
trainment of dry air from the top and sides of a cloud. This approximation will
overestimate the amount of liquid within a cloud. To partially compensate for this
overestimation, cloud-type-dependent "entrainment factors" have been used [88].
In any case, the use of the combined sensors can determine if SLW exists above
the radiometer.

4.6 ADDITIONAL APPLICATIONS

4.6.1 Comparison of Clear-Air Absorption Models

In many applications of radiometry to geophysics, it is important to have accurate
models relating meteorological variables to the fundamental radiometric observa-
ble—the brightness temperature. Because current radiometers have absolute ac-
curacies of 0.5 to 1.0 K, a similar degree of accuracy is required when calculating
brightness temperatures from known profiles of meteorological variables. For clear-
air conditions, vertical profiles of temperature, pressure, and water vapor are re-
quired to calculate absorption and emission as a function of frequency, using Eq.
1.8. Westwater et al. [31a] used data taken at the WPL radiometric facilities at
Stapleton Airport to compare calculations of brightness temperatures, based on
NWS radiosonde data, with measurements. Similar comparisons were made using
data from the steerable radiometer when radiosonde soundings were available. As
an example of such comparisons, Figures 4.37 to 4.39 show summary results com-
paring the water vapor absorption models of Liebe [89] and of Waters [90]. For
these calculations, the oxygen absorption was calculated by the model of Rosen-
kranz [8]. Note that in these figures, Waters' model outperforms the one of Liebe
at 20.6 and 31.65 GHz, and the converse is true at 90.0 GHz. A complete descrip-
tion of the individual data sets entering into these comparisons is given by West-
water et al. [31a].

4.6.2 Mass-Absorption Coefficients for Water Vapor

For clear conditions, there is an accurate and simple parameterization that relates
zenith attenuation to integrated amounts of precipitable water vapor $V$:

$$\tau = \tau_{\text{dry}} + \kappa_V \cdot V$$

(4.44)

where

$$\kappa_V = \frac{1}{V} \int_0^\infty \alpha_V \, dh$$

and

$$\tau_{\text{dry}} = \int_0^\infty \alpha_{\text{dry}} \, dh$$
In Eq. 4.44, the mass absorption coefficient $\kappa_V$ and the dry attenuation term $\tau_{dry}$ are related to the path integrals of the respective absorption coefficients for vapor $\alpha_V$ and for oxygen $\alpha_{dry}$. Due to profile variations of the relevant meteorological variables, the quantity $\kappa_V$ will also vary. However, for a given location and season, and at the frequencies of 20.6 and 31.65 GHz, calculations have shown that the variations in $\kappa_V$ are about 5% [65]. Using $V$ as a parameter, researchers [90a] tried both a linear and a quadratic fit to their 3.3-mm (90.0-GHz) absorption data taken during clear conditions. There was no improvement over a linear fit by a quadratic. Thus, we will use the linear form suggested by Eq. 4.44 as our parameterization.
4.6 ADDITIONAL APPLICATIONS


treating \( \kappa_V \) and \( \tau_{dry} \) as constants (to be determined) for each location and season. Because radiosonde humidity profiles can be integrated to derive \( V \), the determination of effective \( \tau_{dry} \) and \( \kappa_V \) is straightforward; that is, we determine regression coefficients \( A, B \):

\[
\hat{\tau}_{clr} = A + BV \tag{4.45}
\]

The constants \( A \) and \( B \) that were derived by Westwater et al. [31a] are shown in Table 4.4. The data in these tables show excellent correlation between radiomet-
Figure 4.39. Comparison of measured and calculated brightness temperatures at 90.0 GHz. After Westwater et al. [31a].

Ricelly determined absorption \( \tau \) and radiosonde determined \( V \), all correlation coefficients being greater than 0.93. Note also, that, as expected, dry coefficients \( A \) increase with frequency, and also are greater at San Nicolas Island, California, which is at sea level, than at Denver, Colorado, which is 1.611-m above sea level. Note also, for a given frequency, that there is at most a 15% variation in the mass absorption coefficients \( B \), either for location or for season.
### TABLE 4.4 Regression Coefficients, Determined for Three Frequencies, for Predicting Clear-Air Zenith Absorption $\tau$ (dB) from Radiosonde Measurements of Precipitable Water Vapor $V$ (cm)

<table>
<thead>
<tr>
<th>Location: San Nicolas Island, California. July 1987. CLASS Radiosondes.</th>
<th>20.6 GHz</th>
<th>31.65 GHz</th>
<th>90.0 GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^aN = 14$; $V = 1.3 \pm 0.29$ cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A$ (dB)</td>
<td>$0.08 \pm 0.01$</td>
<td>$0.14 \pm 0.01$</td>
<td>$0.24 \pm 0.04$</td>
</tr>
<tr>
<td>$B$ (dB/cm)</td>
<td>$0.18 \pm 0.01$</td>
<td>$0.08 \pm 0.01$</td>
<td>$0.35 \pm 0.03$</td>
</tr>
<tr>
<td>Mean $\tau$ (dB)</td>
<td>$0.32 \pm 0.05$</td>
<td>$0.24 \pm 0.02$</td>
<td>$0.72 \pm 0.11$</td>
</tr>
<tr>
<td>Std. error est. $\tau$ (dB)</td>
<td>$0.01$</td>
<td>$0.01$</td>
<td>$0.03$</td>
</tr>
<tr>
<td>$(\text{Std. error/mean}) \times 100$</td>
<td>$3.4$</td>
<td>$2.9$</td>
<td>$4.4$</td>
</tr>
<tr>
<td>Corr. coeff.</td>
<td>$0.98$</td>
<td>$0.96$</td>
<td>$0.96$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Location: Denver, Colorado. December 1987. NWS radiosondes.</th>
<th>20.6 GHz</th>
<th>31.65 GHz</th>
<th>90.0 GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^aN = 22$; $V = 0.50 \pm 0.28$ cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A$ (dB)</td>
<td>$0.053 \pm 0.005$</td>
<td>$0.097 \pm 0.003$</td>
<td>$0.139 \pm 0.008$</td>
</tr>
<tr>
<td>$B$ (dB/cm)</td>
<td>$0.210 \pm 0.008$</td>
<td>$0.075 \pm 0.005$</td>
<td>$0.34 \pm 0.01$</td>
</tr>
<tr>
<td>Mean $\tau$ (dB)</td>
<td>$0.16 \pm 0.06$</td>
<td>$0.13 \pm 0.02$</td>
<td>$0.31 \pm 0.10$</td>
</tr>
<tr>
<td>Std. error est. $\tau$ (dB)</td>
<td>$0.01$</td>
<td>$0.01$</td>
<td>$0.02$</td>
</tr>
<tr>
<td>$(\text{Std. error/mean}) \times 100$</td>
<td>$6.9$</td>
<td>$4.5$</td>
<td>$5.8$</td>
</tr>
<tr>
<td>Corr. coeff.</td>
<td>$0.98$</td>
<td>$0.96$</td>
<td>$0.98$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Location: Denver, Colorado. August 1987. NWS radiosondes.</th>
<th>20.6 GHz</th>
<th>31.65 GHz</th>
<th>90.0 GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^aN = 37$; $V = 2.02 \pm 0.52$ cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A$ (dB)</td>
<td>$0.07 \pm 0.02$</td>
<td>$0.07 \pm 0.01$</td>
<td>$0.09 \pm 0.04$</td>
</tr>
<tr>
<td>$B$ (dB/cm)</td>
<td>$0.19 \pm 0.01$</td>
<td>$0.075 \pm 0.005$</td>
<td>$0.35 \pm 0.02$</td>
</tr>
<tr>
<td>Mean $\tau$ (dB)</td>
<td>$0.46 \pm .10$</td>
<td>$0.22 \pm 0.04$</td>
<td>$0.81 \pm 0.20$</td>
</tr>
<tr>
<td>Std. error est. $\tau$ (dB)</td>
<td>$0.02$</td>
<td>$0.02$</td>
<td>$0.06$</td>
</tr>
<tr>
<td>$(\text{Std. error/mean}) \times 100$</td>
<td>$5.2$</td>
<td>$7.2$</td>
<td>$8.1$</td>
</tr>
<tr>
<td>Corr. coeff.</td>
<td>$0.97$</td>
<td>$0.93$</td>
<td>$0.95$</td>
</tr>
</tbody>
</table>

$^aN = \text{sample size.}$

*Source: After Westwater et al. [31a].

### 4.6.3 Observations of Attenuation from Clouds

Calculations of microwave emission and attenuation from clouds are difficult to verify because conventional radiosondes do not measure cloud liquid. Even if they did, the highly variable temporal and spatial characteristics of clouds would make comparisons difficult. With the WPL radiometer design of equal beamwidths at all three channels, emission from a common volume can be observed simultaneously. By estimating oxygen and water-vapor emission when clouds are present, relative cloud effects between the three channels can be studied [31a]. The WPL procedure is straightforward, but suffers from the defect that it derives cloud liquid $L$ and vapor $V$ from a dual-frequency algorithm that implicitly contains vapor- and liquid-absorption models. However, we believe that interfrequency comparisons between 20.6 and 90.0 GHz and between 31.65 and 90.0 GHz are meaningful. In addition, the comparison between 20.6 and 31.65 is a check of consistency between mea-
measurements and theory; however, the comparison cannot be used for independent validation. The WPL procedure is described as follows. First, establish a threshold $L_t$ for the presence of liquid-bearing clouds, using the 20.6- and 31.65-GHz channels. In the past, this threshold has proved to be effective in separating clear and cloudy conditions. Next, derive $V$ from the dual-channel measurements. The retrieval coefficients used in deriving $V$ are semiempirical and do not use the models of [89, 90]. However, this determination of $V$ has been extensively verified by comparison with radiosonde data, and, indeed, is of the same order of accuracy as the radiosonde data. For data whose inferred $L_t$ is less than $L_t$, that is, the “clear” set, derive a regression relation between the measured absorption $\tau_{\text{clr}}$ and $V$ as expressed by Eq. 4.45, again determining $A$ and $B$. Finally, for the data whose inferred $L_t$ is greater than $L_t$, that is, the “cloudy” set, determine the cloud attenuation $\hat{\tau}_{\text{cld}}$ by

$$\hat{\tau}_{\text{cld}} = \tau - \hat{\tau}_{\text{clr}}$$
$$= \tau - A - B\hat{V}$$
$$= C + DL$$  \hspace{1cm} (4.46)$$

The coefficient $D$ has the physical significance of the mass-absorption coefficient for cloud liquid, whereas if the procedure of subtracting clear attenuation from cloud attenuation were perfect, $C$ would be zero. It should be understood that $\hat{V}$ in Eq. 4.46 has been derived from the absorptions in cloudy conditions measured at 20.6 and 31.65 GHz. One can also derive $\hat{L}$, but, of course, the accuracy of this determination has not been experimentally established, although theoretical estimates yield an accuracy of 0.0033 cm rms [68]. In Table 4.5, the results of regression analyses from which cloud-attenuation ratios were determined are shown. In addition, we show values of the attenuation ratio as derived from WPL’s radiosonde-based cloud-modeling technique [39].

The values presented in this table show that there is agreement to within 30% of modeling and experiment. However, much more meaningful comparisons could be done if independent measurements of cloud liquid water were available.

**TABLE 4.5 Comparison of Measured and Theoretical Cloud-Attenuation Ratios for 20.65, 31.65, and 90.0 GHz.**

<table>
<thead>
<tr>
<th></th>
<th>31.65</th>
<th>90.0</th>
<th>90.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>20.6</td>
<td>20.6</td>
</tr>
<tr>
<td>San Nicolas Island, Measured</td>
<td>14168</td>
<td>2.0 (\pm) 0.3</td>
<td>10.9 (\pm) 1.8</td>
</tr>
<tr>
<td>July 1987 Theoretical</td>
<td>111</td>
<td>2.30 (\pm) 0.01</td>
<td>15.07 (\pm) 0.06</td>
</tr>
<tr>
<td>Denver, Colorado, Measured</td>
<td>2166</td>
<td>2.8 (\pm) 0.4</td>
<td>10.9 (\pm) 1.7</td>
</tr>
<tr>
<td>December 1987 Theoretical</td>
<td>500</td>
<td>2.23 (\pm) 0.02</td>
<td>11.77 (\pm) 0.08</td>
</tr>
<tr>
<td>Denver, Colorado, Measured</td>
<td>2091</td>
<td>2.6 (\pm) 0.4</td>
<td>10.7 (\pm) 2.0</td>
</tr>
<tr>
<td>August 1988 Theoretical</td>
<td>2217</td>
<td>2.25 (\pm) 0.02</td>
<td>12.53 (\pm) 0.07</td>
</tr>
</tbody>
</table>

*Source: After Westwater and Snider [32a]*
4.6 ADDITIONAL APPLICATIONS

Figure 4.40. Cumulative distribution of zenith attenuation measured by a three-channel radiometer at San Nicolas Island, California, July 1987. Data consist of 4805 5-min averages. After Westwater and Snider [32a].

4.6.4 Attenuation Statistics

Attenuation can be accurately derived from measurements of brightness temperature using the mean radiating-temperature approximation of Eq. 4.38. Although the errors in derived attenuation increase with increasing brightness temperature, better than 10% accuracy is achieved for brightness temperatures less than about...
150 K. In Westwater et al. [31a], attenuation statistics were derived for Denver, Colorado, during December 1987, and during August 1988, as well as for San Nicolas Island, California, during July 1987. Not surprisingly, the statistics for the three data sets differed considerably. An example of these results is shown in Figure 4.40.

4.6.5 Cloud Liquid and Radiative Transfer

Theory indicates, and recent measurements have shown, that the 90.0-GHz channel is about five to six times more sensitive to liquid than is the cloud-sensitive 31.65-GHz channel, which is typically used for cloud detection (see Sections 4.4 and 4.5). Thus, the ability of the system to measure small amounts of liquid is correspondingly increased with the 90.0-GHz channel. The theoretical rms accuracy of the dual-channel system in deriving cloud liquid amount is 0.003 cm, which corresponds to a cloud liquid density of 0.03 g/m³ for a 1-km thick cloud. With the increased sensitivity of the 90-GHz channel, the threshold is lowered to 0.005 mm. This sensitivity may allow the observation of liquid in cirrus clouds, if it exists.

Recently, research has shown that cloud liquid is very important in the transfer of solar radiation to the Earth, and thus is important to many climate-related problems such as so-called “cloud feedbacks” [91]. Consequently, various researchers have used cloud liquid measured by ground-based radiometers in cloud-radiation research [92, 93]. Figure 4.41 shows an example of results [93] in which liquid,

![Figure 4.41](image-url)
measured by the WPL three-channel radiometer, correlated well with reflected solar irradiance, as measured from a satellite. With the recent emphasis on climate and global change, radiometric measurements of cloud liquid may become increasingly in demand.

### 4.6.6 Satellite Validation

The Special Sensor Microwave/Imager (SSM/I) was launched on a polar-orbiting satellite on June 20, 1987, and is a seven-channel, four-frequency radiometer. The frequencies are 19, 22, 37, and 85 GHz. One of the many geophysical parameters to be derived from the SSM/I is the liquid-water content of clouds. Because conventional meteorological instruments do not measure liquid; upward-looking ground-based radiometers were used to validate these measurements, both over land and over ocean [94]. Over land, data from the Colorado Research Network were used; over ocean, data from the steerable radiometer, taken at San Nicholas Island were used [31a]. Preliminary results indicate that the satellite cloud liquid algorithms were not valid over land, but that they gave reasonable agreement with the steerable system over the ocean. Figure 4.42 shows results from this comparison.

**Figure 4.42.** A plot of retrieval versus observed cloud liquid water for the combined San Nicholas and Kwajalein data sets. The units are in kg/m². The San Nicholas points are shown as pluses and the Kwajalein points are shown as diamonds. The solid line is the "perfect-agreement" line. The retrieval values are from the dependent data set. After Alishouse et al. [94].
4.7 CONCLUDING REMARKS

In this chapter, we have reviewed the application of ground-based microwave radiometry to atmospheric remote sensing. All of these applications depend on the ability of microwave instruments to make unattended observations, during near-all weather conditions, of integrated quantities, such as precipitable water vapor,
integrated cloud liquid, and geopotential heights and thicknesses. Only coarse vertical-resolution profiles are available from the passive measurements alone. We have also illustrated how vertical resolution can be improved by combining radiometers with active measurements: acoustic, radar, and lidar.

Even a network of ground-based remote sensors will not be able to provide measurements of sufficient horizontal resolution for mesoscale observation and prediction. As illustrated in Sections 4.4 and 4.5, the combination of surface-based and satellite data may be able to extend the effective horizontal resolution of the remote-sensing system. Highly accurate surface-based measurements can be used as "tie-down" points for satellite sensors; conversely, the satellite data can be used to interpolate between grid points of a surface-based network.

An effective way to combine the remote-sensor data is through a numerical model, in which the physics and dynamics of the atmosphere are accurately modeled. State-of-the-art four-dimensional assimilation and forecast models, such as being developed by Y. H. Kuo [45, 51a] are ideal for this combination. The ideas of combining surface- and satellite-based remote-sensor data with an advanced numerical model are being exploited in WPL through a concept known as TELESONDE. In TELESONDE, the Wind Profiler network is a foundation from which meteorological requirements on winds are already met. In addition, mid tropospheric temperature profiles can be derived from the wind data. Other surface-based instruments, RASS and radiometers, are required to supply additional temperature and humidity information. The data from surface instruments and satellites will be integrated by a regional-scale numerical forecast and assimilation model. A conceptual model of TELESONDE is depicted in Figure 4.43. The development of these ideas may well lead to the weather-observing system of the next century.

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CHAPTER 4: REMOTE SENSING OF METEOROLOGICAL VARIABLES


57. V. M. Plechkov, Preliminary results of determining the moisture content of the atmosphere from measurements of its thermal emission near \( \lambda = 1.35 \text{ cm} \). *Atmos. Oceanic Phys.* **4**, 102–105 (1968).


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The path distortions that radio signals undergo when traversing the atmosphere of the Earth are important for many applications in areas such as space geodesy using radio-positioning systems, radar altimetry from satellites, radio-propagation experiments, and radio astronomy. This refraction introduces uncertainties in the time of arrival of the signal due to bending and retardation along the propagation path. The physical phenomena behind the delays are the dispersion due to the free electrons of the ionosphere, the induced dipole moments of neutral atmospheric molecules, and the permanent dipole moment of water-vapor molecules. The ionospheric delay is approximately inversely proportional to the square of the frequency and is treated elsewhere [1-3]. We concentrate here on the delay in the neutral atmosphere, which is often considered to be the sum of a "dry" component, about 2.3 m in the zenith direction at sea level, caused by induced dipoles, mainly in N₂ and O₂; and a "wet" component caused by the permanent dipole moment of water vapor. Even though the wet term is smaller, it is highly variable, and can range from less than 1 cm to 40 cm or more in the zenith direction. A remote-sensing approach is called for because of the difficulty in predicting line-of-sight water-vapor content from surface measurements. The weak spectral line of H₂O centered between 22 and 23 GHz is particularly well suited for radiometric remote sensing of water vapor along any direction through the atmosphere. The
state of the art of this aspect of microwave remote sensing is discussed in detail in this chapter.

5.1 THE DELAY OF RADIO WAVES PROPAGATING THROUGH THE NEUTRAL ATMOSPHERE

In this section, we discuss the physics behind the delays caused by the neutral atmosphere and define terms fundamental to this subject. The goal is to obtain an expression for a wet delay to be inferred from microwave radiometer measurements. Furthermore, we require this wet delay to be consistent with a dry delay, which will be determined from measurements of the total pressure at the ground, so that we will obtain the best possible accuracy for the resulting total delay.

5.1.1 Definition of the Excess Propagation Path

Let us assume that we know the refractive index \( n \) in a three-dimensional atmosphere. The electrical path length \( L \) of a signal propagating along \( S \) is defined as

\[
L = \int_{S} n \, ds
\]  

(5.1)

The path \( S \) is determined from the index of refraction in the atmosphere using Fermat’s Principle, to wit: the signal will propagate along the path that gives the minimum value of \( L \). In practice, a ray-tracing technique is often used to estimate \( S \) [4]. The geometry is illustrated in Figure 5.1. The geometrical straight-line distance \( G \) through the atmosphere is always shorter than the path \( S \) of the propagated signal. However, the electrical path length of the signal propagating along \( G \) is longer than that for the signal propagating along \( S \). The reason is that it would travel a longer distance with lower velocity close to the surface of the Earth, where the index of refraction is largest. The difference between the electrical path length

![Figure 5.1. The signal from the extraterrestrial source will propagate to the antenna at the Earth’s surface along the path S, instead of the geometrically shorter path G, due to the decreasing refractive index with height in the atmosphere. The path S is determined using Fermat’s Principle.](image)
and the geometrical straight-line distance is called the "excess propagation path," "path delay," or, simply, "delay":

\[ \Delta L = \int_S n \, ds - G \]  \hspace{1cm} (5.2)

We can rewrite this expression as

\[ \Delta L = \int_S (n - 1) \, ds + S - G \]  \hspace{1cm} (5.3)

where \( S = \int_S ds \). The \((S - G)\) term is often referred to as the "geometric delay," or the delay due to bending, denoted \( \Delta L_g \):

\[ \Delta L_g = S - G \]  \hspace{1cm} (5.4)

In the case of a horizontally stratified atmosphere, we note that the two paths \((S\) and \(G\)) are identical in the zenith direction, and hence the geometric delay becomes equal to zero at this angle. The geometric delay is typically 3 cm at an elevation angle of 10° and 10 cm at 5°.

Alternatively, we can expand \( G \) in Eq. 5.2 to obtain

\[ \Delta L = \int_G (n - 1) \, ds - \int_G n \, ds + \int_S n \, ds \]  \hspace{1cm} (5.5)

The corresponding correction in Eq. 5.5, where the integral of \((n - 1)\) is estimated along the straight line \( G \) instead of the curved path \( S \), produces a slightly different definition for the "geometric delay":

\[ \Delta L_g' = \int_S n \, ds - \int_G n \, ds \]  \hspace{1cm} (5.6)

The "geometric delays" in Eqs. 5.4 and 5.6, corresponding to calculating \( \Delta L \) according to Eqs. 5.3 and 5.5, are different and care should be taken because the literature available on this subject is not consistent. The two corrections, \( \Delta L_g \) and \( \Delta L_g' \), are of approximately the same size but have different signs [5]. In this chapter, we use the delay and the corresponding geometric delay according to Eq. 5.3 because these terms are most straightforwardly calculated by using the ray-tracing technique.

The index of refraction is conveniently expressed in terms of the refractivity \( N \) defined as

\[ N = 10^{-6} (n - 1) \]  \hspace{1cm} (5.7)
A common expression for $N$ is [6]

$$N = k_1 \frac{p_d}{T} Z_{d}^{-1} + k_2 \frac{e}{T} Z_{w}^{-1} + k_3 \frac{e}{T^2} Z_{w}^{-1}$$

(5.8)

where $p_d$ is the partial pressure of the dry constituents of air in mbars, $e$ is the partial pressure of water vapor in mbars (i.e., the total pressure $P = p_d + e$), $T$ is the absolute temperature in K, and $Z_{d}^{-1}$ and $Z_{w}^{-1}$ are the inverse compressibility factors for dry air and water vapor, respectively (corrections for the departure of air from an ideal gas) [6]. The first two terms are due to the induced dipole effect, whereas the third term is caused by the permanent dipole moment of the water-vapor molecule. The values of $k_1$, $k_2$, and $k_3$ can be estimated from laboratory experiments. In order to decrease the uncertainties of these values, it has been suggested that $k_1$ and $k_2$ could be extrapolated from their values at optical frequencies [7]. As pointed out by Hill et al. [8], this assumption is not correct because there is a contribution to the refractivity at radio frequencies from several water-vapor vibrational resonance lines in the infrared part of the spectrum. However, the theoretical values presented by Hill et al. [8] and updated by Hill [9] do not agree with experimental values [10, 11]. The disagreement is unexplained and the recommendation made by Hill et al. [8], which is followed here, is to use the experimental values for $k_1$, $k_2$, and $k_3$, for example, those given by Boudouris [10], which are $77.593 \pm 0.08$ K/mbar, $72 \pm 10$ K/mbar, and $(3.754 \pm 0.03) \times 10^5$ K$^2$/mbar, respectively.

Of the dry atmospheric gases, carbon dioxide (CO$_2$) shows the largest variations in concentration. Because this molecule has a linear symmetric configuration, it has no permanent dipole moment and hence contributes with only a "1/T" term in Eq. 5.8. The concentration of CO$_2$ is approximately 353 ppm (in 1990) of dry air and the effect of 300 ppm is already included in the constant $k_1$ in the previous dry pressure term. This constant is reduced by 0.02% for air free from carbon dioxide (corresponding to a change in the zenith delay of only 0.5 mm). The concentration of CO$_2$ shows an annual variation (peak to valley 6 ppm) and is currently increasing at the rate 1.7 ppm/year [12]. Measured variation in the atmospheric profiles of CO$_2$ [13] corresponds to uncertainties well below the mm level in the zenith delay.

The refractivity also has dispersive components [14]. Their maximum values are found at the absorption spectral lines of the atmospheric gases—mainly O$_2$ and H$_2$O. The delay due to the dispersive components of the refractivity (in addition to the frequency-independent part in Eq. 5.8) is much less than 1 mm in the zenith direction for signals at frequencies below 30 GHz. It reaches a level of a few mm around the O$_2$ spectral-line complex at 60 GHz. At frequencies above 300 GHz, the dispersive delay becomes important at the cm level due to several strong H$_2$O lines. In this chapter, we concentrate on the delay for signal frequencies below 30 GHz and the dispersive delays due to atmospheric gases will not be further discussed.
5.1.2 From Refractivity to Delay

Following Davis et al. [15], we now derive an expression for the excess propagation path in terms of the refractive index as given by Eq. 5.8. We can call the first term in Eq. 5.8 the "dry" refractivity, and the second and third terms together the "wet" refractivity. However, the integral of the dry refractivity (dry delay) is difficult to determine from this definition because the hydrostatic equation is valid for the total pressure and not for the partial pressure of dry air only.

Fortunately, the first two terms in Eq. 5.8 have the same temperature dependence, and using the gas law for each gas $i$,

$$p_i = \frac{\rho_i R}{m_i} T Z_i$$

(5.9)

where $\rho_i$ is the density, $m_i$ the molar mass, and $R$ the universal gas constant ($8314.34 \pm 0.35$ J/kmol K). Equation 5.8 can be rewritten as

$$N = k_1 \frac{R}{m_d} \rho_d + k_2 \frac{R}{m_w} \rho_w + k_3 \frac{e}{T^2} Z_w^{-1}$$

$$= k_1 \frac{R}{m_d} \rho + \left(k_2 - k_1 \frac{m_w}{m_d}\right) \frac{e}{T} Z_w^{-1} + k_3 \frac{e}{T^2} Z_w^{-1}$$

(5.10)

where $\rho$ is the total density, and $\rho_d$ and $\rho_w$ are the densities of dry and wet air, respectively; $m_d$ and $m_w$ are the molar masses of dry (28.9644 $\pm$ 0.0014 kg/kmol) and wet (18.0152 kg/kmol) air, respectively. The hydrostatic equation [16]

$$\frac{dP}{dh} = -\rho(h) g(h)$$

(5.11)

can be used to formulate a zenith delay that is a function of the total pressure $P_0$ measured at ground level. Integrating Eq. 5.11, we obtain:

$$P_0 = g_{\text{eff}} \int \rho(h) \, dh$$

(5.12)

where

$$g_{\text{eff}} = \frac{\int \rho(h) g(h) \, dh}{\int \rho(h) \, dh}$$

(5.13)

In order to obtain an integral that can be replaced with the ground pressure according to Eq. 5.12, we insert the total density term in Eq. 5.10 into Eq. 5.3. We obtain a delay, which we call the hydrostatic delay. This is now our definition of
“dry” delay. Note, however, that several different definitions of dry and wet delays are present in the literature. The hydrostatic delay in the zenith direction can be evaluated as

$$
\Delta L_h = [0.0022768 \pm 0.0000024 \text{ (m/mbar)}] \frac{P_0}{f(\Phi, H)} \quad (5.14)
$$

where

$$
f(\Phi, H) = 1 - 0.00266 \cos 2\Phi - 0.00028H \quad (5.15)
$$

is used to model the variation of the acceleration due to gravity [17], $\Phi$ is the latitude, and $H$ is the height in km of the station above the ellipsoid. The uncertainty in Eq. 5.14 is calculated assuming uncorrelated errors and takes into account the uncertainties in $k_1$, the acceleration due to gravity, and the universal gas constant, the variability of the dry mean molar mass, but not departures from hydrostatic equilibrium. The error introduced by the assumption of hydrostatic equilibrium will depend on the wind profile above the site, but is typically of the order of 0.01% [16]. This corresponds to 0.2 mm in the zenith delay. During extreme conditions, deviations from hydrostatic equilibrium may cause errors of several mm in the zenith delay [18].

The hydrostatic delay in the zenith direction will be consequently determined with high accuracy from the total pressure at the ground level and an effective value of the acceleration due to gravity in the atmosphere above the site. Its elevation dependence can be defined by a “dry mapping function” [15, 19, 20], which is often defined to also include the small but significant effect of the geometric delay discussed at the beginning of this section.

The wet delay is then defined by inserting the last two terms in Eq. 5.10 in Eq. 5.3. The wet delay can then be written

$$
\Delta L_w = 10^{-6} \left[ (24 \pm 10) \int_S \frac{e}{T} Z_w^{-1} \, ds + (3.754 \pm 0.030) \right] 
\times 10^5 \int_S \frac{e}{T^2} Z_w^{-1} \, ds \quad (5.16)
$$

Because the first term is only about 1% of the second term, Eq. 5.16 can be simplified without loss of accuracy by introducing a mean temperature $T_m$, defined as

$$
T_m = \frac{\int_S \frac{e}{T} Z_w^{-1} \, ds}{\int_S \frac{e}{T^2} Z_w^{-1} \, ds} \quad (5.17)
$$
whereupon we obtain

$$\Delta L_w = [1 + (6 \pm 3) \times 10^{-5} T_m](0.3754 \pm 0.0030) \int e T^{-2} Z_w^{-1} ds$$ \quad (5.18)$$

The term $\Delta L_w$ is much more difficult to estimate than the hydrostatic path delay because there is no valid hydrostatic-equilibrium equation relating the integral of water-vapor density with its partial pressure at the surface of the Earth. For most sites and weather situations, it is very difficult to predict the altitude distribution of the water vapor from the ground value with high accuracy; ideally, complete information of the distribution of water vapor and the temperature in the troposphere is needed.

Examples of hydrostatic and wet delays in the zenith direction are shown in Figure 5.2 for three sites with different climates. The delays are calculated using meteorological profiles obtained from radiosonde launches made every 12 hours. In Figure 5.3, the variability of the delays are shown as the change occurred over a period of 12 hours. We note that the variations in the hydrostatic delays increase with increasing distance from the equator (a well-known meteorological effect [21]) and that the wet delays are quite variable for all three sites.

### 5.1.3 The Path Delay due to Condensed Water

Even though the path delay is caused mainly by atmospheric gases, there is a possible contribution also from condensed water in the atmosphere—clouds and rain. In order to account for this extra delay, we must have some knowledge of the integrated amount of liquid water in a column of air in the direction of interest. Let us first study the case when clouds have drops of liquid water much smaller than the wavelength of the radio signal. For the special case of a water temperature of 283 K, the following expression can be used for the nondispersive delay due to clouds [22, 23]:

$$\Delta L_c = 0.15 \rho_c h_c$$ \quad (5.19)$$

where the delay $\Delta L_c$ is in cm, the liquid water density $\rho_c$ is in g/m$^3$, and the path length $h_c$ through the cloud is in km. The dispersive component of the delay due to liquid water droplets is at least ten times smaller than is the nondispersive component for frequencies below 30 GHz [23].

Upper bounds of 1-g/m$^3$ liquid water density and of 5 km for the cloud height give a value of the zenith delay due to clouds of 0.75 cm. Therefore, the delay due to clouds, in general, can be neglected or modeled if the integrated amount of liquid water is known. As is discussed in Chapter 4, the microwave radiometer used to estimate the wet delay is usually designed so that the integrated amount of liquid water is estimated simultaneously with the wet delay.
Figure 5.2. The wet and the hydrostatic delay in the zenith direction for West Palm Beach, Florida, Göteborg-Landvetter Airport, Sweden, and Fairbanks, Alaska. The delays are calculated with Eqs. 5.13 and 5.17 using radiosonde data obtained twice daily at noon and midnight universal time (UT), implying true solar times about 7 A.M. and P.M. in Florida, 1 A.M. and P.M. in Sweden, and 2 A.M. and P.M. in Alaska.
Figure 5.3. Changes with time in the wet and the hydrostatic delay calculated using the data presented in Figure 5.2. The variations of the wet delay show a clear annual signature for Fairbanks, whereas this signature is weak for Landvetter and nonexistent for West Palm Beach. The changes in the hydrostatic delay are larger for the stations at high latitudes where the larger variations in pressure during the fall and winter can also be seen.
Figure 5.4. The expected delay due to rain per km path length within the rain cell as a function of the rainfall rate for a linearly polarized 11-GHz signal propagating along a ground path. Horizontal ($H$) and vertical ($V$) polarizations are shown. The graph is based on data presented by Uzunoglu et al. [24].

The delay due to rain is much more difficult to estimate and, in principle, we must know the drop-size distribution as well as the shape and orientation of the drops along the propagation path. Figure 5.4 is based on results from a model presented by Uzunoglu et al. [24] and shows the expected delay due to rain along a ground path for a signal at 11 GHz with vertical or horizontal polarization as a function of the rainfall rate. The delay becomes approximately $0.6$ cm per km path length within the rain cell for the extreme rainfall rate of 100 mm/h. A moderate rainfall of 10 mm/h gives an approximate delay of $0.1$ cm/km. In practice, this type of calculation cannot be used to estimate the delay with high accuracy from rainfall rate measurements at the ground site only. The distribution and size of the raindrops are highly variable both in space and time. Therefore, the accuracy of the method will rapidly decrease with increasing zenith angle. Furthermore, as will be seen in the next section, the method of using microwave radiometry to correct the delay due to water vapor breaks down during rain.

5.2 WET-DELAY ALGORITHMS USED WITH MICROWAVE RADIOMETRY

The microwave emission from the atmosphere depends upon, among other things, its water-vapor content. Radiometric measurements of this emission can be used to estimate the wet delay as defined in the previous section and expressed in Eq. 5.18. A microwave radiometer working at frequencies around the water-vapor spectral line centered at 22.235 GHz can be used for this purpose, and we will refer to such an instrument as a water-vapor radiometer (WVR). This spectral line is rather weak, which implies that radiation emitted by water-vapor molecules at high altitudes will only be slightly attenuated when it arrives at the Earth's surface.
This fact makes this spectral line suitable for studying quantities that depend on the total amount of water vapor in the atmosphere. A complication is that liquid water, when present, also emits radiation of comparable and sometimes stronger intensity in this frequency range. Fortunately, however, these two radiation processes exhibit quite different spectral features, as shown in Figure 5.5 [25-27], and it is possible to separate the contributions from water vapor and liquid by measuring the atmospheric emission at two different frequencies. The influence of oxygen can be modeled by measuring the pressure and the temperature at the ground. As will be shown in the following, the choice of operating frequencies of the WVR depends on the application, the climate, and the expected noise performance of the instrument [28-32].

There is no unique relation between the measured brightness temperatures and the wet delay because the state of the atmosphere is defined by many more parameters than there are independent measurements. A possible approach is first to estimate the atmospheric water-vapor and temperature profiles using the radiometer observables and statistical information, which thereafter can be integrated to give the wet delay according to Eq. 5.18 (see Chapter 4 and References 33-35). A more common approach is to derive an algorithm that directly relates the brightness temperatures to the wet delay. Either approach must use statistical information concerning the atmosphere. This use leads to many possible parameters that can be statistically modeled, and implies that we can formulate many different algorithms. We will outline a general approach first, and then concentrate on a particular formulation. The derivation of this formulation will describe the background physics of the problem and the result will also justify the use of the general statistical retrieval algorithm.

![Figure 5.5. Atmospheric attenuation calculated for the most important constituents in the frequency range used in water-vapor radiometry. The solid lines give the attenuation for three different densities of water vapor using expressions given by Waters [25]. The dashed line gives the attenuation due to oxygen using expressions given by Meeks and Lilley [26]. The dashed-dotted lines give the attenuation for two different densities of liquid water in the form of drops in clouds using expressions given by Staelin [27]. All calculations use a pressure of 1013 mbars and a temperature of 283 K.](image-url)
5.2.1 General Statistical Retrieval Algorithms

The most straightforward statistical approach is to express the wet delay as a linear function of measured quantities:

\[ \Delta L_w = c_0 + \sum_{i=1}^{n} c_i X_i \]  

where \( c_i \) are retrieval coefficients, and \( X_i \) are observables or known parameters directly related to the observables. The observables may include information other than the measured brightness temperatures, such as surface air temperature, pressure, and humidity. The measured brightness temperatures can be used directly as observables [36]; however, it is usually advantageous to express the \( X_i \) as functions of either linearized brightness temperatures [30] or opacities [37] (see also Eqs. 5.24 and 5.37). These quantities do not saturate when there are large amounts of water vapor and liquid water in the atmosphere or at low elevation angles, and thus their use yields a higher accuracy. The retrieval coefficients can be obtained by linear regression using a data set consisting of wet delays and their corresponding observables. The brightness temperature depends on the atmospheric profiles of pressure, temperature, and humidity as defined in Eq. 1.8

\[ T_{b,\nu} = T_{b0,\nu} e^{-\tau_w} + \int_0^\infty T(s) \Re(\nu, T(s))^{-1} \alpha(\nu, s) e^{-\tau(s)} ds \]  

where \( T_{b0,\nu} \) is the equivalent temperature of the cosmic background radiation; \( T(s) \) is the physical temperature of the atmosphere along the path \( s \); and \( \alpha \) is the total attenuation coefficient, which is the sum of the attenuation due to water vapor, oxygen, and liquid water:

\[ \alpha = \alpha_v + \alpha_{ox} + \alpha_l \]  

The opacity \( \tau(\nu, s) \) is defined as

\[ \tau(\nu, s) = \int_0^s \alpha(\nu, s') ds' \]  

The data set used in the linear regression for the retrieval coefficients can be obtained in two ways:

1. Use observed values \( X_i \) from a WVR and \( \Delta L_w \) calculated from simultaneous radiosonde measurements (or any other independent measurement of the wet...
delay). Measurement errors in either the wet delay or in the brightness temperature will limit the accuracy of the derived retrieval coefficients.

2. Calculate all $X_i$ as well as $\Delta L_i$ from a representative set of radiosonde profiles. The limiting accuracy of the derived retrieval coefficients is, in this case, mainly determined by the errors in the expressions used for the different attenuation coefficients.

Both methods have been used extensively [37–40]. The general statistical retrieval algorithm has the advantage of simplicity, and it is easy to include other relevant observables like ground-surface meteorology.

### 5.2.2 Modified Statistical Retrieval Algorithm: Linearized Brightness Temperatures

It is possible to derive more physically complete expressions for the retrieval coefficients by combining the equation for the wet delay (Eq. 5.18) with the measured brightness temperature (Eq. 5.21) at one [41] or two frequencies [30, 42]. For this discussion, we assume that radiometric measurements are obtained at two different frequencies in order to determine two unknowns, the wet delay and the liquid water influence. We will first derive the algorithm using linearized brightness temperatures and thereafter give the corresponding expressions using opacities.

The two linearized brightness temperatures are defined as

$$T'_{b,v} = T_{b0,v} + \int_0^\infty [T(s) - T_{b0,v}] \alpha(v,s) \, ds$$  \hspace{1cm} (5.24)

for $\nu = \nu_1$ and $\nu_2$.

The equation used to calculate the linearized brightness temperatures from the observed brightness temperatures is obtained by first using the relation $\int_0^\infty \alpha e^{-T} \, ds = 1 - e^{-T_{\infty}}$ to rewrite Eq. 5.21 as

$$T_{b,v} = T_{b0,v} e^{-T_{\infty}} + T_{\text{eff},v} (1 - e^{-T_{\infty}})$$  \hspace{1cm} (5.25)

where

$$T_{\text{eff},v} = \frac{\int_0^\infty T \mathcal{R}(T)^{-1} \alpha e^{-T} \, ds}{\int_0^\infty \alpha e^{-T} \, ds}$$  \hspace{1cm} (5.26)

By extending Eq. 5.24 with $T_{\infty}$, solving for $T_{\infty}$ in Eq. 5.25, and combining these equations, one obtains the following expression for linearized brightness temperature as a function of the measured brightness temperature $T_{b,v}$:

$$T'_{b,v} = T_{b0,v} - (T'_{\text{eff},v} - T_{b0,v}) \ln \left(1 - \frac{T_{b,v} - T_{b0,v}}{T_{\text{eff},v} - T_{b0,v}}\right)$$  \hspace{1cm} (5.27)
where

\[ T'_{\text{eff},\nu} = \frac{\int_0^\infty T\alpha \, ds}{\int_0^\infty \alpha \, ds} \quad (5.28) \]

We note that both \( T'_{\text{eff},\nu} \) and \( T'_{\text{eff},\nu} \) are frequency-dependent "average" temperatures of the attenuating medium. As will be discussed in Section 5.3, they may be estimated from measurements of the ground-surface temperature.

Using two linearized brightness temperatures at the frequencies \( \nu_1 \) and \( \nu_2 \) (Eq. 5.24), we want to obtain an expression for the wet delay. We separate the absorption coefficient with its constituent parts (Eq. 5.22) in Eq. 5.24. We multiply the expression for the linearized brightness temperature at the frequency \( \nu_1 \) with \( \frac{\nu_2^2}{\nu_1^2} \) and, thereafter, subtract the expression for the linearized brightness temperature at the frequency \( \nu_2 \) to obtain the expression:

\[
\left( \frac{\nu_2}{\nu_1} \right)^2 \left( T'_{b,\nu_1} - T'_{b,\nu_2} \right) - \int_0^\infty \left( T - T_{b_0,\nu_1} \right) \left( \frac{\nu_2}{\nu_1} \right)^2 \alpha_{\nu_1} \, ds 
- \Delta T_{b_0} \int_0^\infty \alpha_{\nu_2} \, ds + T_{ox} + T_l \quad (5.29)
\]

where

\[ T_{ox} = \left( \frac{\nu_2}{\nu_1} \right)^2 \int_0^\infty \left( T - T_{b_0,\nu_1} \right) \alpha_{ox,\nu_1} \, ds - \int_0^\infty \left( T - T_{b_0,\nu_2} \right) \alpha_{ox,\nu_2} \, ds \quad (5.30) \]

is a function of the oxygen attenuation,

\[ T_l = \int_0^\infty \left( T - T_{b_0,\nu_2} \right) \left( \frac{\nu_2}{\nu_1} \right)^2 \alpha_{\nu_1} \, ds - \Delta T_{b_0} \int_0^\infty \alpha_{\nu_2} \, ds \quad (5.31) \]

is the contribution from liquid water, and

\[ \Delta T_{b_0} = T_{b_0,\nu_1} - T_{b_0,\nu_2} \quad (5.32) \]

will differ from zero due to departures from the Rayleigh-Jeans law. The value of this approach is that the first integral in Eq. 5.31 will be zero when water drops in the atmosphere are small enough so that the attenuation due to liquid water is proportional to the square of the frequency [27]. The terms involving \( \Delta T_{b_0} \) will be
very small: for example, for \( \nu_1 \) and \( \nu_2 \) equal to 21 and 31 GHz, respectively, \( \Delta T_{b0} \) is 0.2 K, and the opacities are all normally much less than unity. We will neglect these terms and assume that \( T_i \) equals zero in the following.

We move \( T_{ox} \) to the left-hand side of Eq. 5.29 and extend the right-hand side with the expression for the wet delay according to Eq. 5.18 to obtain

\[
\left( \frac{\nu_2}{\nu_1} \right)^2 T_{b,v_1} - T_{b,v_2} - \left( \frac{\nu_2}{\nu_1} \right)^2 T_{b0,v_1} + T_{b0,v_2} - T_{ox}
\]

\[
\int_0^\infty (T - T_{b0,v_1}) \left[ \left( \frac{\nu_2}{\nu_1} \right)^2 \alpha_{v,v_1} - \alpha_{v,v_2} \right] ds
\]

\[
= \frac{k_3(10^{-6})(1 + 6 \times 10^{-5}T_m)}{\int_0^\infty \frac{e}{T^2} Z_w^{-1} ds} \Delta L_w
\]

This expression is rewritten as

\[
\Delta L_w = c_b X_b
\]

where we have defined a new observable

\[
X_b = \left( \frac{\nu_2}{\nu_1} \right)^2 T_{b,v_1} - T_{b,v_2} - \left( \frac{\nu_2}{\nu_1} \right)^2 T_{b0,v_1} + T_{b0,v_2} - T_{ox}
\]

and an "inversion coefficient" \( c_b \) for the algorithm using linearized brightness temperatures:

\[
c_b = \frac{k_3(10^{-6})(1 + 6 \times 10^{-5}T_m)}{\int_0^\infty \frac{e}{T^2} Z_w^{-1} ds}
\]

Let us study the inversion coefficient \( c_b \). The attenuation coefficient for water vapor is approximately proportional to the partial pressure of water vapor. Hence, if we make the assumptions that the temperature is constant in the lower part of the atmosphere, where most of the water vapor exists, and that we measure at frequencies chosen so that the pressure dependence of the attenuation coefficients can be neglected, then we obtain a constant inversion coefficient. However, the attenuation coefficient of water vapor depends also on pressure and temperature, and temperatures vary with height and time as well as between sites. The accuracy of the wet delay that is retrieved using this algorithm will depend on the operating frequencies of the WVR and on our ability to model the variations in the coefficient \( c_b \). Equations 5.34–5.36 are close to the form of the general statistical retrieval algorithm for linearized brightness temperatures. Differences are that for the gen-
eral statistical retrieval algorithm, linear corrections using surface meteorology are used instead of modeling the variations in the inversion coefficient and the coefficients in front of the linearized brightness temperatures are not forced to be proportional to the square of the inverse frequency.

5.2.3 Modified Statistical Retrieval Algorithm: Opacities

If opacities are used instead of linearized brightness temperatures, it is straightforward to derive a set of equations using a similar procedure. The opacity can be calculated from the observed brightness temperature by rewriting Eq. 5.25 as

$$\tau_{\nu, \infty} = -\ln \left( \frac{T_{\text{eff}, \nu} - T_{b, \nu}}{T_{\text{eff}, \nu} - T_{b0, \nu}} \right)$$  \hspace{1cm} (5.37)

In the following, all opacities will be for the entire atmosphere and the "\( \infty \)" subscript will be dropped. Because the two observed opacities can also be written as

$$\tau_{\nu_1} = \int_0^\infty (\alpha_{\nu_1} + \alpha_{\text{ox}, \nu_1} + \alpha_{\ell, \nu_1}) \, ds$$  \hspace{1cm} (5.38)

and

$$\tau_{\nu_2} = \int_0^\infty (\alpha_{\nu_2} + \alpha_{\text{ox}, \nu_2} + \alpha_{\ell, \nu_2}) \, ds$$  \hspace{1cm} (5.39)

it is possible to combine Eqs. 5.38 and 5.39 in the same manner as we did with the expressions for the two linearized brightness temperatures (Eq. 5.24). The resulting expression for the wet delay is

$$\Delta L_w = c_{\tau} X_{\tau}$$  \hspace{1cm} (5.40)

where again we have defined a new observable

$$X_{\tau} = \left( \frac{\nu_2}{\nu_1} \right)^2 \tau_{\nu_1} - \tau_{\nu_2} - \tau_{\text{ox}}$$  \hspace{1cm} (5.41)

where

$$\tau_{\text{ox}} = \int_0^\infty \left[ \left( \frac{\nu_2}{\nu_1} \right)^2 \alpha_{\text{ox}, \nu_1} - \alpha_{\text{ox}, \nu_2} \right] ds$$  \hspace{1cm} (5.42)
and

\[ c_r = \frac{k_3 (10^{-6}) (1 + 6 \times 10^{-5} T_m) \int_0^\infty \frac{e}{T^2} Z_w^{-1} ds}{\int_0^\infty \left[ \left( \frac{\nu_2}{\nu_1} \right)^2 \alpha_{\nu, \nu_1} - \alpha_{\nu, \nu_2} \right] ds} \]  

(5.43)

As with \( c_b \), \( c_r \) will be constant for the conditions of atmospheric temperature and water-vapor attenuation discussed previously. However, this inversion coefficient will have a different temperature dependence than \( c_b \). The expected performance of the two derived algorithms is discussed in Section 5.3.

### 5.3 Expected Accuracy of Wet-Delay Algorithms

We now examine the accuracy of the wet-path-delay algorithms presented in the previous section. We will compute simulated observables for a set of model atmospheres using the radiative transfer equation, and then apply our retrieval algorithms as realistically as possible to these observables. Comparison of the retrieved wet-path delays with those already known for these models will then give a measure of how well these algorithms work, and how they can be best applied. We will concentrate on the modified statistical algorithms discussed before, noting that similar studies performed with other statistical algorithms lead to the same general conclusions with regard to the optimum frequencies of observation, measurement errors, and accuracy [30–32, 35, 37, 42]. We will use a set of radiosonde data as a basis for our atmospheric models. This data set is representative of a wide range of worldwide meteorological conditions, consisting of the same radiosonde data whose zenith delays were presented in Figures 5.2 and 5.3.

#### 5.3.1 Simulated WVR Observations

The radiosonde data set was first edited to discard incomplete profiles or profiles with obvious failures. Because radiosondes do not measure liquid water density, the presence of clouds was inferred according to the model described in what follows. Although probably in significant error for individual profiles, this model provides a statistically realistic ensemble of liquid water cases, which is necessary for our study. The actual wet delays were then computed by performing a numerical integration of Eq. 5.18, and the brightness temperatures were similarly computed using Eq. 5.21. All quantities were computed for the zenith direction.

The cloud, that is, liquid water, model we used was adapted from Westwater [43, 44], and is illustrated in Figure 5.6. The model assumes that when the relative humidity exceeds a certain value, then this indicates the presence of liquid water, the density of which is correlated with cloud thickness. We assume that the lower limit for the relative humidity within a cloud is 95%. These clouds in reality usually have average water-particle diameters in the range 10–50 micrometers [45,
46]; however, we allow for the possibility of larger drops by assuming that the frequency dependence of the cloud absorption may differ from $\nu^2$ by allowing for a frequency dependence
\[ \alpha_l \propto \nu^x \] (5.44)
where we can have $x < 2$.

The computed brightness temperatures are ideal in that they assume pencil-beam measurements made by a noise-free radiometer. We use expressions for the attenuation coefficients of water vapor from Waters [25], for oxygen from Meeks and Lilley [26], and for liquid water from Staelin [27]. The effects of errors in these quantities are discussed later. Finally, we use the radiosonde data to compute $T_{\text{eff}}$ and $T'_{\text{eff}}$ as well as the contribution from oxygen ($T_{\text{ox}}$ and $\tau_{\text{ox}}$). These are used to obtain the $X$ observables in the modified statistical retrieval. However, this method is not used after the stage where the retrieval coefficients are derived. When the performance of the algorithm is studied, surface meteorology has to be used to estimate these quantities because radiosonde profiles cannot be assumed to be available during the normal operation of a WVR.

### 5.3.2 Simulated Retrieval Approach

The values for the inversion coefficients $c_b$ computed for 1 year at the Landvetter site are plotted in Figure 5.7. The ground temperature is included in the same figure in order to show the good (but not perfect) correlation between the two parameters. This encourages us to attempt to model the variations in the inversion coefficient using ground meteorology, or, if that is not available, simply the time of the year. The following three formulations for the inversion coefficient will be studied:

\[ c = c_{\text{eff}}[1 + a_1(P_0 - \bar{P}_0) + a_2(T_0 - \bar{T}_0) + a_3(X - \bar{X})] \] (5.45)
\[ c = c_{\text{eff}}[1 + a_1 \sin \Omega t + a_2 \cos \Omega t + a_3(X - \bar{X})] \] (5.46)
\[ c = c_{\text{eff}} \] (5.47)
5.3 EXPECTED ACCURACY OF WET-DELAY ALGORITHMS

Figure 5.7. The inversion coefficient $c_0$ obtained from simulated radiometer observations using the frequency pair 21.0/31.4 GHz. The calculations are based on radiosonde data taken at Göteborg-Landvetter Airport during 1981. The ground temperatures from the same radiosonde profiles are clearly anticorrelated with the inversion coefficient, although not perfectly.

where $\Omega = 2\pi/365$; $t$ is the time in days since January 1; the overbars denote mean values; and the empirical coefficients $c_{\text{eff}}, a_1, a_2,$ and $a_3$ are determined by regression analysis. The quantity $X$ is our modified observable ($X_b$ from Eq. 5.35 or $X_T$ from Eq. 5.41), approximately proportional to the amount of water vapor in the atmosphere.

The off-line frequency should be well separated from the on-line frequency in order to separate best effects of vapor and liquid water. The off-line frequency, however, should not be too high because the algorithm was derived with the assumption that any drops of liquid water are much smaller than the wavelength of the observed emission; furthermore, oxygen absorption becomes more significant at higher frequencies. The frequency 31.4 GHz is a suitable choice because it lies in an atmospheric absorption window, and in a protected frequency band [47]. We will fix one frequency of the WVR at 31.4 GHz and search for the optimum frequency of the other channel around the water-vapor line. The analysis is carried out as follows:

1. Calculate the inversion coefficients $c_0$ or $c_T$ for each site and each frequency pair, thereafter determining the empirical coefficients $c_{\text{eff}}, a_1,$ etc., for each algorithm, site, and frequency pair using regression analysis.

2. Add an assumed instrumental error to the same simulated WVR observations of brightness temperature. The real measurement error consists of two parts:
a random part, such as that which might be due to instabilities in the receiver
gain and reference temperatures, and a systematic bias, such as that which
might be caused by a calibration error or an error in the local-oscillator
frequency. Gaussian random noise is added to our simulated brightness tem­
peratures. We assume that these measurement errors are independent of the
brightness temperature. The effect of a systematic bias can easily be exam­
ined once the constants of the algorithm are determined.

3. Calculate the effective temperatures by multiplying the ground temperature
with an empirical coefficient derived with regression analysis for each fre­
quency and site. (See Reference 42, for example.)

4. Calculate the oxygen contribution using a linear empirical formula obtained
with regression analysis using the ground temperature and the ground pres­
sure. (See Reference 48, for example.)

5. Calculate the modified observable $X_b$ or $X_T$. Use the derived empirical coef­
cficients in the algorithm to calculate the wet delay from the simulated mea­
surements and determine the rms difference to the wet delays calculated from
the same radiosonde profiles. These rms values then give a quantitative mea­
sure of the performance for each frequency pair and algorithm used.

### 5.3.3 Evaluation of Performance

The search for optimum frequencies for the algorithms defined by Eqs. 5.45-5.47
using linearized brightness temperatures was carried out both for a noise-free WVR
and for different instrumental errors. Figure 5.8 shows the result for different fre­
quency pairs using a noise-free WVR and Figure 5.9 shows the effect of measure­
ment errors on the expected accuracy of the wet delay. When opacities are used
instead of linearized brightness temperatures, we obtain the same optimum fre­
quencies within 0.1 GHz as those inferred from Figures 5.8 and 5.9. The impor­
tance of the bandwidth of the microwave radiometer can be studied in these graphs.
A large bandwidth is an advantage when short integration times are to be used; on
the other hand, it is clear that it will increase the error of the estimated wet delay
using a WVR with “optimum” (center-)frequencies.

It is important to note that the instrumental error becomes smaller relative to
the algorithm error for off-zenith observations. The algorithm error is proportional
to the observed air mass, whereas the instrumental error may have only a weak
dependence on the observed brightness temperature, which we ignore. To optimize
our frequency pair for observations other than in the zenith direction, we can still
use Figure 5.9. Assume that our “average” elevation angle is 30° (two air masses)
and that the rms instrumental error is 1 K. The expected error is then two times
the error expected for zenith observations with an instrumental error of 0.5 K. This
means that the optimum frequency pair of a WVR with an rms error of 1 K ob­
serving at an average elevation of 30° should be determined using an rms error of
0.5 K in Figure 5.9.

The choice of optimum frequencies of a WVR depends on the site, the noise
performance of the WVR, and the range of elevation angles used in the observa-
5.3 EXPECTED ACCURACY OF WET-DELAY ALGORITHMS

Figure 5.8. Algorithm errors in the zenith wet-path delay obtained for three different approaches to modeling the inversion coefficient: (*) $c_b$ is a constant (Eq. 5.47); (○) $c_b$ is a function of time of year and the quantity $X$ (Eq. 5.46); and (×) $c_b$ is a function of ground pressure, temperature, and the quantity $X$ (Eq. 5.45). The results are presented as a function of the first frequency channel of the WVR when the second is held constant at 31.4 GHz. In this case, we can see that the optimum frequency of the first channel is either around 20.6 or 23.9 GHz.

Figure 5.9. The error in the zenith wet-path delay when the algorithm errors shown in Figure 5.8 are combined with instrumental errors using the two algorithms with the smallest errors. In this case, we can see how the optimum frequency of the first channel is moved closer to the center of the water­vapor line when the instrument noise is increased.
The optimum frequency for the channel on the water-vapor line is above 21.0 GHz at all sites for zenith-equivalent instrumental noise of 0.6 K or more. For example, the relatively weak emission line at Fairbanks (less water vapor) moves the optimum frequency close to the center of the line for large instrumental errors. This is in contrast to results obtained for a noise-free WVR: the optimum frequencies in Figure 5.8, as well as those reported in other studies [28, 30, 31] neglecting instrumental errors, are well below 21.0 GHz. There is a protected frequency band around 23.6 GHz but the 20–22 GHz band, where many of the optimum frequencies are found, is not protected [47]; for example, part of this frequency band is allocated to satellite-to-earth communication, which is a potential problem.

The algorithm including the ground temperature (Eq. 5.45) uses the daily maximum temperature, which consistently improved the rms residuals compared to when the actual temperature is used. The largest improvement is at Landvetter with a frequency pair of 20.7 and 31.4 GHz, where the rms residual decreased from 0.15 to 0.13 cm when actual ground temperatures were replaced with daily maximum temperatures. Such a change in rms, if due only to statistical causes, would be significant at a level greater than 99.99%, due to the large sample population (2133 radiosonde profiles). The fact that algorithms with or without ground meteorology Eqs. 5.45 and 5.46, respectively, give about the same residual for West Palm Beach data implies that there is not much variation in the temperature profile beyond seasonal variations and variations that correlate with the quantity \( x \).

The influence of clouds is small as long as the assumption holds that the attenuation due to liquid water is proportional to the square of the frequency. Inserting our modeling liquid water profiles in the radiosonde data only increases the value of the rms differences a few percent. However, if we assume that \( x = 1.6 \) in Eq. 5.44 when the observables used to derive the retrieval coefficients are calculated, but still use the algorithm (Eqs. 5.34–5.36), we typically obtain a factor of 2 larger rms differences for the algorithm that includes ground meteorology data and uses the best frequency pair. In this case, the contribution from liquid water (Eq. 5.31) cannot be neglected. Of course, the increase becomes less dominating when we also take instrumental errors into account. On the other hand, these numbers reflect the decreased accuracy averaged over the whole data set, and for single occasions with high liquid water content, the error will be several cm. A related source of error of equal importance is the possibility of liquid water on the antenna system of the radiometer [49].

Let us examine the algorithm errors, that is, the errors in the wet delay that would be incurred using the derived coefficients with radiometer data. Errors obtained using the algorithm with ground meteorology (Eq. 5.45) and the 21.0/31.4 GHz frequency pair are shown for the three sites in Figure 5.10 plotted vs. the total wet delay. The fractional error is much higher for Fairbanks and Landvetter compared to West Palm Beach, indicating that the atmospheric profiles (mainly, the temperature) are less correlated with values at the ground at these sites. Ac-
5.3 EXPECTED ACCURACY OF WET-DELAY ALGORITHMS

Figure 5.10. Algorithm errors for the three studied sites as a function of the total wet delay. The 21.0/31.4 GHz frequency pair and the algorithm defined in Eq. 5.45 is used. The rms error is 0.16 cm for a mean wet delay of 6.8 cm at Fairbanks. The corresponding values for Landvetter and West Palm Beach are 0.15 and 8.4 cm, and 0.22 and 22.4 cm, respectively.

Eventually, the largest positive errors were obtained when there were different types of temperature inversions close to the ground, meaning that a too low temperature at the ground caused the algorithm to predict delays for a colder atmosphere and thereby overestimate the wet delay. Information about the temperature profile and the water-vapor profile can be obtained with other remote-sensing equipment such as a temperature-profiling radiometer (see Chapter 4), radar [50], acoustic sounder [50], or lidar [51].

If changes in the algorithm error were correlated with changes in the observed wet delay, an algorithm including a term dependent on previously measured delays could be introduced. However, Figure 5.11 shows that if such a correlation exists, it is very weak for the time scale of 12 hours, which was the minimum spacing of radiosonde launches in this data set.

Table 5.1 shows the expected error of the “best” algorithms using linearized brightness temperatures from a noise-free WVR for the 20.7/31.4 GHz frequency pair. It is seen that the modified algorithm gives slightly better accuracy of the inferred wet delay compared to the general linear algorithm. However, the difference in the expected errors for the different algorithms becomes less important when we include the instrumental error and errors in the expressions for the attenuation coefficients in our error budget. The effects of attenuation due to liquid water have already been discussed. The error due to uncertainties in attenuation coefficients of oxygen and water vapor can be studied by comparing algorithms derived using different formulas. Using different oxygen attenuation formulas [14, 26, 48, 52-54] mainly introduces a systematic error of 1–2 mm. More serious are
CHAPTER 5: TROPOSPHERIC RADIO-PATH DELAY

Figure 5.11. The change in algorithm error over a 12-h period using the data presented in Figure 5.10 plotted against the corresponding change in the total zenith wet delay. The rms values are 0.12 cm/12 h at Fairbanks, 0.14 cm/12 h at Landvetter, and 0.24 cm/12 h at West Palm Beach. The lack of correlation suggests that there are very small possibilities of reducing the algorithm error further by introducing a time-dependent correction for time scales of 12 hours or longer.

Errors in the formula used for the attenuation of water vapor. Different formulas available in the literature are presented in Figure 5.12 (see caption). They are discussed in Chapter 2. Work by Hill [55] has shown that the Van Vleck-Weisskopf line shape used by Liebe [14, 52, 53] is appropriate. The formula presented by Waters [25] does, however, use the Gross line shape and this formula agrees better with measurements at 20.6 and 31.65 GHz [56]. Other radiometric measurements at 20.7, 22.2, and 23.8 GHz show the best agreement with the Van Vleck-Weisskopf line shape [57], but a comparison with simultaneously acquired

| TABLE 5.1 Expected Algorithm Errors for a Noise-Free 20.7/31.4-GHz WVR |
|---------------------------------|-----------------|-----------------|
| Radiosonde Data Set            | Zenith rms Error in the Wet delay (cm) |
|                                 | General Algorithm* | Modified Algorithm** |
| Fairbanks                       | 0.18             | 0.15             |
| Landvetter                      | 0.17             | 0.13             |
| West Palm Beach                 | 0.21             | 0.18             |

*\( \Delta L_w = c_0 + c_1 T_{b,n} + c_2 T_{b,n}^2 + c_3 P_0 + c_4 T_0 + c_5 a_0 \) (cf. Eq. 5.20).

**\( \Delta L_w = c_{eff}[1 + a_1(P_0 - \bar{P}_0) + a_2(T_0 - \bar{T}_0) + a_3(a_0 - \bar{a}_0) + a_4(X_b - \bar{X}_b)]X_b \) (cf. Eqs. 5.34 and 5.45).
5.3 EXPECTED ACCURACY OF WET-DELAY ALGORITHMS

Figure 5.12. The attenuation coefficient for water vapor. Its uncertainty is the limiting factor of the total accuracy when the WVR method is used to estimate the wet delay. Three different widely used expressions are used to calculate the attenuation for water-vapor densities of 5 gm$^{-3}$ and 10 gm$^{-3}$ and constant pressure and temperature at 1013 mbars and 283 K, respectively. The dashed line, the dashed-dotted line, and the solid line use expressions by Liebe [14, 52, 53], Staelin [27], and Waters [25], respectively.

radiosonde data suggests an increase of about 10% in the line strength in the "Liebe model," which is consistent with the results at 20.6 and 31.65 GHz just mentioned. In order to get a feeling for the size of these uncertainties, let us here assume that the accuracies of these formulas are of the same order as their differences. We derive the empirical coefficients in the algorithm (Eq. 5.45) for the 21.0/31.4 GHz frequency pair at the Landvetter site. Using the expressions given by Liebe [14, 52, 53] instead of those given by Waters [25] implies about 6–8% larger wet delays for cold weather (zenith wet delays of a few cm). For warm and humid weather (zenith wet delays of 20–30 cm), the difference is reduced to 4–5%, depending on the combination of temperature and humidity. The uncertainty in the attenuation coefficients for water vapor is the most important error when the absolute value of the wet delay is to be inferred from WVR observations. Ongoing and proposed work [58] could reduce the size of this error. This may include repeating the laboratory measurements of the water-vapor attenuation coefficient published by Becker and Autler in 1946 [59].

The errors in the attenuation coefficients would not degrade the algorithm if real WVR data are used together with wet delays simultaneously measured with an independent instrument, for example, a radiosonde. However, in this case, the accuracy of the derived algorithm will be influenced by possible biases in the radiosonde data and in the measured brightness temperatures. The wet delay calculated from radiosonde data may have a systematic error because each instrument is normally calibrated with the same equipment on the ground before launch. Assuming that a dry- and wet-bulb psychrometer has systematic errors of 0.2 K implies that the relative-humidity calibration and the wet delay have a bias of a few percent [60]. Simultaneous measurements with a WVR and an independent method,
of course, also can be used to verify the accuracy of an algorithm derived using simulated data based on certain expressions for the attenuation coefficients. This verification will be discussed in Section 5.5.

5.4 RADIOMETER CALIBRATION

The results presented in Figure 5.9 show that a major error source for the wet-delay retrieval is the errors in the brightness-temperature measurements, even when these errors are as low as a few tenths Kelvin. Hence, the calibration of a WVR is of major importance when the best performance is desired. The problem of calibration is particularly demanding when one considers that the typical instrument is a Dicke radiometer (see Chapter 1), which measures the brightness of the sky relative to a target at a fixed temperature. The temperature of a reference target for a practical radiometer is typically near ambient, whereas the sky brightness temperature is usually in the range 10–100 K. Therefore, the quantity actually measured by a WVR—the difference between the sky and reference temperatures—is typically in the range 200–300 K, from which it follows that the calibration of the instrument must be better than 0.2% in order to achieve a measurement accuracy of ∼0.5 K. This is a severe requirement for the calibration of a microwave radiometer.

Fortunately, the conditions of the measurement also permit the use of a calibration technique commonly known as a "tip-curve" calibration. Measurements over a range of zenith angles can be used to achieve a precise calibration, at least to the extent that the atmosphere is horizontally uniform. We can show explicitly the zenith-angle dependence of the sky brightness temperature by rewriting Eq. 5.25 as

\[ T_b(z) = T_{b0} + (T_{\text{eff}} - T_{b0})(1 - e^{-\tau(z)}) \]  

(5.48)

where \( \tau(z) \) is the total opacity through the atmosphere at a zenith angle \( z \). To demonstrate the calibration approach, let us consider the particularly simple case of an optically thin isothermal atmosphere for which we can approximate the factor \( 1 - e^{-\tau(z)} \approx \tau(z) = \tau_z \sec z \), where \( \tau_z \) is the opacity at the zenith, and \( \sec z \) is effectively the increase in air mass relative to the zenith along the line of sight. With this approximation, Eq. 5.48 reduces to

\[ T_b(z) = T_{b0} + (T_{\text{eff}} - T_{b0})\tau_z \sec z \]  

(5.49)

which is linear with the air mass factor \( \sec z \). The calibration of the radiometer can be expressed by the formula

\[ T_b(z) - T_{\text{ref}} = cV(z) \]  

(5.50)

where \( V(z) \) is the radiometer output voltage for a Dicke radiometer that switches between the sky at a given zenith angle and a reference target at temperature \( T_{\text{ref}} \).
Figure 5.13 illustrates how the calibration constant $c$ can be determined for this case by extrapolating uncalibrated data obtained for different air masses, $\sec z \geq 1$, to the hypothetical zero air mass case for which the sky brightness temperature $T_b = T_{bo}$.

The calibration can be obtained just as well in the more general case, although with somewhat more effort, by considering Eq. 5.48 with less restrictive approximations. Equation 5.50 can be solved for $T_b$ and substituted into Eq. 5.48 for each measurement of the radiometer output $V(z)$, yielding a set of simultaneous nonlinear equations than can be solved for $c$ by nonlinear regression analysis. Equation 5.48 can be treated at levels of approximation up to and including a full radiative transfer computation that includes a physical description of the atmospheric profiles and the antenna-gain pattern of the radiometer. It is common to consider $T_{eff}$ to be a known constant or a simple function of ground temperature, allowing $c$ to be readily determined by nonlinear regression. Other considerations involved in the determination can be ignored or approximated depending on the level of accuracy desired, various instrumental characteristics, and the atmospheric information that is available. Several considerations are listed here in approximate order of importance:

1. The brightness temperature measured in the direction of the beam axis will always be greater than the true brightness temperature because of the nonzero beamwidth. This effect is due to the nonlinear increase in brightness temperature with decreasing elevation angle. It is possible to correct measured brightness temperatures for this effect with an adjustment that depends on elevation angle, effective beamwidth, and atmospheric zenith opacity [61, 62]. Antennas possessing significant sidelobes well away from the beam axis will also suffer from ground pickup, which may be difficult or impossible to take into account. It is important
to consider other instrumental effects, such as receiver nonlinearity, which can yield errors that are also systematic with elevation angle.

2. The effective temperature $T_{\text{eff}}$ and its dependence on elevation angle is determined by the atmospheric profiles of temperature and water vapor, which are often not available. $T_{\text{eff}}$ is usually estimated using the surface temperature, and its elevation angle dependence can be modeled [30].

3. The actual propagation path through the atmosphere will differ from that of the simple example given due to the curvature of the Earth as well as to refraction. Full correction again requires knowledge of the atmospheric profiles, but can be approximately corrected by the use of mapping functions. Different wet mapping functions are given in Table 5.2.

The errors introduced by neglecting the foregoing effects increase both with opacity and the minimum elevation angle used for the tip-curve calibration. The magnitudes of these errors depend on many factors and it is beyond the scope of this chapter to detail all such considerations. However, the achievement of an instrument calibration that permits the measurement of brightness temperature to the 0.5 K level or better requires that these effects at least be considered, and be taken into account where necessary.

The inhomogeneity of the atmosphere supplies an observational limit to the precision of a given tip-curve calibration. The presence of clouds containing liquid water that are viewed by the radiometer can render the tip-curve data meaningless. Normal variations in atmospheric vapor content are treated by obtaining measurements at many points in the sky and using regression analysis to provide a least-squares fit for the calibration constant. The scatter in result from individual tip curves can be used to indicate the level of observational error in the calibration, and a series of such calibrations can be usefully averaged to improve the overall

**TABLE 5.2 Mapping Functions for the Wet Atmosphere**

<table>
<thead>
<tr>
<th>Elevation Above Atm., $\varepsilon$ (deg)</th>
<th>Bending [60]* (mdeg)</th>
<th>Wet Mapping Function Values</th>
<th>Models Based on Ray Tracing†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>csc $\varepsilon$</td>
<td>2-km Thick</td>
<td>4-km Thick</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
<td>1.1547</td>
<td>1.1546</td>
</tr>
<tr>
<td>30</td>
<td>30</td>
<td>2.0000</td>
<td>1.9991</td>
</tr>
<tr>
<td>20</td>
<td>50</td>
<td>2.9238</td>
<td>2.9203</td>
</tr>
<tr>
<td>15</td>
<td>70</td>
<td>3.8637</td>
<td>3.8553</td>
</tr>
<tr>
<td>10</td>
<td>100</td>
<td>5.7588</td>
<td>5.7300</td>
</tr>
<tr>
<td>5</td>
<td>180</td>
<td>11.4737</td>
<td>11.2476</td>
</tr>
</tbody>
</table>

*Ground refractivity assumed to be 315.

**For a flat Earth (cosecant) and for two different thicknesses of the atmosphere around a spherical Earth.

†Ground values: pressure = 1013 mbars, temperature = 290 K, and partial pressure of water vapor = 10 mbars.
calibration if the radiometer is sufficiently stable in its properties. The typical observational uncertainty in a single tip-curve calibration in a clear sky allows calibration of sky brightness temperatures to near the 0.5 K level, although the degree of clear-sky homogeneity can vary widely with time and site.

5.5 VERIFICATION OF THE ACCURACY OF THE WVR TECHNIQUE

The accuracy of the wet delay inferred from WVR observations is determined by the instrumental error and the algorithm error. The instrumental error is straightforward to examine by using two or more WVRs observing simultaneously. The algorithm error can be treated as consisting of two parts. The first part was studied using the model atmospheres from radiosonde data. By using a representative set of radiosonde data, it is easy to calculate the expected error for a given algorithm (as was done to obtain Figure 5.10). The second part of the algorithm error is due to the errors in the attenuation coefficients used to derive the algorithm. The actual size of this error is difficult to determine. Upper bounds can be set by using a completely independent technique to determine the wet delay with high accuracy. After a discussion on WVR comparison measurements, we will therefore summarize alternative methods to model, estimate, or measure the wet delay.

5.5.1 Side-by-Side WVR Measurements

Several side-by-side comparisons using different WVRs have been carried out [64–68]. As an example of such a comparison, some results are shown in Figure 5.14. The brightness temperatures cannot be compared directly because the two WVRs were using different frequency pairs. The agreement in the equivalent zenith wet delay is within a few mm. Assuming that the errors of the four WVR channels (two in each WVR) are of the same order, Gaussian, and independent, we obtain a zenith equivalent rms error of less than 0.5 K. This number is significantly better than what is expected from the specifications of the two instruments. The reason may be that the errors of the two channels in each WVR are correlated. There may also be systematic errors that cannot be seen over this relatively short time period.

5.5.2 Estimating Wet Delay Using Surface Meteorological Data

A number of different models for estimating wet delay from surface data alone have been evaluated using data from different sites and climates [39, 69–73]. The rms accuracies for zenith wet delays are very rarely better than 2 cm. Therefore, it is impossible to verify the superior accuracy of the WVR using models based on ground meteorology. On the other hand, WVR measurements can be used to derive and improve atmospheric models. The stochastic behavior of wet-delay
5.5.3 Measuring with Radiosondes

The wet delay can be calculated using atmospheric profiles of temperature and humidity. There is, however, a rather large uncertainty in the estimation of the wet delay from radiosonde profiles due to the error in the relative humidity sensor. One problem is that water may condense on the relative humidity sensor as the radiosonde passes through clouds. It should also be noted that (i) a large amount of manpower is needed to operate a radiosonde station; (ii) continuous measurements necessitate launching balloons continuously, which is difficult and expensive; (iii) it is impossible to control the path of the radiosondes through the atmosphere; and (iv) the radiosonde takes about one-half hour to transverse the troposphere.

The total uncertainty in the radiosonde measurement of the wet delay is difficult to estimate. Most studies claim an rms error of about 10% in the zenith direction [38, 62]. It should, however, be noted that many different types of radiosondes exist and it is likely that they vary in accuracy from approximately 5 to 10%. This variation is supported by the WVR and radiosonde comparisons presented in Table 5.3 [81–86]. The radiosondes launched in Sweden appear to have an accuracy...
TABLE 5.3  Radiosonde (RS) and WVR Comparisons of the Zenith Wet Delay

<table>
<thead>
<tr>
<th>Site</th>
<th>Time</th>
<th>Frequencies</th>
<th>RMS Diff.</th>
<th>Wet Delay</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>El Monte, California</td>
<td>May 1974</td>
<td>22.2/31.4</td>
<td>1.6**</td>
<td>10</td>
<td>[62]</td>
</tr>
<tr>
<td>El Monte, California</td>
<td>May 1975</td>
<td>22.2/31.4</td>
<td>1.1**</td>
<td>8</td>
<td>[62]</td>
</tr>
<tr>
<td>Haystack, Massachusetts</td>
<td>Aug 1975</td>
<td>19.0/22.2</td>
<td>1.5**</td>
<td>15</td>
<td>[81]</td>
</tr>
<tr>
<td>Point Mugu, California</td>
<td>Mar 1976</td>
<td>22.2/31.4</td>
<td>1.5**</td>
<td>10</td>
<td>[62]</td>
</tr>
<tr>
<td>Point Mugu, California</td>
<td>Mar 1976</td>
<td>22.2/31.4</td>
<td>1.4**</td>
<td>13</td>
<td>[62]</td>
</tr>
<tr>
<td>Denver, Colorado</td>
<td>July–Dec. 1978</td>
<td>20.6/31.6</td>
<td>1.1†</td>
<td>10</td>
<td>[38]‡</td>
</tr>
<tr>
<td>Landvetter, Sweden</td>
<td>May–June 1980</td>
<td>21.0/31.4</td>
<td>0.7**</td>
<td>10</td>
<td>[39]</td>
</tr>
<tr>
<td>Landvetter, Sweden</td>
<td>May–June 1980</td>
<td>21.0/31.4</td>
<td>0.8†</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Sterling, Virginia</td>
<td>Aug.–Oct. 1981</td>
<td>20.6/31.6</td>
<td>1.7†</td>
<td>23</td>
<td>[82]‡</td>
</tr>
<tr>
<td>Onsala, Sweden</td>
<td>May 1983</td>
<td>21.0/31.4</td>
<td>0.8†</td>
<td>10</td>
<td>[83]</td>
</tr>
<tr>
<td>Denver, Colorado</td>
<td>June–Aug. 1987</td>
<td>20.6/31.6</td>
<td>1.1†</td>
<td>10</td>
<td>[84]</td>
</tr>
<tr>
<td>Onsala, Sweden</td>
<td>June 1988</td>
<td>20.7/31.4</td>
<td>0.9†</td>
<td>13</td>
<td>[68, 85]</td>
</tr>
<tr>
<td>Onsala, Sweden</td>
<td>June 1988</td>
<td>21.0/31.4</td>
<td>0.9†</td>
<td>13</td>
<td>[68, 85]</td>
</tr>
<tr>
<td>Denver, Colorado§</td>
<td>Aug.–Sep. 1988</td>
<td>20.7/31.4</td>
<td>0.9†</td>
<td>12</td>
<td>[67]‡</td>
</tr>
</tbody>
</table>

* Sensors carried by aircraft.
** The wet-path-delay algorithm was optimized for this particular data set.
† The wet delay is estimated from reported values of the integrated amount of water vapor [86]. The data sets from Denver are samples from a much larger data base. See also Figure 4.24 and the corresponding text in Chapter 4.
‡ Several WVRs were compared to the radiosonde data in this experiment. Reported here is the best agreement obtained using the J03 WVR. Data from this instrument are also shown in Figure 5.14.

closer to 5%, unless the errors from the WVR and radiosondes are highly correlated, which is very unlikely. From this table, we conclude that the rms differences are consistent with expected combined performance of radiosondes and WVRs (including the algorithm noise).

5.5.4  Measuring with a Raman Lidar

A Raman lidar system can be used to obtain profiles of water vapor in the atmosphere. The maximum altitude resolution is 15 m, which is normally smoothed, resulting in a resolution of approximately 100 m [87]. Comparison measurements between a WVR and a lidar have been reported with mean differences in the total water-vapor content ranging from 2 to 8%. The standard deviation of the differences was slightly less [88]. Because the lidar provides information on the water-vapor profile, combined WVR and lidar measurements can be used to study both horizontal and vertical gradients in the water vapor. The absolute calibration of the lidar is, however, normally obtained from simultaneously launched radiosondes.
5.5.5 Measuring with an Infrared Spectral Hygrometer

A common infrared spectral hygrometer (IRSH) measures the radiation from a background source (such as the sun or the moon) at two frequencies, on and off a water-vapor line, in the infrared part of the electromagnetic spectrum [89-94]. The atmospheric emission has also been measured by ground-based [95, 96] as well as satellite-based [97] infrared instruments to estimate the amount of atmospheric water vapor. The main disadvantage with infrared instruments is that they are much more sensitive to condensed water than is a microwave radiometer. In order to obtain reliable estimates of the water-vapor content in the presence of clouds using absorption measurements in the near infrared region, the sun should be visible through the cloud [94]. The IRSH is usually calibrated against an independent instrument to obtain an empirical relation between the wet delay and the observed infrared radiations.

Comparison of IRSH and radiosonde measurements has shown that the precision can be as good as 2% [93]. The possibility of verifying the absolute accuracy of the WVR technique using IRSHs is limited because the uncertainties of the attenuation coefficients in the infrared region are similar to those in the microwave region. However, interesting comparisons of the observed variations in the atmospheric water-vapor content can be made using the two different remote-sensing techniques [98].

5.5.6 Differential Optical/Radio Measurements

The difference in refractivity at optical and radio frequencies is mainly in the \( e/T^2 \) term in Eq. 5.10, where the optical coefficient is small and well known. It is therefore possible to derive an accurate value for the wet delay by measuring the difference in propagation time between an optical and radio signal. Such an instrument has been built and used in measurements along a ground-based path at the Joint Institute for Laboratory Astrophysics (JILA) in Boulder, Colorado [99, 100]. If such measurements were carried out from the ground to an airplane, they could provide an accurate calibration of simultaneous WVR observations. Most of the water vapor in the atmosphere must be penetrated by the signals. However, depending on the altitude of the airplane, it may be necessary to model the wet delay caused by water vapor above the airplane because this is also observed by the WVR.

When this method is used to provide an accurate calibration of the WVR technique, the result can be used to reduce the uncertainty in the attenuation coefficient for water vapor. Simultaneously launched radiosondes will make it possible to estimate that part of the algorithm error that assumes error-free attenuation coefficients (such as those in Figure 5.10). The error caused by the attenuation coefficient can then be estimated from the difference between the measured wet propagation delay and the wet delay from the WVR by placing upper bounds on the instrumental error of the WVR. In this case, it is of course also an advantage to use two or more WVRs in the experiment.
5.5.7 Estimation Using Radio-Interferometry Systems

Although one of the applications of the WVR is in the area of radio interferometry, the interferometer itself can measure the differential atmospheric delay seen by a pair of interferometer elements by observing a "point source" [76, 101]. If the hydrostatic delays are removed with high accuracy, the remaining delay can be assumed to be the site difference in the wet delay, which can be compared with site differences between wet delays measured with WVRs [64].

One can also use a Kalman-filter technique to estimate the wet delay (or, more correctly, a delay in addition to the hydrostatic delay) using data from (1) a geodetic very-long-baseline interferometry (VLBI) experiment [102] or (2) the Global Positioning System [103]. Examples of estimates using VLBI data are presented in Figures 5.15 and 5.16 together with wet delays inferred from WVR observations. Both these figures show a reasonably good agreement given the size of the one standard-deviation error bar shown for the delays estimated with the Kalman filter. Short-time variations, which are only present in the Kalman-filter estimates, can be unmodeled errors in the interferometer data that are being absorbed into the estimate of the wet delay. The more slowly varying difference may be attributable to errors in the mapping functions (for the hydrostatic and the wet delay) used to estimate the delays from the VLBI data. However, instrument errors of the WVR

![Figure 5.15](image-url)
as well as algorithm errors (see Figures 5.10 and 5.11) cannot be ignored. They are expected to vary at the several mm level over time scales of several hours to days.

The Kalman-filter technique has only recently been developed and one can expect interesting results from future comparisons between WVR observations and Kalman-filter estimates of wet delays.

5.6 APPLICATIONS OF WATER-VAPOR RADIOMETRY

This chapter has described the method of ground-based water-vapor radiometry for the estimation of the excess propagation path due to atmospheric water vapor. The main applications are the improvement of the accuracy of space-based geodetic systems. Other applications where knowledge about fluctuations in atmospheric water vapor is important are satellite altimetry [104], high-precision spacecraft tracking [105], attenuation [106], and scintillation [107] in Earth-space communication links, multipath propagation on terrestrial line-of-sight links [108], distortion of synthetic-aperture radar (SAR) images [109], interferometers for radio astronomy at mm wavelengths [110, 111], and meteorology (see Chapter 4). Here we briefly discuss two of the space geodesy applications.
5.6 APPLICATIONS OF WATER-VAPOR RADIOMETRY

5.6.1 WVR Data for Very-Long-Baseline Interferometry (VLBI)

It was realized at the time when the first VLBI system (Mark-I) was used that errors in the models for the wet delay based on ground meteorology could be a major source of error [112] even though it was possible to estimate a delay correction from the VLBI data themselves [113]. Typical uncertainties in estimates of intercontinental baseline lengths due to water-vapor fluctuations have been predicted to be 2–3 cm [78]. Fluctuations in atmospheric water vapor are strongly site-dependent, however. It has been shown that for one specific experiment that the WVR data can decrease the interferometer residuals by a factor of 2 compared to using a ground-based model together with an additional (constant) estimated delay [114]. By using WVR data, an improvement of a factor of 2–3 in accuracy of the local vertical site coordinate is expected if no additional bias of the delay is estimated from the VLBI data. If, however, an additional atmospheric delay has to be estimated, the improvement will be reduced to about 50% [115, 116]. Therefore, it is important that the total atmospheric delay can be inferred accurately from the WVR data on an absolute scale (i.e., no offsets in pressure measurements or large biases due to algorithm errors are allowed).

Limited studies of baseline-length repeatability have been made involving baselines to the Mojave, California [117], the Fort Davis, Texas [66], and the Onsala, Sweden [118], VLBI sites, where 0–25% improvement was obtained when WVR data were used instead of different estimation techniques. However, the situation may be different for other stations like the Richmond VLBI-site in Florida, where the wet-delay variations are larger than those in the Mojave Desert, the semiarid climate in Texas, and on the Swedish West coast, respectively. The main question at present is to what degree it is possible to improve the accuracy of the Kalman-filter or the WVR approach for the wet-delay correction. Comparisons such as those shown in Figures 5.15 and 5.16 will help to improve both techniques.

5.6.2 WVR Data Used with the Global Positioning System (GPS)

When the GPS system is used for relative positioning, it measures the difference in arrival time of signals originating from satellites outside the Earth’s atmosphere. Again, one of the serious error sources is the variation in the atmospheric-path delay due to water vapor. The GPS signal is much stronger than the faint extragalactic sources used in VLBI, and several sources (satellites) are observed simultaneously, implying shorter observing time. In this case, the WVR data should be used to obtain a time-dependent wet delay “map” over the sky.

As mentioned in Section 5.5, it is also possible to estimate atmospheric delays from the GPS data themselves [103, 119]. In the VLBI data analysis, clocks and atmospheres must be estimated simultaneously, implying that very low elevation angle observations should be included in order to separate these effects. An advantage compared to the VLBI technique is that errors in the models for the receiver and satellite clocks can be nearly eliminated by the method of double dif-
ferencing [120], thereby making it easier to model the atmosphere. This is fortunate because the low directivity of GPS antennas can imply an undesired sensitivity to multipath effects of the received signals at very low elevation angles. A GPS experiment involving WVRs at sites with large amounts of water vapor in Central and South America gave geodetic results with small differences when the stochastic estimation technique using the GPS data themselves was compared to the independent wet-delay correction using WVR data. Poor tip-curve calibration of the WVR and horizontal gradients in the wet delay are suggested as possible causes for the lack of improvement when WVR data are used [121].

Experiments have also been made involving WVRs where accuracies of site coordinates have been compared using WVR data or models based on ground meteorology to correct for the wet delays. The accuracy was improved by a factor of 2-3 when WVR data were used [122, 123]. Thunderstorm conditions prevailed during the observations and the wet delays showed large variations. In such a case, a ground-based model is expected to show large errors. The use of ground-based models have also been studied by using simulations of GPS observations together with real WVR data [124].

An important application of GPS is to measure local vertical coordinates using relatively short baselines. For short baselines, the elevation angles of the observed satellites at the two sites are almost the same, making it difficult to separate the atmospheric delays. The use of WVR data has been predicted to decrease the uncertainty of the estimate of the local vertical coordinate from 7 to 2-3 cm under certain conditions [125]. On the other hand, repeatabilities between 1 and 2 cm in the vertical coordinate have been demonstrated for baseline lengths up to 50 km in California without using WVR data [126, 127].

It is not yet clear to what extent and in which applications water-vapor radiometry should be used routinely to provide atmospheric wet-delay corrections. However, it is one of the few methods that can be used to study the variations in the wet delay over time scales ranging from seconds to days. In future years, it will also be an excellent tool for isolating other error sources and thereby provide a ground for future improvements for very-long-baseline interferometry (VLBI) and the Global Positioning System (GPS) applied to geodynamic research.

Acknowledgments

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REFERENCES

REFERENCES


REFERENCES


CHAPTER 5: TROPOSPHERIC RADIO-PATH DELAY


Over the past 20 years, radiometers aboard satellites have measured the Earth’s radiation throughout much of the microwave spectrum. These measurements have been used to determine rainfall, cloud liquid water, water vapor, and the vertical distribution of temperature [1–3]. The instruments have evolved from single-channel radiometers with low spatial resolution to higher-resolution sensors with many channels [4]. In this chapter, we review the evolution of this remote-sensing application up to the present and indicate what can be expected in the next few years. The emphasis is on the retrieval of atmospheric parameters for weather and climatological studies, and we concentrate on the rationale and techniques that have been developed for this application. The introductory section reviews the various microwave instruments that have been placed in orbit to observe the Earth’s atmosphere and surface. The next section develops the underlying principles pertaining to microwave remote sensing from satellites, followed with a description of the retrieval methods used for determining temperatures, cloud liquid water, rain rates, and water vapor from microwave measurements. Lengthier subjects are discussed in the appendixes to avoid interrupting the main concepts.
6.1 INTRODUCTION

6.1.1 Atmospheric Remote Sensing and Microwaves

The transparent (window) regions in the visible, infrared, and microwave bands are used to observe the surface and lower atmosphere from satellites, and the opaque regions are used to observe the upper atmosphere. Figure 6.1 shows the transmissivity of a nominal clear atmosphere at frequencies from the microwave to the ultraviolet region. This scale is expanded in Figure 6.2 to include just the microwave region, and shows the transmittance for three typical atmospheres with different amounts of water vapor. The absorption features are due to oxygen and water vapor, and the relative contributions to the absorption from these two sources are shown in Figure 6.3 for the standard atmosphere case of the previous figure. Resonant absorption occurs at 22 and 183 GHz due to water vapor, and at 118 GHz and between 50 to 70 GHz due to a series of oxygen absorption lines. The absorption features of these constituents are discussed in detail in Chapter 2.

The effects of clouds are not shown in the previous figures, but are a significant factor at all frequencies when viewing the surface and lower atmosphere from space. Both water clouds and the ice crystals comprising cirrus clouds are highly absorbing in the infrared and highly reflecting at visible wavelengths, and limit the use of infrared and visible techniques to clear atmospheres. Fortunately, cirrus clouds are virtually transparent at all microwave frequencies, and even clouds consisting of liquid water droplets produce relatively little absorption at the lower microwave frequencies. The effects of cloud particles (hydrometeors) on microwave radiative transfer are discussed in Chapter 3.

Determination of atmospheric temperature from satellites was first suggested using infrared radiation measurements centered around the 15-μm carbon dioxide band [5, 6], and the method was later extended to the microwave emission band of molecular oxygen [7]. Radiometric measurements in the 50–60 GHz portion of the oxygen band are used to derive temperature profiles in clear and cloudy atmospheres. The influence of water vapor is small and can often be neglected when analyzing measurements within the oxygen band due to the large frequency sepa-
Figure 6.2. Total transmittance in the microwave region for a cloud-free tropical, standard, and polar atmosphere. The main differences in transmittance are due to the varying amounts of water vapor, which are indicated.

Measurement between the water-vapor lines and the oxygen complex (see Figure 6.3). Measurements around the 22-GHz water-vapor line are used to obtain column water abundance [2] and the measurements around the 183-GHz water vapor line are used to obtain humidity profiles using statistical techniques [8, 9].

The unique characteristics of clouds at microwave frequencies are used to full advantage when designing instruments for particular applications. Microwave ab-
sorption by liquid water clouds increases monotonically with frequency. The absorption by clouds is minimal at frequencies below 20 GHz, enabling high-quality observations of the surface from space. At frequencies between 20 to 40 GHz, absorption by clouds and the larger liquid drops in rain can be used to extract information about their water content and horizontal extent. In the production of rain, the large ice particles formed aloft act as efficient scatterers with very little absorption [10], and are readily identified at frequencies around 90 GHz or higher.

6.1.2 Value of Microwave Measurements

Historically, the earliest satellite observations of the Earth were made in the visible and infrared regions, followed later by the use of microwave measurements. We discuss here some of the important differences between infrared and microwave measurements. In general, maximum absorption occurs within the infrared band due to carbon dioxide and water vapor. Also, at temperatures corresponding to the Earth’s environment, the peak emitted radiation occurs at infrared frequencies, and the lowest levels of radiation appear at the Rayleigh–Jeans limit of the Planck function. Therefore, infrared radiometers require less amplification than the very sensitive radiometers needed to detect microwave radiation. In practice, however, sensitivity is rarely a limiting factor in the design of microwave sensors for satellite applications. The absorption and emission by surfaces and clouds are also quite different in the two spectral regions. At the center of the infrared band, natural surfaces (including clouds) act as nearly perfect emitters \( (ε ≈ 1) \) so that the radiation is nearly independent of the material and is only dependent on the temperature. Thus, for example, infrared measurements in window regions are used to determine accurate temperatures of surfaces and cloud tops. The more variable emissivity at microwave frequencies is used for surface identification (see Figure 6A.1 in the Appendix to Chapter 6).

Due to the strong infrared absorption by clouds, the measurements in the window region around the 11-\( \mu \)m (micrometer) wavelength correspond to the temperature of the cloud tops or the surface under cloud-free conditions. To illustrate this feature, Figure 6.4 shows a nighttime satellite image of Typhoon June over the Pacific Ocean using the Very High Resolution Radiometer (VHRR) on NOAA-4. The image was generated using mapped radiometer measurements, where the coldest regions are shown in white and are due to the emission from the cirrus (ice) clouds covering the storm. Warmer temperatures, due to emission from lower clouds, are shown in various gray shades. The darkest areas correspond to clear views of the warm sea surface; they occur in the eye of the storm and the outer cloud-free regions.

Measurements in the absorption regions of uniformly mixed gases such as oxygen and carbon dioxide are proportional to the vertically weighted atmospheric temperature. Figure 6.5 shows such weighting functions (see Section 6.2.2) for an infrared (Vertical Temperature Profile Radiometer, VTPR) and a microwave (Scanning Microwave Spectrometer, SCAMS) temperature sounder, which were selected to provide similarly weighted temperatures centered around the 300-mbar
**Figure 6.4.** Image of Typhoon June on November 21, 1975, at 1140 GMT using 11.5-μm measurements from the Very High Resolution Radiometer (VHRR) on NOAA-4.

**Figure 6.5.** Weighting functions at 55.45 GHz (O₂ band) and 695 cm⁻¹ (CO₂ band) at nadir. The 55.45-GHz channel is one of five frequencies measured by the Scanning Microwave Spectrometer (SCAMS) on Nimbus-6, and the infrared channel at 14.29 μm (695 cm⁻¹) is one of six channels of the Vertical Temperature Profile Radiometer (VTPR) on NOAA-4.
pressure level in the upper troposphere. The infrared and microwave weighting functions were computed using absorption models for carbon dioxide and oxygen, respectively, and are plotted normalized to their peak values. Figure 6.6 shows contour plots of the microwave (left) and infrared (right) brightness-temperature measurements for the typhoon. Both the infrared and microwave measurements are similar under clear conditions. However, the infrared measurements around the 15-µm carbon dioxide band suffer the same cloud problems found in the more transparent region around 11 µm (refer to Figure 6.4). The strong absorption by clouds cuts off the infrared weighting function below the cloud tops so that only the microwave measurements display the true temperature pattern of the typhoon around 300 mbars. The SCAMS measurements indicate increasingly warmer temperatures around the storm center, which results from latent heating due to condensation processes as well as the warming due to subsidence (adiabatic compression) around the eye wall region [11]. Comparisons such as this clearly established the importance of microwave techniques for obtaining temperature information under clear and cloudy conditions.

6.1.3 Satellite Microwave Radiometers

Table 6.1 lists the microwave radiometers that have been or shortly will be placed into orbit for meteorological, hydrological, and oceanographic applications. The first instruments used relatively simple sensors having few channels with limited spatial resolution. Instrumentation and analysis techniques have continued to improve so that the current and future generations of sensors are much more capable of obtaining atmospheric temperature, moisture, and precipitation. We give here a brief description of these instruments and their historical significance. Not listed in Table 1 are special-purpose radiometers such as those used for the correction of radar altimeters for tropospheric path delay; although these use techniques similar to those discussed here, their description is beyond the scope of this chapter [12, 13].

The microwave sensors described in this chapter are generally of two types, which we describe separately in more detail in what follows: imagers, which have channels in the window regions of the spectrum to monitor surface features and precipitation, and sounders, with channels in opaque spectral regions to provide profiles of atmospheric temperature or water vapor. All current and planned sensors are flown aboard low Earth-orbiting satellites. The vantage point of geosynchronous orbit would be valuable for obtaining the synoptic and continuous views of the atmosphere provided by optical and infrared sensors; however, large antenna-aperture sizes are required to provide useful spatial resolution at this distance and their feasibility is still under study [14]. The coverage available from a polar orbiter is illustrated in Figure 6.7. Polar orbiters can only view a given scene every 12 to 24 hours, depending on the latitude. The 12-hour observations are obtained at latitudes >30°, where the ascending and descending orbital swaths overlap. Coverage at lower latitudes is limited to 24 hours with the diamond-shaped areas showing regions that are missed in this period. The significance of the observation
Figure 6.6. Brightness temperatures (K) for Typhoon June from SCAMS 55.45-GHz measurements (left) and VTPR 695 cm⁻¹ measurements (right).
<table>
<thead>
<tr>
<th>Satellite</th>
<th>Sensor</th>
<th>Center Frequencies (GHz)</th>
<th>Nadir IFOV (km)*</th>
<th>Primary Application**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cosmos-243 1969</td>
<td>—</td>
<td>3.5, 8.8, 22.2, 37</td>
<td>13 (Nadir)</td>
<td>V, Q, I, T, M</td>
</tr>
<tr>
<td>Cosmos-384 1970</td>
<td>—</td>
<td>3.5, 8.8, 22.2, 37</td>
<td>13 (Nadir)</td>
<td>V, Q, I, T, M</td>
</tr>
<tr>
<td>Nimbus-5 1972</td>
<td>ESMR</td>
<td>19.35</td>
<td>25 (X-Scan)</td>
<td>I, M, P</td>
</tr>
<tr>
<td>Nimbus-5 1972</td>
<td>NEMS</td>
<td>22.23, 31.40, 53.65, 54.90, 58.80</td>
<td>200 (Nadir)</td>
<td>t, V, Q</td>
</tr>
<tr>
<td>Nimbus-6 1975</td>
<td>SCAMS</td>
<td>22.23, 31.65, 52.85, 53.85, 55.45</td>
<td>150 (X-Scan)</td>
<td>t, V, Q</td>
</tr>
<tr>
<td>Nimbus-6 1975</td>
<td>ESMR</td>
<td>37.0 (V + H)</td>
<td>25 (C-Scan)</td>
<td>I, P, W</td>
</tr>
<tr>
<td>Nimbus-7 1978</td>
<td>SMMR</td>
<td>6.6, 10.69, 18.0 (V + H), 21.0, 37.0 (V + H)</td>
<td>25–100 (C-Scan)</td>
<td>I, M, P, S, V, Q, W, T</td>
</tr>
<tr>
<td>(Also SEASAT)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIROS 1978–1995</td>
<td>MSU</td>
<td>50.30, 53.74, 54.96, 57.95</td>
<td>110 (X-Scan)</td>
<td>t, Q</td>
</tr>
<tr>
<td>DMSP 1979–</td>
<td>SSMT</td>
<td>50.50, 53.20, 54.35, 54.90, 58.40, 58.82, 59.4</td>
<td>175 (X-Scan)</td>
<td>t, Q</td>
</tr>
<tr>
<td>MOS-1 1987</td>
<td>MSR</td>
<td>23.8, 31.4</td>
<td>23–32 (X-scan)</td>
<td>V, Q, I, W</td>
</tr>
<tr>
<td>DMSP 1987–</td>
<td>SSM/I</td>
<td>19.35, 37.0, 85.5 (V + H), 22.23 (V)</td>
<td>15–60 (C-Scan)</td>
<td>I, M, P, S, V, Q, W</td>
</tr>
<tr>
<td>Instrument</td>
<td>Platform</td>
<td>Dates</td>
<td>Channels</td>
<td>X-Scan Count</td>
</tr>
<tr>
<td>-------------</td>
<td>-----------</td>
<td>-----------</td>
<td>----------</td>
<td>--------------</td>
</tr>
<tr>
<td>DMSP 1991–</td>
<td>SSM/T2</td>
<td>90.0, 150.0, 183 ± 7, 183 ± 3, 183 ± 1</td>
<td>50 (X-Scan)</td>
<td>$v, V, P$</td>
</tr>
<tr>
<td>NOAA (1995)</td>
<td>AMSU/A</td>
<td>23.8, 31.4, 89.0, 50.3, 52.80, 53.60, 54.40, 54.94, 55.50, $F = 57.29; F \pm 0.217$, $F \pm 0.322 \pm 0.048$, $F \pm 0.322 \pm 0.022$, $F \pm 0.322 \pm 0.010$, $F \pm 0.322 \pm 0.045$</td>
<td>50 (X-Scan)</td>
<td>$t, v, I, P$, $S, V, Q$</td>
</tr>
<tr>
<td>NOAA (1995)</td>
<td>AMSU/B</td>
<td>89.0, 157.7, 183 ± 7, 183 ± 3, 183 ± 1</td>
<td>15 (X-Scan)</td>
<td>$v, V, P$</td>
</tr>
<tr>
<td>DMSP (1996)</td>
<td>SSM/IS</td>
<td>19.35, 22.23, 37.0, 91.6, 50.30, 52.80, 53.60, 54.40, 55.50, 57.29, 59.40, 63.283 ± .285, $F = 60.79 \pm .357, F \pm 0.050$, $F \pm 0.016, F \pm 0.006, F \pm 0.002$, 150, 183 ± 7, 183 ± 3, 183 ± 1</td>
<td>15—75 (C-Scan)</td>
<td>$t, v, I, M, P$, $S, V, Q, W$</td>
</tr>
</tbody>
</table>

*X-Scan = cross track scanner; C-Scan = conical scanner.

**Atmospheric parameters: $P =$ precipitation (rain rate), $Q =$ cloud liquid water, $t =$ temperature sounding, $v =$ water-vapor sounding, $V =$ total precipitable water. Surface parameters: $I =$ sea ice, $M =$ soil moisture, $S =$ snow cover, $T =$ sea-surface temperature, $W =$ sea-surface wind.
repeat times and spatial resolution can be appreciated with reference to Table 6.2, which lists the spatial and temporal scales of temperature variation for different meteorological systems.

Sounders and imagers both make use of scanning antennas to obtain wider areal coverage. Table 6.1 identifies the sensors as either cross-track or conical scanners. Cross-track scanners typically scan through nadir and view the atmosphere over a range of slant angles. Figure 6.8 shows the discrete scan steps of the SSM/T sounder, for example, and Figure 6.9 illustrates the beam footprints of these steps.

![Figure 6.7. Global coverage of SSM/I measurements over 24 hours.](image)

**TABLE 6.2 Scales of Meteorological Features**

<table>
<thead>
<tr>
<th>Temporal Scale (h)</th>
<th>Spatial Scale (km)</th>
<th>Feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–0.1</td>
<td>0.1–1</td>
<td>Tornados</td>
</tr>
<tr>
<td>0.1–1</td>
<td>1–5</td>
<td>Thunderstorms</td>
</tr>
<tr>
<td>6–12</td>
<td>10–50</td>
<td>Fronts, squall lines</td>
</tr>
<tr>
<td>12–24</td>
<td>10–100</td>
<td>Hurricanes</td>
</tr>
<tr>
<td>12–48</td>
<td>200–500</td>
<td>Synoptic cyclones</td>
</tr>
<tr>
<td>&gt;24</td>
<td>1000–10000</td>
<td>Planetary waves,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>atmospheric tides,</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mean zonal temperature</td>
</tr>
</tbody>
</table>
Figure 6.8. Antenna step-scanning diagram for the SSM/T sounder. Note the seven Earth-viewing positions and the two calibration positions of cold space and the warm calibration target.

Projected onto the Earth. The analysis of the measurements must take into account the differing path lengths through which the atmosphere is viewed. Imagers preferentially scan at a constant slant angle (conical scanning) so that this complication is avoided in the analysis. Polarization plays a role when the surface is seen, and some of the window channels listed in Table 6.1 are identified as having linear horizontal (H) or vertical (V) polarizations according to whether the orientation of the accepted polarization is respectively orthogonal to or lies within the plane of

Figure 6.9. SSM/T scan grid pattern and field of view (half-power) projected on Earth.
incidence defined by the Earth normal and the direction of the scene viewed to the spacecraft.

Imagers

These instruments view the Earth with relatively high spatial resolution (\(< 30\) km), and the measurements are often displayed as enhanced color images. The 12- to 24-hour sampling period achieved from low polar orbit is adequate for monitoring changes in the Earth’s surface (e.g., snow and ice cover), although more frequent observations using multiple satellites are needed to more adequately sample precipitation. This is particularly true in the tropics where the observations generally occur only every 24 hours from a single satellite. However, it will be possible to more adequately sample global precipitation as the number of satellites containing microwave radiometers increases in this decade.

Microwave radiometry of Earth from satellites began with the 1968 launch of Cosmos-243 and the 1970 launch of Cosmos-384. These Soviet satellites contained a nadir-viewing instrument having four channels with frequencies between 3.5 and 37 GHz, and provided determinations of water vapor and cloud liquid water over the oceans in addition to surface parameters [15, 16]. The first U.S. microwave imager was the Electrically Scanning Microwave Radiometer (ESMR), which was launched in 1972 on the Nimbus-5 satellite. It viewed the Earth using a cross-track scanning mechanism and provided linearly polarized measurements at 19 GHz. This was followed by a second ESMR on Nimbus-6, which was launched in 1975 and measured the radiation at 37 GHz. Unlike the earlier ESMR, this instrument used a conical scanner to provide dual polarized measurements at a fixed field of view (25 km) and constant incident angle (50°). Results obtained from the ESMR instruments demonstrated the importance of microwave observations for identifying sea ice and snow cover under cloudy conditions and monitoring precipitation over oceans [17, 18]. However, it became apparent that multispectral measurements were needed to improve the accuracy and reduce the ambiguity in obtaining surface and precipitation measurements.

The Scanning Multichannel Microwave Radiometer (SMMR) was flown aboard the SEASAT and Nimbus-7 satellites in 1978. The SMMR contained five channels with dual polarization at frequencies from 6.6 to 37 GHz, and provided the first multispectral observations in the transparent regions of the microwave spectrum. The combined measurements at 18 and 37 GHz were particularly valuable for monitoring the global variations of snow cover and precipitation [19, 20]. Over the polar oceans, algorithms were developed to estimate the percent coverage of new ice, multiyear ice, and open water [21, 22]. Quantitative measurements of the vertically integrated cloud liquid water and water vapor (precipitable water) were made over oceans using the 21- and 37-GHz channels [23]. Sea-surface temperature and wind speed were also obtained from the 6.6- and 10.7-GHz measurements [24, 25].

The latest microwave imager is the Special Sensor Microwave/Imager (SSM/I), which was developed as part of the Defense Meteorological Satellite
Program (DMSP) and was flown aboard the Air Force Block 5D satellite in 1987 and again in 1991. The SSM/I is a conically scanning radiometer having channels from 19 to 85 GHz [26]. All measurements are obtained with dual polarization except for the 22-GHz channel. The addition of an 85-GHz channel makes the SSM/I unique in comparison to previous instruments. This channel has the highest resolution (15 km) ever flown for a microwave radiometer and provides the highest sensitivity for measuring rainfall over land and ocean. In addition to precipitation, snow and ice cover are identified using the 85-GHz channel in conjunction with the lower-frequency measurements [27]. The first Japanese microwave radiometer, the Microwave Scanning Radiometer (MSR), was launched in February 1987 aboard the Marine Observation Satellite (MOS-1). This was planned as the first of a series of instruments for oceanographic applications [28].

**Sounders**

Radiometers sensing in the vicinity of the oxygen band centered near 60 GHz are used to derive vertical temperature profiles (soundings) and are classified as temperature sounders. Existing radiometers use the lower half of this band, from approximately 50–60 GHz. Similarly, radiometers having channels around the 183-GHz water-vapor line are referred to as water-vapor sounders. Generally, two such satellites are placed in orbit simultaneously so that observations can be made nearly every 6 hours in the polar and midlatitude regions. As indicated in Table 6.2, this temporal resolution is adequate for sampling most meteorological systems.

It is evident from Table 6.2 that mesoscale features such as tornadoes and thunderstorms require the more continuous observations obtained from geostationary satellites. Polar-orbiting satellites are used for measuring the development of hurricanes, frontal systems, and the large-scale features associated with cyclones and planetary waves. The latter two events can be resolved using the modest spatial resolutions (100–200 km) available from current microwave radiometers. However, the smaller spatial scales associated with hurricanes and frontal systems require the resolution of more advanced instruments such as the Advanced Microwave Sounding Unit (AMSU). Note, from Table 6.1, AMSU consists of two separate modules, A and B.

The horizontal variability of atmospheric temperature for large-scale events is smaller than it is for surfaces, and temperature sounders are therefore designed with poorer spatial resolution than imagers. Sounders also scan cross-track rather than conical to obtain wide swath widths resulting in greater areal coverage. Furthermore, polarization measurements are unnecessary for sounding the atmosphere because Zeeman splitting of the oxygen lines due to the Earth’s magnetic field is only noticeable at the very low pressures that occur above about 50 km [29].

Temperature soundings from satellites using microwave radiometry began with the launch of the Nimbus E Microwave Spectrometer (NEMS) on Nimbus-5 in 1972. This nadir-viewing instrument contained three oxygen channels, a 31-GHz window channel, and a 22-GHz water-vapor channel. The weighting functions for
this and the other sounders described here are discussed in detail in Section 6.2.2 and illustrated in Figures 6.13 through 6.17. Prior to the development of microwave sounders, temperature soundings were derived using infrared measurements in the 15-μm carbon dioxide band and were mainly limited to clear areas. Analysis of the NEMS data clearly established the importance of microwave techniques for obtaining temperature soundings and columnar water vapor for nearly all weather conditions. Because the measurements were virtually unperturbed by clouds, temperature profiles were derived by simply ignoring clouds in the NEMS analysis [3]. A major limitation was the nonscanning characteristic of the NEMS, which limited its horizontal coverage for meteorological systems to nadir observations. More sounding channels were also needed to improve the temperature accuracy. These improvements were made in the next generation of instruments.

A scanning version of the NEMS called the Scanning Microwave Spectrometer (SCAMS) was launched aboard the Nimbus-6 satellite in 1975. The weighting functions are elevated for increasing scan angle (see Section 6.2.3), and the 55.45-GHz measurements displayed in Figure 6.6 were corrected to equivalent nadir brightness temperatures. Measurements such as these demonstrated the unique capability of the instrument for mapping the temperature structure of tropical storms as well as other meteorological systems [11, 30]. In addition to temperature, the SCAMS window and water-vapor channels were used to map the global distribution of water vapor and cloud liquid water over the world’s oceans [2, 31].

The NEMS and SCAMS were experimental instruments intended to test the capability for microwave temperature sounding. An operational version of the SCAMS called the Microwave Sounding Unit (MSU) was placed on the National Oceanic and Atmospheric Administration (NOAA) series of polar orbiting satellites beginning in 1978 [32, 33]. It contains four channels within the oxygen band instead of the three used in the experimental versions. At present, several identical MSU instruments have been successfully flown with excellent performance [34]. The high stability of the MSU instruments has been used to accurately measure global temperature changes during the past 14 years [35].

A more advanced instrument, called the Special Sensor Microwave/Temperature (SSM/T) sounder, was developed as part of the Defense Meteorological Satellite Program (DMSP) and was launched in 1979, 1983, 1987, and again in 1991 aboard the Air Force Block 5D satellites [36–38]. Whereas the earlier temperature sounders only contained up to four oxygen channels, the SSM/T contains seven channels, resulting in improved temperature accuracy. The characteristics of the SSM/T channels are given in Table 6.3, including the instrumental noise per measurement on a given field of view (ΔT_{fov}). Besides the SSM/T and SSM/I instruments, a new sensor called SSM/T2 was launched in November 1991 aboard the DMSP satellites (see Table 6.1). This instrument has channels at 90, 150, and near 183 GHz; its use for deriving water-vapor profiles is one of the most challenging problems presently under study.

Beginning in 1995, an Advanced Microwave Sounding Unit (AMSU) will be flown aboard the next generation of NOAA polar-orbiting satellites. This multi-purpose instrument contains 12 oxygen channels and extends the height of the
TABLE 6.3 SSM/T Channel Parameters

<table>
<thead>
<tr>
<th>Channel</th>
<th>Polarization</th>
<th>Frequency (GHz)</th>
<th>Bandwidth (MHz)</th>
<th>( \Delta T_{\text{dev}} ) (K)</th>
<th>Peak Response (km, Mb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>50.50</td>
<td>400</td>
<td>0.32</td>
<td>Surface</td>
</tr>
<tr>
<td>2</td>
<td>Principally</td>
<td>53.20</td>
<td>400</td>
<td>0.24</td>
<td>2, 700</td>
</tr>
<tr>
<td>3</td>
<td>Horizontal</td>
<td>54.35</td>
<td>400</td>
<td>0.36</td>
<td>6, 400</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>54.90</td>
<td>400</td>
<td>0.22</td>
<td>10, 250</td>
</tr>
<tr>
<td>5</td>
<td>Orthogonal</td>
<td>58.40</td>
<td>115</td>
<td>0.39</td>
<td>30, 10</td>
</tr>
<tr>
<td>6</td>
<td>to Channels</td>
<td>58.825</td>
<td>400</td>
<td>0.29</td>
<td>16, 90</td>
</tr>
<tr>
<td>7</td>
<td>1–4</td>
<td>59.40</td>
<td>250</td>
<td>0.31</td>
<td>22, 50</td>
</tr>
</tbody>
</table>

temperature soundings beyond that of the SSM/T. As with the SSM/I and SSM/T2 instruments, AMSU also contains channels near the 183- and 22-GHz water-vapor lines for obtaining water-vapor soundings and includes window channels at 31, 90, and 157 GHz for obtaining precipitation and surface parameters. A similar instrument combining imaging and sounding capabilities is also being developed by the Air Force and called SSM/IS. In addition to combining the SSM/T, SSM/T2 and SSM/I into a single instrument, the SSM/IS also has six channels near the center of the strongest oxygen lines to provide temperature soundings beyond the stratosphere up to an altitude of 80 km [39, 40].

6.2 THEORETICAL BACKGROUND

Remote sensing of the Earth’s atmosphere from satellites differs from other applications in this book because the atmosphere is viewed against the complex and varied background of the Earth’s surface. This requires additions to the radiative transfer equation that takes the surface into account and consequently requires special considerations in the retrieval of atmospheric properties. A simplified but useful expression of the radiative transfer equation is derived here which introduces the concept of atmospheric weighting functions and lays the foundation for subsequent sections.

6.2.1 Brightness Temperature Equation

The radiative transfer equation given by Eq. 1.13 is generally applicable for unpolarized and nonprecipitating atmospheres free from scattering. Temperature as well as the various absorbing constituents of the Earth’s atmosphere are largely horizontally stratified; consequently, this equation is usually modified to describe a plane-parallel atmosphere. If \( \theta \) is the local zenith angle on Earth viewed by the satellite instrument and the \( z \)-direction is normal to the Earth’s surface, then the distance along the slant path \( s \) is well approximated as \( z \sec \theta \) and Eq. 1.13 can
be written as

\[ T_b(\nu, \theta) = T_{b0} e^{-\tau(\nu, 0) \sec \theta} + T_u(\nu, \theta) \]  

(6.1)

where

\[ T_u(\nu, \theta) = \sec \theta \int_0^H T(z) \alpha(\nu, z) e^{-\tau(\nu, z) \sec \theta} \, dz \]  

(6.2)

is the upwelling radiation from the surface at \( z = 0 \) to the satellite altitude \( H \), \( \nu \) is the frequency, \( \alpha \) is the absorption coefficient, and \( \tau \) is the opacity along the vertical axis between height \( z \) and the satellite. The opacity is obtained from Eq. 1.5 and is written for this case as

\[ \tau(\nu, z) = \int_z^H \alpha(\nu, z') \, dz' \]  

(6.3)

Equation 6.1 and the equations that follow from it are often expressed in terms of a transmittance function \( e^{-\tau(\nu, z)} \), which is often also identified by the symbol \( \tau \). Hence, we use opacity rather than transmittance in the following equations to avoid confusion with the notation in other chapters. We will also drop the explicit frequency dependence for opacity and other variables that are clearly frequency-dependent, for example, referring to \( \tau(\nu, z) \) as simply \( \tau(z) \).

The boundary term \( T_{b0} \) is the sum of two components: radiation emitted from the surface, which we denote as \( T_e \), and downwelling radiation reflected from the surface back toward the satellite, which we denote as \( T_r \). Equation 6.1 consequently can be rewritten as

\[ T_b(\nu, \theta) = T_u(\nu, \theta) + T_e(\nu, \theta) e^{-\tau(0) \sec \theta} + T_r(\nu, \theta) e^{-\tau(0) \sec \theta} \]  

(6.4)

These three components are illustrated in Figure 6.10.

Figure 6.10. Schematic showing the brightness temperature \( T_b \) resulting from the upwelling and downwelling atmospheric radiation \( (T_u, T_d) \) and the surface emitted and reflected radiation \( (e_T, T_r, (1 - e_s) T_d) \).
The reflected and emitted radiation from the surface are difficult to treat analytically because of multiple scattering due to surface roughness and inhomogeneities within the material. Even the variations of temperature with depth can complicate the analysis, making it difficult to obtain a general equation for the reflected and emitted radiation. We will treat only the much simpler case of a smooth, homogeneous, isothermal surface for the following. This is sufficient for the majority of cases, and the more general case is discussed in Appendix 6A.

For an isothermal surface viewed at an angle $\theta$, the emitted radiation depends only on the product of the temperature $T_s$ and the emissivity $\varepsilon_s$ of the surface,

$$T_e = \varepsilon_s(\nu, \theta)T_s \quad (6.5)$$

The reflected radiation from a smooth homogeneous surface only contains the downwelling radiation $T_d$ in the specular direction $\theta$, where the power-reflection coefficient is $1 - \varepsilon_s(\nu, \theta)$, so that

$$T_r = [1 - \varepsilon_s(\nu, \theta)]T_d(\nu, \theta) \quad (6.6)$$

The downwelling radiation is also obtained from the radiative transfer equation, Eq. 1.13 except that the path of integration begins from above the atmosphere and extends to the Earth's surface, namely,

$$T_d(\nu, \theta) = T_c e^{-\tau(0)\sec\theta} + \sec\theta \int_0^\theta T(z) \kappa(z) e^{-\tau(0) - \tau(z)\sec\theta} dz \quad (6.7)$$

where the boundary term is now the cosmic microwave background with $T_c = 2.7$ K. This term is generally small compared to the atmospheric contribution and will be neglected for the following. Substituting Eqs. 6.5–6.7 into Eq. 6.4, the brightness temperature becomes

$$T_b(\nu, \theta) = T_u(\nu, \theta) + [\varepsilon_sT_s + (1 - \varepsilon_s)T_d(\nu, \theta)]e^{-\tau(0)\sec\theta} \quad (6.8)$$

Equation 6.8 can be simplified by combining the integrals, $T_u$ and $T_d$, into a single term and expressing the resulting integral in pressure coordinates, or

$$T_b(\nu, \theta) = S(\nu, P_s, \theta)T_s - \int_{-\infty}^{\ln P_s} T(P) \frac{dS(\nu, P, \theta)}{d \ln P} d \ln P \quad (6.9)$$

where

$$S(\nu, P, \theta) = [1 - (1- \varepsilon_s)e^{-2[\tau(P) - \tau(P_s)\sec\theta]}]e^{-\tau(P) \sec\theta} \quad (6.10)$$

Here $T(P)$ is the atmospheric temperature profile and $P_s$ is the surface pressure. Also, from Eq. 6.10, we have $S(\nu, P, \theta) = \varepsilon_s e^{-\tau(P_s) \sec\theta}$. Note that the quantity
Combines the atmospheric opacity $\tau$, surface emissivity $\varepsilon_s$, and local zenith angle $\theta$ into a single parameter. The opacity can be expressed in pressure coordinates using the hydrostatic relationship $dP = -\rho g dz$, or

$$\tau(P) = \int_{z(P)}^{z(0)} \alpha(z) \, dz = \frac{1}{g} \int_0^P \frac{\alpha(z(P))}{\rho \, dP}$$  \hspace{1cm} (6.11)$$

where $g$ is the gravitational constant, and $\rho$ is the density for air.

For most applications, Eq. 6.9 contains all the quantities needed to compute the response of a satellite-based microwave radiometer to changes in atmospheric and surface variables. However, for temperature sounding above 50 km, the opacity due to molecular oxygen becomes a tensor quantity due to the Zeeman effect. The radiative transfer equation then becomes a matrix equation, and it is therefore necessary to account for the changes in magnetic field intensity and polarization [29, 39, 40]. We will not discuss this subject further here except to note that in practice, either circular or dual-polarized antennas are used to reduce the effect of magnetic field polarization on the measurements. Also, excluding the variations due to magnetic storms, climatological data can be used to account for the spatial variation in magnetic field intensity around the globe.

### 6.2.2 Atmospheric Weighting Functions

In this section, we will explore the behavior of the radiative transfer equation in simple cases to gain insight for the subsequent development of atmospheric retrieval algorithms. First, Eq. 6.9 can be simplified for large opacities. For example, temperature sounders operate within the 60-GHz oxygen band where the transmittance $e^{-\tau(P) \sec \theta}$ is typically less than 0.1 (see Figure 6.3). In this case, surface contributions can often be neglected so that Eq. 6.9 can be approximated as

$$T_b(\nu, \theta) \approx -\int_{-\infty}^{\ln P_0} T(P) \frac{dS(\nu, P, \theta)}{d \ln P} \, d \ln P$$  \hspace{1cm} (6.12)$$

with

$$S(\nu, P, \theta) = e^{-\tau(P) \sec \theta}$$  \hspace{1cm} (6.13)$$

where $\tau(P)$ is due almost entirely to oxygen. As discussed next, the opacity has a unique pressure dependence at frequencies where the absorption is due to a uniformly mixed gas such as oxygen. Equation 6.12 then represents the weighted atmospheric temperature, where the weighting function is

$$W(\nu, P, \theta) = -\frac{dS(\nu, P, \theta)}{d \ln P}$$  \hspace{1cm} (6.14)$$

where the shape of this function describes the vertical resolution of a sounding channel measurement.
Next let us consider a single absorption line for the purpose of examining the frequency and pressure dependence of weighting functions. The absorption for the \( n \)th line of a given molecule can be approximated by the Lorentz line shape (see Eq. 2.57),

\[
\alpha \approx s_n N \left[ \frac{v^2 \delta \nu_n}{(\nu - \nu_n)^2 + \delta \nu_n^2} \right]
\]

where \( N \) is the molecular density, and \( s_n \) is the line strength. The resonant character of absorption is described by the bracketed term, which contains the frequency of a spectral line \( \nu_n \) and its line width \( \delta \nu_n \). The linewidth for collision-broadened lines varies in proportion to atmospheric pressure and is given by \( \delta \nu_n = \Gamma_n P \), where \( \Gamma_n \) is a line-dependent broadening parameter (e.g., \( \Gamma_n \approx 1 \text{ MHz/mbar} \) for oxygen in the 60-GHz band). At frequencies sufficiently far from the line center, \( \nu - \nu_n \gg \delta \nu_n \) so that Eq. 6.15 can be approximated as

\[
\alpha \approx s_n N \left[ \frac{v^2 \delta \nu_n}{(\nu - \nu_n)^2} \right]
\]

The line strength and line-width parameters typically have small temperature dependencies, which we will neglect. Also, for uniformly mixed gases such as oxygen, the ratio of the gas density to that of dry air is constant \((N/\rho = \text{constant})\) so that the substitution of Eq. 6.16 in Eq. 6.11 results in the opacity

\[
\tau(P) = \left( \frac{P}{P_v} \right)^2
\]

where

\[
P_v = \left( \frac{\nu - \nu_n}{\nu} \right) \sqrt{\frac{2g}{s_n \Gamma_n}} \left( \frac{\rho}{N} \right)
\]

From Eq. 6.14, we obtain the weighting function

\[
- \frac{dS(\nu, P, \theta)}{d \ln P} = 2 \left( \frac{P}{P_v \sqrt{\cos \theta}} \right)^2 \exp - \left( \frac{P}{P_v \sqrt{\cos \theta}} \right)^2
\]

This weighting function is illustrated in Figure 6.11 and is seen to have the approximate shape of a Gaussian in pressure coordinates. The weighting function has a maximum value of \( 2e^{-1} \) at the pressure level \( P_v \sqrt{\cos \theta} \), and its full width at half maximum is roughly \( P_v \sqrt{\cos \theta} \). From Eq. 6.18, \( P_v \) is proportional to the frequency displacement from the line center and inversely proportional to the square root of the line strength.

Oxygen has a complex of about 45 lines centered at 60 GHz with a total spread of \( \pm 10 \text{ GHz} \), and an isolated line at 118.75 GHz (see Chapter 2). The lines cen-
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Figure 6.11. Lorentz model weighting function.

tered around 60 GHz have separations ranging from 500 MHz for the weaker lines to 120 MHz between the most intense lines. The opacity given by Eq. 6.17 and the corresponding weighting function approximates results obtained using the actual absorption model for oxygen at both low and high pressures. To provide a better fit with the exact absorption model, the pressure power law for a given channel can be modified as \( \tau = \left( \frac{P}{P_v} \right)^n \), where values of \( n \) different than 2 are used to account for the added absorption from overlapping lines at higher pressures [41].

Figure 6.12(a) shows a representative temperature profile for a tropical atmosphere plotted as a function of pressure. Also shown are 13 computed brightness temperatures plotted at the pressure level where the weighting function peaks, \( P_v \). The brightness temperatures are computed using Eq. 6.9 with \( \varepsilon \theta = 1 \) and \( \theta = 0^\circ \). Weighting functions for each channel are obtained from Eq. 6.19 with \( P_v \) set at values from 20 to 1000 mbars. Both atmospheric pressure and \( P_v \) are indicated on the vertical axis with the same logarithmic scale, and the horizontal axis is used for temperature and brightness temperature. The temperature scale is made twice as large as the brightness-temperature scale to account for the smaller changes in brightness temperature compared to temperature.

The brightness temperatures in Figure 6.12(a) respond to different pressure regions and closely follow the temperature profile of the tropical atmosphere. However, the same set of weighting functions results in brightness temperatures that are less correlated with the more variable temperature profiles found in the polar regions and midlatitudes. Figure 6.12 shows significant smoothing of the temperature inversions above the tropopause (b) and lower troposphere (c) by the brightness temperatures. The individual brightness temperatures appear incapable of resolving the more abrupt variations in temperature associated with these soundings. A formal procedure used for the retrieval of temperature profiles is discussed in Section 6.3.

6.2.3 Weighting Functions for Flight Instruments

The various channels in microwave sounders measure the radiation over a narrow bandwidth whose center frequency is chosen almost midway between adjacent ox-
6.2 THEORETICAL BACKGROUND

\[ \text{Figure 6.12. Temperature profiles and computed brightness temperatures for weighting functions peaking at the levels indicated by the crosses. Results are shown for a (a) tropical, (b) polar, and (c) midlatitude atmosphere over land at nadir.} \]

Figure 6.12. Temperature profiles and computed brightness temperatures for weighting functions peaking at the levels indicated by the crosses. Results are shown for a (a) tropical, (b) polar, and (c) midlatitude atmosphere over land at nadir.

gen lines. In this way, the radiometer bandpass for a given channel can include the full region between lines without appreciably smoothing the spectral information. This results in the sharpest possible weighting functions, and bandwidths as large as 400 MHz are used to reduce instrument noise (see Figure 1.13).

Figures 6.13 through 6.17 show the respective weighting functions for the NEMS, SCAMS, MSU, SSM/T, and AMSU instruments. The weighting functions were calculated using a more complete oxygen absorption model [42] and peak at lower pressure levels as the frequency comes closer to the strong oxygen
Figure 6.13. NEMS nadir-viewing weighting functions over land.

Figure 6.14. SCAMS weighting functions at nadir and scan-limit positions over land.
lines around 60 GHz (consistent with Eq. 6.18). Of particular interest are the SSM/T weighting functions in Figure 6.16, shown for both the nadir position and far scan angle ($\theta = 42^\circ$). Observe how the weighting functions peak at lower pressures at the off-nadir scan position. This "limb effect" is consistent with Eq. 6.18, which indicates a shift in the peak height of the weighting function by the amount $P(\theta) = P(0^\circ)\sqrt{\cos \theta}$. Limb correction procedures that adjust the measurements to nadir are described in Section 6.3.

The SSM/T contains more channels and covers a wider range of pressures than earlier sounding instruments—the 59.40- and 58.40-GHz channels sense temperatures higher in the atmosphere than all previous microwave sounders. Figure 6.18 indicates the bandpass of the different SSM/T channels on the overall frequency spectrum. Brightness temperatures at frequencies between 50 and 60 GHz are calculated using a more complete oxygen-absorption model and applying Eq. 6.9 at nadir with $\varepsilon = 1$. The temperature profile used in the calculations is that of Figure 6.12(a), and contains the typical temperature decrease with altitude in the troposphere and increase in the stratosphere. The sharp increases in brightness temper-
Figure 6.16. SSM/T weighting functions at nadir and scan-limit positions over land.

Temperature near the line centers are caused by the strong stratospheric contribution. Note that the 58.80-GHz channel is between two of the strongest and closest spaced lines; consequently, from Eq. 6.18, its weighting function peaks higher than the two highest-frequency channels. The radiation in the weaker absorption regions between lines corresponds to the relatively colder temperatures near the tropopause and forms valleys in the spectrum. The least absorption occurs at frequencies below 53 GHz, where the radiation corresponds to temperatures near the much warmer surface. One can view this spectral plot as a representation of the temperature profile in frequency coordinates, rather than pressure. Inversion techniques are used to reconstruct the pressure-temperature profile from the spectral information, where this is the next subject.

The AMSU is to be launched aboard the NOAA polar-orbiting satellites beginning in the mid-1990s and will be able to sound temperatures at even higher altitudes than the SSM/T. This instrument contains the 12 oxygen channels listed in Table 6.1, where Figure 6.17 shows their weighting functions computed at nadir.

6.3 TEMPERATURE RETRIEVALS

6.3.1 Retrieval Approach

The brightness temperature measurements in the oxygen band respond to different regions of the atmosphere in a way that depends on the frequency and viewing angle. We now explore the techniques that are used to retrieve the atmospheric temperature profile from the measurements. The general problem has long been
Figure 6.17. AMSU weighting functions at nadir viewing over land. Channels 3–14 are listed in Table 6.1, beginning with the lowest frequency oxygen channel at 50.3 GHz for AMSU/A.

Figure 6.18. Brightness-temperature spectrum for the 50- to 60-GHz portion of the oxygen band. Shaded regions denote the bandpass for SSM/T channels.
recognized as the inversion of the radiative transfer equation in a form such as Eq. 6.9 with known weighting functions [5, 6]. The practical approach that has evolved is to approximate the integral in Eq. 6.9 as a finite series of terms, or

\[
T_b(\nu, \theta) = \sum_{i=0}^{N} K_i(\nu, \theta) T(P_i) + \epsilon \tag{6.20}
\]

and treat the problem as a matrix inversion. The quadrature coefficients \( K_i \) bridge the gap between the integral and series approximation. For each term in the series, \( P_i > P_{i+1} \), where \( K_0 T(P_0) \) is the surface contribution and includes the term \( S(\nu, P_s, \theta) T_s \) from Eq. 6.9. A simple quadrature formula (based on the trapezoidal rule) is obtained by connecting the values of \( T(P) W(\nu, P, \theta) \) in the integral of Eq. 6.9 by straight lines between consecutive intervals of \( \ln P \). The resulting coefficients are given by

\[
K_i(\nu, \theta) = \begin{cases} 
\frac{1}{2} W(\nu, P_i, \theta) \ln (P_{i+1}/P_{i-1}) & i \neq 0 \\
\frac{1}{2} W(\nu, P_i, \theta) \ln (P_i/P_s) + S(\nu, P_s, \theta) & i = 0 
\end{cases} \tag{6.21}
\]

More accurate coefficients can be derived (e.g., Gaussian quadrature), but the form of the brightness-temperature equation is still given by Eq. 6.20. The residual term \( \epsilon \) denotes the quadrature error, which decreases as the number of terms \( N \) increases. The \( \epsilon \) parameter can also be used to account for errors in the brightness-temperature measurements that are uncorrelated with temperature, such as instrumental noise and emissivity variations.

An alternative method of approximating the brightness-temperature equation in discrete form is to represent the temperature profile by a series of polynomials, or empirical functions \( T(P) = \sum c_i F_i(P) + \epsilon \). When \( T(P) \) is substituted into Eq. 6.9, the resulting equation has the same form as Eq. 6.20. The residual error \( \epsilon \) now arises from the approximation of \( T(P) \) as a finite series of terms.

As is evident by the weighting functions of Figure 6.15, the brightness-temperature measurements respond to different regions of the atmosphere, depending on both the frequency and viewing angle. Both parameters can generally be used to derive the temperature profile; however, existing satellite instruments have been designed to view each spot on Earth simultaneously with many frequencies rather than at different angles. Hence, we will consider algorithms in which only a discrete set of brightness temperatures at different frequencies is used to estimate the temperature profile. If we consider that the brightness temperature is given by Eq. 6.20 for each frequency, then the resulting set of equations is conveniently expressed in matrix form

\[
T_b = \mathbf{K} \mathbf{T} + \epsilon \tag{6.22}
\]

where \( T_b \), \( \epsilon \), and \( T \) are column matrices containing the set of brightness temperature measurements at each frequency, their errors, and atmospheric temperatures.
at prescribed levels, respectively. The number of pressure levels must be greater than the number of frequency measurements to reduce quadrature errors; hence, \( \mathbf{K} \) is a nonsquare matrix. Least-squares techniques have been used to invert Eq. 6.22 by minimizing the quantity \( \mathbf{T}_b - \mathbf{K} \mathbf{T} - \varepsilon \) where the superscript \( t \) represents matrix transposition. However, a more accurate result is obtained using a priori information on the temperature structure to constrain the solution. The inversion procedure most widely used is the a priori statistical method discussed in Chapter 4.

Statistical inversion techniques such as regression analysis use brightness-temperature measurements as "predictors" to estimate the temperature, or the "predictands." The temperature estimate is written as

\[
\mathbf{T}' = \langle \mathbf{T} \rangle + \mathbf{D} [\mathbf{T}_b - \langle \mathbf{T}_b \rangle]
\]  

where the \( \mathbf{D} \) matrix operates on the "data vector" \( \mathbf{T}_b \) to obtain the temperature profile \( \mathbf{T}' \), with \( \langle \mathbf{T} \rangle \) and \( \langle \mathbf{T}_b \rangle \) being the a priori expected vectors. The \( \mathbf{D} \) matrix is obtained by minimizing the least-squares difference between the actual temperature \( \mathbf{T} \) and the estimate given by Eq. 6.23. This minimization gives

\[
\mathbf{D} = \mathbf{C}(t, d) \cdot \mathbf{C}(d, d)^{-1}
\]  

where the covariance matrix \( \mathbf{C}(X, Y) = X \cdot Y^t \) and the column matrices \( t = \mathbf{T} - \langle \mathbf{T} \rangle \) and \( d = \mathbf{T}_b - \langle \mathbf{T}_b \rangle \).

Equation 6.23 is a linear regression solution, where the \( \mathbf{D} \) matrix coefficients, \( D(v_j, P_i) \), correlate the temperature at a given pressure with the brightness temperature at different frequencies. The covariance matrices together with the a priori information can be obtained empirically, or they can be based on a more physical approach. Radiosondes (RAOBs) are used to provide the atmospheric temperature data in either case. The brightness temperatures can either consist of measured values using coincident satellite observations, or can be simulated by a forward radiative transfer calculation using Eq. 6.9. The physical approach based on simulated data is simpler to implement, although the empirical approach is necessary when large differences occur between the calculated and measured brightness temperatures. However, microwave sounders have been shown to produce small stable differences between the measured and computed brightness temperatures. In the physical approach, the measured brightness temperatures are adjusted to agree with the radiative transfer calculations using an initial sample of measurements and calculated brightness temperatures based on collocated RAOB matchups (see Appendix 6B).

Equation 6.23 expresses the temperature at any given pressure level as a linear combination of \( M \) brightness-temperature measurements. In expanded form, the temperature is written as

\[
T'(P) = \langle T(P) \rangle + \sum_{j=1}^{M} D(v_j, P, \theta) [T_b(v_j, \theta) - \langle T_b(v_j, \theta) \rangle]
\]  

(6.25)
For cross-track scanning instruments, the weighting functions vary with local zenith angle so that separate $\mathbf{D}$ matrices are needed for each local zenith angle $\theta$. Alternatively, the brightness temperature can be adjusted to the nadir-viewing position so that a single set of coefficients can be used. The so-called limb-correction procedure has the additional advantage of enabling one to examine the individual channel measurements in terms of fixed weighting functions (see Figure 6.6). These angular adjustments can involve constant offsets for each scan position, or can be obtained more accurately using regression analysis to relate the nadir brightness temperature $T_b(v_j, 0^\circ)$ to the linear combination of all channel measurements at a particular angle, $T_b(v_j, \theta)$; in other words,

$$T_b(v_j, 0^\circ) = L_0(v_j, \theta) + \sum_{k=1}^{M} L_k(v_j, \theta) T_b(v_k, \theta)$$  (6.26)

where the summation includes the channel at frequency $v_j$. As in the case of the $\mathbf{D}$ matrix, the limb-correction coefficients $L_k(v_j, \theta)$ can be obtained empirically using actual measurements, or determined using simulated brightness temperatures computed from a climatological set of atmospheres.

### 6.3.2 Surface Emissivity Effects

The brightness temperature from Eq. 6.9 is a function of surface emissivity and surface pressure; consequently, the retrieval coefficients must be stratified according to these parameters as well as local zenith angle, that is, $D(v_j, P_j; \varepsilon_s, P_s, \theta)$. This approach appears simple, but it is impractical to implement when a wide range of parameters is required. The surface effect and the method of correction depend on the surface type and the atmospheric absorption for a given channel.

At frequencies around 50 GHz, the emissivity over land can vary between near unity for dry or vegetated land to less than 0.8 for snow cover, bare wet land, and rivers and lakes, which only partly fill the instruments' field of view [43]. This corresponds to a maximum emissivity variation of $\pm 0.10$ from a 0.90 nominal value. The emissivity for oceans varies because of wind-induced foam and surface roughness [25], increasing from 0.50 to about 0.55 for winds ranging from calm to 20 m/s. A similar increase in emissivity results from a decrease in sea-surface temperature [44], so that the total emissivity variation is $\pm 0.05$ about an average value of 0.55. Hence, the emissivity over both land and ocean usually only varies about 10 percent from its mean value. Fortunately, for most of the sounding channels, the emissivity variations are strongly attenuated by the atmospheric absorption due to oxygen.

Figure 6.19 shows the brightness temperature change as a function of frequency due to a 10 percent increase in emissivity over land and ocean. The calculations are based on Eq. 6.9 and result in brightness temperature variations less than 0.5 K for frequencies greater than 53.7 GHz. The local variations in emissivity at these frequencies can be neglected and it is only necessary to account for the abrupt change between land ($\varepsilon_s \approx 0.95$) and ocean ($\varepsilon_s \approx 0.50$). Emissivity effects for
the 53.74-GHz MSU channel can be accounted for using separate $\tilde{D}$ matrices for land and ocean [30]. However, the method used operationally by the National Environmental Satellite Data and Information Service (NESDIS) of NOAA is based on the limb-correction algorithm of Eq. 6.26 with separate coefficients generated over land and ocean. The limb coefficients are obtained from simulations and are used to adjust the brightness temperatures to a unity emissivity surface in addition to nadir viewing. The procedure uses the 50.3-GHz channel with appropriate threshold values to identify the surface type, and the other three MSU channels provide the limb corrections for that surface.

The SSM/T instrument contains a 53.2-GHz channel located near the outer edge of the oxygen band, which allows an improvement of the temperature-retrieval accuracy near the surface over that of the MSU. Figure 6.19 shows appreciable surface effects for this channel, however. The measurements, therefore, must be corrected for a wider range of emissivity parameters than just the average values over land and ocean in order to reduce the brightness temperature variations to within 0.5 K. Appendix 6C describes the correction procedure used for the SSM/T instrument to account for local changes in surface emissivity in addition to the elevation effects over land.

Equation 6.9 offers additional insight on the effects of emissivity on the brightness temperature measurements. The equation contains two surface contributions: the surface emission term, $S(\nu, P_s, \theta) T_s$, and the integral term, which contains the downwelling radiation as part of the weighting function. For decreasing emissivity, the surface emission decreases and the reflected radiation (integral term) increases. The combination of these opposing effects on the brightness temperature is approximated by considering an isothermal atmosphere with $T(P) = T_s$, in which case, Eq. 6.9 reduces to

$$T_b = T_s (1 - e^{-2\tau(P_s)\sec\theta}) + T_s \varepsilon_s e^{-2\tau(P_s)\sec\theta}$$  \hspace{1cm} (6.27)
where $T_s$ is the surface temperature, and $e^{-\tau(P_s) \sec \theta}$ is the transmittance along the slant path between the satellite and Earth’s surface. The first term defines the atmospheric contribution of brightness temperature, and for a nonisothermal atmosphere can be obtained from Eq. 6.9 with $\varepsilon_s = 0$. The second term contains the emissivity contributions due to reflected and emitted radiation, and contains the transmittance “squared” multiplied by the surface emission, $\varepsilon_s T_s$. This equation can be rewritten as

$$\Delta T_b = T_s \Delta \varepsilon_s e^{-2\tau(P_s) \sec \theta} \quad (6.28)$$

to show the change in brightness temperature as a function of the emissivity variation $\Delta \varepsilon_s$ and the transmittance.

The atmospheric transmittance at nadir is 0.23 for the 53.2-GHz SSM/T channel. Equation 6.28 predicts a brightness-temperature change of 1.5 K for a surface temperature of 285 K and a 10% emissivity variation ($\Delta \varepsilon_s = 0.10$) over land. The same 10% variation in emissivity ($\Delta \varepsilon_s = 0.05$) over oceans results in a brightness-temperature change of 0.7 K. These values are consistent with those shown in Figure 6.19, although the isothermal approximation slightly overestimates the magnitudes. The emissivity variations represent a source of noise in brightness temperature because they are uncorrelated with temperature, and therefore reduce the overall effectiveness of the 53.2-GHz channel in monitoring small changes in temperature. The 53.74-GHz channel of the MSU instrument has a transmittance of 0.10 and is therefore more suitable for measuring small temperature changes in the lower troposphere. This channel has been used for climate monitoring, for example [34, 35].

### 6.3.3 Water Vapor and Cloud Effects

The influence of water vapor is small when obtaining measurements in the oxygen band because of the large frequency separation between water vapor and oxygen absorption. Also, only those channels having weighting functions in the lower atmosphere are affected because most of the moisture is at altitudes below the 700-mbar pressure level. The effect for these channels is proportional to the vertically integrated water vapor and the underlying surface emissivity. As an example, Figure 6.20 shows the simulated change in brightness temperature as a function of frequency for a 10-mm change in the integrated water vapor. The results correspond to average variations expected for a given latitude band and are shown separately for land and ocean. The perturbations in the brightness temperature are less than 0.2 K for frequencies greater than 53.7 GHz, and are therefore negligible.

The effect of clouds depends on the liquid water content and the underlying surface emissivity, and is analogous to the water-vapor effect. In contrast to the shallow distribution of water vapor, however, clouds can have appreciable water content throughout the troposphere and therefore can result in a considerable modification of the weighting functions and corresponding brightness temperatures [45]. From a study of various cloud types [46], liquid water is found to decrease rapidly
for temperatures below freezing, where the decrease can be approximated as $e^{0.12(T-273)}$. As a result, clouds mainly affect the lowest sensing channels in the polar regions, whereas clouds in the midlatitudes and tropics can affect channels having higher peaking weighting functions [47].

Simulations are used to calculate the change in brightness temperature as a function of frequency due to cloud effects. Figure 6.21 shows the results for both land ($\varepsilon_s = 1$) and ocean surfaces ($\varepsilon_s = 0.5$). As in the previous simulations (Figures 6.19 and 6.20), the brightness temperature is calculated from Eq. 6.9 using a standard temperature profile having a surface temperature of 280 K with a constant lapse rate of 6.5 K/km in the troposphere. The opacity for clouds is given in Appendix 6D and depends on the liquid water density. Both low- and high-level clouds are simulated by distributing liquid water between the pressure levels indicated in Figure 6.21. The liquid water distribution was adjusted to produce 0.3 mm of total liquid for both cloud types. This value approximately corresponds to the maximum amount of liquid water found from satellite measurements for non-precipitating clouds [2, 47].

Clouds are shown to produce different effects depending on the frequency and underlying surface. Over oceans, the clouds can either increase or decrease the brightness temperature, with the null effect occurring at about 53.7 GHz, which corresponds to the lowest sounding MSU channel. The brightness temperature measured by the SSM/T channel at 53.2 GHz generally increases for increasing liquid water, where cloud corrections are obtained using liquid water measurements [48]. Over high-emissivity land surfaces, the clouds always decrease the brightness temperature, with the maximum effect occurring for high clouds. High clouds with considerable liquid water (e.g., nimbostratus) often occupy small por-
Figure 6.21. Brightness temperature change as a function of frequency due to clouds having 0.3 mm of liquid water within the indicated pressure levels. Results are shown separately for land and ocean.

tions of the viewing area, however, and generally produce smaller effects than the broader, lower (stratiform) clouds.

Effects due to precipitation are more important than cloud effects, which is exemplified by the fact that only severe storms and hurricanes have resulted in measurable brightness temperature decreases for the 53.74-GHz MSU channel [43, 49]. The decreased measurements in these cases is mainly due to the scattering of the upwelling radiation by large ice particles formed around the tops of precipitating clouds (see Section 6.4.2). Sharp decreases in brightness temperature (> 1 K) due to heavy rain are readily identified in MSU data by using a median filter, and the affected measurements are edited out of the data stream [50].

6.3.4 Temperature-Retrieval Accuracy

Accurate temperatures are obtained from microwave sounders over land and ocean in spite of surface-emissivity variations and cloud effects. The best accuracy is
achieved when retrieving temperatures at 700 mbars and lower pressures, because the major contributions arise from frequencies greater than 53.5 GHz. In this region of the atmosphere, the temperature-retrieval accuracy depends mainly on the number of channels and the \textit{a priori} temperature information used to constrain the solution. These features are best illustrated by referring to the results of an early study involving simulated data and analysis [33].

Figure 6.22 compares the retrieval accuracy obtained using the three MSU sounding channels with that obtained from a five-channel sounder having weighting functions similar to the SSM/T instrument. The weighting functions for the three- and five-channel sounders are also shown. The simulation results were obtained using Eq. 6.9 to compute brightness temperatures from a climatological set of 400 radiosondes (RAOBs) over the midlatitudes. Instrumental noise of 0.3 K and the random effect of a 10\% variation in surface emissivity were introduced in the computations. These RAOB temperature profiles and the corresponding brightness temperatures were then used to generate the \( \mathbf{D} \) matrices and \textit{a priori} parameters contained in Eq. 6.25 for the two sounders. Finally, the two retrieval algorithms were applied to the 400 simulated measurements to estimate the temperature at the different pressure levels. Figure 6.22 shows the error as a function of pressure for the three- and five-channel sounders relative to the RAOB temperatures.

The smallest differences between the two error curves occur below 700 mbars, near 250 mbars, and above 100 mbars. The region below 700 mbars also corresponds to the largest errors because of the lack of sharp weighting functions in

---

**Figure 6.22.** Simulated retrieval errors (left) for the MSU and five-channel sounder using climatological data. Temperature weighting functions (right) for the MSU and five-channel sounder.
addition to the atmosphere being most variable in the boundary layer. Large errors also occur around the 250-mbar tropopause region where the reversal of temperature with height results in small changes in brightness temperature. Compared to the MSU, however, the five-channel sounder provides more accurate temperatures throughout the middle troposphere (centered around 500 mbars) and the lower stratosphere (centered around 150 mbars). Above 100 mbars, the errors would be substantially reduced if additional stratospheric channels were included. Results such as these prompted the development of microwave sounders like the AMSU with yet more channels.

Equation 6.9 is used to relate the temperature accuracy to the a priori information contained in the retrieval algorithm, Eq. 6.25. An expression for the retrieval error, \( T'(P) - T(P) \), is obtained by combining Eq. 6.9 with Eq. 6.25 to eliminate the brightness-temperature terms:

\[
\Delta T(P) = \langle \Delta T(P) \rangle - \int_{\ln P_s}^{-\infty} \langle \Delta T(P') \rangle \frac{dK(P', P')}{d \ln P} d \ln P' - \langle \Delta T_s \rangle K(P, P_s)
\]  

(6.29)

where \( \Delta T = T' - T \), \( \langle \Delta T \rangle = \langle T' \rangle - T \), and \( \langle \Delta T_s \rangle = \langle T'_s \rangle - T_s \). The quantity \(-dK(P, P')/d \ln P'\) is called the averaging kernel, where

\[
K(P, P') = \sum_{j=1}^{M} D(v_j, P)S(v_j, P')
\]

(6.30)

It is evident from Eq. 6.29 that minimum retrieval errors occur for the narrowest averaging kernels. To illustrate this, Figure 6.23 displays the kernels at several pressure levels using the weighting functions and \( \tilde{D} \) matrices obtained for the three- and five-channel sounders. Note that the width of the 500-mbar function is significantly reduced by the additional two channels, which results in much smaller retrieval errors according to Figure 6.22. Little improvement occurs at 850 and 250 mbars for both the averaging kernels and retrieval errors compared to the three-channel results. The 150-mbar kernel is bimodal because of the large negative correlation between this level and the lower tropospheric sounding channels. The five-channel function displays a sharper positive and negative mode compared to the three-channel kernel, which again results in smaller retrieval errors (see Figure 6.22). Much less interlevel correlation exists between the stratospheric and tropospheric channels for the other kernels. Also, the 70-mbar kernel (not shown) is mainly defined by the 57.95-GHz weighting function for both the three- and five-channel sounder. In summary, the averaging kernels are basically unimodal, peaking at the pressure level of the retrieved temperature and become narrower for increasing channels, resulting in smaller retrieval errors.

A detailed analysis of Eq. 6.29 leads to a more physical relationship between the retrieval error and the a priori mean temperature. The result is obtained by
expressing $\langle \delta T \rangle$ in the integral term as a Taylor expansion about $\ln P' = \ln P$ so that

$$\Delta T(P) = [1 - F_0(P)] \langle \Delta T(P) \rangle - \sum_{n=1}^{\infty} F_n(P) \frac{d^n \langle \Delta T(P) \rangle}{d \ln P^n}$$

(6.31)

where

$$F_n(P) = \frac{1}{n!} \int_{\ln P}^{-\infty} \ln \left( \frac{P'}{P} \right)^n \frac{dK(P, P')}{d \ln P'} d \ln P'$$

(6.32)

and the small surface term in Eq. 6.29 is neglected in Eq. 6.31.
Equation 6.31 contains two error terms: the first term depends on the difference between the *a priori* mean and true temperature, and the remaining series of terms contains the local derivatives of this difference temperature. It is found that the area under the averaging kernel, $F_0(P)$, is close to unity so that the first term is small compared to the derivative terms and Eq. 6.31 can be approximated as

$$\Delta T(P) \approx - \sum_{n=1}^{\infty} F_n(P) \frac{d^n \langle \Delta T(P) \rangle}{d \ln P'^n}$$

(6.33)

It follows that the major source of error in the temperature retrievals arises from local differential changes between the *a priori* mean and true temperature, and the absolute difference between the two temperatures only weakly contributes to the error. Consequently, similar variations must be contained in the *a priori* mean temperature to accurately retrieve the abrupt changes in temperature structure shown in Figure 6.12.

### 6.3.5 Retrieval Accuracy of the SSM/T Sounder

An example of the retrieval accuracy of the SSM/T sounder is given in Figure 6.24, which shows profile errors relative to RAOBs for matchups collected between November 14–17, 1983 [37]. The temperature-retrieval algorithm used at this time is given by Equation 6.25 with the retrieval coefficients generated from simulated data with the surface corrections described in Appendix 6C. Matchups between satellite and RAOB data are based on a maximum time difference of 3 hours and a 1-degree latitude-longitude window. Results are shown for all matchups within the midlatitudes (30–60° N) at pressure levels down to 20 mbars. Separate comparisons are shown for clear, partly cloudy, and completely cloudy conditions, where the sample size is indicated at each pressure level. The rms errors are generally between 2–3 K for pressure levels between 700 to 20 mbars and are independent of cloud cover. These results are identical to those obtained at other time periods and are consistent with simulation results [36]. The largest temperature errors generally occur at pressure levels where (a) weighting functions are inadequate and (b) strong correlation is lacking between level temperatures and the weighted temperatures sensed by the instrument.

Figure 6.24 also displays the errors for the operational sounding system of NOAA/NESDIS, using the same set of RAOB measurements. This system, called the TIROS Operational Vertical Sounder (TOVS), consists of three separate instruments: the MSU and two infrared sounding instruments. The four-channel MSU provides temperature information in cloudy regions, and the two infrared instruments contain more than 20 channels that are used in conjunction with the MSU in clear and partly cloudy areas [32]. The MSU channels are the main predictors for completely cloudy situations, so that it is not surprising to find the seven-channel SSM/T retrievals to be more accurate than TOVS. This was also determined from the simulations in Figure 6.22, where rms differences as large as 1 K were found near 500 and 150 mbars. Smaller differences between the two satellite
systems occur for clear and partly cloudy areas, and agree with results obtained at other time periods. Interestingly, for the clear case, the larger TOVS errors at 500 mbars and above have been identified with elevation effects that are not accounted for in the TOVS retrieval procedure. Six of the 64 matches at 500 mbars and above had surface pressures less than 700 mbars.

6.4 RAINFALL AND CLOUD LIQUID WATER

Rainfall-estimation techniques were originally developed using satellite-based visible and infrared sensors. In this approach, cloudtop temperature and cloud patterns are used to obtain an empirical relationship with ground-level precipitation [51]. A more direct measure of rain rate can be obtained using microwave radiometry because of its ability to penetrate clouds. The accuracy of the microwave approach depends on many factors. We discuss here the importance of the channel frequencies and algorithms employed in deriving rain rates, with emphasis on the channels available from the SSM/I sensor. Effects due to beam filling, which av-
erages rain and rain-free areas within the field of view, are also significant but are not discussed.

6.4.1 Emission Measurement

Rain, when present, is the major source of attenuation when viewing the surface from space at frequencies less than 50 GHz. Brightness temperatures of the warmer, more emissive precipitating regions over sea surfaces are highlighted by 50 K or more in contrast to clear areas. Such large contrasts between rain and its surroundings have been used to display the precipitation for tropical storms as well as to map the global distribution of rainfall over oceans [52-54]. In most situations, the discrimination between rain and nonraining clouds can be obtained using appropriate thresholds on the measurements, and it is sufficient to determine the rain intensity from increases in brightness temperature. Effects due to sea-surface winds on emissivity or the contribution due to water vapor absorption are generally of minor importance and can be accounted for using additional channels.

The atmosphere can be considered isothermal in window channels where only the surface or lowermost troposphere are seen, in which case, the radiative transfer equation, Eq. 6.8, simplifies to

\[ T_b(\nu) = T_s [1 - (1 - \epsilon_s) e^{-2\tau(P_s) \sec \theta}] \]  \hspace{1cm} (6.34)

where \( T_s \) is the temperature of both the lower atmosphere and the surface. The contribution due to oxygen is small and the absorption depends primarily on the vertically integrated liquid water \( Q \) due to rain and cloud droplets, and on the integrated water vapor \( V = V(P_s) \) in the column (also called total precipitable water), where

\[ V(P) = \frac{1}{g} \int_0^P w(P') \, dP' \]  \hspace{1cm} (6.35)

and \( w(P) \) is the water-vapor mixing ratio, or the ratio of water-vapor density \( N \) to that of dry air. We can approximate the opacity through the atmosphere as

\[ \tau(P_s) = \left( \frac{V}{V_v} + \frac{Q}{Q_v} \right) \]  \hspace{1cm} (6.36)

where the coefficients \( V_v \) and \( Q_v \) depend on the frequency and can be determined using atmospheric models. The liquid water parameter also depends on cloud temperature and drop size, as discussed in Appendix 6D. Although not indicated, the emissivity is a function of polarization as well as frequency and local zenith angle, so that the brightness temperature also depends on polarization.

Over oceans, the variations in emissivity due to wind-generated roughness and foam are small compared to the changes in transmittance due to water vapor and liquid water. Therefore, the liquid water content of clouds and rain can be obtained
from dual frequency measurements, where a second channel must be used to account for the water-vapor contribution. From Eqs. 6.34 and 6.36, the linearized algorithm has the form

\[ Q = C_0 \{ \Theta (\nu_1) - [C_1 + C_2 \Theta (\nu_2)] \} \]  
(6.37)

where

\[ \Theta (\nu) = \ln [T_s - T_b (\nu)] \]  
(6.38)

A similar algorithm is obtained for the integrated water vapor based on Eqs. 6.34 and 6.36:

\[ V = D_0 \{ \Theta (\nu_1) - [D_1 + D_2 \Theta (\nu_2)] \} \]  
(6.39)

and will be referred to in the next section on water-vapor retrievals.

The coefficients \( C_0, C_1, \) and \( C_2 \) in Eq. 6.37 can be expressed in terms of the model parameters contained in Eqs. 6.34 and 6.36; however, they are more accurately determined through simulations using the more exact Eq. 6.8. An analysis based on such simulations is presented here to demonstrate the performance of this algorithm. The brightness temperatures for the SSM/I channels were computed from data on temperature, water vapor, clouds, and sea-surface wind. Temperatures and water vapor data were based on radiosonde profiles from the midlatitudes and tropics. For each sounding, clouds with various amounts of liquid water were introduced at low, middle, and high levels, with a total of 668 different combinations of atmospheric and surface conditions being simulated. The liquid water content \( Q \) was varied between 0 to 1 mm (1 kg/m\(^2\)), and the effect of winds on the surface emissivity was also modeled [25]. Table 6.4 lists the mean values and standard deviations of the sea-surface temperature, winds, integrated water vapor, and cloud liquid water for the data set. The predictors given by Eq. 6.38 with \( T_s = 290 \) K were then regressed against the liquid water contained in the data set to derive the coefficients. The simulations were also used to define the optimum pair of SSM/I channels for deriving liquid water.

Figure 6.25 shows the standard errors and explained variance obtained using different combinations of two channels. Errors obtained from single-channel measurements \( (C_2 = 0 \) in Eq. 6.37) are also shown. The results are shown separately for the case of zero wind and variable wind speed. For single-frequency measure-

<table>
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<th>TABLE 6.4 Parameters Used In Simulations</th>
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<td>Parameter</td>
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<td>Sea temperature</td>
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<td>Water vapor</td>
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<td>Liquid water</td>
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ments, the 37-GHz algorithm is most accurate, followed by the 85-GHz results, whereas the liquid water obtained from the lowest-frequency channels at 19 and 22 GHz is the least accurate. The 37-GHz measurements explain 80% of the variance in liquid water; however, substantial improvement is obtained using a second channel at 19 or 22 GHz to separate out the water vapor contribution. The second channel also reduces the effect of sea-surface temperature variations on the 37-GHz measurements, which is accomplished indirectly by the statistical correlation between temperature and water vapor implicitly contained in the data base.

By using the 37- and 22-GHz channels as predictors, the liquid water algorithm is given by

$$ Q = -1.68 \{ \Theta(37V) - [3.085 + 0.295 \Theta(22V)] \} \text{ mm} \quad (6.40) $$

where the vertically polarized channels (designated $37V$, $22V$) are chosen to minimize the effects of wind speed. The liquid water must exceed the amount that can be present in nonraining clouds to identify precipitation. Liquid water obtained using Eq. 6.40 typically ranges between 0 to about 2 mm, and values exceeding 0.3 mm may be associated with precipitation.

The algorithm using the 37-GHz frequency provides the best overall results, although its accuracy is somewhat dependent on the liquid water in the data sample. If the simulation study were performed using thin stratiform clouds having little liquid water, the results using the 85-GHz channels would be most accurate. Similarly, for convective clouds having large amounts of liquid water, the most accurate results are obtained using low-frequency measurements. Therefore, various combinations of the low- and high-frequency channels are needed to measure the full dynamic range of liquid water, although no general procedure exists at present.
In computing liquid water using Eq. 6.40, the 37-GHz measurements must be adjusted to account for the scattering due to the large ice particles formed aloft in precipitating clouds. Scattering results in a decrease in the brightness temperature and the corresponding liquid water amount. As we discuss in Section 6.4.2, scattering effects at 37 GHz are identified when the scattering index given by Eq. 6.46 exceeds a threshold of 7 K. Under this condition, the 37-GHz measurements are replaced by the value in the absence of ice particles, which is estimated based on the 19-GHz channel using Eq. 6.47. Furthermore, the 37-GHz measurements approach saturation for liquid water exceeding 1 mm even in the absence of scattering effects. The algorithm given by Eq. 6.40 is therefore mainly used to measure the liquid water for nonprecipitating clouds and to identify the rain/no-rain boundary.

A more accurate measure of rain rate is obtained using low-frequency emission measurements [54]. Although the 19-GHz SSM/I channel is less accurate for determining cloud liquid water than the 37-GHz channel, it is less influenced by the saturation effects of rain and the scattering due to ice particles and thus provides a more accurate measure of rain water. The algorithm obtained based on the 19- and 22-GHz channels is given by

\[ Q = -6.72 \{ \Theta(19V) - [3.006 + 0.373 \Theta(22V)] \} \text{ mm} \quad (6.41) \]

Figure 6.26 compares the instantaneous liquid water amounts obtained using Eqs. 6.40 and 6.41 with the hourly amounts of rainfall in units of mm/h. Rain
rates are obtained using hourly averaged radar measurements that were calibrated against raingage data over land. The results are based on more than 2000 matchups between the SSM/I and radar data obtained off the coast of Japan between June and August 1989. Only average values over 1 mm/h intervals are shown for each rain rate due to large scatter in the data. The number of observations within each rain interval is indicated on the figure. Saturation is quite apparent for the 37-GHz liquid water algorithm and is also seen in Figure 6.27, which displays the corresponding average brightness-temperature measurements for the vertically polarized SSM/I channels. Minimal saturation occurs at 19- and 22-GHz; the high brightness temperature and smaller variations at 22 GHz are due to water vapor absorption. The SSM/I data were convolved using the antenna pattern defined by the 19-GHz channel and the radar data were averaged over a circular area having a 60-km diameter to enable meaningful comparisons.

### 6.4.2 Scattering Measurements

Although the emission-based method discussed before is limited to ocean areas, it is found to be accurate in identifying light as well as heavy precipitation. A completely different algorithm, based on the scattering properties of ice particles, is applicable over land as well as oceans. The scattering-based algorithm depends on the existence of millimeter-size ice particles above the rain layer. This gives a less direct measure of rainfall than the emission approach; nevertheless, it has been very successful in measuring a wide range of rain events.

![Figure 6.27. SSM/I vertically polarized brightness temperatures corresponding to data shown in Figure 6.25.](image-url)
The ice particles produced aloft in rain-bearing clouds scatter microwave radiation with negligible absorption or emission. The incident radiation is reduced by scattering energy out of the beam while passing through regions containing ice particles, as shown schematically in Figure 6.28. If $T_i$ represents the incident radiation, then the total energy removed by spherical particles of radius $a$ and density $n(a)$ can be approximated as

$$T_b(v, \theta) = T_i e^{-\tau_{sc} \sec \theta}$$  \hspace{1cm} (6.42)$$

where

$$\tau_{sc} = L \int_0^\infty \pi a^2 Q_e (a/\lambda) n(a) \, da$$  \hspace{1cm} (6.43)$$

This model assumes single-particle scattering, where $T_b$ is the brightness temperature emerging from a uniform layer of ice particles of thickness $L$ and opacity $\tau_{sc}$. The opacity depends on the efficiency factor $Q_e$, which is the ratio of scattering cross-section to geometrical cross-section $\pi a^2$ and depends on the ratio of the particle radius to the radiation wavelength $\lambda$. The incident radiation $T_i$ is produced by emission sources below the scattering layer.

The single most important parameter defining the brightness temperature is the scattering cross-section $\pi a^2 Q_e$. Figure 6.29 shows the efficiency factors for spherical ice particles at 85, 37, and 19 GHz plotted as a function of particle diameter. The ice particle diameters are generally less than 2 mm for light rain so that Rayleigh scattering applies ($Q_e \sim \nu^4$), and the cross-section at 85 GHz is about 27 times greater than at 37 GHz. From Eq. 6.42, this results in a much larger decrease in brightness temperature at 85 GHz than at 37 GHz. The larger ice particles produced due to intense convection results in smaller differences between the two channel measurements (see Figure 6.29). However, the particle diameters are less than 5 mm even in this case, so that the brightness temperature decreases for increasing frequency, with the maximum decrease occurring at 85 GHz.

Figure 6.28. Schematic of different radiation components and variables contained in the scattering model.
Figure 6.29. Scattering efficiency for spherical ice particles as a function of diameter.

**Multifrequency Method**

Brightness-temperature differences at two frequencies have been used to identify scattering caused by precipitation-size ice particles [55, 56]. A more precise technique for measuring scattering effects is to use combinations of the lower-frequency SSM/I channels at 19 and 22 GHz to estimate the nonscattering contribution $T_i$ at 85 GHz. The difference between the estimate $T_i$ and the high-frequency measurement $T_b$ is called a scattering index:

$$\text{SI}(85V) = T_i - T_b(85V)$$

where significant positive values are used to identify the scattering due to precipitation [27].

The accuracy of the scattering index depends on the estimate $T_i$, which is inferred from low-frequency measurements, which are relatively unaffected by scattering. To obtain the functional form of $T_i$, the low-frequency channels are regressed against the high-frequency channel using a global data set that excludes scattering surfaces (e.g., snow cover and aged sea ice) and precipitation. The data set only contains measurements where the 85-GHz channel exceeds the 22-GHz measurements by more than 5 K to eliminate any possibility of scattering surfaces or precipitation. Data over land are chosen to contain large variations in vegetation cover, soil moisture, and surface temperature. Oceanic measurements are chosen to contain a wide distribution of temperature, water vapor, and cloud liquid water.
The 85-GHz measurements are correlated with the lower-frequency channels using all of the data to obtain regression relationships involving different channel combinations. The most accurate two-channel relationship for estimating the 85-GHz vertically polarized measurements was obtained using the result given by Grody [27]:

\[
T_i = 450.2 - 0.506T_b(19V) - 1.874T_b(22V) + 0.00637T_b^2(22V)
\]

where \( T_i \) provides an estimate of the 85-GHz brightness temperature with a standard error of 2.8 K and an explained variance of 98%. The additional use of the 37-GHz SSM/I channel results in smaller errors (2.4 K) than the two-channel estimate of \( T_i \); however, this channel can exhibit scattering effects and was therefore not used.

Scattering index values greater than 10 K are used to ensure an accurate identification of precipitation. Smaller values are found to result in false signatures. Figure 6.26 shows the scattering index at 85 GHz compared against the radar-derived rain rates and the SSM/I liquid water measurements obtained over the ocean. The 85-GHz measurements as well as all other measurements were convolved to the same spatial resolution. Note the high correlation between the 85-GHz scattering index, the liquid water measurements based on the 19- and 22-GHz channels, and the radar data. However, these results are based on averaging the measurements over a wide variety of rain events, and larger differences between the emission and scattering measurements are found for individual cases. The scattering index can drop below the 10 K threshold for regions containing large amounts of liquid water (>0.5 mm) in cases of stratiform rain or warm-core rain events. A combination of the emission and scattering methods is preferred for this reason.

It is important to discuss the use of the 37-GHz channel before continuing with an alternate method of identifying scattering effects. The 37-GHz channels available from the SMMR instruments on SEASAT and Nimbus-6 were used for identifying precipitation as well as other scattering features prior to the launch of the SSM/I instruments [55, 56]. Based on the same scatter-free global data set used in generating the 85-GHz scattering index, the index for the vertically polarized 37-GHz channel is given by

\[
\text{SI}(37V) = T_i - T_b(37V)
\]

with

\[
T_i = 60.1 + 0.781T_b(19V)
\]

where \( T_i \) provides an estimate of the 37-GHz measurement with a standard error of 1.9 K. A 7 K threshold is used in applying the 37-GHz scattering index to identify precipitation. Comparisons between the 85- and 37-GHz scattering indices can provide information on the size distribution of ice particles. Due to a lower sensitivity to small ice particles (see Figure 6.29), the 37-GHz scattering index is
found to be about three times smaller than the 85-GHz index over land. Over oceans, however, precipitation results in even smaller scattering indices at 37 GHz than at 85 GHz, suggesting that smaller ice particles are formed over oceans than over land.

**Dual-Polarization Method**

The previous method used multifrequency measurements at a single (vertical) polarization to detect rain over land and ocean; however, dual-polarization measurements at a single frequency can be used to normalize the measurements to a unity emissivity surface and thereby enhance the scattering signature.

In deriving the polarization algorithm, it is assumed that the surface emissivity for vertical $\varepsilon_v$ and horizontal polarization $\varepsilon_h$ are highly correlated, that is,

$$\frac{1 - \varepsilon_v}{1 - \varepsilon_h} = B$$  \hspace{1cm} (6.48)

Parameter $B$ is considered independent of surface type. As shown below (see Eq. 6.51), global values are determined by comparing the vertical and horizontally polarized measurements using the ocean–land data set referred to before, where $B = 0.455$ at 85 GHz and $B = 0.543$ at 37 GHz.

If the incident brightness temperature $T_i$ appearing in Eq. 6.42 is given by Eq. 6.8, then the respective vertical and horizontal polarized brightness temperatures are given by

$$T_v = e^{-\tau_a} [T_u + (\varepsilon_v T_s + (1 - \varepsilon_v) T_d) e^{-\tau_a}]$$  \hspace{1cm} (6.49)

$$T_h = e^{-\tau_a} [T_u + (\varepsilon_h T_s + (1 - \varepsilon_h) T_d) e^{-\tau_a}]$$  \hspace{1cm} (6.50)

where $\tau_a$ is the opacity below the ice layer due to the absorption by clouds and water vapor (see Figure 6.28). The angle and frequency dependence are omitted in the foregoing equations for simplicity.

Substituting Eq. 6.48 into Eqs. 6.49 and 6.50, we obtain

$$\frac{T_v - BT_h}{1 - B} = e^{-\tau_a} (T_u + T_s e^{-\tau_a})$$  \hspace{1cm} (6.51)

where the transformed brightness temperatures on the left side of Eq. 6.51 represent the measurements over a unity emissivity surface. The quantity $T_u + T_s e^{-\tau_a}$ is proportional to surface temperature [57]. Decreases in the transformed measurements below a 268 K threshold is associated with the increased opacity due to ice scattering. The resulting measurements have been used to identify precipitation and retrieve rain rate [57, 58].
6.5 WATER VAPOR RETRIEVALS

Knowledge of the large variations in water vapor is of the utmost importance for understanding the development of tropical cyclones and cloud clusters as well as for monitoring climate change. Retrievals using the 22-GHz water vapor line provide the vertically integrated water vapor over oceans with accuracies comparable to radiosonde observations [2, 23], as illustrated in Figure 6.30. The retrieval algorithm generally has a form similar to Eq. 6.39 with the primary channel near the 22-GHz line center and a secondary channel on either side of the line to correct for cloud absorption. Many radiometers have included these channels so that there are numerous publications on the algorithms and applications of the water vapor measurements [2, 11, 23, 59, 60].

Most numerical prediction models require at least two vertical layers of water vapor rather than the integrated amounts derived from past microwave instruments. Either the total moisture must be parameterized into a profile [61] or new instruments must be developed to provide more useful data. Although investigators have examined the feasibility of using ground-based measurements around the 22-GHz water-vapor line [62, 63] to provide water-vapor profiles, a current approach is to use satellite measurements around the 183-GHz water-vapor line. Such channels are included in the AMSU and SSM/T-2 instruments.

The first SSM/T-2 instrument was launched aboard the latest DMSP satellite in November 1991, and microwave water-vapor soundings will soon be obtained globally for the first time—only infrared techniques based on the strong water-vapor absorption region around 6.5 μm have been available until now [32]. Little is known of the effects of clouds at frequencies around the more opaque 183.3-GHz water-vapor line, however, and only the clear retrievals are discussed here. The retrieval of water-vapor profiles is more complex than the retrieval of temperature profiles and represents a challenging problem.

6.5.1 Retrieval of Water Vapor Burden

By substituting Eq. 6.15 into Eq. 6.11, the opacity due to water vapor can be expressed as

$$\tau_{H_2O} = \frac{1}{g} \int_0^P w(P') F_r(P') \, dP'$$  \hspace{1cm} (6.52)

where $F_r(P) = \alpha/N$ is the line shape factor, and $w(P)$ is the water vapor mixing ratio. Retrievals of mixing ratio can be obtained in principle by substituting Eq. 6.52 into Eq. 6.9 and inverting the radiative transfer equation using measurements within 10 GHz of the 183-GHz line.

Unlike the linear relationship between brightness temperature and temperature, the radiative transfer equation is a nonlinear function of the water vapor distribution. Also, the coupling between temperature and moisture in Eq. 6.9 increases the complexity of retrieving water vapor profiles. Numerical techniques are used...
Figure 6.30. Comparisons between Nimbus-6 SCAMS retrieved precipitable water (mm) and radiosonde measurements for August 20–22, 1975. Such large variations in the water vapor distribution over oceans could previously only be surmized from the limited number of radiosonde stations and by subjective analysis of satellite–cloud observations.
to solve the nonlinear problem [8, 64], whereas linear solutions are obtained about a first guess using statistical regression techniques [9, 65].

One can neglect the slower variations of \( F_v(P) \) in comparison with \( w(P) \) in formulating the nonlinear retrieval algorithm, so that Eq. 6.52 can be approximated as [8]

\[
\tau_{\text{H}_{2}\text{O}} \approx V(P) / V_v
\]  

(6.53)

where \( V_v \) is a frequency-dependent parameter, and \( V(P) \) is the water-vapor burden given by Eq. 6.35. By substituting this into the expression for \( S \) given by Eq. 6.10, the latter becomes a function of water-vapor burden \( V \) rather than a direct function of pressure as in the case of oxygen channels. Expressing the radiative transfer Eq. 6.9 in terms of water vapor burden rather than pressure, we obtain

\[
T_{b}^{\text{H}_{2}\text{O}}(\nu, \theta) = S(\nu, V(P_s), \theta) T_s - \int_0^{V(P_s)} T(V) \frac{dS(\nu, V, \theta)}{dV} dV
\]  

(6.54)

where \( T_{b}^{\text{H}_{2}\text{O}}(\nu, \theta) \) is the brightness temperature for a water vapor channel, and \( V(P_s) \) is the total water vapor burden. \( V(P_s) \) can be accurately determined over oceans using measurements around the 22-GHz line, as discussed in the previous section.

The quantity \( dS(\nu, V, \theta)/dV \) represents a water vapor weighting function for frequencies dominated by water vapor absorption similar to the manner in which \( dS(\nu, P, \theta)/d \ln P \) defines the temperature weighting function for frequencies around the oxygen-absorption lines. Figure 6.31 displays the weighting functions as a function of water vapor burden for the AMSU and SSM/T-2 channels, which are displaced 1, 3, 5, and 7 GHz from the 183-GHz water vapor line. These weighting functions have the unique property of being independent of the water vapor profile.

The temperature profile is given by Eq. 6.25,

\[
T'(P) = \langle T(P) \rangle + \sum_{j=1}^{M_{\text{O}_2}} D(\nu_j, P, \theta)[T_b^{\text{O}_2}(\nu_j, \theta) - \langle T_b^{\text{O}_2}(\nu_j, \theta) \rangle]
\]  

(6.55)

where the \( T_b^{\text{O}_2} \) specifically identify the \( M_{\text{O}_2} \) oxygen-channel measurements. A similar solution is obtained for \( T'(V) \) based on Eq. 6.54 and using water-vapor-channel measurements \( T_b^{\text{H}_{2}\text{O}} \),

\[
T'(V) = \langle T(V) \rangle + \sum_{j=1}^{M_{\text{H}_{2}\text{O}}} H(\nu_j, V, \theta)[T_b^{\text{H}_{2}\text{O}}(\nu_j, \theta) - \langle T_b^{\text{H}_{2}\text{O}}(\nu_j, \theta) \rangle]
\]  

(6.56)

where \( D(\nu_j, P, \theta) \) and \( H(\nu_j, V, \theta) \) are the retrieval coefficients for temperature and water vapor, respectively, and \( M_{\text{H}_{2}\text{O}} \) is the number of water-channel measurements. As discussed by Rosenkranz et al. [8], the water vapor burden is computed numerically as a function of pressure by combining Eq. 6.55 with Eq. 6.56 and
solving the set of equations simultaneously. The mixing ratio profile is obtained by differentiating the water burden, or finding \( w(P) = dV(P)/dP \). Unfortunately, the solutions for \( V(P) \) and \( w(P) \) are not unique if the retrieved temperature varies other than monotonically with pressure.

### 6.5.2 Linearized Retrieval Approach

The radiative transfer equation can be linearized about an *a priori* mixing-ratio profile to provide an alternate retrieval method. The linearized equation is obtained by first expressing the mixing ratio as

\[
w(P) = \langle w(P) \rangle + \delta w(P)
\]

where \( \langle w(P) \rangle \) is the *a priori* mean profile, and \( \delta w(P) \) is the deviation about the mean. An accurate estimate of \( \langle w(P) \rangle \) over oceans can be obtained using the 22-GHz measurements of total precipitable water in conjunction with the retrieved temperature profiles and statistical information [61]. Over land, the initial estimate can be obtained only using temperature retrievals and statistical information. This, among other factors, reduces the accuracy of the water vapor soundings over land compared to that obtained over oceans.

Considering \( \langle w(P) \rangle \gg \delta w(P) \), the water vapor transmittance can be approximated as

\[
e^{-\tau(P) \sec \theta} \approx \left[ 1 - \sec \theta \int_0^P \delta w(P') F_\nu(P') \right] e^{-\langle \tau(P) \rangle \sec \theta}
\]

\((6.58)\)
where $\langle \tau(P) \rangle$ is obtained using Eq. 6.52 with $w(P) = \langle w(P) \rangle$. Substituting this expression into Eq. 6.10, we find

$$S(\nu, P, \theta) = \langle S(\nu, P, \theta) \rangle + \delta S(\nu, P, \theta) \quad (6.59)$$

where $\langle S(\nu, P, \theta) \rangle$ is obtained from Eq. 6.10 with $\tau(P) = \langle \tau(P) \rangle$, and $\delta S(\nu, P, \theta)$ is given by

$$\delta S(\nu, P, \theta) = U(\nu, P, \theta) \int_{0}^{P} \delta w(P') F_{\nu}(P') \, dP' \quad (6.60)$$

with

$$U(\nu, P, \theta) = \langle S(\nu, P, \theta) \rangle - 2e^{-\langle \tau(P) \rangle \sec \theta} \cdot$$

A linearized form of the radiative transfer equation is obtained by substituting Eq. 6.59 into Eq. 6.9 and performing an integration by parts:

$$T_{b}^{H_{2}O}(\nu, \theta) = \langle T_{b}^{H_{2}O}(\nu, \theta) \rangle + \int_{-\infty}^{\ln P_{s}} \frac{\delta w(P')}{\langle w(P') \rangle} DT(P') \langle W(\nu, P', \theta) \rangle \, d \ln P' \quad (6.61)$$

where the first term on the right, $\langle T_{b}^{H_{2}O}(\nu, \theta) \rangle$, is the brightness temperature corresponding to the *a priori* estimate of the mixing ratio. Note the similarity between Eq. 6.61 and the general radiative transfer equation, Eq. 6.9. The integrand now contains water vapor in the form of $\delta w(P)/\langle w(P) \rangle$ in place of temperature, and is weighted by the temperature weighting function $\langle W(\nu, P, \theta) \rangle$ given by Eq. 6.14 and computed using the mixing ratio $\langle w(P) \rangle$. The integrand in Eq. 6.61 also contains a temperature-dependent quantity

$$DT(P') = \int_{\ln P'}^{\ln P_{s}} \frac{U(\nu, P, \theta)}{U(\nu, P', \theta)} \, d T(P') \, d \ln P \quad (6.62)$$

which can be estimated using the temperature information available from the oxygen channel measurements.

Figure 6.32 displays the weighting functions for different atmospheres at frequencies displaced 1, 3, 4, and 7 GHz from the 183-GHz water vapor line. These results show the sensitivity of the weighting functions to the *a priori* water vapor profile, whereas the weighting functions based on water vapor burden (see Figure 6.31) are independent of the profile.

Equation 6.61 can be inverted to obtain the water vapor mixing ratio using the same statistical method that was developed for temperature sounding. The solution is written as

$$\frac{w(P) - \langle w(P) \rangle}{\langle w(P) \rangle} = \sum_{j=1}^{M_{H_{2}O}} R(\nu_{j}, \theta) [T_{b}^{H_{2}O}(\nu_{j}, \theta) - \langle T_{b}^{H_{2}O}(\nu_{j}, \theta) \rangle] \quad (6.63)$$
Figure 6.32. Weighting functions near the 183-GHz water vapor line as a function of pressure over land. Results are shown separately for tropical and mid latitude atmospheres.
where the retrieval coefficients $R(v_j, \theta)$ reflect the information contained in the weighting functions. The coefficients must be stratified according to $\langle w(P) \rangle$ because the weighting functions vary for different mean profiles. Also, Eq. 6.61 and 6.62 show that the coefficients depend on the temperature-lapse rate $dT(P)/d \ln P$ and should be stratified according to this parameter as well. The estimate of $\langle w(P) \rangle$ was discussed before and the estimate of the lapse rate can be obtained using the difference in two or more oxygen channels.

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APPENDICES TO CHAPTER 6

6A SURFACE EMISSIVITY

The radiation emanating from the Earth’s atmosphere and surface depends on the temperature and emission properties of the medium. In principle, the radiation from atmospheric gases and surface materials can be treated using electromagnetic field theory, but to obtain tractable solutions, approximations are made depending on particle dimensions and correlation lengths relative to the radiation wavelength [1–3]. In general, the spatial scales are quite different for atmospheres and surfaces, and as such, their radiative transfer properties are treated differently. Atmospheres are typically dilute and have large correlation lengths so that the electromagnetic wave solution takes the form of the simple radiative transfer equation discussed in Chapter 1 [1, 2]. Surfaces are another matter, however. We expand here on some of the factors that must be considered when we attempt to account for the surface-emission term in our analysis to obtain atmospheric parameters.

6A.1 Theoretical Formulation

Radiation is both emitted and reflected by the surface. The radiation reflected at the surface is the angular integrated downwelling radiation given by Eq. 6.7 over the upper portion of the surface. It is written as

\[ T_r = \frac{1}{4\pi} \int_{0}^{2\pi} \int_{0}^{\pi/2} T_d(v, \theta') \sigma(\theta, \theta', \phi') \sin \theta' \, d\theta' \, d\phi' \]  

(6A.1)

where \( \sigma \) is the bistatic scattering cross-section of the surface and relates the energy scattered in the direction \( \theta \) due to the radiation incident at all other angles \( (\theta', \varphi') \). Although not specifically indicated, \( \sigma \) is also a function of frequency and the polarization of the incident and reflected radiation.

The emitted radiation is given by Eq. 6.5, or \( T_e = \varepsilon_s T_s \), for surfaces at a uniform temperature, where Kirchoff’s law states that the emission equals the radiation absorbed by the environment. From the conservation of energy between the emitted, reflected, and incident radiation, the surface emissivity can be related to
the integrated scattering cross-section [4]:

\[ \epsilon_s(v, \theta) = 1 - \frac{1}{4\pi} \int_0^{\pi/2} \int_0^{2\pi} \sigma(\theta, \theta', \phi') \sin \phi' \, d\theta' \, d\phi' \]  

(6A.2)

The emissivity given by Eq. 6A.2 assumes isothermal conditions. A more complex analysis is required for materials whose temperature varies with depth [5]. The simplest situation occurs when the material is highly tenuous and the spatial variations of the absorption coefficient change slowly compared to wavelength. In this case, the radiative transfer model can be used to calculate the upwelling radiation (i.e., emission) leaving the surface. An effective emissivity is obtained by dividing the upwelling radiation given by Eq. 6.2 by the surface temperature. This technique has been applied to homogeneous materials such as soils and fresh ice [6], but cannot be used rigorously when the material has inhomogeneities approaching wavelength dimensions.

6A.2 Modeling Surface Parameters

Theoretical analysis has been used to determine the emissivity and scattering cross-section for different surfaces. Because most materials contain closely spaced (interacting) particles, coherent effects become important and the scattered radiation from surfaces described by \( \sigma(\theta, \theta', \phi') \) cannot be determined rigorously using radiative transfer theory. It must be obtained using the more fundamental theory of electromagnetic fields, where the surface materials are defined by their dielectric property and the scattered radiation field is computed using Maxwell's equations.

Variations due to surface roughness have been analyzed using geometric optics or small-scale perturbation theory depending upon the scale of roughness relative to the radiation wavelength. These methods have been particularly useful in analyzing ocean surfaces [7, 8]. However, unlike the analysis for homogeneous materials such as water and fine soil, the theoretical analysis can be a formidable task for heterogeneous materials such as snow pack and sea ice (which consist of ice-air mixtures). For such granular materials, the individual particle effects are accounted for using an inhomogeneous (random) dielectric constant and solving the electromagnetic problem using high-order perturbation theory [9, 10]. The theoretical description for these surfaces is most complex and generally involves many free parameters.

The simplest analytical solution is obtained for smooth homogeneous materials, where the surface is described using a bulk dielectric constant and fixed boundary conditions. For smooth surfaces, the scattered radiation peaks in the specular direction (\( \theta' = \theta, \phi' = \phi + \pi \)) and the bistatic scattering cross-section is given by

\[ \sigma = (4\pi / \sin \theta') |R_p(v, \theta)|^2 \delta(\theta - \theta') \delta(\phi - \phi' - \pi) \]  

(6A.3)

where \( R_p \) is the Fresnel reflection coefficient, and \(|R_p|^2\) is the reflectivity. As indicated by Eq. 3.44, the Fresnel coefficient is calculated using the dielectric constant of the surface and is a function of frequency, local zenith angle \( \theta \), and the
polarization $p$ of the reflected radiation. For winds less than about 7 m/s, the ocean appears smooth and its reflectivity has been accurately computed using the dielectric constant for salt water [44 in Chapter 6]. Equation 6A.3 has also been used to model cultivated land using the dielectric properties of soil [11].

Substituting Eq. 6A.3 into Eq. 6A.2, we obtain

$$\epsilon_s(\nu, \theta) = 1 - |R_p(\nu, \theta)|^2 \quad (6A.4)$$

Substituting Eq. 6A.3 into Eq. 6A.1 gives Eq. 6.6 for $T_r$. Equations 6.6 and 6A.4 are then used to obtain the simplified expression for the brightness temperature $T_b(\nu, \theta)$ given by Eq. 6.8. Although derived for a smooth surface, Eq. 6.8 has been used to approximate rough surfaces. In this case, the emissivity must include a roughness parameter (e.g., wind speed for oceans) that is empirically determined using experimental data.

### 6A.3 Surface-Emissivity Measurements

Theoretical analysis is important for understanding the physical properties of surfaces; however, measurements are needed to display the actual characteristics of natural surfaces. Ground-based, aircraft, and satellite radiometers have been used to measure the emissivity of natural surfaces at different frequencies and polarizations. The reflected radiation requires knowledge of the scattering cross-section, which cannot be inferred from radiometric measurements, but requires scattering measurements for a variety of angles at dual polarization. In comparison to the emissivity measurements, much less data exist on the bistatic cross-section for natural surfaces. Therefore, in practice, the specular approximation of Eq. 6A.3 is used to describe the reflected radiation. The brightness temperature is then given by Eq. 6.8 with the emissivities obtained experimentally for different surfaces.

Based on theoretical models and experimental measurements, it is found that the microwave radiation emitted from natural materials depends primarily on the absorption properties of water. Because the absorption due to water increases with frequency, the emitted radiation also increases with frequency for surfaces such as soil, vegetation, and melting snow. These surfaces are classified as "absorbers," whereas other materials, such as snow cover and precipitating clouds, are composed of ice particles, which scatter microwave radiation. Ice formations on land and water also scatter microwave radiation as the ice ages and voids occur in an otherwise homogeneous ice layer. Because the scattering cross-section of inhomogeneities generally increases with frequency, the radiation emerging from "scattering materials" drops as the frequency increases (refer to Section 6.4.2).

Figure 6A.1 shows the average emissivity at nadir as a function of frequency for a few important surfaces. The emissivity of wet land is obtained from model calculations for average soil moisture [11]. Calculations are also used to obtain the smooth sea-surface emissivity, which is accurate for winds less than about 7 m/s. In the case of sea ice and snow, the models become much more uncertain so that aircraft and ground-based measurements must be used [12, 13]. The overall frequency response is obtained by fitting the data (at widely separated frequencies)
to the empirical function

\[ \varepsilon_n(w) = \frac{\varepsilon_0 + \varepsilon_\infty(w/w_0)^n}{1 + (w/w_0)^n} \]  

(6A.5)

where the parameters \(\varepsilon_0\), \(\varepsilon_\infty\), \(w_0\), and \(n\) depend on the local zenith angle and polarization. The parameters are listed in Table 6A.1 for the nadir-viewing angle. A plot of the function and the corresponding measurements (indicated by different symbols) are shown in Figure 6A.1. The frequency characteristics of this empirical model is that of a low- or high-pass filter, depending on whether the material acts more as an absorber or scatterer of radiation, respectively. For a scattering material \(\varepsilon_0\) is greater than \(\varepsilon_\infty\), and the parameter \(w_0\) denotes the lowest frequency at which scattering becomes important. Also, the parameter \(n\) is proportional to the slope of emissivity with frequency near \(w_0\).

As shown in Figure 6A.1, the emissivity varies little or increases with frequency for homogeneous materials such as water, soil, and newly formed ice. Also, water has the lowest emissivity because it has the highest dielectric constant.

**TABLE 6A.1 Coefficients for Emissivity Model**

<table>
<thead>
<tr>
<th>Surface</th>
<th>(\varepsilon_0)</th>
<th>(\varepsilon_\infty)</th>
<th>(w_0) (GHz)</th>
<th>(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ice</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>New</td>
<td>0.95</td>
<td>0.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Second Year</td>
<td>0.93</td>
<td>0.83</td>
<td>31</td>
<td>2</td>
</tr>
<tr>
<td>Multiyear</td>
<td>0.92</td>
<td>0.64</td>
<td>31</td>
<td>2</td>
</tr>
<tr>
<td>Snow</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wet</td>
<td>0.76</td>
<td>0.99</td>
<td>9</td>
<td>2</td>
</tr>
<tr>
<td>Dry</td>
<td>0.90</td>
<td>0.75</td>
<td>33</td>
<td>3</td>
</tr>
<tr>
<td>Refrozen</td>
<td>0.97</td>
<td>0.53</td>
<td>32</td>
<td>4</td>
</tr>
</tbody>
</table>
Consequently, dry soil, which contains little water, has the highest emissivity. Depending on the soil moisture, the emissivity can decrease to that of a free-water surface. However, vegetation acts as a canopy that absorbs the upwelling surface radiation. For frequencies having high absorption (>5 GHz) the emissivity for densely vegetated wet soil can appear similar to dry soil. New ice also has a low dielectric constant (similar to that of dry soil) and therefore has a high emissivity.

The emissivity characteristics change dramatically for heterogeneous materials, which contain particles of wavelength dimensions. This is the case of multiyear (also summer melt) ice, which has voids (scattering centers) in the ice sheets due to brine depletion. Dry snow consists of ice particles that also scatter microwave radiation. The volume scattering effects result in a decrease in emissivity with increasing frequency by scattering some of the upwelling radiation out of the field of view. Note from Figure 6A.1 that the emissivity of sea ice also decreases with increasing concentration and size of brine pockets (i.e., ice age). Similarly, for dry snow, the emissivity decreases with increasing snow density and crystal size (i.e., refrozen snow). The strong scattering in the case of refrozen snow results in emissivities less than that of water for high frequencies. However, when snow melts, its structure and electromagnetic properties change markedly. As temperatures increase to the melting point, the effective dielectric constant of the melting ice increase to that of water-coated ice particles, which mainly absorb microwave radiation. Moist snow, therefore, becomes highly emissive, with an emissivity that varies between that of wet and dry land depending on melting conditions.

6B CORRECTIONS FOR CALIBRATION AND MODELING ERRORS

Algorithms for deriving geophysical parameters can be obtained empirically using regression analysis to relate the antenna temperature measurements to the desired atmospheric parameters. Alternatively, the algorithms can be derived theoretically using the radiation transfer equation and an atmospheric data base to simulate the microwave measurements. To use such theoretically based algorithms on actual measurements, it is necessary to account for errors in both the measurements and the theoretical model. Adjustments due to instrumental errors and modeling errors are addressed here, and we show that both can be combined into a single expression.

6B.1 Calibration Corrections

The accuracy of the measured antenna temperature depends on the accuracy of the calibration sources. The typical flight radiometer uses a two-point temperature calibration as described in Section 1.3.1, where an onboard warm target and the cold-space background are used to obtain the calibration. For example, the SSM/T views a warm target and space once each during a 32-s cycle (see Figure 6.8). Ideally, the brightness temperature of the warm target is given by its physical
temperature of about 300 K (monitored using platinum resistance sensors), and the antenna temperature of cold space is 2.7 K. This assumes a perfect warm load with unity emissivity, and that the antenna’s field of view encompasses all the energy from the warm load or cosmic background.

Shrouded enclosures are used on the SSM/T to direct the radiation from the warm load and cold space to the antenna aperture, and greatly reduce any unwanted radiation due to the spacecraft and the Earth’s atmosphere. Consequently, the operational procedure initially assumes ideal calibration conditions for this instrument. However, empirical adjustments are later made based on comparisons between measured and calculated antenna temperatures.

A calibration-error model is obtained by considering that the true warm and cold targets can differ from the operational values. The appropriate radiometer calibration equation can be obtained with a slight manipulation of Eq. 1.35 as

\[
T_a = T_2 + \frac{T_2 - T_1}{V_2 - V_1} (V - V_2)
\]

(6B.1)

where \(T_a\) is the antenna temperature to be obtained from the measured radiometer output voltage \(V\), \(T_1\) and \(T_2\) are the respective antenna temperatures of the cold and warm loads, and \(V_1\) and \(V_2\) are the respective measured voltages when these loads are observed. The effect of calibration target errors on the antenna temperature is obtained by replacing the operational values \(T_1\) and \(T_2\) with the “true” values \(T'_1\) and \(T'_2\) in Eq. 6B.1. The resulting antenna temperature is denoted as \(T'_a\) and given by

\[
T'_a = T'_2 + \frac{T'_2 - T'_1}{V_2 - V_1} (V - V_2)
\]

(6B.2)

The relationship between the true measurement \(T'_a\) and that using the operational values, \(T_a\), is obtained by combining Eq. 6B.1 with 6B.2 and eliminating the voltage ratio:

\[
T_a = \alpha_v T'_a + \beta_v
\]

(6B.3)

where

\[
\alpha_v = \frac{T_2 - T_1}{T'_2 - T'_1}
\]

(6B.4)

and

\[
\beta_v = \frac{T'_2 T_1 - T_2 T'_1}{T'_2 - T'_1}
\]

(6B.5)

Equation 6B.3 is the calibration correction algorithm, where the \(\alpha_v\) and \(\beta_v\) parameters correct the antenna temperature measurements \(T'_a\) for errors in the space and warm target temperatures. The parameters are given by Eqs. 6B.4 and 6B.5.
and depend on the difference between the actual temperatures \((T_1', T_2')\) and the operational values \((T_1, T_2)\) for the space view and warm target. A frequency dependence is indicated because the parameters can vary for the different channels. Also, when only one of the calibration values are in error, the two parameters are related; that is, for \(T_2' = T_2\), \(\beta_v = (1 - \alpha_v)T_2\). Values of \(\alpha_v\) are generally within 1% of unity with \(\beta_v\) values averaging about 1 K for most of the channels.

Determination of the \(\alpha_v\) and \(\beta_v\) parameters requires a minimum of two calibration targets on Earth. The parameters are obtained by comparing the Earth-viewing measurements, \(T_a\), with estimates of the true antenna temperature, \(T_\infty\). Fortunately, in the case of the sounding channels, accurate estimates of the true antenna temperature can be calculated using radiosonde data as input to the radiation-transfer equation. However, in addition to the \(\alpha_v\) and \(\beta_v\) parameters, factors must be included to account for errors in the theoretical oxygen-absorption model used in the calculations, and are discussed in Section 6B.3.

### 6B.2 Antenna Sidelobe Corrections

The antenna temperature is given by Eq. 1.28 as an integration of the antenna gain over the brightness temperature of the entire sky. Although antennas for flight radiometers are typically highly efficient at collecting radiation within their narrow main lobes, it is necessary to account for radiation received from their small but nonnegligible sidelobes. We can express Eq. 1.28 as the sum of respective integrations over the main lobe and the remainder of the sky, or

\[
T_a = \int \int_{\text{main lobe}} G(\theta', \phi') T_b(\nu, \theta', \phi') \sin \theta' \, d\theta' \, d\phi' + \int \int_{\text{sidelobes}} G(\theta', \phi') T_b(\nu, \theta', \phi') \sin \theta' \, d\theta' \, d\phi' \tag{6B.6}
\]

The far sidelobes (typically, \(\theta > \pm 60^\circ\) from nadir) receive radiation outside the Earth’s atmosphere so that Eq. 6B.6 can be written as

\[
T_a = \eta T_m + (1 - \eta) T_c \tag{6B.7}
\]

where

\[
\eta = 1 - \int \int_{\text{far sidelobes}} G(\theta', \phi') \sin \theta' \, d\theta' \, d\phi' \tag{6B.8}
\]

and

\[
T_m = \frac{1}{\eta} \int \int_{\text{main lobe}} G(\theta', \phi') T_b(\nu, \theta', \phi') \sin \theta' \, d\theta' \, d\phi' + \int \int_{\text{nearsidelobes}} G(\theta', \phi') T_b(\nu, \theta', \phi') \sin \theta' \, d\theta' \, d\phi' \tag{6B.9}
\]
In Eq. 6B.7, $T_m$ is the total Earth contribution and $T_c$ is the 2.7 K cosmic background. The quantity $\eta$ defined in Eq. 6B.8 represents the fraction of energy received by the antenna that only arises from the Earth. For example, this parameter has been computed using the SSM/T antenna patterns and derived for the different scan angles. The values of $\eta$ are very close to unity so that

$$T_m \approx T_a / \eta$$  \hspace{1cm} (6B.10)$$

where the sidelobe-corrected measurement $T_m$ is slightly greater than the antenna temperature by about 1 K.

Calculations of the parameter $\eta$ are complicated by the small but uncertain contribution of Earth radiation entering the far sidelobes of the antenna. This effect becomes most noticeable as the antenna scans away from the nadir direction, causing the sidelobes to view Earth rather than space. Because the sidelobes are generally asymmetric on opposite sides of the cross-track scan direction, this results in an asymmetry of the brightness-temperature measurements between the right and left scan positions. To improve the calculated values of $\eta$, empirical corrections are added to Eq. 6B.8 as a function of scan position by comparing the measurements on opposite sides of the scan.

6B.3 Modeling Corrections

Based on the radiative transfer theory, the antenna temperature is calculated using Eq. 6.9 with the weighting function obtained using an absorption model for oxygen. In the following analysis, $S(\nu, P)$ is approximated by Eq. 6.13 so that the results are applicable for unity emissivity surfaces or at frequencies having very small transmittance. High surface emissivities are obtained for vegetated land (see Figure 6A.1), and small transmittances less than 0.1 occur in the oxygen band for $\nu > 53.5$ GHz.

To account for errors in the theoretical oxygen model, Eq. 6.9 can be written as

$$T_a'(\nu) = \int_{\ln P_s}^{\ln P} T(P) \frac{dS_{\nu}(\nu, P)}{d \ln P} d \ln P + S_{\nu}(\nu, P_s) T_s$$  \hspace{1cm} (6B.11)$$

where $T_a'$ denotes the true antenna temperature measurements of the scene. It contains an empirical correction to the oxygen-absorption model $\gamma_{\nu}$, which is frequency-dependent. Deviations in $\gamma_{\nu}$ about unity can be related to errors in the theoretical line strength, line width, or interference parameters at the temperatures and pressures near where the weighting-function peaks.

Equation 6B.11 is considered the true antenna temperature, where the calculated (theoretical) antenna temperature $T_{calc}(\nu)$ is obtained by setting $\gamma_{\nu}$ to unity. If $\gamma_{\nu}$ is close to unity, then Eq. 6B.11 can be approximated by the first two terms of a Taylor expansion about $\gamma_{\nu} = 1$:

$$T_a'(\nu) \approx (\gamma_{\nu} - 1) R_{\nu} + T_{calc}(\nu)$$  \hspace{1cm} (6B.12)$$
where

\[ R_v = \int_{\ln P_v}^{-\infty} T(P) \frac{dK(\nu, P)}{d \ln P} d \ln P + K(\nu, P_v) T_s \]  

(6B.13)

and

\[ K(\nu, P) = S(\nu, P) \ln S(\nu, P) \]  

(6B.14)

The factor \( R_v \) in Eq. 6B.12 depends on frequency as well as the temperature structure, where the values are listed in Table 6B.1 for the SSM/T channels of interest. Average temperature profiles for the three basic latitude zones were used in the calculations.

Substituting Eq. 6B.12 into Eq. 6B.3, we obtain

\[ T_a(\nu) = \alpha_v T_{\text{calc}}(\nu) + \alpha_v (\gamma_v - 1) R_v + \beta_v \]  

(6B.15)

which shows the relationship between the radiometer measurement \( T_a \) and the calculated antenna temperature \( T_{\text{calc}} \). The equation contains the combined effects of transmittance and calibration errors on the antenna temperature measurement. Although all three parameters can be determined, usually only two of the three parameters are required to account for the differences between the measured and calculated values. Most investigators have assumed \( \gamma_v = 1 \), and have determined the \( \alpha_v \) and \( \beta_v \) parameters by regressing the measurements against the calculated values [14 and 37, 43 of Chapter 6]. These studies showed that \( \alpha_v \approx 1 \), where almost all of the correction is in the form of the bias \( \beta_v \). In the context of Eq. 6B.15, it is appropriate to assume \( \alpha_v = 1 \) and approximate the equation as

\[ T_a(\nu) = T_{\text{calc}}(\nu) + (\gamma_v - 1) R_v + \beta_v \]  

(6B.16)

where the application of this result is discussed next.

### 6B.4 Calibration and Modeling Correction Parameters

The adjustment parameters in Eq. 6B.16 were obtained for the SSM/T channels by comparing the satellite measurements with collocated radiosonde measurements of temperature (the water vapor contribution is generally insignificant when com-

<table>
<thead>
<tr>
<th>Channel</th>
<th>Frequency (GHz)</th>
<th>Polar</th>
<th>Midlatitude</th>
<th>Tropical</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>54.35</td>
<td>-13.118</td>
<td>-18.727</td>
<td>-23.900</td>
</tr>
<tr>
<td>4</td>
<td>54.90</td>
<td>-9.218</td>
<td>-13.572</td>
<td>-20.863</td>
</tr>
<tr>
<td>6</td>
<td>58.825</td>
<td>-1.127</td>
<td>1.627</td>
<td>5.872</td>
</tr>
<tr>
<td>7</td>
<td>59.40</td>
<td>-0.745</td>
<td>2.500</td>
<td>8.245</td>
</tr>
</tbody>
</table>
puting the antenna temperature for oxygen channels). As part of the operational procedure, SSM/T data are collected twice a day and matched up with data from a radiosonde (RAOB) file supplied by the National Weather Service. To minimize the effects due to spatial and temporal differences, the RAOBs, which are balloon-launched at 0 and 12 GMT, are matched within 1 degree latitude-longitude and 3 hours of the satellite data.

In generating the matchup files, the RAOBs are required to have a surface pressure of 1000 mbars or greater and extend up to 10 mbars. Also, a climatological lapse rate is used to extend the RAOB temperature profiles beyond their cutoff to 0.1 mbar. This additional requirement on the RAOB profiles ensures adequate vertical resolution for the calculation of antenna temperatures for most of the channels. Furthermore, it guarantees the same number of matchups \((T_a, T_{calc})\) for all channels. Unfortunately, the amount of global RAOB data is reduced from around 1000 to about 50 per day due to the tight restriction on pressure levels. Therefore, many days of matchup data are required to obtain a reasonable sample size.

Most studies comparing satellite measurements against computed antenna temperatures use individual matchups for periods less than a week. Besides obtaining correction factors, the data are used to obtain the combined noise from the instrument and RAOB data [14]. However, the data used here consist of weekly averages over a 7-month period for the purpose of averaging out much of the random noise.

Table 6B.2 gives results using the weekly averaged matchup data for the SSM/T instrument launched in 1983 and covers a complete time period beginning in April 1985 and ending in October (28 weeks). Mean differences and standard deviations between the calculated and measured values are shown separately for the three latitude zones in the northern hemisphere and are presented for all the channels except 1 and 5. The window channel at 50.5 GHz is affected by emissivity and the 58.4-GHz channel peaks at 10 mbars, where radiosonde data is inadequate for computation purposes. For each latitude band, there is a total of 28 points per channel.

Table 6B.2 gives the mean difference and standard deviation for each channel and latitude zone. The 53.20-GHz channel shows the most scatter, due mainly to emissivity variations over land that are not adequately corrected. Also, the 59.4-GHz channel has a portion of its weighting function extending beyond the 10-mbar cutoff of most RAOBs, resulting in slightly greater standard deviations than the lower sounding channels. Of greater significance is the large bias for the "tropopause" channel at 54.90 GHz, which decreases with increasing latitude. The MSU instrument contains a similar channel and has shown nearly identical results [14 and 43, 49 of Chapter 6]. The "bias with latitude" is consistent with the error characteristics of the oxygen-absorption model, and is accounted by the \(\gamma\) parameter in Eq. 6B.16.

In addition to the increased bias in the tropics compared to other latitudes, Table 6B.2 also displays a change in sign between the bias for the tropospheric and stratospheric channels. The computed values for the tropospheric channels (53.2, 54.35, and 54.90 GHz) are much warmer compared to the measurements, whereas the stratospheric channels (58.40 and 58.825 GHz) are colder compared to the
### Table 6B.2 Calculated ($T_{\text{calc}}$) Minus Measurements ($T_a$)

<table>
<thead>
<tr>
<th>Channel Number</th>
<th>Frequency (GHz)</th>
<th>Latitude Zone</th>
<th>Mean Difference (K)</th>
<th>Standard Deviation (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>53.20</td>
<td>Polar</td>
<td>0.69</td>
<td>0.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midlatitude</td>
<td>0.31</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tropical</td>
<td>1.60</td>
<td>0.30</td>
</tr>
<tr>
<td>3</td>
<td>54.35</td>
<td>Polar</td>
<td>0.62</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midlatitude</td>
<td>1.39</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tropical</td>
<td>1.91</td>
<td>0.12</td>
</tr>
<tr>
<td>4</td>
<td>54.90</td>
<td>Polar</td>
<td>1.32</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midlatitude</td>
<td>1.61</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tropical</td>
<td>2.41</td>
<td>0.14</td>
</tr>
<tr>
<td>6</td>
<td>58.825</td>
<td>Polar</td>
<td>-0.24</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midlatitude</td>
<td>-0.63</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tropical</td>
<td>-0.59</td>
<td>0.28</td>
</tr>
<tr>
<td>7</td>
<td>59.40</td>
<td>Polar</td>
<td>-0.45</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Midlatitude</td>
<td>-1.16</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tropical</td>
<td>-1.39</td>
<td>0.32</td>
</tr>
</tbody>
</table>

**Figure 6B.1.** Mean differences between calculated and measured antenna temperature (refer to Table 6B.2) are plotted against the $R_v$ parameters (listed in Table 6B.1). The slope of the regression lines corresponds to $\gamma - 1$ and the intercept is $\beta$. Values of $\beta$ and $\gamma$ are listed in Table 6B.3.
TABLE 6B.3 Calibration and Transmittance Correction Parameters

<table>
<thead>
<tr>
<th>Channel</th>
<th>Frequency (GHz)</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>54.35</td>
<td>0.9468</td>
<td>1.121</td>
</tr>
<tr>
<td>4</td>
<td>54.90</td>
<td>-0.1967</td>
<td>1.109</td>
</tr>
<tr>
<td>6</td>
<td>58.825</td>
<td>0.5992</td>
<td>1.055</td>
</tr>
<tr>
<td>7</td>
<td>59.40</td>
<td>0.9278</td>
<td>1.091</td>
</tr>
</tbody>
</table>

measurements. This suggests that the weighting functions are too low in the atmosphere and requires an overall increase in the theoretical oxygen absorption (i.e., $\gamma_v > 1$ in Eq. 6B.11).

Corrections for errors in the oxygen model and instrument calibration are given by the $\gamma_v$ and $\beta_v$ parameters. These parameters are obtained by plotting $T_{\text{calc}}(\nu) - T_{\text{a}}(\nu)$ against $R_v$, where, according to Eq. 6B.16, the slope of the regression line is $\gamma_v - 1$, and the intercept is $\beta_v$. To apply this method, the mean values of $T_{\text{calc}} - T_{\text{a}}$ listed in Table 6B.2 are plotted against the correspond $R_v$ values of Table 6B.1. Figure 6B.1 shows the plots for all of the frequencies except the noisy 53.20-GHz channel. The data corresponding to the three latitude zones lie along regression lines having slopes $\gamma_v - 1$ and intercepts equal to $\beta_v$, where Table 6B.3 lists the values of $\beta_v$ and $\gamma_v$.

6C CORRECTIONS FOR SURFACE EMISSIVITY AND ELEVATION

Temperature profiles can be derived from brightness-temperature measurements using Eq. 6.25 with the $\hat{D}$ matrix coefficients stratified by scan angle and land-water surface. However, when using channels less than 53.7 GHz to measure the temperature in the lower atmosphere ($P \geq 850$ mbars), it is necessary to account for the local variations in emissivity (dry land, wet land, snow cover, etc.) in addition to the elevation effects on the channel measurements. Different coefficients could be used to account for these effects, depending on elevation information and the emissivity estimates obtained using window channel measurements. As an alternate approach, the measurements can be adjusted to sea-level conditions at a fixed emissivity. Although different procedures are currently being developed, this Appendix describes the method currently used for the SSM/T instrument [36 of Chapter 6].

6C.1 Emissivity and Elevation Corrections

Effects of elevation and emissivity on the brightness temperature are obtained by modifying Eq. 6.8 as

$$T_b(h, \varepsilon_s) = T_u(\nu, \theta) + [\varepsilon_s T_s(h) + (1 - \varepsilon_s) T_d(\nu, \theta)] e^{-\tau(h) \sec \theta} \quad (6C.1)$$
where \( h \) is the elevation height, and \( T_s(h) \) is the surface temperature at the elevation. All of the terms in Eq. 6C.1 show the explicit dependence on surface elevation, emissivity, and frequency. To account for nonzero elevation, the opacity \( \tau(0) \sec \theta \) in Eq. 6.9 becomes \( \tau_s(h) \sec \theta \) and the upward and downward radiation components are given by Eqs. 6.2 and 6.7 with the lower limit of integration set to \( h \) rather than 0. Also, the downward component given by Eq. 6.7 now contains \( \tau(h) \) in place of \( \tau(0) \).

Although it has been customary to normalize the brightness temperatures to unity emissivity [32 of Chapter 6], the SSM/T measurements were normalized to zero emissivity. This simplifies the retrieval procedure because then the brightness temperature only contains atmospheric information. By using the notation of Eq. 6C.1, the \( T_b(0, 0) \) corresponds to the brightness temperature at sea-level pressure \( P_0 \) with a surface emissivity of zero, and is given by Eq. 6.9 with \( \varepsilon = 0 \) and \( P_s = P_0 \):

\[
T_b(0, 0) = \int_{\ln P_0}^{-\infty} T(P) \frac{dS_v(v, P, \theta P, \theta)}{d \ln P} d \ln P \quad (6C.2)
\]

where

\[
S(v, P, \theta) = [1 - e^{-2(\tau(P) - \tau(0)) \sec \theta}] e^{-\tau(0) \sec \theta} \quad (6C.3)
\]

Based on Eq. 6C.1, the brightness temperature at sea level for an emissivity of zero is given by

\[
T_b(0, 0) = T_b(h, \varepsilon_s) + A_v(h) \varepsilon_s(v) T_s(h) \quad (6C.4)
\]

where

\[
A_v(h) = T_u(v, 0) - T_u(v, h) + T_d(v, 0) e^{-\tau(0) \sec \theta} - T_d(v, h) e^{-\tau(h) \sec \theta} \quad (6C.5)
\]

and

\[
B_v(h) = [1 - T_d(v, h) / T_s(h)] e^{-\tau(h) \sec \theta} \quad (6C.6)
\]

In Eq. 6C.4, \( T_b(h, \varepsilon_s) \) is the uncorrected measurement, and coefficients \( A_v \) and \( B_v \) depend on frequency, elevation height, temperature, and local zenith angle. For convenience, only the dependence on frequency and elevation height is indicated, and the coefficients are approximated as a power series in elevation height. By keeping only the first- and second-order terms, the coefficients have the general form

\[
A_v(h) = [a_1(v) + a_2(v) h] h \quad (6C.7)
\]

\[
B_v(h) = b_0(v) + [b_1(v) + b_2(v) h] h \quad (6C.8)
\]
where \( b_0 \) provides the emissivity correction under sea-level conditions and is given by

\[
b_0(\nu) = e^{-\tau_\nu(0) \sec \theta} [1 - T_d(\nu, 0)/T_s(0)]
\]

To obtain a measure of the emissivity corrections, \( T_d(\nu, 0) \) is approximated using Eq. 6.7 for an isothermal atmosphere so that \( b_0 \) becomes \( e^{-2\tau_\nu(0) \sec \theta} \). By using transmittances of 0.70, 0.20, and 0.02 for the 50.50-, 53.20-, and 54.35-GHz SSM/T channels, and a mean surface temperature of 285 K, the emissivity corrections, \( b_0 \epsilon_s T_s \), are 140, 11, and 0.1 K at nadir for the respective channels. Only the lowest-frequency sounding channel (53.20 GHz) has an appreciable surface contribution, and therefore requires emissivity corrections. The remaining terms in Eqs. 6C.7 and 6C.8 correct for the elevation effects contained in the transmittance, where simulations are used to determine all the coefficients.

Because the correction equation 6C.4 only contains the surface-emission term, \( \epsilon_s T_s(h) \), this quantity can be determined using surface (window) channels. In the case of the SSM/T instrument, the 50.5-GHz channel is the most transparent channel and is used to estimate this term. From Eq. 6C.4, we can write

\[
\epsilon_s(\nu) T_s(h) = \frac{T_b(h, \epsilon_s) - T_b(0, 0) + A_s(h)}{B_s(h)}
\]

where \( T_b(h, \epsilon_s) \) is the brightness-temperature measurement at 50 GHz and all other parameters are obtained from simulations at this frequency. Except for the measurements, \( T_b(h, \epsilon_s) \), all other quantities must be estimated using the \( a \ priori \) data. Of all the parameters, the atmospheric contribution, \( T_b(0, 0) \), is the most dependent on \( a \ priori \) information. This and the other terms are computed as a function of viewing angle and have been stratified by latitude zone and season. For more advanced instruments containing lower frequency channels (e.g., AMSU), better estimates of surface emission are possible without appreciable atmospheric effects. However, the emission term in Eq. 6C.4 must be obtained around 50 GHz so that one must account for the frequency variation of emissivity when using lower frequency channels.

### 6C.2 Emissivity and Elevation-Correction Parameters

Equations 6C.4 and 6C.10 have been used to adjust the lower sounding channels (53.2 and 54.35) to a zero emissivity surface at sea-level conditions. The elevation and emissivity corrections in Eq. 6C.4 is \( A_s(h) - B_s(h) \epsilon_s T_s(h) \), where \( T_s(h) \) is the ground temperature at elevation \( h \). Average values for the parameters are obtained from simulations. Brightness-temperature differences are computed for each of the \( a \ priori \) radiosonde profiles before and after removing the lower portion of the sounding at prescribed elevations. The elevation parameters are computed for each channel at the different scan angles and stratified according to latitude zone and season.
Figure 6C.1 displays the elevation corrections for the 53.20- and 54.35-GHz channels for emissivities of 0.9 and 1.0, where again only the nadir values are shown. Note that the correction increases the measurements to compensate for the decrease in brightness temperature due to terrain height. The 53.20-GHz measurements decrease by more than 2 K for elevations exceeding 2 km. The elevation must exceed 4 km to observe the same decrease at 54.35 GHz.

A sample of SSM/T measurements is used to examine the emissivity and elevation corrections. The region chosen for this study is the ocean and land areas surrounding equatorial East Africa, where temperature variations are small and the land contains high mountainous terrain. To observe the maximum surface effects only the nadir observations are considered. Figure 6C.2 shows the mapped viewing positions and the corresponding surface elevation. The uncorrected brightness temperatures are plotted in Figure 6C.3 for the 50.5-, 53.20-, and 54.35-GHz channels. Measurement locations are indicated along the horizontal axis and the elevation height is displayed on the 53.20-GHz plot for reference.

Compared to the ocean ($\varepsilon_s \approx 0.5$), the brightness temperature over land ($\varepsilon_s \approx 1$) is increased by as much as 60 K for the 50.5-GHz channel and 8 K for the 53.20-GHz channel. Also, at the point of maximum elevation (2.9 km at 7.4 N, 39.3 W), the 50.5-GHz channel decreases by about 8 K and the 53.20-GHz channel decreases by almost 2 K. The 54.35-GHz channel appears unaffected by emissivity or elevation effects.

![Figure 6C.1](image-url) Brightness temperature corrections as a function of elevation for different emissivities. Calculations are shown for (a) the 53.20-GHz and (b) the 54.35-GHz channels for the nadir-viewing position.
Figure 6C.2. Mapped nadir-viewing scan positions for October 5, 1984, at 0724-0732 GMT. Surface elevation (km) is indicated next to each beam position.

Results of the emissivity- and elevation-correction procedures are shown in Figure 6C.4 for the 53.20- and 54.35-GHz measurements. Separate plots are shown for each channel, where one set displays the measurements corrected only for emissivity ($h = 0$ in Eq. 6C.4), and the second contains the elevation adjustments as well. For reference, the elevation heights are indicated on the 53.20-GHz emissivity corrected plot. Compared to Figure 6C.2, the emissivity adjustment lowers the 53.20-GHz brightness temperature to that of a zero-emissivity surface with no apparent variation between the ocean and land areas. As expected, the 54.35-GHz channel shows no change due to emissivity. With regard to elevation, note that
the correction increases the measurements (see Figure 6C.2) to compensate for the effect of terrain height on the brightness temperatures. At the point of maximum elevation (2.9 km), this increase amounts to 2.7 K at 53.20 GHz and 0.7 K at 54.35 GHz. There appears to be a slight overcorrection at 53.20 GHz, which may be due because the terrain height was not averaged over the SSM/T field of view before applying Eq. 6C.4. However, it is interesting to observe a slight increase

Figure 6C.3. Brightness temperature at 50.30, 53.20, and 54.35 GHz for the cross-section shown in Figure 6C.2. Surface elevation is indicated on the 53.20-GHz plot.

Figure 6C.4. Brightness temperature at 53.20 and 54.35 GHz (compare with Figure 6C.3) after applying the emissivity correction and the combined emissivity and elevation corrections. Surface elevation is shown on the 53.20-GHz plot.
with increasing latitude for the fully corrected 53.20-GHz measurements. This change in brightness temperature with latitude is supported by the 54.35-GHz channel and is due to actual temperature variations.

6D CLOUD LIQUID WATER ABSORPTION

The interaction of electromagnetic energy with ice and water particles depends on the dielectric properties of the droplets (the Debye model) as well as their geometry, and has been discussed in Chapter 3. If we consider only drops whose diameters are much smaller than the wavelength, then scattering is unimportant and the absorption coefficient is given by the Rayleigh approximation. This is generally written as Eq. 3.5 and is independent of the drop size. Using the dielectric constant for liquid water [15], the absorption coefficient for frequencies less than 100 GHz is approximated by the single-Debye relationship,

\[
\alpha = 0.0241M \frac{\nu^2 \nu_0}{\nu^2 + \nu_0^2} \text{ km}^{-1}
\]  

(6D.1)

where

\[
\nu_0 \approx 160e^{7.2(1 - 287/T_{cl})} \text{ GHz}
\]  

(6D.2)

Here \( M \) is the liquid water density in g/m\(^3\), and \( \nu_0 \) represents a relaxation frequency that accounts for the cohesion that resists the free rotation of water molecules to an applied electric field. The relaxation frequency is temperature-dependent and varies from 133 GHz for warm clouds (\( T_{cl} = 280 \) K) to 75 GHz for higher colder clouds (\( T_{cl} = 260 \) K). The absorption coefficient is thus seen to increase monotonically with frequency, having a quadratic form for frequencies less than \( \nu_0 \). The spectral increase is less pronounced at higher frequencies.

The Rayleigh approximation is accurate within several percent when the radiation wavelength is about 50 times larger than the droplet diameters. This would apply to frequencies up to 60 GHz for radii less than 100 \( \mu \)m. It is important to note that for frequencies less than \( \nu_0 \), the absorption increases with the square of frequency and contains the same dependence on cloud temperature. The opacity due to clouds under this condition is approximated by substituting 6D.1 into Eq. 6.11,

\[
\tau_{cl}(P_s) = Q/Q_{\nu}
\]  

(6D.3)

where \( Q_{\nu} = \nu_0^2/(0.0241\nu^2) \), and \( Q \) is the vertically integrated cloud liquid water in kg/m\(^2\) (or mm). An equation of this form has been used to determine the cloud liquid water content at frequencies up to about 40 GHz (see Section 6.4).
In the case of rain, the liquid water particles can have diameters larger than 1000 \mu m, and the Rayleigh approximation would then only apply for frequencies less than about 3 GHz. In this case, the relationship between absorption and liquid water given by Eq. 6D.1 must be expanded to include higher-order diffraction effects. The linear relationship between the absorption coefficient and liquid water density also approximately holds for large drops, although the proportionality constant is larger and depends on the size distribution as well as the frequency. For the same liquid water density, the absorption due to large drops is about a factor of 3 greater than that due to small drops.

Clouds and precipitation contain ice particles in addition to water drops. Unlike water, however, the dielectric constant of ice is nearly independent of frequency and provides very little loss in the microwave region [10 of Chapter 6]. Ice crystals found in cirrus clouds and dry falling snow are virtually transparent at microwave frequencies because of the extremely low dielectric loss. It is only when the ice particles became large, as in the case of graupel for convective storms, that their scattering becomes important at high frequencies (see Section 6.4.2). Wet snow results in absorption similar to liquid drops, however.

REFERENCES


7

GROUND-BASED MICROWAVE SPECTROSCOPY OF THE EARTH’S STRATOSPHERE AND MESOSPHERE

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7.1 INTRODUCTION

7.1.1 The Middle Atmosphere

The stratosphere and mesosphere span the altitude region 15–85 km in the terrestrial atmosphere and are collectively referred to as the middle atmosphere. The exact lower and upper boundaries are defined by a temperature minimum at the cold tropopause (190 K) at a pressure level of 200–400 mbars and a still lower mesopause temperature minimum at a pressure level of 0.001 mbar. Figure 7.1 indicates the mean winter temperature profile within the middle atmosphere at mid-latitude. The stratosphere–mesosphere boundary at a pressure of 1 mbar is defined by a temperature maximum of 280 K at the stratopause.

The temperature inversion within the stratosphere is driven by direct solar heating, which is largely due to O$_3$ absorption of solar ultraviolet flux. As illustrated in Figure 7.1, O$_3$ mixing ratios peak near a pressure of 5 mbars. The decline of atmospheric temperatures in the mesosphere is a consequence of decreased O$_3$ abundances and increased cooling rates from CO$_2$ infrared radiation, which escapes more easily to space above the stratosphere. The larger infrared opacities in the stratosphere, which include smaller contributions from O$_3$, CH$_4$, CFC’s, and
N\textsubscript{2}O as well as CO\textsubscript{2}, provide a significant greenhouse effect that increases tropospheric temperatures by 30 K.

The photochemistry of O\textsubscript{3} is a complex system in which the production of O\textsubscript{3} by O\textsubscript{2} photolysis is balanced by at least four catalytic loss cycles for O\textsubscript{3}. These loss cycles include the HO\textsubscript{x} family (OH, HO\textsubscript{2}, H), which dominates destruction of O\textsubscript{3} in the mesosphere; the NO\textsubscript{x} family (NO, NO\textsubscript{2}), which nominally controls destruction of O\textsubscript{3} in the lower stratosphere; and the O\textsubscript{x} family itself (O\textsubscript{3}, O), which controls O\textsubscript{3} abundances above the mesosphere. A fourth catalytic cycle, which was only discovered in the 1970s [1], is driven by the Cl\textsubscript{x} family (Cl, ClO) and contributes a significant loss to upper stratospheric ozone. Cl\textsubscript{x} chemistry also plays a major role in the recently discovered Antarctic ozone hole [2, 3]. Additional atmospheric parameters that influence middle atmospheric photochemistry are solar flux, atmospheric temperature, and dynamical transport.

Although middle-atmospheric research stands alone as a scientifically important study of a complex balance of photochemical, radiative, and dynamically processes, an added urgency and intensity in this research stems from changes in the middle atmosphere, which are predicted to impact significantly the global habitability of the Earth. In particular, long-term changes in climate and the stability of ozone shielding of solar middle ultraviolet radiation are primarily middle-atmosphere problems. Middle-atmosphere research must provide both an understanding of the natural processes that control stratospheric radiative and photochemical balances, and an assessment of the related impacts of increased atmospheric levels of CO\textsubscript{2}, CH\textsubscript{4}, N\textsubscript{2}O, and Cl\textsubscript{x} due to anthropogenic activity [4].

### 7.1.2 Microwave Applications

Early applications of microwave spectroscopy [5–7] to stratospheric and mesospheric studies were limited in part by the relative weakness of microwave lines
compared to infrared, visible, and ultraviolet spectral lines. The increased signal at visible and ultraviolet frequencies reflects the frequency dependence of incident and scattered solar radiance, whereas increased signal-to-noise ratios for infrared transitions are a consequence of the frequency dependence of blackbody radiation from the warm atmosphere. The Wein wavelength for the terrestrial atmosphere lies in the middle infrared (10–15 µm).

However, in the late 1970s and 1980s, microwave spectroscopy facilitated a number of important middle-atmospheric measurements. Rotational transitions in the ground vibrational state, which occur at microwave frequencies, have been measured for H₂O, O₃, O₂, ClO, CO, HO₂, NO, and HCN in the terrestrial stratosphere and mesosphere [8–16a]. Most of these observations return information relevant to O₃ photochemistry. The ClO and HO₂ molecules are not easily measured at shorter wavelengths. Furthermore, ground-based microwave observations allow pressure scale-height resolution of the vertical mixing profile of the measured species, information that is not usually obtained from ground-based visible and ultraviolet observations.

Two further advantages of microwave wavelengths are their relative insensitivities to aerosol scattering and uncertainties in atmospheric temperatures. At shorter observing wavelengths, aerosol scattering, particularly in the stratosphere, must be corrected for accurate monitoring of stratospheric ozone. As the particle size of such aerosols is much smaller than microwave wavelengths ($r \sim \lambda/1000$), neither aerosol scattering nor emission significantly impacts microwave measurements. The strong temperature dependence of infrared emission through the Planck source function requires coincident, accurate (1 K) measurement of atmospheric temperatures. As a rule, infrared instruments must be flown above the warm troposphere on spacecraft, rockets, aircraft, or balloons in order to obtain measurements of the stratosphere and mesosphere. Microwave emission is linearly dependent on atmospheric temperature in the Rayleigh–Jeans approximation to the source function and can be observed from the ground with moderate influence due to tropospheric transmission.

### 7.1.3 Microwave Instrumentation

Only a very general outline of the microwave spectroscopic-observing system is presented here, partly because the diversity of such systems is quite large, and also because the rapid evolution of microwave technology guarantees that detailed descriptions are quickly outdated. The basic elements of a microwave spectroscopic system include an antenna, for directional reception of the microwave flux; a radio receiver, for phase-coherent amplification of the signal passband; and a spectrometer, for frequency decomposition and square-law detection of the microwave spectrum [17–19]. These elements are described in some detail in Section 1.3. In the following discussion, we indicate how these elements both constrain and facilitate microwave observations of the middle atmosphere.

The microwave antenna system may be one of two extremes, depending on the
type of observation. High angular resolution on the sky is not a critical criterion for most ground-based systems that measure atmospheric emission. A diffraction-limited beam of $\sim 2^\circ$ is attained by a 5-cm feedhorn operating at a wavelength of 2 mm (angular resolution in radians $\sim \lambda/D_{\text{antenna}}$). The primary limitation on the beam size for emission measurements is that the air mass ($1/\mu; \mu = \cos \theta; \theta = \text{zenith angle}$) of observation over the beam does not change drastically. On the other hand, absorption measurements that measure the atmospheric extinction of an extraterrestrial microwave continuum source, such as the Sun or the Moon, require a pointable antenna ($\geq 1 \text{ m}$) that is capable of astronomical tracking.

The receiver includes a heterodyne subsystem that phase-coherently mixes a bandwidth of signal radiance about the frequency of observation ($20-500 \text{ GHz}$) with a highly phase-stable local oscillator (LO) frequency. The relatively low power in the lower-frequency term of the signal–LO product is phase-coherently amplified within the receiver before it is sent to the spectrometer, where it is spectrally decomposed and detected. The noise level of the observation is determined by the background level of microwave radiation within the receiver. This receiver background level must be subtracted from the total system power density in order to separate the signal power density. Several techniques employed in middle-atmosphere observations to remove the receiver background level are presented in later discussion. In any case, the measurement uncertainty of the signal power density is determined by the system noise temperature, as given by Eq. 1.26. One other important observational constraint dictated by the receiver is the bandwidth of useful operation. This bandwidth, which is generally of the order of $\leq 1 \text{ GHz}$, limits the frequency range of a single observation. The bandwidth of a given receiver can be moved over a limited range of frequencies ($\Delta f/f < 0.2$) with retuning and/or changing of receiver mixer components. The net result is that each receiver is effectively designed to measure at best a few molecular species.

A variety of techniques is available for spectral decomposition of the receiver output (see Chapter 1). The Doppler widths of microwave transitions in the middle atmosphere are easily resolved by microwave spectrometer systems. With regard to middle-atmosphere studies, a more important parameter is the total bandwidth covered by the spectrometer. Microwave transitions in the lower stratosphere have line widths well in excess of 100 MHz due to pressure broadening. Acoustooptical, filter bank, and chirp transform spectrometer systems can easily span such a frequency range. However, most molecular lines in the stratosphere are weak, and considerable care must be given to remove any low-order frequency dependence in the system response over the spectrometer bandwidth (often referred to as baseline problems).

The complete microwave spectral line system can span a wide range in size and weight. Helium-cooled systems, such as for the 22-GHz water line, may be too large for current spacecraft applications, but are portable for ground-based observations. Ambient-temperature systems can be designed at under 30 kg mass for spacecraft applications. Technological improvements in detectors, mixers, and spectrometers promise greater reductions in size, weight, and power requirements for microwave spectrometer systems.
7.1.4 Microwave Transitions

Microwave transitions of interest to middle-atmospheric studies occur primarily as rotational electric-dipole transitions in the ground vibrational state of molecules, and encompass wavelengths from 1 cm to 0.5 mm (frequencies of 20 to 500 GHz). The quantum mechanical theory of molecular transitions was developed with remarkable completeness in the 1950s [20]. The quantum physics of microwave transitions has been reviewed in several publications [21, 22], and is presented in detail in Chapter 2. Only the more salient features of microwave transitions are summarized here.

The microwave rotational spectrum for a linear molecule consists of a set of lines separated in frequency by $\Delta \nu = 2B$, where $B$ is the molecular constant (e.g., $N_2O$ transitions of Table 2A.4). This leads to wide frequency separations between the different rotational transitions of a given linear molecule. Nonlinear molecules such as $O_3$ (Table 2A.5) present much richer and more complicated spectra. A fairly exhaustive tabulation of microwave transitions and integrated line strengths can be found in Poynter and Pickett [23; see also Chapter 8]. Integrated line strengths increase as $\nu^{-3}$ for increasing order rotational transitions of a given linear molecule (see Table 2A.4). Although line strengths for nonlinear molecules are much more complicated, the strongest line transitions for a given nonlinear molecule also scale roughly as $\nu^{-3}$ in line strength. The increase in line strength with higher-frequency transitions reflects the energy dependence of stimulated emission-absorption, the Boltzmann population of energy states, and the increasing statistical weight, $g_J$, of larger $J$ values (to the degree to which these states remain degenerate). As a result, transitions at higher frequencies present greater optical depths, a point that is significant given the signal/noise limitations that are usually inherent in ground-based observations. Almost all microwave observations of the middle atmosphere involve optically thin lines. In selecting a particular transition for observation, one must balance signal-to-noise trade-offs presented by smaller optical depths at low frequencies and the smaller tropospheric transmissions (see the following section) and the greater technological challenges that are presented at higher frequencies.

7.1.5 Microwave Line Shapes

The line-shape factor $F(\nu, \nu_0)$, describes the spread in frequency or energy over which the integrated transition strength is dispersed about the line center frequency, $\nu_0$. The two important line-broadening effects for transitions in the middle atmosphere are Doppler (thermal) and collisional (pressure) broadening. Because the microwave line shape plays such a crucial role in middle-atmospheric microwave spectroscopy, we summarize the basic microwave line shape, which is presented in much greater detail in Chapter 2. Doppler broadening is described by the Gaussian distribution of kinetic velocities for the absorbing-emitting molecules. The Doppler line-shape function is given by

$$D(\nu, \nu_0) = \frac{(\ln 2/\pi)^{1/2} \exp \left[ -\ln 2[(\nu - \nu_0)/\Delta \nu_d]^2 \right]}{\Delta \nu_d}$$

(7.1)
and the Doppler full width at half maximum ($\Delta \nu_d$) is given by

$$\Delta \nu_d = \frac{\nu}{c} \left(2kT \ln \frac{2}{m}\right)^{1/2} \quad (7.2)$$

where $m$ is the molecular mass.

Interactions between molecules provide additional line broadening, which, for microwave frequencies, exceeds Doppler line broadening at atmospheric pressures greater than $\sim 0.1$ mbar (65-km altitude). For middle-atmospheric line widths, collisional broadening can be approximated by the Lorentzian line shape.

$$C(\nu, \nu_0) = \frac{1}{\pi} \left[ \frac{\Delta \nu_c}{(\nu - \nu_0)^2 + \Delta \nu_c^2} \right] \quad (7.3)$$

The collisional line width, $\Delta \nu_c$, is linearly dependent on atmospheric pressure $P$ and roughly inversely dependent on atmospheric temperature $T$:

$$\Delta \nu_c = \Delta \nu_{c0} \left(\frac{P}{P_0}\right) \left(\frac{T}{T_0}\right)^{-x} \quad (7.4)$$

where the exponent $x$ is approximately 0.75 for collisional broadening in the terrestrial middle atmosphere [13]. The total line shape, which is the convolution of the Doppler and collisional line shapes,

$$F(\nu, \nu_0) = \int_{-\infty}^{\infty} C(\nu - \nu') D(\nu') \, d\nu' \quad (7.5)$$

is called the Voigt line shape. It is important to point out that it is the pressure dependence of the line shape of microwave transitions that allows definition of the vertical distribution of an observed species. Above $\sim 65$-km altitude, where the line shape becomes relatively constant (i.e., the Doppler line shape), one can derive only a vertical column from the integrated line depth. Below $\sim 65$ km, it is possible to retrieve vertical resolution of the species concentration on the order of a pressure scale-height. The signal at frequencies further from line center corresponds to emission/absorption at correspondingly higher atmospheric pressures. This is an important contrast to visible and infrared transitions for which the Doppler line shape applies throughout the entire middle atmosphere.

### 7.1.6 Atmospheric Transmission

Ground-based observations of the middle atmosphere suffer transmission losses that are controlled primarily by broadband extinction from tropospheric $O_2$ and $H_2O$. Figure 7.2 from Waters [22] presents the zenith opacity for a completely dry atmosphere (no water, lower curve) and a typical summer midlatitude atmosphere (2-gm-cm$^2$ water column, upper curve). For a perfectly dry atmosphere, pressure-
Figure 7.2  (a) Background microwave opacities and (b) brightness temperatures for a wet (H$_2$O = 2 gm/cm$^3$) and completely dry atmosphere. The background transmission of the atmosphere is defined by microwave absorption by O$_2$, H$_2$O, and stratospheric O$_3$ (reprinted from Waters [22]).
broadened magnetic dipole transitions of O₂ at 60 and 118 GHz contribute substantial opacities within ±20 and ±5 GHz of these transitions. Much narrower lines due to stratospheric ozone become numerous beyond 100 GHz. The mid-latitude summer atmosphere exhibits prohibitively high opacities for frequencies beyond ~90 GHz, due to electric-dipole transitions of H₂O at 183 GHz and higher frequencies. In practice, even good observing conditions (such as in winter) still exhibit water opacities of 0.1 to 0.2 for frequencies greater than 200 GHz, as the atmosphere is never completely dry. Sea-level observations suffer serious transmission losses during summer months. High-altitude observatories, such as Mauna Kea provide better year-round observing conditions.

7.1.7 Microwave Radiative Transfer

We begin development of the transfer of microwave line radiation within the middle atmosphere from the formalism presented in Chapter 1. Equation 1.13 is rewritten in a form more applicable to ground-based observations through the atmosphere:

\[ T_b^*(\nu) = \int_0^\infty T(h) \exp \left(-\int_0^h \alpha(\nu, s) \, ds/\mu \right) \alpha(\nu, h) \, dh/\mu + T_c(\nu) \exp \left[-\int_0^\infty \alpha(\nu, s) \, ds/\mu \right] \]

where the path of integration is taken from the ground \((h = 0)\) along a straight-line path through an atmosphere at an angle from zenith, \(\theta\) \((\mu = \cos \theta)\). The background term, \(T_c(\nu)\), can be either the cosmic background emission or, in the case of absorption observations (see the following section), an external source such as the Moon. The absorption coefficient per unit length, \(\alpha(\nu, h)\), includes both the spectral line absorption and any other source of microwave opacity present in the atmosphere.

A simplification of the middle atmosphere is that \(\alpha(\nu, h)\) usually pertains only to the absorption coefficient of the specific molecule or molecules that are of observational interest. This approximation is appropriate because microwave lines are well separated in frequency. In addition, the primary continuum opacity at microwave frequencies is due to H₂O, which is essentially confined to the troposphere. As a result, the line-opacity integrals of Eq. 7.6 are not usually integrated down to the surface \((h = 0)\). Rather, a brightness temperature \(T_b^*(\nu)\) is defined as that due only to emission/absorption from the altitude region of interest:

\[ T_b^*(\nu) = \int_{h_0}^\infty T(h) \exp \left[-\int_{h_0}^h \alpha(\nu, s) \, ds/\mu \right] \alpha(\nu, h) \, dh/\mu + T_c(\nu) \exp \left[-\int_{h_0}^\infty \alpha(\nu, s) \, ds/\mu \right] \]
where the lower altitude limit of integration, \( h_0 \), is placed well below the lower-altitude limit for which information on the unknown \( \alpha(\nu, h) \) is to be retrieved. The total brightness temperature \( T_b(\nu) \) can be approximated as the sum of \( T_b^\tau(\nu) \) uniformly attenuated by tropospheric transmission \((e^{-\tau_{TROP}})\) and a frequency-independent tropospheric emission term approximated by \((1 - e^{-\tau_{TROP}/\mu})T_{TROP}\) for \( \tau_{TROP}/\mu \ll 1 \), namely,

\[
T_b(\nu) = T_b^\tau(\nu)e^{-\tau_{TROP}/\mu} + (1 - e^{-\tau_{TROP}/\mu})T_{TROP}
\]  

(7.8)

The quantity \( \tau_{TROP} \) is given by the sum of tropospheric \( O_2 \) and \( H_2O \) opacities. A weighted-average tropospheric temperature \( (T_{TROP}) \) is assumed. Both the tropospheric emission and transmission are nearly independent of frequency across the measured brightness temperature spectrum \( T_b(\nu) \), due to highly pressure-broadened line widths within the troposphere.

7.2 OBSERVATIONAL METHODS

The primary goal of observational microwave spectroscopy is to measure the signal response \( S(\nu) \) of an atmospheric molecular species and to convert \( S(\nu) \) into a brightness-temperature spectrum, \( T_b(\nu) \). From this point, it is possible to invert the \( \nu = \nu_1, \nu_2, \cdots \) set of integral equations represented by Eq. 7.7 for the unknown \( \alpha(\nu, h) \) which ultimately yields the number-density profile of the molecular species observed. Discussion of such inversions is treated in the following section. Here we briefly describe observational methods for measurement of \( S(\nu) \) and subsequent derivations of \( T_b^\tau(\nu) \) from these measurements.

7.2.1 Emission Measurements

In Figure 7.3, we reproduce from an earlier review of ground-based microwave spectroscopy of the middle atmosphere [19] an illustration of the two basic methods of middle-atmospheric microwave observations, the emission and absorption measurements. For the more widely applied emission observations, the antenna (typically, a small feed horn) is pointed at a fixed zenith angle on the sky. A zenith angle of 60–70° is usually chosen to maximize the path length of middle-atmospheric emission while maintaining acceptable tropospheric transmission. The observed signal \( S(\nu) \) is defined as an uncalibrated radiometer response to an input signal,

\[
S(\nu) = G(\nu) \left[ T_b^\tau(\nu)e^{-\tau_{TROP}/\mu} + (1 - e^{-\tau_{TROP}/\mu})T_{TROP} + T_{REC} \right]
\]  

(7.9)

where \( T_b^\tau(\nu) \), \( \tau_{TROP} \), and \( T_{TROP} \) are defined in Eq. 7.8. \( T_{REC} \) represents the internal receiver noise power as a receiver background brightness temperature. The system gain factor \( G(\nu) \) determines the scaling between the voltage units of \( S(\nu) \) and the
temperature units of $T_b^*(\nu)$, $T_{TROP}$, and $T_{REC}$. The frequency dependence of $G(\nu)$ reflects both channel-to-channel variations in the spectrometer detector sensitivities and broadband variability in the receiver output level.

For the purposes of removing the receiver background level, $T_{REC}$, and normalizing the frequency variations of $G(\nu)$, a reference continuum signal $S_{REF}(\nu)$ is measured:

$$S_{REF}(\nu) = G(\nu) (T_{REF} + T_{REC})$$

(7.10)

In practical terms, the antenna is alternately illuminated by the sky and a continuum reference, such as a noise tube. (Parrish et al. [17] describe an alternative allowing use of the sky itself as a reference, which is useful to minimize the degree of gain nonlinearity, as described in what follows.) Continuous “beam switching” between the reference and signal can be achieved by placing a chopper wheel in
front of the feed horn. The difference spectrum, \( S(\nu) - S_{\text{REF}}(\nu) \), is normalized by \( S_{\text{REF}}(\nu) \) to obtain

\[
\frac{S(\nu) - S_{\text{REF}}(\nu)}{S_{\text{REF}}(\nu)} = \frac{T^*_b(\nu) e^{-\tau_{\text{TROP}}/\mu} + (1 - e^{-\tau_{\text{TROP}}/\mu}) T_{\text{TROP}} - T_{\text{REF}}}{T_{\text{REF}} + T_{\text{REC}}} \tag{7.11}
\]

It is still necessary to determine \( \tau_{\text{TROP}} \), \( T_{\text{TROP}} \), \( T_{\text{REC}} \), and \( T_{\text{REF}} \) before \( T^*_b(\nu) \) can be derived from the observed difference spectrum of Eq. 7.11.

**Gain Nonlinearity**

In deriving Eq. 7.11, we have assumed a linear relationship between \( S(\nu) \) and \( T^*_b(\nu) \), as indicated in Eq. 7.9. In fact, the precise relationship between \( S(\nu) \) and \( T^*_b(\nu) \) is slightly nonlinear. From a signal-to-noise viewpoint, this nonlinearity can be very significant because the ratio of \( S(\nu) - S_{\text{REF}}(\nu) \) to \( S_{\text{REF}}(\nu) \) cannot completely remove the channel-to-channel variations in \( G(\nu) \). These residual variations in the spectral baseline contribute systematic channel-to-channel, noiselike spectral artifacts that do not decrease with increased integration time, as does the random noise generated within the receiver (see Eq. 1.26).

In order to minimize the effects of gain nonlinearity, it is necessary to maintain a very accurate balance between \( S(\nu) \) and \( S_{\text{REF}}(\nu) \). Rather than demonstrate this relationship between signal-reference balance and gain nonlinearity, we refer the reader to a detailed analysis by Parrish et al. [17]. Using a servomechanism to maintain constant balance between \( S(\nu) \) and \( S_{\text{REF}}(\nu) \) by adjusting the zenith angle of observation for \( S(\nu) \), Parrish et al. have developed highly optimized observing systems capable of measuring 276.9-GHz spectra of \( O_3 \) with signal-to-noise ratios in excess of 500.

**Calibration**

A calibrated determination of \( T^*_b(\nu) \) requires absolute determinations for \( T_{\text{REC}} \) and \( \tau_{\text{TROP}} \). A weighted mean tropospheric temperature can be adopted for \( T_{\text{TROP}} \). It is possible to obtain modest accuracy in the determination of \( \tau_{\text{TROP}} \) and \( T_{\text{REC}} \) and the ambient temperature for \( T_{\text{REF}} \) by measuring a “tipping curve” or “sky dip” [24]. Employing beam switching with a fixed reference signal, one observes the zenith-angle dependence of tropospheric continuum emission

\[
\frac{S_\nu(\mu) - S_{\text{REF}}}{S_{\text{REF}}} = \frac{T_{\text{TROP}}(1 - e^{-\tau_{\text{TROP}}/\mu}) - T_{\text{REF}}}{T_{\text{REF}} + T_{\text{REC}}} \tag{7.12}
\]

\( S_\nu(\mu) \) is the tropospheric continuum emission signal, \( \mu \) is the cosine of the zenith angle, and \( \tau_{\text{TROP}} \) is the normal \( (\mu = 1) \) tropospheric opacity. By assuming values for \( T_{\text{TROP}} \) and \( T_{\text{REF}} \), it is possible to solve Eq. 7.12 for \( \tau_{\text{TROP}} \) and \( T_{\text{REC}} \) from two or more observations at different \( \mu \).

Parrish et al. discuss more accurate calibrations for emission spectra using cold- and warm-temperature loads placed in front of the antenna (e.g., see Figure 1.12.
and Eq. 1.35). The resulting receiver voltage outputs are measured to obtain an accurate scaling between signal intensity (brightness temperature) and receiver output. This allows accurate measurements of $T_{REC}$ and $T_{TROP} (1 - e^{-\tau_{TROP}/\mu})$. A value for $\tau_{TROP}$ is derived by assuming a mean tropospheric temperature for $T_{TROP}$.

Parrish et al. [17] estimate that $2\sigma$ calibration accuracies of 12% are possible with such techniques.

**Frequency Switching**

In addition to beam switching to a reference continuum signal, it is also possible to switch the receiver LO frequency between two positions, $v + FS$ and $v - FS$. The difference spectrum of integrations between the two frequency settings can be normalized by a reference continuum signal $S_{REF}(v)$ in order to remove $G(v)$:

$$\frac{S(v - FS) - S(v + FS)}{S_{REF}(v)} = \frac{[T_b^*(v - FS)e^{-\tau_{TROP}/\mu} - T_b^*(v + FS)e^{-\tau_{TROP}/\mu}]}{T_{REF} + T_{REC}}$$

(7.13)

A frequency-switched spectrum exhibits optimum gain stability because the power level within the difference spectrum is minimized. Note also that $T_{TROP}(1 - e^{-\tau_{TROP}/\mu})$ and the continuum level of any external field, $T_c$ (Eq. 7.6), are automatically removed in a frequency-switched spectrum.

The middle-atmospheric emission term $T_b^*(v)$ appears as negative and positive emission lines separated by the frequency difference ($2FS$) between the two LO settings. Figure 7.4 presents such a frequency-switched spectrum for the mesospheric CO line. The major drawback of frequency switching is a limitation in the

*Figure 7.4* An emission spectrum (in brightness-temperature units) of the 230-GHz spectrum of CO, employing frequency switching.
constancy of the receiver gain \( G(\nu) \) when switching much more than 5–10 MHz. This makes it difficult to measure broad microwave lines with this technique. Nevertheless, many of the early microwave observations of \( \text{O}_3 \) employed frequency switching [8, 25].

### 7.2.2 Absorption Observations

Absorption measurements require observation of a continuum source above the Earth’s atmosphere in order to determine the transmission of the atmosphere across a microwave spectral line. Middle-atmosphere absorption measurements have been made using the Sun [24], the Moon [26], and Venus as background continuum sources. The weaker continuum sources, such as Venus, require radio-astronomy telescopes (~ 10 meters) to obtain sufficient continuum signal. All such extraterrestrial sources require astronomical tracking with the antenna. In spite of these added instrumental difficulties, microwave absorption measurements possess the advantage that they are self-calibrating.

Background subtraction for absorption measurements proceeds by differencing integrations with the antenna alternately pointed on and off the continuum source. Antenna pointing for the off spectra should be several antenna beamwidths offset in azimuth from the continuum source to ensure that none of the continuum signal is incorporated in the off spectra, and that the atmospheric path length remains constant between the on and off spectra. The individual on and off spectra are normalized by a reference continuum signal \( S_{\text{REF}} \) and then differenced:

\[
\Delta S(\nu) = \frac{S_{\text{ON}(\nu)} - S_{\text{OFF}(\nu)}}{S_{\text{REF}(\nu)}} = \frac{T_c e^{-r_{\text{TROP}}/\mu} \exp \left[ - \int_{h_0}^{\infty} \alpha(\nu, s) \frac{ds}{\mu} \right]}{T_{\text{REF}} + T_{\text{REC}}}
\]

(7.14)

Note that the atmospheric emission term of \( T^*_b(\nu) \) from Eq. 7.6 is removed in this difference spectrum.** One clear drawback with this difference spectrum is the inherent receiver power imbalance between the off and on spectra due to the continuum power of the external source in the on spectra (see the previous discussion of “gain nonlinearity”). This generally leads to poorer signal-to-noise ratios in absorption/emission spectra for a given integration period [27].

Equation 7.14 represents a transmission spectrum for a line opacity \( \tau(\nu) \) given by

\[
\tau(\nu) = -\int_{h_0}^{\infty} \alpha(\nu, h) \frac{dh}{\mu}
\]

(7.15)

*Some care must be taken to ensure that the atmospheres of continuum sources such as Venus and Mars do not contain interfering microwave absorption lines.

**We have assumed that the cosmic microwave background 3 K \(<\ T_c \) of the observed continuum source.
In the wings of the spectrum $\Delta S(\nu), \tau(\nu) \to 0,$ and

$$\Delta S_w \equiv \frac{S_{ON}(\nu_w) - S_{OFF}(\nu_w)}{S_{REF}(\nu)} \rightarrow \frac{T_c e^{-\tau_{TRP}/\mu}}{T_{REF} + T_{REC}} \quad (7.16)$$

Normalization of Eq. 7.14 by Eq. 7.16 leads to

$$\Delta S(\nu)/\Delta S_w = \exp \left[ - \int_{h_0}^{\infty} \alpha(\nu, s) \, ds / \mu \right] \quad (7.17)$$

Equation 7.17 represents an internally calibrated spectrum of the integrated line opacity of the observed species. Figure 7.5 presents such a self-calibrated absorption spectrum from Clancy et al. [27], employing the Moon as a continuum source. A more detailed analysis of the self-calibration of microwave absorption spectra can be found in Clancy et al. [27].

It is instructive to compare the atmospheric integral equations measured in emission spectra to the line-opacity integral equations described in Eq. 7.17 for absorption measurements. If we omit the small absorption term due to the cosmic microwave background, ($3 \,\text{K} \ll T(h)$), we can express the calibrated emission spectrum, $T_b^*(\nu)$, from Eq. 7.7, as follows.

$$T_b^*(\nu) = \int_{h_0}^{\infty} T(h) \exp \left[ - \int_{h_0}^{h} \alpha(\nu, s) \, ds / \mu \right] \alpha(\nu, h) \, dh / \mu \quad (7.18)$$

Figure 7.5 An absorption spectrum (in self-calibrated units of $\tau_{CO}$) of the 230-GHz spectrum of CO, observed in absorption against the Moon.
7.3 DATA-ANALYSIS TECHNIQUES

At first glance, the sets of integral equations defined for the emission (Eq. 7.18) versus the absorption (Eq. 7.17) measurement appear quite different. The emission measurement is, in fact, identical in form to pressure–temperature soundings of atmospheres at infrared and microwave frequencies. Temperature soundings require optically thick line opacities and an opacity source whose concentration profile within the atmosphere is very well known (see Chapter 4).

For middle-atmospheric spectroscopic observations, the unknown to be determined is the concentration or volume-mixing profile of the absorbing species. In order to include the unknown mixing profile more explicitly in our equations, we express the absorption coefficient, $\alpha(v, h)$, as the product of the unknown volume-mixing ratio profile, $X(h)$, and the absorption coefficient per unit volume mixing ratio, $\kappa(v, h)$:

$$\alpha(v, h) = \kappa(v, h)X(h)$$  \hspace{1cm} (7.19)

Hence, the absorption and emission integral equations become

$$\frac{\Delta S(v)}{\Delta S_w} = \exp \left[ - \int_{h_0}^{\infty} X(h) \kappa(v, h) \, dh / \mu \right]$$  \hspace{1cm} (7.20)

and

$$T_b^*(v) = \int_{h_0}^{\infty} X(h) T(h) \kappa(v, h) e^{-\tau(v, h)} \, dh / \mu$$  \hspace{1cm} (7.21)

respectively, where the partial transmission $e^{-\tau(v, h)}$ is defined by

$$\tau(v, h) = \int_{h_0}^{h} X(s) \kappa(v, s) \, ds / \mu$$  \hspace{1cm} (7.22)

Equations 7.20 and 7.21 represent a nonlinear set of integral equations due to the exponential dependence of the unknown, $X(h)$. However, microwave opacities of observed species in the middle atmosphere are invariably small such that

$$e^{-\tau(v, h)} \sim 1 - \tau(v, h)$$

For heuristic purposes, the absorption equations can be approximated as

$$\frac{\Delta S(v)}{\Delta S_w} \sim 1 - \int_{h_0}^{\infty} X(h) \kappa(v, h) \, dh / \mu$$
to illustrate the basically linear character of the set of equations represented by Eq. 7.20. In a similar manner, we approximate the transmission term in the emission equation (Eq. 7.21) as unity to show that a similar set of linear integral equations in $X(h)$ characterize the emission equation:

$$T^b_T(v) \sim \int_{h_0}^{\infty} X(h) T(h) \kappa(v, h) \, dh / \mu$$

A variety of inversion techniques have been applied to derive concentration profiles of molecular species from microwave spectra. Stable, well-behaved solutions for $X(h)$ depend on the kernels or weighting functions of the integral equations. The weighting functions of Eqs. 7.20 and 7.21 are primarily controlled by the pressure–frequency dependence of the microwave specific absorption coefficient, $\kappa(v, h)$.

### 7.3.1 Microwave Weighting Functions

Let us consider a specific example of a microwave emission line in order to demonstrate the information that can be retrieved from such a spectrum. In Figure 7.6, we present a synthetic emission spectrum of the 142.175-GHz rotational transition of ozone for zenith viewing ($\mu = 1$). The frequency scale is given in MHz from the line center. The units of intensity are calibrated brightness temperatures (K). As the optical depth of a given molecular species at a given frequency increases, the brightness temperature of the emission spectrum at that frequency approaches the physical temperature of the absorbing molecules (i.e., the atmospheric temperature). The line center opacity for this ozone transition is 0.095, assuming nom-
inal winter midlatitude values for the atmospheric ozone and pressure–temperature profiles (see Figure 7.1).

The determination of the ozone mixing profile from the emission spectrum of Figure 7.6 is facilitated by the specific altitude–frequency dependence of the specific absorption coefficient, $\kappa(\nu, h)$. As depicted schematically in Figure 7.7, individual pressure levels within the middle atmosphere contribute emission spectra whose line widths are proportional to the local atmospheric pressure (see Eq. 7.4). The emission brightness temperature at a given frequency offset from the line center is most sensitive to the concentration of the emitting molecule within the atmospheric pressure layer for which the half-width-half-maximum (HWHM) of the line emission roughly equals this frequency offset.

A more quantitative description of the concentration-profile information contained in microwave emission spectra can be obtained by considering the weighting functions for the ozone spectrum of Figure 7.6. The weighting functions are defined from Eq. 7.21 as

$$W(\nu, h) = T(h) e^{-\tau(\nu, h) \kappa(\nu, h) / \mu}$$

(7.23)

The altitude dependence of $W(\nu, h)$ for a selection of frequency offsets from line center is presented in Figure 7.8. The observed signal $T_b(\nu)$ is given by the altitude integral of the product $X(h) W(\nu, h)$, where $W(\nu, h)$ is given in units of K/ppmv-km.

---

**Figure 7.7** Schematic of the collisional and Doppler line-shape dependence of microwave spectral lines within the stratosphere and mesosphere. Line widths increase to greater than 500 MHz in the lower stratosphere, but remain constant and less than 1 MHz within the mesosphere.
Figure 7.8 Weighting functions computed for the 142-GHz spectrum of O\textsubscript{3} (Figure 7.6). The nadir brightness temperature at a given frequency from line center \((v - v_0)\) is equal to the altitude integral of the product of the appropriate weighting function and the atmospheric temperature profile (Figure 7.1).

For example, the observed brightness temperature at a frequency 20 MHz from line center \((v_{#5}\) in Figure 7.8), is most sensitive to the average ozone mixing ratio below 35-km altitude. Ozone above 40-km altitude contributes almost no signal to the brightness temperature at this frequency. Similarly, the brightness temperature at line center \((v_{#14}\) in Figure 7.8) is sensitive to the entire ozone-mixing profile below 70–80 km altitude. The secondary maxima in the weighting functions near line center \((v_{#10-14}\) are a consequence of the transition between the relative importance of collisional and thermal broadening near the line center for altitudes above \(\sim 50\) km.

Although the weighting functions of Figure 7.8 present all of the fundamental information that the spectral line measurement contains on the altitude distribution of ozone, it is useful to construct weighting functions that peak at distinct altitudes. Such weighting functions are more commonly presented because they are amenable to the Chahine-type inversion methods (see the next section). Altitude-peaked weighting functions from ground-based microwave observations can be formed by reconstructing the measurements as brightness temperature differences between frequency pairs. It is clear from Figure 7.8 that the difference between brightness temperatures at \(v_{#5}\) and \(v_{#6}\) is most sensitive to the ozone mixing ratio between 35- and 40-km altitude. In Figure 7.9, we present these "difference" weighted functions for the ozone spectrum of Figure 7.6 versus brightness temperature differences \([BT(v_1) - BT(v_2)]\) at frequencies \(v_1\) and \(v_2\).
Figure 7.9 Weighting functions computed for differential emission of the 142-GHz transition of O$_3$. The difference in the nadir brightness temperatures of two frequency offsets from line center is equal to the altitude integral of the product of the appropriate difference weighting function and the atmospheric temperature profile (Figure 7.1).

Several important features of ground-based microwave observations are apparent in these difference weighting functions. Firstly, the weighting functions exhibit distinct maxima as a function of the frequency difference. The differential line emission between the frequency pairs is most sensitive to the unknown, $X(h)$, at a particular altitude. This ensures that the emission integral equations (Eq. 7.21) can be solved for $X(h)$ over the altitude range for which the weighting functions are relatively independent of one another, given sufficient signal/noise in the measurement. Secondly, the weighting functions tend to converge to a frequency-independent profile for $\nu - \nu_0 < 200$ KHz, indicating that the altitude dependence of $X(h)$ above 70 km is not well determined by the observations. This follows because the frequency dependence of $\kappa(\nu, h)$ above 70 km is no longer pressure-dependent; the emission line widths are set by Doppler rather than pressure broadening. Thirdly, the amplitudes of the brightness temperature differences $[BT(\nu_1) - BT(\nu_2)$ in Figure 7.10] decrease rapidly above $\sim 60$ km and below $\sim 25$ km, requiring greater signal-to-noise ratios in the line center and wings in order to achieve comparable accuracy in the derivation of $X(h)$ in these regions. Furthermore, for altitudes below $\sim 25$ km, the difference frequencies become widely separated. Hence, $X(h)$ at these altitudes becomes increasingly sensitive to small, systematic uncertainties in the low-order frequency dependence of the system calibration over the measurement bandpass (i.e., curvatures in the spectral baselines).
Figure 7.10  Narrowband microwave spectra of nighttime (squares, fitted by a dashed line) and daytime (triangles, fitted by a solid line) emission about the line center of the 142-GHz O₃ transition. The enhanced nighttime emission near the line center indicates a nighttime increase in mesospheric ozone (reprinted from Lobsiger and Kunzi [43]).

It is this aspect of ground-based microwave spectroscopy that generally sets a limit of ~20–25 km for the lowermost altitude of information retrieval.

Finally, it is instructive to derive a measure of the altitude resolution of $X(h)$ that can be retrieved by analysis of microwave spectra. Results of a simple least-squares inversion (see the next section) of the synthetic ozone spectrum in Figure 7.6 for the mixing profile of O₃ between 25 and 75 km are presented in Table 7.1. The formal 1σ errors in the ozone mixing ratio at 37-km altitude are indicated versus the vertical resolution of the O₃ profile specified in the inversion. Notice that the errors increase dramatically for altitude resolutions less than 6–8 km. The specific errors listed in Table 7.1 assume a 1σ error of 0.1 K in the measured brightness temperature spectrum of the 142.175-GHz transition of ozone.

This result is consistent with more rigorous studies of the altitude resolution afforded by ground-based microwave spectroscopy [28–30]. An optimum resolution of 6–8 km, or approximately one atmospheric pressure scale height, can be achieved for signal-to-noise ratios of ~100. Vertical resolution degrades to poorer

<table>
<thead>
<tr>
<th>Vertical Resolution (km)</th>
<th>% Error (1σ) in 37-km O₃ Mixing Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>$\gg 100$</td>
</tr>
<tr>
<td>4</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
</tr>
</tbody>
</table>
than 10 km in the lower mesosphere as the line shape approaches the thermal line shape.

7.3.2 Iterative Inversion Solutions

Two separate approaches to the solution of the integral equations, Eqs. 7.20 and 7.21 have been followed by various workers. An approximate, mean-valued solution, developed by Chahine [31], adopts an optimized set of weighting functions from the integral kernels, which are assumed to map a one-to-one relationship between a solution set, \( X(h_j) \), and a brightness-temperature set, \( T_b(\nu_j) \).* Hence the integral equations (Eq. 7.21) become

\[
T_b(\nu_i) = \sum_{j=1}^{N} W(\nu_i, h_j) X(h_j) \quad (i = 1, N) \quad (7.24)
\]

An initial guess for the solution, \( X^0(h_{j=1,N}) \) is inserted in Eq. 24 to calculate a first approximation to the observations, \( T_b^0(\nu_j) \). The initial solution is adjusted by the ratio of the observed to the approximated brightness temperatures:

\[
X^1(h_j) = X^0(h_j)[T_b(\nu_j)/T_b^0(\nu_j)] \quad (j = 1, N) \quad (7.25)
\]

The iterative application of Eq. 25 produces a solution \( X^n(h_j) \), which converges to \( X(h_j) \) as \( T_b^0(\nu_j) \) converges to \( T_b(\nu_j) \). The continuous solution \( X(h) \) is derived from interpolation of the discretized solution, \( X(h_j) \). Such a simple solution algorithm works because the frequencies \( \nu_j \) and the altitudes of solution \( h_j \) have been chosen to make the weighting function matrix \( W_{ij} \) nearly diagonal. However, there are several drawbacks to this algorithm. Only a small portion of the full observational set of frequencies is actually used in the solution, as the dimensions of the vectors \( X \) and \( T_b \) are required to be equal. Furthermore, if the weighting-function matrix is not sufficiently diagonal or if it depends too strongly on the solution (due to the nonunity transmission term, for example), then this iterative solution may not converge to a proper solution. Both of these drawbacks are alleviated to a large degree by modifications in the iterative multipliers in Eq. 7.25, as suggested by Twomey [32],

\[
M^a_i = 1 + \gamma W(\nu_i, h_j)[T_b(\nu_i)/T_b^0(\nu_i) - 1] \quad (7.26)
\]

\[
X^n(h_j) = X^{a-1}(h_j) \prod_{i=1}^{R} M^a_i \quad (j = 1, N; R \geq N) \quad (7.27)
\]

A normalization constant \( \gamma \) for the weighting functions can be adjusted to balance the stability and speed of the solution convergence. Equations 7.26 and 7.27

*In order to simplify notation in the following discussion, we have dropped the asterisk from the brightness temperature, \( T_b^*(\nu) \).
do not require equal dimensions for the vectors $X(h_j)$ and $T_p(\nu_i)$, and, as such, require no *a priori* selection of weighting functions based upon the solution vector $X(h_j)$.

### 7.3.3 Matrix-Inversion Solutions

Matrix-inversion solutions for the set of integral equations (Eq. 7.21) are often applied in analysis of middle-atmospheric spectroscopic observations. It is customary to express the integral equations in matrix notation as

$$T_{bi} = \sum_{j=1}^{M} A_{ij} E_j \quad (i = 1, N) \quad (7.28)$$

where we have expressed the solution $X(h)$ in terms of a set of basis functions, $b_j(h)$:

$$X(h) = \sum_{j=1}^{M} E_j b_j(h) \quad (7.29)$$

$$A_{ij} = \int_{h_0}^{\infty} W(\nu_i, h) b_j(h) \, dh \quad (7.30)$$

By representing the solution as a sum of basis functions, we define a solution that is continuous in altitude even though the solution vector $E_j$ is finite. Square-step (i.e., constant layers), linear [33], and exponential [26] basis functions have been used in the application of Eq. 7.29 to microwave emission spectra. For $M = N$, Eq. 7.28 can be directly inverted for a solution:

$$E_j = \sum_{i=1}^{N} A_{ij}^{-1} T_{bi} \quad (7.31)$$

However, for all practical applications, $A_{ij}^{-1}$ is overwhelmingly singular. That is to say, there are far fewer pieces of information on $X(h)$ contained in the observations than there are brightness temperature measurements, $T_{bi}$. The ozone spectrum of Figure 6 may contain several hundred spectral intervals, but as the weighting functions of Figure 7.9 indicate, there are only 5 to 10 independent measurements of $X(h)$ that can be retrieved.

One of the consequences of specifying too large a dimension $M$ for $E_j$ is that the solution $X(h)$ becomes unacceptably sensitive to noise in the measurements $T_{bi}$. This behavior can be quantified by consideration of the contribution functions $C_i(h)$ of the solution [30]:

$$C_i(h) = \sum_{j=1}^{M} A_{ij}^{-1} b_j(h) \quad (7.32)$$
The derived solution can then be expressed in terms of the contribution functions as

$$X(h) = \sum_{i=1}^{N} C_i(h) T_{bi}$$  (7.33)

Hence, noise variances $\sigma^2$ in the observations $T_{bi}$ are amplified in the solution by

$$C^2(h) = \sum_{i=1}^{N} C_i^2(h)$$  (7.34)

### 7.3.4 Constrained Matrix-Inversion Solutions

With the condition that $M < N$, the system of equations (Eq. 7.28) is overdetermined such that a direct solution is no longer attainable. It becomes necessary to specify minimization of some functional of the solution in order to proceed with inversion of Eq. 7.28. The most straightforward constraint requires that the sum of the squared residuals between the observed $T_{bi}$ and the computed $T_{bi}$ be a minimum,

$$\frac{\Delta}{\Delta E_j} \sum_{i=0}^{N} \left( T_{bi} - \sum_{j=1}^{M} A_{ij} E_j \right)^2 = 0 \quad (j = 1, M)$$  (7.35)

In vector notation, the solution of Eq. 7.35 is given by

$$E = (A^T A)^{-1} A^T T_b$$  (7.36)

where $E$, $T_b$, and $A$ represent the arrays $E_j$, $T_{bi}$, and $A_{ij}$, respectively, and $A^T$ is the transpose, $A_{ji}$, of $A_{ij}$. Solution (Eq. 7.36) is called the least-squares solution, providing the best possible fit to the data.

There is a variety of other functionals of the solution one may wish to minimize. A particularly useful solution developed by Twomey [33] combines minimization of the sum of the squared derivatives of the solution with the least-squared residuals constraint. Minimization of the derivatives of the solution essentially constrains the smoothness of the solution. Application of Twomey's algorithm requires that the basis functions $b_i(h)$ are constant-layer or linear in $h$ such that the altitude derivatives of the solution can be expressed by the vector

$$\Delta E_j = E_{j+1} - E_j \quad (j = 1, M - 1)$$  (7.37)

We can then express the sum of the squared derivatives of the solution as

$$\Delta^2(E) = E^T D E$$  (7.38)
where $\mathbf{E}^T$ is the transpose of the solution vector $\mathbf{E}$ and $\mathbf{D}$ is the $M \times M$ derivative matrix:

$$
D = 
\begin{bmatrix}
1 & -1 & 0 & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\
-1 & 2 & -1 & 0 & \cdots & \cdots & \cdots & \cdots & \cdots \\
0 & -1 & 2 & 1 & 0 & \cdots & \cdots & \cdots & \cdots \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\cdots & \cdots & \cdots & \cdots & 0 & -1 & 2 & -1 & 0 \\
\cdots & \cdots & \cdots & \cdots & 0 & -1 & 2 & -1 & 1 \\
\cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots & \cdots
\end{bmatrix}
$$

(7.39)

The Twomey method minimizes the functional

$$
F(\mathbf{E}(h)) = [\mathbf{T}_b - \mathbf{A}\mathbf{E}]^2 + \epsilon \mathbf{E}^T \mathbf{D} \mathbf{E}
$$

(7.40)

where $\epsilon$ is an arbitrary constant that can be varied to optimize the solution with respect to minimum derivatives (large $\epsilon$) or minimum residuals to the data (small $\epsilon$).

The solution for (Eq. 7.40) is given by

$$
\mathbf{E} = (\mathbf{A}^T \mathbf{A} + \epsilon \mathbf{D})^{-1} \mathbf{A}^T \mathbf{T}_b
$$

(7.41)

This solution is easily extended to the minimization of higher-order derivatives of the solution [33].

Two other minimization problems bear mention, although we refer the reader to appropriate references rather than attempt to present their solutions here. The Backus-Gilbert method [34] can be used to optimize the solution with regard to maximum vertical resolution and minimum noise amplification (i.e., minimize the sum of the squares of the contribution functions, $C_i$, Eq. 7.32) at a particular altitude. This method has been adapted to atmospheric sounding [33], and has been applied to the 22-GHz mesospheric water line [28]. The “most probable,” or optimal estimation solution can be used for cases in which the unknown mixing profile can be characterized by an $a$ priori probability distribution. Such a solution returns the most probable profile based upon input Gaussian probability distributions for the measurements and the solution [35]. This technique is particularly adaptable to ozone studies, as a large amount of information on the distribution and variability of middle-atmospheric ozone has been accumulated in the past two decades.

### 7.4 MIDDLE-ATMOSPHERE OBSERVATIONS

A variety of microwave spectra of middle atmospheric species has been observed, particularly in the last decade. A large subset of these observations is unique in
that the science returned would be unavailable without microwave observations. We present a general survey of the major molecular species of the middle atmosphere that have been measured using ground-based microwave spectroscopy. We also provide brief descriptions of the scientific applications of the individual measurements. The wide range of altitudes and physical quantities associated with the microwave observations leads to a rewarding diversity of middle-atmospheric processes that can be studied.

7.4.1 \( \text{O}_3 \)

As indicated in Figure 7.1, the altitude profile of \( \text{O}_3 \) mixing in the middle atmosphere exhibits a fairly complex structure. The photochemistry of \( \text{O}_3 \) changes considerably throughout the stratosphere and mesosphere due to distinct altitude dependencies in the photolysis rates of \( \text{O}_3 \) and \( \text{O}_2 \) and in the dominant chemical reactions that balance the production and loss of \( \text{O}_3 \) [36]. Between altitudes of \( \sim 40 \) and 80 km, the photochemical lifetime of \( \text{O}_3 \) is relatively short (\( \leq 2 \) h) such that the \( \text{O}_3 \) abundance is controlled primarily by the local chemical composition and radiation field. As a result, if one obtains measurements of the key molecular species (such as \( \text{H}_2\text{O}, \text{HO}_2, \text{ClO}, \text{NO}_2 \)) in this altitude region, it is possible to predict \( \text{O}_3 \) abundances with relatively simple one-dimensional photochemical models [37]. One of the strong advantages of microwave spectroscopy is the ability to measure many of these species, including \( \text{O}_3 \), from the ground. For altitudes above \( \sim 80 \) km and below \( \sim 40 \) km, the photochemical lifetime of \( \text{O}_3 \) becomes long enough to allow the local \( \text{O}_3 \) abundance to be seriously affected by horizontal and vertical transport of \( \text{O}_3 \). For these regions, it is necessary to employ far more complex two- and three-dimensional dynamical-photochemical models to predict the distribution of \( \text{O}_3 \) [38, 39].

Microwave observations of middle-atmospheric \( \text{O}_3 \) have been carried out at a number of frequencies, including 101.7 [8], 110.8 [9], 142.2 [40], 206.1 [41], and 276.9 [42] GHz. The mixing profile of \( \text{O}_3 \) and the transition strengths of \( \text{O}_3 \) microwave lines lead to fairly strong line emission throughout the stratosphere and mesosphere. Typical brightness temperatures of \( \text{O}_3 \) emission spectra range from 5 to 25 K at the line center. Observing systems are generally designed to determine the stratospheric ozone profile using broadband (250–500-MHz) spectrometers with coarse spectral resolution (1–2 MHz) or to determine the mesospheric ozone distribution using narrowband (5–20-MHz) spectrometers with fine spectral resolution (50–250 KHz). Fairly automated observing systems with dual spectrometers have been operated to measure both fine- and coarse-resolution spectra of \( \text{O}_3 \) [40].

In Figure 7.10, we present the narrowband \( \text{O}_3 \) spectra of Lobsiger and Kunzi [43], in which separate spectra of day and night mesospheric \( \text{O}_3 \) were measured. The difference in the day and night spectra indicates the diurnal variation of \( \text{O}_3 \) that occurs in the mesosphere (Figure 7.11). The diurnal variation of ozone results from the recombination of \( \text{O}_3 \) from \( \text{O} \) and \( \text{O}_2 \), which is no longer balanced by the reverse process of photodissociation of \( \text{O}_3 \) into \( \text{O} \) and \( \text{O}_2 \) in the nightside atmosphere. This imbalance leads to a diurnal variation of \( \text{O}_3 \) above \( \sim 50 \)-km altitude,
where the daytime abundance of O is sufficient to contribute a noticeable increase in the nighttime O\textsubscript{3} abundance [44, 45].

We present, in Figure 7.12, broadband spectra of O\textsubscript{3} measured at McMurdo Station, Antarctica, in the austral springtime of 1986. These high signal-to-noise measurements by Connor et al. [42] were analyzed to retrieve O\textsubscript{3} mixing ratios to as low as 23-km altitude. The distinction between the two spectra presented in Figure 7.12 reflects the difference between high- and low-latitude stratosphere ozone abundances. The stronger of the two emission lines was observed on September 23 when the polar vortex above McMurdo Station was displaced by a lower-latitude airmass [42]. The increased emission between ±50 MHz of line center is a consequence of ozone mixing ratios of 6–8 ppm at altitudes between 25 and 40 km (such as in Figure 7.11). The weaker emission spectrum was observed on September 20, when the winter polar vortex remained over McMurdo Station. The polar vortex acts to confine stratospheric air near the winter poles (≥ 70S, N) and leads to much reduced stratospheric ozone abundance (i.e., 4–5 ppm at 20–40-km altitude) [36, 42]. Connor et al. employed a time series of such O\textsubscript{3} observations during the development of the Antarctic ozone hole in 1986 to demonstrate that the Antarctic ozone hole (which is a separate phenomenon) does not extend sig-

![Figure 7.11](image_url)
7.4 MIDDLE-ATMOSPHERE OBSERVATIONS

7.4.2 H\textsubscript{2}O

The mixing ratio of water vapor in the middle atmosphere is controlled by only a few processes. Very low temperatures at the equatorial tropopause act as a cold trap to restrict transport of water from the wet troposphere into the dry middle atmosphere. Stratospheric water mixing ratios typically range between 4 and 7 ppm, and exhibit a $\sim 50\%$ increase between 30 and 60 km due to chemical formation of water vapor from the photolysis products of CH\textsubscript{4} in the upper stratosphere. Above 70–75-km altitude, the water mixing ratio begins to decline due to photolysis of H\textsubscript{2}O by solar Lyman alpha flux. The photochemical lifetime of H\textsubscript{2}O throughout the middle atmosphere is $\geq$ month, such that its variability is dominated by transport. As indicated in Figure 7.13, existing ground-based observations of the 22.2-GHz rotational transition of H\textsubscript{2}O return information on the water mixing profile between approximately 50 and 85 km [46].

The 22-GHz emission spectrum for H\textsubscript{2}O is quite weak due to the frequency-squared dependence of the microwave absorption coefficient (e.g., Eq. 2.16). Notice that the line-center brightness temperature of a typical 22-GHz H\textsubscript{2}O emission line, such as presented in Figure 7.14 [47], is approximately 100 times smaller than for the mesospheric CO line (cf Figure 7.4). To date, 22-GHz H\textsubscript{2}O observations have employed narrow bandwidths ($< 10$ MHz) such that water mixing ratios below 50 km have not been measured by this technique. However, this restriction should be removed in the near future. Furthermore, the 22-GHz frequency results in a very narrow Doppler line width ($\sim 20$ KHz, as compared to
Figure 7.13  Mesospheric water mixing profiles derived from various microwave observations of the 22-GHz transition of H₂O (reprinted from Tsou et al. [46]).

Figure 7.14  Emission spectrum of the 22-GHz transition of H₂O, observed by Bevilacqua et al. at the Jet Propulsion Laboratory in Pasadena, California. The spectrum represents 24 h of integration and has been folded about the line center (reprinted from Bevilacqua et al. [47]).
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~200 KHz for the 230-GHz CO line). As a result, one is able to derive profile information from the collisional line shape to higher altitudes.

Synoptic observations of the mesospheric water line have provided unique information on the seasonal variability of vertical transport in the mesosphere [47, 48]. Upper mesospheric water abundances appear to exhibit annual variability due to the annual variation in vertical advection. Maximum water mixing ratios are observed in winter, minimum values in summer [48]. Mesospheric water vapor plays a major role in mesospheric ozone photochemistry. Photolysis of water vapor in the mesosphere provides the major source for odd hydrogen (OH, HO₂, H), which is the major agent for catalytic destruction of ozone in the mesosphere [36]. Finally, it is worth noting that a much stronger microwave H₂O transition that occurs at 183 GHz has been observed (Waters et al. [49] profile in Figure 7.13, see Chapter 8). However, very low atmospheric transmission due to tropospheric water vapor (Figure 7.2) requires observation of this H₂O transition from aircraft or balloonborne instrumentation. Alternatively, the mesospheric distribution of water can be inferred from weak microwave lines of H₂¹⁸O and HDO, which have recently been observed by the authors.

7.4.3 CO

The CO molecule exhibits a vertical mixing profile that is controlled by two very different production mechanisms in the terrestrial atmosphere. As indicated in Figure 7.15, CO mixing ratios reach maxima in the troposphere and thermosphere, where the primary production sources are oxidation of biologically produced methane and photolysis of CO₂, respectively. Low CO mixing ratios between 20- and 60-km altitude are due to relatively high CO recombination rates, slow CO production rates, and very slow vertical eddy diffusion in the stratosphere [50, 51]. The rapid decline of CO mixing ratios below 60 km leads to a very narrow microwave line for CO (see Figures 4 and 5).

A diverse set of emission and absorption observations of mesospheric CO has been obtained since the initial measurement by Waters et al. [11] in 1976. Measurements of the 115-GHz and 230-GHz rotational transitions of CO have been analyzed to return limited information on the CO mixing profile in the 60–75-km altitude range, and for the column of CO between 75 and 90 km [26, 52]. A measurement of the 691-GHz transition of CO allows inference of the CO mixing profile down to ~50-km altitude, due to the higher opacities encountered at this frequency [53]. Several of the mesospheric CO profiles derived from ground-based microwave observations are included in Figure 7.15 [54].

A time dependence in the intensity of the mesospheric CO line has been observed, and interpreted in terms of seasonal variability of vertical advection in the mesosphere [26, 27]. The relatively long photochemical lifetime of mesospheric CO (~ month) leads to its sensitivity to dynamical transport in the mesosphere. The average seasonal variation of mesospheric CO can be described by roughly a factor of two enhancement in the winter midlatitude CO column relative to the summer column. The mesospheric CO column also exhibits comparable variations
Figure 7.15 A compendium of atmospheric CO mixing profiles derived from ground-based microwave (above 50 km) and balloonborne infrared (below 50 km) spectral observations. The altitude range of microwave retrievals is approximately 50–80 km (reprinted from Solomon et al. [54]).

during periods of winter planetary-wave activity. In Figure 7.16, we show the mesospheric column density inferred from lunar absorption 230-GHz spectra on January 24, 25, and 29 of 1982. The abrupt increase in the CO column between the 25th and the 29th coincides with the descent of air from the winter polar vortex over the Kitt Peak observing site [54]. This particular event also increased the width of the CO line due to unusually large CO abundances between 55 and 65 km [55].

7.4.4 ClO

The fundamental importance of the ClO species lies in its ability to catalytically destroy the O₃ molecule with remarkable efficiency, and because its atmospheric abundance is rapidly rising due to anthropogenic activities. The overall Cl budget of the middle atmosphere is predicted to increase by $\sim 4\%$ /yr in the foreseeable future due to worldwide industrial production of chlorofluorocarbons (CFCs). Throughout most of the middle atmosphere, the bulk of the Cl budget is tied up in relatively inert forms (such as HCl and ClONO₂). However, in the upper stratosphere, a significant amount of the active Cl₂ species, ClO and Cl, are present to contribute $\sim 30\%$ of the total O₃ destruction in this region. The continuing increase in CFCs will lead to a long-term decrease in upper stratospheric ozone (as much as $\frac{1}{2}\%$ /yr) [1, 4, 36].
Microwave observations provide the primary technique for ground-based measurement of the middle-atmospheric CIO profile. Microwave transitions of stratospheric CIO have been observed at 204.4 [12, 56] and 278.6 [57, 58] GHz. We present the Solomon et al. [56] 1982 measurement of the 278.6-GHz transition versus local time in Figure 7.17. Note that the emission is quite weak (line center $T_b \sim 0.05$ K), that the line is also fairly broad and that it is diurnally dependent. In Figure 7.18, we also reproduce from Solomon et al. [56] the model profiles of Ko and Sze [59] (solid lines) and Froidevaux et al. [37] (dashed lines). CIO profiles for local times of 4 A.M. and 2 P.M. are provided to indicate the predicted diurnal variation in stratospheric CIO. The diurnal variation is driven by formation of the ClONO$_2$ species, which is a stable reservoir for Cl, in the nighttime when ClONO$_2$ photolysis is absent. The daytime abundance and diurnal behavior of the CIO line emission are roughly consistent with the the model CIO profiles of Figure 7.18; the nighttime CIO line emission in Figure 7.17 is down by almost an order of magnitude from the daytime emission.

More recently, microwave observations of CIO in the Antarctic lower stratosphere have provided invaluable information on the causes of the Antarctic ozone hole. Leading theories for the causes of the springtime depletion of Antarctic ozone [2] involve heterogeneous release of the active CIO species in the lower stratosphere [3]. Under normal conditions almost all of the lower stratospheric Cl budget is tied up in the inert HCl and ClONO$_2$ species. However, widespread polar stratospheric aerosols during the Antarctic winter appear to trigger decomposition of HCl and ClONO$_2$, releasing large amounts of Cl [3]. The details of this heterogeneous chemistry are complex and still remain uncertain, but several key predic-
Figure 7.17 A 24-h sequence of emission spectra of the 278.6-GHz transition of ClO. These observations were obtained by Solomon et al. [56] at Mauna Kea Observatory in December 1982. The apparent diurnal variation in the line intensity and width reflects diurnally dependent partitioning of stratospheric Cl, (reprinted from Solomon et al. [56]).

Figure 7.18 Model predictions by Ko and Sze [59] (solid lines) and Froidevaux et al. [37] (dashed lines) for the diurnal dependence of the stratospheric mixing profile of ClO. Separate profiles are given for local times of 4 A.M. and 2 P.M. (reprinted from Solomon et al. [56]).
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Tions of this chemistry are supported by microwave observations of Antarctic springtime ClO profiles. In Figure 7.19, we present a 278.6-GHz emission spectrum of ClO observed at McMurdo Station, Antarctica, in the austral spring of 1986 [57, 58]. Notice the presence of broad emission shoulders, which are not present in the Mauna Kea spectrum [56], also indicated in Figure 7.19. De Zafra et al. [60] repeated the Antarctic ClO observations during the austral spring of 1987, obtaining a larger bandwidth and improved diurnal coverage. Figure 7.20 presents both the altitude and diurnal dependence of ClO within the Antarctic ozone hole based upon these 1987 microwave observations [60]. Note the presence of a large lower stratospheric enhancement in daytime ClO abundances (peak \( \sim 1.6 \text{ ppbv} \)) in addition to the normal upper stratospheric peak (peak \( \sim 1.0 \text{ ppbv} \)) near 35–40 km [58]. It is this lower stratospheric enhancement in ClO that leads to the broadened microwave line for ClO in the Antarctic ozone hole. The Antarctic microwave observations of ClO indicate distinct seasonal [57] and diurnal [58, 60] variations in the lower stratospheric ClO layer, which are generally consistent with model predictions of the Antarctic ozone hole.

7.4.5 \( \text{N}_2\text{O} \) and NO

The profile of atmospheric \( \text{N}_2\text{O} \) is controlled by production at the Earth’s surface, vertical transport from the troposphere into the middle atmosphere, and photolytic destruction in the stratosphere. Biologically driven nitrification and denitrification processes in surface soils provide the major source of atmospheric \( \text{N}_2\text{O} \), although as much as 25% of \( \text{N}_2\text{O} \) production is associated with industrial and agricultural activities [36]. The \( \text{N}_2\text{O} \) molecule is a fairly long-lived species in the troposphere and lower stratosphere, where it serves as a useful indicator of vertical transport rates. \( \text{N}_2\text{O} \) is also a key ingredient in the photochemical cycle of middle-atmospheric \( \text{O}_3 \) because chemical decomposition of \( \text{N}_2\text{O} \) in the stratosphere provides the sole source for atmospheric \( \text{NO}_x \) compounds. The active \( \text{NO}_x \) species, NO and \( \text{NO}_2 \), dominate the photochemical destruction of \( \text{O}_3 \) within the middle and lower stratosphere, where the bulk of atmospheric \( \text{O}_3 \) resides. \( \text{N}_2\text{O} \) also plays a minor

\[
\begin{align*}
\frac{\text{Channel \# MHz}}{0} & \quad \frac{\text{Frequency resolution corresponding to a single channel is 1 MHz (figure supplied by R. L. de Zafra).}}{0.00} & \quad \frac{0.05}{} & \quad \frac{0.10}{} & \quad \frac{0.15}{} \\
0 & \quad 100 & \quad 200 & \quad 300 \\
\end{align*}
\]

\textbf{Figure 7.19} A comparison of the midday 278-GHz spectrum of ClO as observed at Mauna Kea (19°N, lower spectrum) in December 1982 [56], and at McMurdo Station (78°S, upper spectrum) within the Antarctic ozone hole of 1986 [57, 58]. The presence of very broad emission wings in the Antarctic ozone hole indicates \( >100 \) times the normal ClO abundance at 20-km altitude. The frequency resolution corresponding to a single channel is 1 MHz (figure supplied by R. L. de Zafra).
Figure 7.20 The diurnal and altitudinal dependencies of the stratospheric mixing profile of ClO within the Antarctic ozone hole as inferred from 1987 observations of the 278-GHz spectrum of ClO at McMurdo Station, Antarctica [60]. The local time is binned at intervals of (a) (2–0 h before sunrise), (b) (0–2 h after sunrise), (c) (2–4 h after sunrise), ... , (j) (0–2 h after sunset). The large enhancement of ClO at 20 km, which is not present under normal stratospheric conditions (cf. Figure 7.18), results from heterogeneous decomposition of HCl on polar stratospheric cloud particles [3] (reprinted from de Zafra et al. [60]).

but important role as a greenhouse gas within the stratosphere. The atmospheric content of N₂O is enormous relative to the Cl budget, such that anthropogenic activity leads to smaller percentage changes in this important atmospheric constituent.

Microwave spectra of middle atmospheric N₂O from Connor et al. [14] are presented in Figure 7.21. These 276.3-GHz spectra were measured from Mauna Kea in June 1983 and in May and June 1986. They were inverted for N₂O mixing profiles, which are generally consistent with model [61, 62] and infrared satellite observations [62], as indicated in Figure 7.22. A much more surprising result is that obtained by Parrish et al. [63] from N₂O 276.3-GHz observations at McMurdo Station, Antarctica, during the austral spring of 1986. Parrish et al. provide a comparison between their Antarctic spectrum and the Connor et al. Mauna Kea observation, which is reproduced in Figure 7.23. The column of N₂O is apparently down by at least a factor of 10 above 25 km in the Antarctic springtime. This phenomenon is not directly related to development of the ozone hole, which occurs at lower altitudes, but is presumably tied to downward advection within the winter polar vortex [63].

At the very top of the middle atmosphere, the combined effects of solar x-ray flux and ion chemistry produce a distinct layer of lower thermospheric (90–180 km) NO [64]. Previous observations of lower-thermospheric NO have required

Figure 7.21 Four separate emission spectra of the 276.3-GHz transition of N₂O observed on May 23 and June 2, 3, and 6, 1986, at Mauna Kea Observatory by Connor et al. [14]. The variability among the spectra is estimated to be twice the calibration uncertainties, hence, indicative of true N₂O variability (reprinted from Connor et al. [14]).
ultraviolet instruments carried either on rockets or spacecraft. Recently, Clancy et al. [16a] observed the 250.8-GHz spectrum of NO, which is presented in Figure 7.24. The Gaussian line shape and the \( \sim 300 \text{ K} \) thermal line width of this NO line and the diurnal invariability of the NO emissions were analyzed to identify the 250.8-GHz NO emission with the lower thermospheric NO layer [16a]. A significant feature of lower-thermospheric NO is its extreme sensitivity to solar-cycle variations. Spacecraft ultraviolet observations indicate that the peak NO density varies by a factor of 10, apparently due to large solar-cycle variability in coronal x-ray flux [64]. More recent microwave NO observations during the 1991–1992 solar maximum also indicate an order-of-magnitude variation in the 255.8-GHz NO emission, which correlates well with 27-day solar-cycle variations. We also note that the microwave NO line does not exhibit Zeeman splitting as might be

Figure 7.22 A comparison of the stratospheric \( \text{N}_2\text{O} \) mixing profile retrieved from the range of \( \text{N}_2\text{O} \) emission spectra [14] in Figure 21 (shaded region); modeled by Jones and Pyle [62] (long dashed); modeled by Ko et al. [61] (short dashed); and observed by the SAMS satellite experiment (solid line) [61] (reprinted from Connor et al. [14]).

Figure 7.23 A comparison of the \( \text{N}_2\text{O} \) 276.3-GHz spectrum as observed at Mauna Kea [14] (upper line) and observed at McMurdo Station (lower line) within the Antarctic ozone hole of 1986 [63]. The channel width is 1 MHz. The decrease in Antarctic \( \text{N}_2\text{O} \) above 25 km (i.e., above the ozone hole) must be at least a factor of 10 within the springtime polar region relative to low latitudes to account for the difference in these emission lines (reprinted from Parrish et al. [63]).
Figure 7.24  The 250.8-GHz line of NO was observed [62] at Kitt Peak, Arizona, in April, 1991. This weak emission is due to lower thermospheric NO (altitudes of 90–120 km), which exhibits very large solar-cycle variations [64].

expected from the $\frac{1}{2}$ electron spin of the NO molecule. The magnetic-dipole moments of the electron spin and orbital motion cancel one another such that the Zeeman splitting in the terrestrial magnetic field is less than a few KHz (Philip Rosencranz, personal communication, 1992).

7.4.6 \( \text{HO}_2, \text{H}_2\text{O}_2, \) and HCN

The molecular species \( \text{H}_2\text{O}_2 \) and \( \text{HO}_2 \) comprise 30–100% of the middle- and upper-stratospheric abundance of odd hydrogen (HO$_x$). Both of these species are extremely difficult to measure by any technique, as is the third major HO$_x$ species, OH. Because HO$_x$ plays an important role both in the direct destruction of upper-stratospheric–mesospheric ozone and in the partitioning of Cl$_x$ and NO$_x$ species, detections or upper limits derived from microwave observations of \( \text{H}_2\text{O}_2 \) and \( \text{HO}_2 \) provide unique and important insight into middle-atmospheric ozone chemistry. De Zafra et al. [13] obtained measurements of \( \text{HO}_2 \) emission lines at 265.690, 265.732, and 265.770 GHz, which are shown in Figure 7.25. The weakness and narrow line widths of these spectral lines result from the generally low \( \text{HO}_2 \) mixing ratios in the stratosphere (5 x 10$^{-10}$ at 40-km altitude) and a rapid decline in the \( \text{HO}_2 \) mixing ratio below 40-km altitude. The smooth-line fit to the observed spectra in Figure 7.25 was determined by de Zafra et al. to be consistent with typical
model predictions, although the signal/noise of the observations precluded determination of an altitude mixing profile for \( \text{HO}_2 \) by direct inversion of the line shapes.

Photochemical model calculations for the \( \text{H}_2\text{O}_2 \) mixing profile indicate a local maximum of \( 2-3 \times 10^{-10} \) near 30-km altitude [36]. Above 35 km, \( \text{H}_2\text{O}_2 \) mixing ratios are predicted to fall below \( 1 \times 10^{-10} \). Such low concentrations, particularly in the upper stratosphere, lead to very weak and broad spectral line emissions. De Zafra et al. [65] integrated for 55 h on one of the stronger \( \text{H}_2\text{O}_2 \) microwave transitions (270.610 GHz). Although \( \text{H}_2\text{O}_2 \) emission was not detected, de Zafra et al. were able to place upper limits on the \( \text{H}_2\text{O}_2 \) mixing profile between 30- and 50-km altitude. These upper limits are approximately twice model \( \text{H}_2\text{O}_2 \) mixing ratios, and a factor of 2 less than a tentative determination by Waters et al. [66] from balloonborne microwave measurements at 30-km altitude.

Studies of the stratospheric profile of HCN have focused on derivation of vertical-transport time scales. The photochemical lifetime of HCN, which is produced at the Earth's surface, is of the order of a few years. However, infrared observations [67] of stratospheric HCN suggested an enhancement of the HCN mixing ratio between 30- and 40-km altitude, which would indicate additional stratospheric production source for HCN. Observations of the 265.989-GHz rotational transition of HCN by Jaramillo et al. [15] confirm the existence of an increasing HCN mixing ratio above 30 km, as shown in Figure 7.26. In Figure 7.27, shaded regions indicate the range of inverted HCN mixing profiles allowed by the observed spectrum [15]. Noise and the limited bandwidth (140 MHz) of the spectrum contribute the major portion of uncertainties in the HCN profile. A measurement of the same HCN transition within the Antarctic ozone hole in 1986 revealed substantial depletion of HCN above 25-km altitude, a fact that further indicates substantial downward advection within the winter polar vortex [68] (cf \( \text{N}_2\text{O} \)).

Figure 7.25  Microwave emission spectra of \( \text{HO}_2 \) near 265.7-GHz, observed at Mauna Kea in September-October 1982 by de Zafra et al. [13]. Additional microwave opacities due to \( \text{O}_3 \) and \( \text{HNO}_3 \) are modeled in the smooth-line fit to the data (reprinted from de Zafra et al. [13]).
7.4.7 Mesospheric Winds

Ground-based studies of middle-atmospheric winds have relied primarily on radar techniques. However, the high spectral resolution afforded by microwave spectroscopy allows accurate definition of the Doppler shifts in microwave spectral lines resulting from winds. At a frequency of 230 GHz, a 10-m/s wind speed results in a 7.5-kHz shift in the line center frequency. In practice, detections of such line shifts are limited by signal/noise rather than spectral resolution. Muhleman [69] has measured line shifts in the 230-GHz mesospheric CO emission to determine zonal wind velocities over the 70–85-km altitude range. The CO line is
observed in emission (employing frequency switching) while pointing the aperture alternately in East and West directions. An elevation of $20^\circ$ is typically adopted for these observations. Differencing of the East and West CO spectra leads to the residual CO emission presented in Figure 7.28. For a zero zonal wind speed, no residual signal would be apparent, as the East and West spectra would exhibit no frequency separation. The smooth-line fit corresponds to a $50 \pm 5$ m/s westerly zonal wind.

In Figure 7.29, we show a set of five such determinations of the zonal wind velocity between 70 and 85 km, determined by Muhleman [69] for various months of the year. All of the observations of Figure 7.29 correspond to latitudes between $30^\circ$N and $40^\circ$N. Note that summer months are not well represented in the observations, due to generally poorer atmospheric transmission for these months. Two-dimensional dynamical models predict a reversal of zonal flow from westerlies to easterlies in the month of April for midlatitudes [38]. The measurement of lower-mesospheric winds (50–60 km) can also be obtained through similar measurements of appropriate O$_3$ lines.

**Figure 7.28** Emission spectra of the 230-GHz transition of CO observed at Amherst, Massachusetts, by Muhleman [69] while pointing East (solid circles) and West (open circles) at an elevation of $20^\circ$. The difference between the East and West spectra (solid line) provides a measure of the Doppler shift due to mesospheric zonal winds, which is $\sim 40$ kHz or 50 m/s in this example.
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Mesospheric zonal winds: latitudes near 35°N

Figure 7.29 Set of mesospheric wind measurements obtained at latitudes near 35°N using the 230-kHz mesospheric CO line [69].

7.4.8 Middle-Atmospheric Temperatures, O₂, O₂ (¹Δg)

One of the advantages of microwave observations with regard to middle-atmospheric compositional studies is their relative insensitivity to atmospheric temperatures. The microwave thermal source function is linearly dependent on atmospheric temperatures, as compared to the much higher-order dependence of the Planck function at infrared frequencies. The temperature sensitivity of microwave emission generally varies between $T^1$ and $T^{-1}$, depending on the microwave absorption coefficient for the particular molecular species and the frequency of observation. For a more detailed examination of the temperature sensitivity of microwave emission, we consider the microwave absorption coefficient for O₃, which scales with the ambient temperature according to the relationship

$$\frac{S(v, T)}{S(v, T_0)} \sim \frac{F(v, T)}{F(v, T_0)} e^{-(E_f + E_i)/kT} \left(\frac{T_0}{T}ight)^{5/2}$$

(7.42)

where $S(v, T)$, and $(E_f + E_i)$ are defined by Eqs. 2.17 and 2.19; and $F(v, T)$ by Eqs. 7.1 to 7.5.

For lower energy rotational states, $E_f + E_i \ll kT$, and the term $e^{-(E_f + E_i)/kT}$ contributes very weakly to the temperature sensitivity of $S(v, T)$. For energetic rotational states, such as for the 276.924-GHz rotational transition of O₃ for which $E_f + E_i \sim kT$, $e^{-(E_f + E_i)/kT}$ contributes correspondingly greater to the temperature sensitivity of $S(v, T)$. The temperature dependence of the line-shape function $F(v, T)$ enters primarily through the temperature dependence of the collisional linewidth parameter $\Delta \nu e$ at stratospheric pressures; and through the temperature dependence of the Doppler linewidth parameter $\delta \nu_D$ at mesospheric pressures (see Eqs. 7.2 and 7.4). Connor et al. demonstrate that the temperature dependence of
line center emission in the optically thin 276.924-GHz spectrum of O\textsubscript{3} is essentially zero [42]. However, the temperature dependence of the Lorentzian line shape is distinctively different for frequencies near and away from the line center.

\[
\frac{\Delta \nu_c}{[(\nu - \nu_0)^2 + \Delta \nu^2_c]} \rightarrow \frac{1}{\Delta \nu_c}
\]

\[
\frac{\Delta \nu_c}{[(\nu - \nu_0)^2 + \Delta \nu^2_c]} \rightarrow \frac{\Delta \nu_c}{(\nu - \nu_0)^2}
\]

As a result, the temperature sensitivity for the retrieval of ozone from 276.924-GHz emission varies from near zero in the upper stratosphere to \(-1/T\) in the lower stratosphere. Substantially different temperature sensitivities are exhibited for linear molecules and for lower-order rotational transitions. Furthermore, absorption measurements and emission measurements exhibit different temperature sensitivities due to the exclusion of the thermal emission source function in the absorption radiative transfer equation (compare Eqs. 7.20 and 7.21). In any case, many microwave measurements are generally insensitive enough to atmospheric temperatures to allow accurate (1\%) corrections based upon meteorological temperature data sets (such as the National Meteorological Center stratospheric temperatures [70]) or seasonal/latitudinal models.

Greater temperature sensitivities for microwave emission do exist (see Figure 2.8) that permit ground-based temperature sounding of middle-atmospheric-temperature profiles. Observation of the \(^{18}\text{O}^{16}\text{O}\) oxygen isotope at 233.946 GHz can also be analyzed, in principle, to retrieve middle-atmospheric-temperature profiles. In Figure 7.30, we present a 233.946 GHz \(^{18}\text{O}^{16}\text{O}\) spectrum observed in absorption.

![Figure 7.30](image)

**Figure 7.30** An absorption spectrum of the 233.9-GHz transition of \(^{18}\text{O}^{16}\text{O}\), taken at the Kitt Peak NRAO facility in December 1986 by Muhrleman [16]. The line center reflects Zeeman splitting of this magnetic-dipole transition. The depth and separation of these multiplets varies with the orientation of the received polarization to the Earth's magnetic field.
against Venus, by Muhleman [16]. Zeeman splitting of this magnetic-dipole transition by the terrestrial magnetic field is apparent near the line center. The optical thinness of this transition and the high degree of accuracy with which the O₂ mixing ratio is known are both necessary qualifications for ground-based sounding of middle-atmospheric temperatures with microwave spectroscopy. However, very accurate calibration (for emission measurements) and high signal-to-noise ratios are required before significantly accurate (≈1%) temperature retrievals are possible by this technique.

For completeness, we also point out that the electronically excited O₂ (1Δg) state of molecular oxygen exhibits ~0.5K line emission (recently observed by Clancy) at a frequency of 255.018 GHz. The electronically excited O₂ (1Δg) molecule results from the photolysis of O₃ in the mesosphere, which leads to large (1–5 ppm) concentrations of mesospheric O₂ (1Δg). Zeeman splitting of ~0.5 MHz is apparent in the line center of the observed emission.

### 7.5 Future Developments

Many of the recent advances in microwave spectroscopy have been realized by improvements in the sensitivity and stability of microwave instrumentation. This has been achieved partly by improvements in receiver noise characteristics, but primarily it is a consequence of refinement in the observational techniques. In particular, the ability to maintain a high degree of accuracy in the spectral baselines returned by microwave spectrometer systems has allowed measurements in the lower stratosphere. This has proved invaluable in the study of such important phenomena as the Antarctic ozone hole.

The next major advance in microwave spectroscopy of the middle atmosphere may well be an improvement in calibration accuracies. Measurements of small trends in O₃ (< 1%/yr) and ClO (< 5%/yr) in the middle atmosphere are of fundamental importance in determining the global changes in atmospheric chemistry that humankind’s activities have brought. Currently, there exist no reliable ground-based techniques for measuring middle-atmospheric profiles of such trends (see Ozone Trends Panel Report [71]). Furthermore, satellite-based observational systems rely on ground-based observations for long-term calibration. Microwave spectroscopy provides a reliable technique for ground-based monitoring of vertical mixing profiles of O₃ and other important minor species, such as ClO and H₂O. Improvements in calibration accuracies to better than 5% should allow accurate monitoring of long-term trends in middle-atmospheric chemistry, and provide key ground calibration for satellite remote-sounding data sets in the future. A ground-based network of microwave ozone spectrometers is currently under study, as part of a larger ground-based Network for Detection of Stratospheric Change (NDSC). The prototype system includes six well-separated sites, each incorporating ozone observations at 109.559 and 110.836 GHz (Alan Parrish, personal communication, 1989). A comparable set of microwave ClO spectrometers is also under consideration. Development and deployment of lower noise temperature receivers (TREC
Finally, it is interesting to note the convergence of microwave and infrared observations at submillimeter wavelengths. Due to diminishing atmospheric transmission at submillimeter wavelengths, far infrared observations of the middle atmosphere have utilized balloonborne instrumentation, similar to the balloonborne microwave observations of O$_3$, H$_2$O$_2$, and ClO by Waters et al. [41]. The distinction between microwave and infrared measurements in the submillimeter wavelength region is purely instrumental in nature. Far infrared observations, such as by Abbas et al. [67], employ optical techniques such as Michelson interferometry. Microwave observations at submillimeter wavelengths employ radio techniques through heterodyne mixing of the observational frequency down to radio frequencies. However, recent advances in microwave spectrometer systems (e.g., acoustooptical devices) have begun to adopt optical techniques. Conversely, laser heterodyne techniques have been applied at infrared wavelengths [72].

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water vapor in 1984 and 1985: Results and implications for middle atmospheric trans­


MICROWAVE LIMB SOUNDED

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8.1 INTRODUCTION

Microwave* limb sounding measures atmospheric thermal-emission spectra at millimeter and submillimeter wavelengths as the instrument field of view (FOV) is scanned through the limb from above.** Atmospheric profiles of molecular abundances, temperature, pressure, wind, and magnetic field can be determined from the measured emission spectra. Intensity of the emission can provide abundance and temperature. Measured linewidths, and emission from temperature-insensitive O₂ lines, can provide pressure. Differentiation of measured pressure with respect to measured height differential (obtained from the instrument FOV scan encoder) can also provide temperature through atmospheric hydrostatic equilibrium (which relates temperature to pressure and height differential). Doppler shifts of spectral lines can provide wind, and Zeeman splitting of the magnetic dipole lines of O₂ can provide magnetic field. Limitations on spatial resolution are ~1.5 km in the

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*The term "microwave" is used here to denote heterodyne measurement techniques at millimeter and submillimeter wavelengths. Development of microwave limb sounding follows earlier development of microwave remote sensing [1] and its application from satellite [2], and the development of infrared limb sounding [3, 4]. Techniques for retrieving atmospheric profiles from limb-sounding measurements [5, 6] and methods for characterizing the resulting errors [7] are well-developed.

**Atmospheric spectral absorption of solar radiation can also be measured, but is much less desirable because of its limitations in spatial and temporal coverage. Other measurement geometries (e.g., scanning through the nadir direction) could also be used, but these (1) give much degraded vertical resolution and (2) do not have a "cold space" background and the "thermal contrast" needed to measure emission lines is much less. An attractive measurement geometry is to scan the limb both vertically and horizontally with an instrument containing heterodyne detector arrays—this can provide three-dimensional maps, but must await the development of the appropriate array technology.
vertical and ~300 km in the horizontal direction along the line of sight, as can be estimated from the appropriate weighting functions discussed in Section 8.4. Low signal strengths limit the highest altitudes that can be measured. Tropospheric attenuation by water (both vapor and liquid), coupled with low signal strengths for other molecules, limit the lower altitudes that can be measured. Ice clouds and other particulates (such as volcanic aerosols) have negligible effects on the signals; this allows measurements in regions where heterogeneous chemistry can occur.

Unique to microwave limb sounding is instrumentation that simultaneously gives best possible spectral resolution and sensitivity for thermal-emission measurements at longer wavelengths. Spectral resolution can be made arbitrarily fine, being fundamentally limited only by the measurement integration time, so the only limitation in resolving spectral features is the overlapping of atmospheric spectral lines. Additional features of microwave limb sounding, some of which are shared by other techniques, are as follows:

1. Many upper-atmospheric molecules, especially chemical radicals important in ozone destruction, have spectral lines that can be measured.
2. The viewing geometry optimizes vertical resolution and signal strengths.
3. Thermal emission is observed, allowing measurements at any time without requiring background sources (e.g., the Sun) or intermediate processes (e.g., backscattering).
4. The spectroscopy data base is generally more accurate than in other spectral regions. This is because line strengths are determined from the permanent dipole moment of the molecule, which can be measured in the laboratory to better than 1% from Stark or Zeeman effects without requiring simultaneous measurement of the abundances in the laboratory cell. Uncertainties in quantum-mechanical calculations of matrix elements for individual line transitions are also typically less than 1%.
5. Measurements require no simultaneous ancillary data. Spectral lines for composition measurements can be chosen that have temperature-insensitive limb thermal emission, so that highly accurate temperature measurements are not required for deducing abundances. The data contain atmospheric pressure information, as discussed before, so that precise platform pointing information is not essential.
6. Instruments can be developed for orbiting satellites that have long (many years) operational lifetimes and reliable long-term calibration.

*At 200 GHz, for example, optical depths smaller than unity (which generally indicates acceptably small attenuation) occur for limb paths having tangent heights greater than ~5 km at high latitudes and ~10 km at low latitudes (the variation is due to the water-vapor variation with latitude). Tropospheric attenuation increases greatly with increasing frequency (due to strong H₂O rotational lines at submillimeter wavelengths).

**However, heterodyne systems generally have smaller spectral coverage than nonheterodyne systems.
8.2 THE NEED FOR MEASUREMENTS

There is now a general appreciation of the upper atmosphere's importance to life on Earth, and of its vulnerability. The ozone molecule (O₃) in Earth's stratosphere protects life from solar ultraviolet radiation, but can be depleted by pollution from economically important industrial products. It is important to understand stratospheric ozone and the processes that control it. Advances in this understanding arise from a combination of measurement and theory. Dobson's [8] pioneering measurements and Chapman's [9] original theory provided an initial description. Discrepancies between measured and predicted ozone abundances led to theories for hydrogen [10] and nitrogen [11] catalytic destruction of ozone. Chlorine catalytic destruction of stratospheric ozone, discovered more recently [12, 13], is of especial concern because industrial chlorofluorocarbons (CFCs) are the major chlorine source. Discovery of the spectacular springtime Antarctic ozone hole [14], and subsequent measurements of its abnormal composition [15 especially] have led to a realization of the importance of stratospheric heterogeneous chemistry [16], and that the ozone hole is caused by greatly enhanced chlorine destruction of ozone that is triggered by heterogeneous reactions in polar stratospheric clouds [17, 18, for example].

Although tremendous progress has recently been made in understanding stratospheric ozone, significant problems remain. For example, upper-stratospheric ozone abundance is not correctly predicted by current theory, although it is in this region that the theory should be most reliable [19, 20]. Also, 1969-1986 northern hemisphere high-latitude ozone decreased significantly more than expected [22]. Enhanced levels of active chlorine, presumably due to heterogeneous processes similar to those in the Antarctic, were observed in the Arctic in 1989 with anticorrelation in ozone abundances [23]. The extent and potential growth of these processes are unknown, but they can have serious consequences. Early results from the Microwave Limb Sounder experiment on the Upper Atmosphere Research Satellite have shown large abundances of active chlorine over populated areas of the northern hemisphere in January 1992 (see Section 8.6). Volcanic injections into the stratosphere can also produce particulates upon which heterogeneous chemistry can occur and potentially add to ozone depletion, for example, by converting chlorine from chemically inactive to chemically active forms [24]. Even if the industrial use of chlorocarbons and related products were completely eliminated, the amount of stratospheric chlorine will continue to increase over the next several years (due to the reservoir of chlorine that already exists) and approximately one century will be required for this chlorine to decrease below that at which the Antarctic ozone hole formed [25, Figure 13.1]. Nonvolcanic sulfuric acid aerosols at ~20-km height appear to have increased by ~5% per year in the past 10 years [26], perhaps due to sulfur emission by jet aircraft [27], and have increased the potential for heterogeneous chemistry in the lower stratosphere. Re-

*Study of processes involving vibrationally excited O₂ may help resolve this [21].
cent assessment [28] shows greater ozone loss in all seasons at mid- and high latitudes than previously thought, and identifies coupling between lower-stratospheric ozone chemistry and potential climate change. Careful monitoring and study of the stratosphere are needed. Many atmospheric molecules and atoms are involved in the complex chemistry [18, 29, 30, for example].

8.3 STRATOSPHERIC MOLECULES AND SPECTROSCOPY

The millimeter and submillimeter spectral regions, for which microwave limb sounding applies, are very rich in atmospheric spectral lines. Figure 8.1 illustrates spectra of just a few important upper-atmospheric molecules, including the rate-limiting radicals in ozone-destruction cycles. The vertical scale is the logarithm (base 10) of the opacity at spectral line center for a limb path through the middle stratosphere.

Stratospheric emission over the submillimeter spectral region has been surveyed with ~100-MHz resolution [31, 32] so that the more-sensitive higher-resolution heterodyne experiments can be planned without worry of excessive interference.
8.3 STRATOSPHERIC MOLECULES AND SPECTROSCOPY

Figure 8.2. 620–670 GHz stratospheric emission spectra. Top panel: from Figures 1 and 2 of Baldecchi et al. [32], measured from balloon with ~100-MHz resolution and a limb path through the middle stratosphere. Bottom panel: calculated by W. G. Read with 1 MHz resolution for a limb path having tangent height of ~30 km. The vertical scale of each panel is linear in emission intensity: the strongest lines, mainly O₃, have emission approximately equal to that of a blackbody at 230 K. Lines of HCl and ClO are indicated in the bottom panel.

from unknown strong lines. Figure 8.2 shows 620–670 GHz stratospheric spectra measured with ~100-MHz resolution and spectra calculated with 1-MHz resolution. This interesting spectral region contains the strongest rotational line of ClO, the first rotational line of HCl, and lines of many additional molecules of atmospheric interest. Figure 8.3 shows the first measurements in this region made with a balloon-borne heterodyne radiometer [33].

The JPL Submillimeter, Millimeter, and Microwave Spectral Line Catalog [34, 35] contains relevant spectroscopic data. Appendix 8A of this chapter gives plots of 0–3000 GHz spectra of stratospheric molecules and atoms that have spectral lines with expected optical depth greater than 10⁻³ for a limb-measurement path. As discussed in Section 8.5, such lines can be measured with integration times of less than 1 minute. Appendix 8B gives theoretical expressions for calculating atmospheric signals from JPL catalog data; Appendix 8C gives examples of FORTRAN code for absorption coefficients.

Tables 8.1 to 8.6 list upper-atmospheric molecules and atoms grouped by chemical families. As discussed in Appendix 8B, a useful “figure of merit” for indicating expected strengths of submillimeter signals is the quantity $M = f\mu^2/Q_\alpha$, where $f$ is the volume mixing ratio, $\mu$ is the molecule’s permanent dipole moment,

*The fractional abundance on a per molecule basis.
Figure 8.3. Measured stratospheric emission near 625 and 649 GHz (from Stachnik et al. [33]). Measurements are indicated by crosses whose horizontal extent gives the spectral width of the individual filter, and whose vertical extent gives estimated accuracy. Some of the measurement crosses near the center of the HCl and O₃ lines are obscured due to several occurring over a narrow spectral range. The measurements were made by a balloonborne heterodyne radiometer having a local oscillator at 637.05 GHz and 10.5–13 GHz intermediate frequency. They are for an observation path having ~33 km tangent height. The smooth curve is a spectrum calculated for atmospheric profiles retrieved from the balloon measurements. The three horizontal scales indicate the radiometer’s (1) intermediate frequency [IF], (2) upper sideband [USB] frequency, and (3) lower sideband [LSB] frequency. The vertical scale gives the “double-sideband” [DSB] brightness temperature, which is the intensity of the measured signal relative to that of a blackbody observed simultaneously through both radiometer sidebands (the USB and LSB responses are approximately equal).

$Q_{rs}$ is its “rotation–spin” partition function. Values of log $M$, $f$, $\mu$, and $Q_{rs}$ are given in the tables. Values of $f$ are for maximum values generally expected in the stratosphere. Values of $\mu$ are in Debye ($D$) units used in spectroscopy: $1D = 10^{-18}$ esu cm $= 3.336 \times 10^{-30}$ C m [SI units]. Values of $Q_{rs}$ are for a typical stratospheric temperature of 225 K. Molecules and atoms that have been included in the JPL catalog at the time of writing this chapter are identified by an entry in the “JPL SPECTAG” column. The three most significant digits of SPECTAG are the molecular mass of the entry; the three least significant digits are the chronological order, for that mass, in which entries were added to the catalog. General references for mixing ratios given in Tables 8.1 to 8.6 are [29] and [36]; relative isotopic mixing ratios are based on data in Table 8.7.
<table>
<thead>
<tr>
<th>Molecule or Atom</th>
<th>JPL SPECTAG</th>
<th>( \mu ) (D)</th>
<th>( Q_{rs} ) at 225 K</th>
<th>( \log_{10} \frac{f \mu^2}{Q_{rs}} )</th>
<th>Height (km)</th>
<th>Notes</th>
<th>Approximate Maximum Stratospheric Mixing Ratio</th>
</tr>
</thead>
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<tr>
<td>( ^{16}\text{O} )</td>
<td>16001</td>
<td>0.0186</td>
<td>6.324</td>
<td>1.0 \times 10^{-7}</td>
<td>50</td>
<td>-11.3</td>
<td>1, 2</td>
</tr>
<tr>
<td>( ^{18}\text{O} )</td>
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<td>6.324</td>
<td>2.0 \times 10^{-10}</td>
<td>50</td>
<td>-14.0</td>
<td>1, 2</td>
<td></td>
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<td>1, 2</td>
<td></td>
</tr>
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<td>( \text{O}_2 )</td>
<td>32001</td>
<td>0.0186</td>
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<td>2.1 \times 10^{-1}</td>
<td>&lt; 90</td>
<td>-6.4</td>
<td>1</td>
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<td>( \text{O}_2 (v = 1) )</td>
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<td>0.0186</td>
<td>1.64 \times 10^{2}</td>
<td>1.0 \times 10^{-5}</td>
<td>&lt; 90</td>
<td>-10.7</td>
<td>1, 3</td>
</tr>
<tr>
<td>( \text{O}_2 (\Delta) )</td>
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<td>0.0186</td>
<td>1.13 \times 10^{2}</td>
<td>3.0 \times 10^{-6}</td>
<td>70</td>
<td>-11.0</td>
<td>1, 4</td>
</tr>
<tr>
<td>( ^{18}\text{OO} )</td>
<td>34001</td>
<td>0.0186</td>
<td>3.47 \times 10^{2}</td>
<td>8.5 \times 10^{-4}</td>
<td>&lt; 90</td>
<td>-9.1</td>
<td>1</td>
</tr>
<tr>
<td>( ^{17}\text{OO} )</td>
<td>33002</td>
<td>0.0186</td>
<td>3.47 \times 10^{2}</td>
<td>1.6 \times 10^{-4}</td>
<td>&lt; 90</td>
<td>-10.1</td>
<td>1</td>
</tr>
<tr>
<td>( \text{O}_3 )</td>
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<td>0.5337</td>
<td>2.23 \times 10^{3}</td>
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<td>35</td>
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<td>2.23 \times 10^{3}</td>
<td>9.0 \times 10^{-9}</td>
<td>35</td>
<td>-12.0</td>
<td>3, 6, 8</td>
</tr>
<tr>
<td>( \text{O}_3 (v_4) )</td>
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<td>2.23 \times 10^{3}</td>
<td>9.0 \times 10^{-9}</td>
<td>35</td>
<td>-12.2</td>
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<td>( \text{O}_3 (2v_2) )</td>
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<td>0.519</td>
<td>2.23 \times 10^{3}</td>
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<td>35</td>
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<tr>
<td>( \text{O}_3 (v_2 + v_3) )</td>
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<td>2.23 \times 10^{3}</td>
<td>1.1 \times 10^{-10}</td>
<td>35</td>
<td>-13.9</td>
<td>3, 6, 8</td>
</tr>
<tr>
<td>( \text{O}_3 (v_1 + v_2) )</td>
<td>48008</td>
<td>-0.52</td>
<td>2.23 \times 10^{3}</td>
<td>7.0 \times 10^{-11}</td>
<td>35</td>
<td>-14.1</td>
<td>3, 6, 8</td>
</tr>
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<td>( \text{O}_3 (2v_3) )</td>
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<td>2.23 \times 10^{3}</td>
<td>1.1 \times 10^{-11}</td>
<td>35</td>
<td>-14.8</td>
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<td>2.23 \times 10^{3}</td>
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<td>2.23 \times 10^{3}</td>
<td>1.0 \times 10^{-12}</td>
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<td>2.23 \times 10^{3}</td>
<td>5.6 \times 10^{-12}</td>
<td>35</td>
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<tr>
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<td>4.69 \times 10^{3}</td>
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<td>35</td>
<td>-11.8</td>
<td></td>
</tr>
<tr>
<td>( ^{18}\text{OOO} (v_2) )</td>
<td>50006</td>
<td>0.532</td>
<td>5.00 \times 10^{3}</td>
<td>3.5 \times 10^{-10}</td>
<td>35</td>
<td>-13.7</td>
<td>3</td>
</tr>
<tr>
<td>( ^{18}\text{OO} )</td>
<td>50003</td>
<td>0.532</td>
<td>2.29 \times 10^{3}</td>
<td>1.4 \times 10^{-8}</td>
<td>35</td>
<td>-11.8</td>
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<tr>
<td>( ^{18}\text{OOO} (v_2) )</td>
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<td>2.45 \times 10^{3}</td>
<td>1.8 \times 10^{-10}</td>
<td>35</td>
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<td>49002</td>
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<td>2.73 \times 10^{4}</td>
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<td>( ^{17}\text{OO} )</td>
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<td>0.532</td>
<td>1.30 \times 10^{4}</td>
<td>2.6 \times 10^{-9}</td>
<td>35</td>
<td>-13.2</td>
<td></td>
</tr>
</tbody>
</table>

Notes: 1. Magnetic dipole. Value given for \( \mu \) is 2 Bohr magnetons converted to equivalent Debye (D) units.
2. The mixing ratio of atomic \( \text{O} \) increases rapidly with increasing height. The \( 10^{-7} \) mixing ratio used here is typical for 50 km (the "top" of the stratosphere); values are \( -10^{-6} \) at \( -70 \) km and \( -10^{-4} \) at \( -105 \) km. (These data and the catalog spectra are for atomic oxygen in its ground \( \ell^2 \) electronic state.)
3. The mixing ratio given here for excited vibrational states is that of ground state multiplied by \( e^{-E_e/kT} \) at \( T = 225 \) K, where \( E_e \) is the energy of the excited state above the ground state. The values used for \( E_e/\hbar c \) are from the JPL catalog or, for states not in the catalog, from E. A. Cohen (private communication).

Molecule (state) \( E_e/\hbar c \) (cm\(^{-1}\)) \( e^{-E_e/kT} \) at \( T = 225 \) K
| \( \text{O}_2 (v_1) \) | 1556 | \( 4.8 \times 10^{-5} \) |
| \( \text{O}_3 (v_2) \) | 701 | \( 1.1 \times 10^{-2} \) |
| \( \text{O}_3 (v_3) \) | 1042 | \( 1.3 \times 10^{-3} \) |
| \( \text{O}_3 (v_4) \) | 1103 | \( 8.6 \times 10^{-4} \) |
| \( \text{O}_3 (2v_2) \) | 1400 | \( 1.3 \times 10^{-4} \) |
4. $\text{O}_2 (^1\Delta)$ is a metastable state, with energy 7918 cm$^{-1}$ above the ground state, and is not in thermal equilibrium in the upper atmosphere; the mixing ratio given here is from R. P. Wayne, *J. Photochem.* 25, 345 (1984).
6. The JPL catalog has a single entry covering (1) both $\text{O}_3(v_1)$ and $\text{O}_3(v_3)$, and (2) both $\text{O}_3(v_2 + v_3)$ and $\text{O}_3(v_1 + v_2)$; common quantum-mechanical models were used for these combined states in producing the catalog data.
7. Spectroscopic parameters for these states are from E. A. Cohen (private communication).
8. The JPL catalog partition function for $\text{O}_3$ is a summation over all vibrationally excited states of this molecule that are in the catalog.

**TABLE 8.2 Nitrogen Molecules**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>JPL SPEC-TAG</th>
<th>$\mu$ (D)</th>
<th>$Q_{225}$ Value $\equiv f$</th>
<th>Height (km)</th>
<th>$\log_{10}$ of $f\mu^2/Q_{\text{rs}}$</th>
<th>Notes $^b$</th>
</tr>
</thead>
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<tr>
<td>$\text{N}_2\text{O}$ (NNO)</td>
<td>44004</td>
<td>0.1608</td>
<td>$3.74 \times 10^2$</td>
<td>20</td>
<td>$-10.9$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}$ ($v_2$)</td>
<td>44009</td>
<td>0.1608</td>
<td>$3.74 \times 10^2$</td>
<td>20</td>
<td>$-12.5$</td>
<td>1</td>
</tr>
<tr>
<td>$\text{N}_2\text{O}$ (2$v_1$)</td>
<td>44010</td>
<td>0.1608</td>
<td>$3.74 \times 10^2$</td>
<td>20</td>
<td>$-14.1$</td>
<td>1, 2</td>
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<td>$-0.16$</td>
<td>$3.87 \times 10^2$</td>
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<tr>
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<td>45007</td>
<td>$-0.16$</td>
<td>$3.74 \times 10^2$</td>
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<tr>
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<td>$-14.3$</td>
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### TABLE 8.2 (Continued)

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<th>Molecule</th>
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<th>(Q_\alpha), at 225 K</th>
<th>Value = (f)</th>
<th>Height (km)</th>
<th>(\log_{10} f \mu^2/Q_\alpha)</th>
<th>Notes</th>
<th>Notes^b</th>
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<tr>
<td>(^{15}\text{NO})</td>
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<td>40</td>
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<td>4</td>
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<tr>
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<td>(~8.2 \times 10^2) | (2.0 \times 10^{-11})</td>
<td>40</td>
<td>-15.2</td>
<td>4</td>
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<td></td>
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<tr>
<td>(\text{N}^{17}\text{O})</td>
<td>~0.16</td>
<td>(~8.2 \times 10^2) | (3.7 \times 10^{-12})</td>
<td>40</td>
<td>-15.9</td>
<td>4</td>
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<td>1</td>
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<td>-15.6</td>
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<td>(\text{HNO}_3)</td>
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<td>-15.7</td>
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<tr>
<td>(\text{HNO}_3)</td>
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<tr>
<td>(\text{HNO}_3)</td>
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<td>-15.9</td>
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<tr>
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<tr>
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<td>(1.93 \times 10^4) | (1.0 \times 10^{-11})</td>
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<td>-14.7</td>
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<tr>
<td>(\text{HON}^{18}\text{OO (trans)})</td>
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<td>(1.93 \times 10^4) | (1.0 \times 10^{-11})</td>
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<tr>
<td>(\text{N}_2)</td>
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<td>(7.8 \times 10^{-1}) | (&lt; 100)</td>
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<td>7</td>
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</tr>
</tbody>
</table>

8.3 STRATOSPHERIC MOLECULES AND SPECTROSCOPY 391
### Spectroscopic parameters, unless otherwise noted, are from the JPL Catalog.

### Notes:
1. The mixing ratio given here for excited vibrational states is that of the ground state multiplied by $e^{-E_r/kT}$ at $T = 225$ K, where $E_r$ is the energy of the excited state above the ground state. The values used for $E_r/hc$, given below, are from E. A. Cohen (private communication).

<table>
<thead>
<tr>
<th>Molecule (state)</th>
<th>$E_r/hc$ (cm$^{-1}$)</th>
<th>$e^{E_r/kT}$ at $T = 225$ K</th>
</tr>
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<tbody>
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<td>$\text{N}_2\text{O}$ ($v_3$)</td>
<td>576</td>
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<td>1168</td>
<td>$5.7 \times 10^{-4}$</td>
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<tr>
<td>$\text{N}_2\text{O}$ ($2v_2^0$)</td>
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<td>$5.5 \times 10^{-4}$</td>
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<td>$\text{HNO}_3$ ($v_8$)</td>
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<td>$\text{HNO}_3$ ($2v_9$)</td>
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<td>$\text{HNO}_3$ ($v_7 + v_9$)</td>
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<td>$1.3 \times 10^{-3}$</td>
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<tr>
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<td>$4.1 \times 10^{-4}$</td>
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<td>$\text{HNO}_3$ ($v_6 + v_7$)</td>
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<tr>
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<td>$1.4 \times 10^{-10}$</td>
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</table>

2. The JPL catalog has a single entry covering both $\text{N}_2\text{O}$ ($2v_2^0$) and $\text{N}_2\text{O}(2v_2^0)$; a common quantum-mechanical model was used for these states in producing the catalog data. These states have been added since release of Version 3 of the catalog in June 1992.

3. Spectroscopic parameters are from E. A. Cohen (private communication).

4. The value $1.0 \times 10^{-8}$ used here for the NO mixing ratio is the approximate maximum expected in the stratosphere. The mixing ratio is much larger at higher altitudes; typical values at $-100$ km are $-10^{-5}$.

5. Magnetic dipole. Value given for $\mu$ is 1 Bohr magneton converted to equivalent Debye (D) units.

6. The value of $Q_{ns}$ for $\text{HNO}_3$ ($v_9$) given here is reduced two times from the JPL catalog value—because the catalog contains pairs of lines (due to torsional splitting of states) that are not resolved in the stratospheric spectrum.

7. No spin or rotational spectrum.
### TABLE 8.3 Hydrogen Molecules

<table>
<thead>
<tr>
<th>Molecule</th>
<th>JPL Spec-</th>
<th>$\mu$ (D)</th>
<th>$Q_{rs}$ at 225 K Value $f$</th>
<th>Height (km)</th>
<th>log$<em>{10}$ of $f\mu^2/Q</em>{rs}$</th>
<th>Notes$^b$</th>
</tr>
</thead>
<tbody>
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<td>H$_2$O</td>
<td>18003</td>
<td>1.85</td>
<td>$1.6 \times 10^2$ $5.0 \times 10^{-6}$</td>
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<td>-6.8</td>
<td>1</td>
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<tr>
<td>H$_2$O ($v_2$)</td>
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<td>1.85</td>
<td>$1.6 \times 10^2$ $1.9 \times 10^{-10}$</td>
<td>50</td>
<td>-11.3</td>
<td>1, 2</td>
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<tr>
<td>$^{17}$H$_2$O</td>
<td>19003</td>
<td>1.85</td>
<td>$1.6 \times 10^2$ $1.0 \times 10^{-8}$</td>
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<td>-9.5</td>
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<td>-13.8</td>
<td>3, 4</td>
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<td>$1.9 \times 10^{-13}$</td>
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<td>$1.2 \times 10^{-12}$</td>
<td>50</td>
<td>-15.0</td>
<td></td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>34004</td>
<td>1.573</td>
<td>$5.7 \times 10^3$ $1.0 \times 10^{-10}$</td>
<td>35</td>
<td>-13.4</td>
<td></td>
</tr>
<tr>
<td>HO$_2$N$O$</td>
<td>79001</td>
<td>1.288</td>
<td>$8.6 \times 10^4$ $3.0 \times 10^{-10}$</td>
<td>30</td>
<td>-14.2</td>
<td>6</td>
</tr>
<tr>
<td>CH$_4$</td>
<td></td>
<td></td>
<td>$1.0 \times 10^{-6}$</td>
<td>20</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td></td>
<td></td>
<td>$5.0 \times 10^{-7}$</td>
<td></td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

$^a$Spectroscopic parameters, unless otherwise noted, are from the JPL Catalog.

Notes:
1. The JPL catalog partition function for H$_2$O is a summation over all vibrationally excited states of this molecule that are in the catalog.
2. The mixing ratio given here for excited vibrational states is that of ground state multiplied by $e^{-E_r/kT}$ at $T = 225$ K, where $E_r$ is the energy of the excited state above the ground state. Values used for $E_r/kT$ are below; they are from the JPL catalog or, for states not in the catalog, from E. A. Cohen (private communication).

<table>
<thead>
<tr>
<th>Molecule (state)</th>
<th>$E_r/kT$ (cm$^{-1}$)</th>
<th>$e^{-E_r/kT}$ at $T = 225$ K</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O ($v_2$)</td>
<td>1595</td>
<td>$3.7 \times 10^{-5}$</td>
</tr>
<tr>
<td>HDO ($v_2$)</td>
<td>1403</td>
<td>$1.3 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

3. Spectroscopic parameters are from E. A. Cohen (private communication).
4. HD$^{17}$O has been added to the catalog since Version 3 released in June 1992.
5. OH mixing ratios in the mesosphere are larger than in the stratosphere; values at 75 km are $1.0 \times 10^{-8}$.
6. Abundance from Caltech model (L. Froidevaux, private communication).
7. No rotational spectrum except for very weak perturbation-allowed spectrum (E. A. Cohen, private communication).
8. No spin or rotational spectrum.
### TABLE 8.4 Halogen Molecules with Expected $\log_{10} \left[ \frac{f \mu^2}{Q_{sr}} \right] \geq -15^\circ$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>JPL SPEC- TAG</th>
<th>$\mu$ (D)</th>
<th>$Q_{sr}$ at 225 K</th>
<th>Value $\equiv f$</th>
<th>$\log_{10} \left[ \frac{f \mu^2}{Q_{sr}} \right]$</th>
<th>Height (km)</th>
<th>Notes $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3$H$^35$Cl</td>
<td>36001</td>
<td>1.109</td>
<td>$6.09 \times 10^1$</td>
<td>$1.5 \times 10^{-9}$</td>
<td>50</td>
<td>-10.5</td>
<td>1</td>
</tr>
<tr>
<td>$^3$H$^37$Cl</td>
<td>38001</td>
<td>1.109</td>
<td>$6.10 \times 10^1$</td>
<td>$0.5 \times 10^{-9}$</td>
<td>50</td>
<td>-11.0</td>
<td>1</td>
</tr>
<tr>
<td>$^3$D$^35$Cl</td>
<td>37001</td>
<td>$\sim 1.1$</td>
<td>$1.19 \times 10^2$</td>
<td>$2.3 \times 10^{-13}$</td>
<td>50</td>
<td>-14.3</td>
<td>1</td>
</tr>
<tr>
<td>$^3$D$^37$Cl</td>
<td>39004</td>
<td>$\sim 1.1$</td>
<td>$1.19 \times 10^2$</td>
<td>$0.8 \times 10^{-13}$</td>
<td>50</td>
<td>-14.8</td>
<td>1</td>
</tr>
<tr>
<td>$^3$ClO</td>
<td>51002</td>
<td>1.2974</td>
<td>$2.85 \times 10^3$</td>
<td>$3.7 \times 10^{-10}$</td>
<td>35</td>
<td>-11.7</td>
<td>2, 3, 4</td>
</tr>
<tr>
<td>$^3$ClO</td>
<td>53002</td>
<td>1.2974</td>
<td>$2.90 \times 10^3$</td>
<td>$1.3 \times 10^{-10}$</td>
<td>35</td>
<td>-12.1</td>
<td>2, 3, 4</td>
</tr>
<tr>
<td>$^3$HO$^35$Cl</td>
<td>52006</td>
<td>1.471</td>
<td>$6.18 \times 10^3$</td>
<td>$1.6 \times 10^{-10}$</td>
<td>35</td>
<td>-13.3</td>
<td></td>
</tr>
<tr>
<td>$^3$HO$^37$Cl</td>
<td>54005</td>
<td>1.471</td>
<td>$6.29 \times 10^3$</td>
<td>$5.3 \times 10^{-11}$</td>
<td>35</td>
<td>-13.7</td>
<td></td>
</tr>
<tr>
<td>$^3$O$^35$ClO</td>
<td>67001</td>
<td>1.784</td>
<td>$3.44 \times 10^4$</td>
<td>$9.0 \times 10^{-11}$</td>
<td>18</td>
<td>-14.1</td>
<td>5</td>
</tr>
<tr>
<td>$^3$O$^37$ClO</td>
<td>69001</td>
<td>1.784</td>
<td>$3.57 \times 10^4$</td>
<td>$3.0 \times 10^{-11}$</td>
<td>18</td>
<td>-14.6</td>
<td>5</td>
</tr>
<tr>
<td>$^3$ClO$^35$ClO</td>
<td>102001</td>
<td>0.72</td>
<td>$1.07 \times 10^5$</td>
<td>$0.6 \times 10^{-9}$</td>
<td>18</td>
<td>-14.5</td>
<td>5</td>
</tr>
<tr>
<td>$^3$ClO$^37$ClO</td>
<td>104001</td>
<td>0.72</td>
<td>$1.07 \times 10^5$</td>
<td>$0.3 \times 10^{-9}$</td>
<td>18</td>
<td>-14.8</td>
<td>5</td>
</tr>
<tr>
<td>$^3$ClO$^35$NO$_2$</td>
<td>97002</td>
<td>0.72</td>
<td>$6.53 \times 10^4$</td>
<td>$1.0 \times 10^{-9}$</td>
<td>30</td>
<td>-14.1</td>
<td></td>
</tr>
<tr>
<td>$^3$ClO$^37$NO$_2$</td>
<td>99001</td>
<td>0.72</td>
<td>$6.70 \times 10^4$</td>
<td>$3.0 \times 10^{-10}$</td>
<td>30</td>
<td>-14.6</td>
<td></td>
</tr>
<tr>
<td>$^3$CH$^35$Cl</td>
<td>50007</td>
<td>1.899</td>
<td>$1.83 \times 10^4$</td>
<td>$3.0 \times 10^{-10}$</td>
<td>20</td>
<td>-13.2</td>
<td></td>
</tr>
<tr>
<td>$^3$CH$^37$Cl</td>
<td>52009</td>
<td>1.899</td>
<td>$1.86 \times 10^4$</td>
<td>$1.0 \times 10^{-10}$</td>
<td>20</td>
<td>-13.7</td>
<td></td>
</tr>
<tr>
<td>HF</td>
<td>20002</td>
<td>1.826</td>
<td>$1.48 \times 10^1$</td>
<td>$4.0 \times 10^{-10}$</td>
<td>35</td>
<td>-9.9</td>
<td></td>
</tr>
<tr>
<td>DF</td>
<td>21002</td>
<td>1.819</td>
<td>$1.48 \times 10^1$</td>
<td>$6.0 \times 10^{-14}$</td>
<td>35</td>
<td>-13.9</td>
<td></td>
</tr>
<tr>
<td>COF$_2$</td>
<td>66001</td>
<td>0.951</td>
<td>$3.99 \times 10^4$</td>
<td>$1.0 \times 10^{-10}$</td>
<td>35</td>
<td>-14.6</td>
<td></td>
</tr>
<tr>
<td>$^8$H$^81$Br</td>
<td>82001</td>
<td>0.828</td>
<td>$7.34 \times 10^1$</td>
<td>$2.0 \times 10^{-12}$</td>
<td>35</td>
<td>-14.3</td>
<td></td>
</tr>
<tr>
<td>$^8$H$^79$Br</td>
<td>80001</td>
<td>0.828</td>
<td>$7.33 \times 10^1$</td>
<td>$2.0 \times 10^{-12}$</td>
<td>35</td>
<td>-14.3</td>
<td></td>
</tr>
<tr>
<td>$^8$1BrO</td>
<td>97001</td>
<td>1.794</td>
<td>$3.69 \times 10^2$</td>
<td>$5.0 \times 10^{-12}$</td>
<td>35</td>
<td>-13.4</td>
<td>4</td>
</tr>
<tr>
<td>$^7$BrO</td>
<td>95001</td>
<td>1.794</td>
<td>$3.68 \times 10^2$</td>
<td>$5.0 \times 10^{-12}$</td>
<td>35</td>
<td>-13.4</td>
<td>4</td>
</tr>
</tbody>
</table>

$^a$Spectroscopic parameters, unless otherwise noted, are from JPL Catalog.

Notes:
1. Spectroscopic parameters are from E. A. Cohen (private communication).
2. Value of $\mu$ is measurement by D. Yaron, K. Peterson, W. Klemperer [31 of Chapter 8 Appendix].
3. The ClO mixing ratio given here is typical for midlatitude "normal" chemistry. ClO mixing ratios are $1.0 \times 10^{-9}$, or higher, in the "perturbed" chemistry of the spring or winter lower stratosphere.
4. The values of $Q_{sr}$ given here for ClO and BrO are reduced eight times from the JPL catalog values—because there are eight strong (approximately equal-strength) hyperfine components of each rotational transition, which are included in the catalog but are not resolved in the stratospheric spectrum. The amount by which these components are separated decreases with increasing rotational state. Examples for rotational transitions that might be used for stratospheric measurements: ClO components are spread over 16 MHz for the 204-GHz transitions and over 6 MHz for the 649-GHz transitions; BrO components are spread over 17 MHz for the 346-GHz $^8$BrO transitions and over 7 MHz for the 523-GHz $^8$1BrO transitions.
5. The mixing ratios given here are for enhanced levels as might be expected in the Antarctic spring lower stratosphere [69].
### TABLE 8.5 Halogen Molecules with Expected \( \log_{10} \left( f_{\mu^2}/Q_{rs} \right) \leq -15 \)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \mu ) (D)</th>
<th>( Q_{ns} ) at 225 K</th>
<th>Approximate Maximum Stratospheric Mixing Ratio</th>
<th>( \log_{10} ) of ( f_{\mu^2}/Q_{rs} )</th>
<th>Notes&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{35}\text{Cl} )</td>
<td>0.0186</td>
<td>16.01</td>
<td>( 9.0 \times 10^{-12} ) 40</td>
<td>-15.7</td>
<td>1</td>
</tr>
<tr>
<td>( ^{37}\text{Cl} )</td>
<td>0.0186</td>
<td>16.01</td>
<td>( 3.0 \times 10^{-12} ) 40</td>
<td>-16.2</td>
<td>1</td>
</tr>
<tr>
<td>( \text{Cl}_2 )</td>
<td>~1.8</td>
<td>( 1.84 \times 10^5 )</td>
<td>( 4.0 \times 10^{-11} ) 20</td>
<td>-15.2</td>
<td>3</td>
</tr>
<tr>
<td>( \text{CCl}_3 )</td>
<td>0.0</td>
<td>( 4.25 \times 10^2 )</td>
<td>( 1.4 \times 10^{-6} ) &lt;70</td>
<td>-14.8</td>
<td>2</td>
</tr>
<tr>
<td>( \text{CCl}_4 ) (CFC-10)</td>
<td>0.46</td>
<td>( 1.77 \times 10^5 )</td>
<td>( 8.0 \times 10^{-11} ) 20</td>
<td>-16.4</td>
<td>3</td>
</tr>
<tr>
<td>( \text{CCl}_2\text{F} ) (CFC-11)</td>
<td>~0.5</td>
<td>( 1.17 \times 10^5 )</td>
<td>( 2.0 \times 10^{-10} ) 20</td>
<td>-15.4</td>
<td>3</td>
</tr>
<tr>
<td>( \text{CCl}_2\text{F}_2 ) (CFC-12)</td>
<td>~0.5</td>
<td>( 7.19 \times 10^4 )</td>
<td>( 2.0 \times 10^{-12} ) 35</td>
<td>-17.2</td>
<td>3</td>
</tr>
<tr>
<td>( \text{CF}_4 ) (CFC-14)</td>
<td>0.0</td>
<td>( 6.0 \times 10^{-11} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{CHClF}_2 ) (CFC-22)</td>
<td>1.24</td>
<td>( 4.31 \times 10^4 )</td>
<td>( 2.0 \times 10^{-11} ) 20</td>
<td>-15.1</td>
<td>3</td>
</tr>
<tr>
<td>( \text{CCl}_2\text{FClIF}_2 ) (CFC-113)</td>
<td>&lt;0.5</td>
<td>( 3.40 \times 10^5 )</td>
<td>( 4.0 \times 10^{-12} ) 20</td>
<td>&lt;17.5</td>
<td>3</td>
</tr>
<tr>
<td>( \text{CCl}_2\text{FClIF}_2 ) (CFC-114)</td>
<td>&lt;0.5</td>
<td>( 2.50 \times 10^5 )</td>
<td>( 1.0 \times 10^{-12} ) 35</td>
<td>-17.3</td>
<td>3</td>
</tr>
<tr>
<td>( \text{CF}_3\text{F} ) (CFC-115)</td>
<td>0.8</td>
<td>( 2.50 \times 10^5 )</td>
<td>( 2.0 \times 10^{-12} ) 35</td>
<td>-17.4</td>
<td>3</td>
</tr>
<tr>
<td>( \text{CClF}_2\text{CF}_3 ) (CFC-116)</td>
<td>~1.82</td>
<td>( 2.54 \times 10^4 )</td>
<td>( 1.0 \times 10^{-13} ) 20</td>
<td>-16.9</td>
<td>4</td>
</tr>
<tr>
<td>( \text{CBrClIF}_2 ) (CFC-12B1)</td>
<td>~1</td>
<td>( 1.81 \times 10^5 )</td>
<td>( 4.0 \times 10^{-13} ) 20</td>
<td>-17.7</td>
<td>3</td>
</tr>
<tr>
<td>( \text{CBrF}_3 ) (CFC-13B1)</td>
<td>~1</td>
<td>( 1.13 \times 10^5 )</td>
<td>( 5.0 \times 10^{-13} ) 20</td>
<td>-17.4</td>
<td>3</td>
</tr>
</tbody>
</table>

<sup>a</sup>Notes:
1. Magnetic dipole. Value given for \( \mu \) is 2 Bohr magnetons converted to equivalent Debye (D) units. \( Q_{ns} \) is from E. A. Cohen (private communication). Abundance is from J. G. Anderson, J. J. Margitan, D. H. Stedman [Science 198, 501 (1977)] with nominal isotopic distribution assumed. Note: the lowest-frequency transition for Cl is \(~ 25,000 \text{ GHz} \) [M. Dagenais, J. W. C. Johns, A. R. W. McKellar, Can. J. Phys. 54, 1438 (1976)].
2. No spin or rotational spectrum.
3. Spectroscopic parameters are estimates by E. A. Cohen (private communication).
4. \( \mu \) is from J. Gadhi, G. Wlodarczak, J. Legrand, J. DeMaison, Chem. Phys. Lett. 156, 401 (1989). \( Q_{ns} \) is an estimate by E. A. Cohen (private communication).

### TABLE 8.6 Carbon and Sulfur Molecules<sup>a</sup>

<table>
<thead>
<tr>
<th>Molecule</th>
<th>JPL SPEC- TAG</th>
<th>( \mu ) (D)</th>
<th>( Q_{ns} ) at 225 K</th>
<th>Approximate Maximum Stratospheric Mixing Ratio</th>
<th>( \log_{10} ) of ( f_{\mu^2}/Q_{rs} )</th>
<th>Notes&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CO}_2 ) (OCO)</td>
<td></td>
<td>0.0007</td>
<td>( 4.25 \times 10^2 )</td>
<td>( 3.5 \times 10^{-4} ) &lt;70</td>
<td>-14.8</td>
<td>1</td>
</tr>
<tr>
<td>( \text{OC}^{18} \text{O} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{CO} )</td>
<td>28001</td>
<td>0.1098</td>
<td>( 8.17 \times 10^1 )</td>
<td>( 1.0 \times 10^{-7} ) 50</td>
<td>-10.8</td>
<td>3</td>
</tr>
<tr>
<td>( ^{13}\text{CO} )</td>
<td>29001</td>
<td>0.11</td>
<td>( 8.55 \times 10^1 )</td>
<td>( 1.1 \times 10^{-9} ) 50</td>
<td>-12.8</td>
<td>3</td>
</tr>
<tr>
<td>( \text{C}^{18} \text{O} )</td>
<td>30001</td>
<td>0.11</td>
<td>( 8.58 \times 10^1 )</td>
<td>( 2.0 \times 10^{-10} ) 50</td>
<td>-13.5</td>
<td>3</td>
</tr>
<tr>
<td>( \text{C}^{17} \text{O} )</td>
<td>30001</td>
<td>0.11</td>
<td>( 8.58 \times 10^1 )</td>
<td>( 3.7 \times 10^{-11} ) 50</td>
<td>-14.2</td>
<td>3</td>
</tr>
<tr>
<td>( \text{H}_2\text{CO} )</td>
<td>30004</td>
<td>2.331</td>
<td>( 1.87 \times 10^3 )</td>
<td>( 1.0 \times 10^{-10} ) 35</td>
<td>-12.5</td>
<td></td>
</tr>
</tbody>
</table>

<sup>b</sup>Notes:
"Notes:
1. Magnetic dipole. Value given for \( \mu \) is 2 Bohr magnetons converted to equivalent Debye (D) units. \( Q_{ns} \) is from E. A. Cohen (private communication). Abundance is from J. G. Anderson, J. J. Margitan, D. H. Stedman [Science 198, 501 (1977)] with nominal isotopic distribution assumed. Note: the lowest-frequency transition for Cl is \(~ 25,000 \text{ GHz} \) [M. Dagenais, J. W. C. Johns, A. R. W. McKellar, Can. J. Phys. 54, 1438 (1976)].
2. No spin or rotational spectrum.
3. Spectroscopic parameters are estimates by E. A. Cohen (private communication).
4. \( \mu \) is from J. Gadhi, G. Wlodarczak, J. Legrand, J. DeMaison, Chem. Phys. Lett. 156, 401 (1989). \( Q_{ns} \) is an estimate by E. A. Cohen (private communication).
<table>
<thead>
<tr>
<th>Molecule</th>
<th>JPL SPEC-TAG</th>
<th>( \mu ) (D)</th>
<th>( Q_n ) at 225 K</th>
<th>Value ( f )</th>
<th>Height (km)</th>
<th>( \log_{10} ) of ( f\mu^2/Q_n )</th>
<th>Notes(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2^3\text{CO} )</td>
<td>31002</td>
<td>2.331</td>
<td>( 1.93 \times 10^3 )</td>
<td>( 1.1 \times 10^{-12} )</td>
<td>35</td>
<td>-14.5</td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{C}^{18}\text{O} )</td>
<td>32004</td>
<td>2.331</td>
<td>( 1.96 \times 10^3 )</td>
<td>( 2.0 \times 10^{-13} )</td>
<td>35</td>
<td>-15.3</td>
<td></td>
</tr>
<tr>
<td>( \text{HCN} )</td>
<td>27001</td>
<td>2.984</td>
<td>( 1.06 \times 10^2 )</td>
<td>( 1.0 \times 10^{-10} )</td>
<td>30</td>
<td>-11.1</td>
<td>4</td>
</tr>
<tr>
<td>( \text{HCN} (\nu_2^b) )</td>
<td>27003</td>
<td>~2.9</td>
<td>( 1.06 \times 10^2 )</td>
<td>( 1.0 \times 10^{-12} )</td>
<td>30</td>
<td>-13.1</td>
<td>2, 4, 5</td>
</tr>
<tr>
<td>( \text{HCN} (2\nu_3^b) )</td>
<td>~2.9</td>
<td>2.931</td>
<td>( 1.06 \times 10^2 )</td>
<td>( 1.2 \times 10^{-14} )</td>
<td>30</td>
<td>-15.0</td>
<td>2, 5</td>
</tr>
<tr>
<td>( \text{HCN} (2\nu_3^b) )</td>
<td>27003</td>
<td>~2.9</td>
<td>( 1.06 \times 10^2 )</td>
<td>( 1.1 \times 10^{-14} )</td>
<td>30</td>
<td>-15.1</td>
<td>2, 5</td>
</tr>
<tr>
<td>( \text{H}^{13}\text{CN} )</td>
<td>28002</td>
<td>2.984</td>
<td>( 1.09 \times 10^2 )</td>
<td>( 1.1 \times 10^{-12} )</td>
<td>30</td>
<td>-13.0</td>
<td>4</td>
</tr>
<tr>
<td>( \text{HC}^{15}\text{N} )</td>
<td>28003</td>
<td>2.984</td>
<td>( 1.09 \times 10^2 )</td>
<td>( 3.7 \times 10^{-13} )</td>
<td>30</td>
<td>-13.5</td>
<td></td>
</tr>
<tr>
<td>( \text{DCN} )</td>
<td>28004</td>
<td>2.984</td>
<td>( 1.30 \times 10^2 )</td>
<td>( 1.5 \times 10^{-14} )</td>
<td>30</td>
<td>-14.9</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_2\text{CN} )</td>
<td>41001</td>
<td>3.919</td>
<td>( 9.84 \times 10^3 )</td>
<td>( &lt;1.0 \times 10^{-11} )</td>
<td>20</td>
<td>-13.8</td>
<td></td>
</tr>
<tr>
<td>( \text{CH}_3\text{C}^{15}\text{N} )</td>
<td>42001</td>
<td>3.919</td>
<td>( 3.39 \times 10^3 )</td>
<td>( &lt;3.7 \times 10^{-14} )</td>
<td>20</td>
<td>-15.8</td>
<td></td>
</tr>
<tr>
<td>( \text{SO}_2 )</td>
<td>64002</td>
<td>1.633</td>
<td>( 3.77 \times 10^4 )</td>
<td>( 1.0 \times 10^{-9} )</td>
<td>( &lt;\sim 30 )</td>
<td>-13.2</td>
<td>6</td>
</tr>
<tr>
<td>( \text{SO}^{34}\text{O}_2 )</td>
<td>~1.62</td>
<td>~3.8 \times 10^4</td>
<td>( 4.2 \times 10^{-11} )</td>
<td>( &lt;\sim 30 )</td>
<td>-14.4</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>( \text{SO}^{18}\text{O} )</td>
<td>~1.6</td>
<td>~3.8 \times 10^4</td>
<td>( 4.0 \times 10^{-12} )</td>
<td>( &lt;\sim 30 )</td>
<td>-15.4</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>( \text{SO}^{17}\text{O} )</td>
<td>~1.6</td>
<td>~3.8 \times 10^4</td>
<td>( 7.5 \times 10^{-13} )</td>
<td>( &lt;\sim 30 )</td>
<td>-16.3</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>( \text{OCS} )</td>
<td>60001</td>
<td>0.715</td>
<td>( 7.72 \times 10^2 )</td>
<td>( 3.0 \times 10^{-10} )</td>
<td>20</td>
<td>-12.7</td>
<td>7</td>
</tr>
<tr>
<td>( \text{O}^{13}\text{CS} )</td>
<td>61001</td>
<td>0.715</td>
<td>( 7.74 \times 10^2 )</td>
<td>( 3.0 \times 10^{-12} )</td>
<td>20</td>
<td>-14.7</td>
<td></td>
</tr>
<tr>
<td>( \text{OC}^{34}\text{S} )</td>
<td>62001</td>
<td>0.715</td>
<td>( 7.78 \times 10^2 )</td>
<td>( 1.3 \times 10^{-11} )</td>
<td>20</td>
<td>-14.1</td>
<td></td>
</tr>
<tr>
<td>( \text{OC}^{18}\text{OS} )</td>
<td>62002</td>
<td>0.715</td>
<td>( 8.22 \times 10^2 )</td>
<td>( 6.0 \times 10^{-13} )</td>
<td>20</td>
<td>-15.4</td>
<td></td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4 )</td>
<td>98001</td>
<td>2.725</td>
<td>( 5.07 \times 10^4 )</td>
<td>( 5.0 \times 10^{-11} )</td>
<td>25</td>
<td>-14.1</td>
<td>8</td>
</tr>
</tbody>
</table>

\(^a\)Spectroscopic parameters, unless otherwise noted, are from the JPL catalog.

\(^b\)Notes:

1. No spin or rotational spectrum.
2. Spectroscopic parameters are estimates by E. A. Cohen (private communication).
3. Mixing ratio is \( >100 \) times larger at \( \sim 70-140 \) km.
4. Values given here for \( Q_n \) are reduced three times from the JPL catalog values to account for triplets of lines due to nitrogen quadrupole splitting that are included in the catalog, but that are not resolved in the stratospheric spectrum.
5. The mixing ratio given here for excited vibrational states is that of the ground state multiplied by \( e^{-E_v/kT}\) at \( T = 225 \) K, where \( E_v \) is the energy of the excited state above the ground state. The values used for \( E_v/\hbar c \) are from E. A. Cohen (private communication) and given below.

\[
\begin{align*}
\text{Molecule (state)} & & E_v/\hbar c/(\text{cm}^{-1}) & & e^{-E_v/kT}\text{ at } T = 225 \text{ K} \\
\text{HCN} (\nu_2^b) & & 713 & & 1.0 \times 10^{-2} \\
\text{HCN} (2\nu_3^b) & & 1410 & & 1.2 \times 10^{-4} \\
\text{HCN} (2\nu_3^b) & & 1426 & & 1.1 \times 10^{-4} \\
\end{align*}
\]

### TABLE 8.7 Isotopic Data for Atoms that Are Chemically Active in the Stratosphere.

<table>
<thead>
<tr>
<th>Z&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Isotope</th>
<th>Nuclear Spin</th>
<th>Nominal % Natural Abundance&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Notes on Abundances&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt;sup&gt;1&lt;/sup&gt;H</td>
<td>1/2</td>
<td>99.985</td>
<td>See note for &lt;sup&gt;2&lt;/sup&gt;H. Based on average for fresh and ocean water: [1] measure 0.0153–0.0156% for ocean water, and 0.0133–0.0154% for fresh water in the U.S. [2] obtain 0.0418 for Lake Michigan water, and variations of from −17% to +7% of this value for ground-level air collected in the U.S. and Germany. [3] measure a variation in surface air of approximately −10% to +20% relative to the ‘standard’ value for ocean water. [4] measure D/H for ‘Standard Light Antarctic Precipitation’ which is 0.4285 that of ‘Standard Mean Ocean Water’.</td>
</tr>
<tr>
<td>2</td>
<td>&lt;sup&gt;2&lt;/sup&gt;H (D)</td>
<td>1</td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>&lt;sup&gt;12&lt;/sup&gt;C</td>
<td>0</td>
<td>98.89</td>
<td>See note for &lt;sup&gt;13&lt;/sup&gt;C. From [5] who obtains 1.108 for limestone CO&lt;sub&gt;2&lt;/sub&gt; (reanalyzed by [8] who obtains 1.096 to 1.113).</td>
</tr>
<tr>
<td>7</td>
<td>&lt;sup&gt;14&lt;/sup&gt;N</td>
<td>1</td>
<td>99.634</td>
<td>See note for &lt;sup&gt;15&lt;/sup&gt;N. From [5, 6] for N&lt;sub&gt;2&lt;/sub&gt; in air. [7] find no significant change with height up to 52 km.</td>
</tr>
<tr>
<td>8</td>
<td>&lt;sup&gt;16&lt;/sup&gt;O</td>
<td>0</td>
<td>99.758</td>
<td>See notes for &lt;sup&gt;18&lt;/sup&gt;O and &lt;sup&gt;17&lt;/sup&gt;O. From [5] (reanalyzed by [8] who also obtains 0.204 to 0.207 for carbonates) measured for air. [7] find &lt;1% difference from the ‘standard’ value for stratospheric O&lt;sub&gt;2&lt;/sub&gt;; [9] find &lt;~2% difference for surface O&lt;sub&gt;2&lt;/sub&gt;. [10] finds up to ~40% enhancement in stratospheric &lt;sup&gt;18&lt;/sup&gt;O&lt;sub&gt;3&lt;/sub&gt; and perhaps also in &lt;sup&gt;46&lt;/sup&gt;O&lt;sub&gt;3&lt;/sub&gt;.</td>
</tr>
<tr>
<td>8</td>
<td>&lt;sup&gt;18&lt;/sup&gt;O</td>
<td>0</td>
<td>0.204</td>
<td></td>
</tr>
<tr>
<td>$Z^a$</td>
<td>Isotope</td>
<td>Nuclear Spin</td>
<td>Nominal % Natural Abundance</td>
<td>Notes on Abundances$^b$</td>
</tr>
<tr>
<td>------</td>
<td>---------</td>
<td>--------------</td>
<td>----------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>8</td>
<td>$^{17}$O</td>
<td>5/2</td>
<td>0.038</td>
<td>From [5] (and reanalyzed by [8]) measured for air. [5, 7] find essentially no atmospheric variation.</td>
</tr>
<tr>
<td>9</td>
<td>$^{19}$F</td>
<td>1/2</td>
<td>100.</td>
<td>No evidence for any isotope except $^{19}$F [11].</td>
</tr>
<tr>
<td>16</td>
<td>$^{32}$S</td>
<td>0</td>
<td>95.02</td>
<td>Nominal values are from meteoritic sulphur [12]. [13] obtain 95.005 for virgin sulfur from a dome in Wharton County, Texas.</td>
</tr>
<tr>
<td></td>
<td>$^{34}$S</td>
<td>0</td>
<td>4.213</td>
<td>[13] obtain 4.223. See note for $^{32}$S.</td>
</tr>
<tr>
<td></td>
<td>$^{33}$S</td>
<td>3/2</td>
<td>0.75</td>
<td>[13] obtain 0.758. See note for $^{32}$S.</td>
</tr>
<tr>
<td></td>
<td>$^{36}$S</td>
<td>0</td>
<td>0.017</td>
<td>[13] obtain 0.014. See note for $^{35}$S.</td>
</tr>
<tr>
<td>17</td>
<td>$^{35}$Cl</td>
<td>3/2</td>
<td>75.77</td>
<td>From [14] measured for seven samples of halite or sylvite crystals from collections of the U.S. National Museum. [15, 16] found no variations in more extensive surveys. [17] obtain $75.529 \pm 0.016%$ for natural potassium chloride. [18] obtain $75.4 \pm 0.2%$ for HCl.</td>
</tr>
<tr>
<td></td>
<td>$^{37}$Cl</td>
<td>3/2</td>
<td>24.23</td>
<td>From [14]; see note for $^{35}$Cl. [17] obtain $24.471 \pm 0.016%$ for natural potassium chloride. [18] obtain $24.6 \pm 0.2%$ for HCl.</td>
</tr>
<tr>
<td>35</td>
<td>$^{79}$Br</td>
<td>3/2</td>
<td>50.69</td>
<td>From [19] for mineral samples from around the world. [20] find 50.54% with $\sim 0.2%$ variations in natural samples from Michigan brines, West Virginia brines, California Searles (dry) Lake, Pacific Ocean, and Gulf of Mexico. [20] find $50.53 \pm 0.1%$ for potassium bromide. See note for $^{79}$Br. [20] find 49.46%. [21] find $49.47 \pm 0.1%$.</td>
</tr>
<tr>
<td></td>
<td>$^{81}$Br</td>
<td>3/2</td>
<td>49.31</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Nuclear charge of the isotope.

$^b$ Sources of data: [5, 7, 8, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21].
"Z is the atomic number.

Abundances are on a "per atom" basis. [ ] refer to the following references:

Table 8.8 lists molecules in decreasing order of $M$. The author’s experience suggests that a molecule with log $M$ greater than about $-14$ will have spectral lines of sufficient strength for measurement by microwave limb sounding. $M$ should be used only as a rough guideline, however, and a definitive statement on measurement of a molecule requires detailed examination of its spectra, and that of molecules that might have interfering lines. This should include, at least, all molecules having $M$ larger than and comparable to that of the “target” molecule.

### 8.4 GEOMETRICAL CONSIDERATIONS

Figure 8.4 shows the geometry for limb sounding. An instrument is located at an observation point having height $h_o$ above Earth’s surface. The path of a ray of radiation incident upon the instrument is described by the height $h_T$ of its tangent point. The angle $\theta$, which a straight-line ray path makes with the local horizontal at the observation point, satisfies

$$\cos \theta = \frac{h_T + R_E}{h_o + R_E} \quad (8.1)$$

where $R_E$ is Earth’s radius. Note that $\theta$ is also the great circle angle between the observation and tangent points. The distance between the observation and tangent points is

$$S = \sqrt{(R_E + h_o)^2 - (R_E + h_T)^2} \quad (8.2)$$

$$= \sqrt{(2R_E + h_o + h_T)(h_o - h_T)} \quad (8.3)$$

$$= \sqrt{(2R_E + h_o)(h_o - h_T)} \quad (8.4)$$

where the approximation $h_T \ll R_E$, which always holds for the heights in which we are interested, has been used in Eq. 8.4.* An important geometric quantity, which places requirements on the instrument angular stability and FOV width, is the rate of change of $h_T$ with $\theta$. This is just the distance $S$, or

$$\frac{dh_T}{d\theta} = \sqrt{(2R_E + h_o)(h_o - h_T)} \quad (8.5)$$

*Highly accurate calculations must also account for any differences in $R_E$ between the tangent and observation locations, as well as effects of refraction. Centrifugal forces of Earth’s rotation cause a larger equatorial than polar radius: the polar radius is 6357 km, the equatorial is 6378 km, and the mean radius (that of a sphere having Earth’s volume) is 6371 km. Refraction between the tangent point and an observer outside the atmosphere changes the ray’s direction of arrival at the observation point by $0.5^\circ$ for a tangent point near the Earth’s surface, and by $0.05^\circ$ for a tangent point at 20 km [37].
### TABLE 8.8 Stratospheric Molecules and Atoms in Descending Order of $\frac{f}{\mu^2 / Q_{rs}}$  

<table>
<thead>
<tr>
<th>$\log_{10} \frac{f}{\mu^2 / Q_{rs}}$</th>
<th>Molecule or Atom</th>
<th>JPL SPEC- TAG</th>
<th>$\mu$</th>
<th>$Q_{rs}$ at 225 K</th>
<th>Approx. Max. Stratospheric Mixing Ratio</th>
<th>Plot of $\log_{10} \left{ \frac{f}{\mu^2 / Q_{rs}} \right}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Value $\equiv f$</td>
<td>ht/km</td>
</tr>
<tr>
<td>-6.4</td>
<td>O$_2$</td>
<td>32001</td>
<td>0.0186</td>
<td>$1.64 \times 10^2$</td>
<td>$2.1 \times 10^{-1}$</td>
<td>$\sim 90$</td>
</tr>
<tr>
<td>-6.8</td>
<td>H$_2$O</td>
<td>18003</td>
<td>1.855</td>
<td>$1.16 \times 10^2$</td>
<td>$5.0 \times 10^{-6}$</td>
<td>50</td>
</tr>
<tr>
<td>-9.1</td>
<td>$^{18}$O$_2$</td>
<td>34001</td>
<td>0.0186</td>
<td>$3.47 \times 10^2$</td>
<td>$8.6 \times 10^{-4}$</td>
<td>$\sim 90$</td>
</tr>
<tr>
<td>-9.1</td>
<td>O$_3$</td>
<td>48004</td>
<td>0.5337</td>
<td>$2.26 \times 10^3$</td>
<td>$7.0 \times 10^{-6}$</td>
<td>35</td>
</tr>
<tr>
<td>-9.5</td>
<td>H$_2$O$^{18}$</td>
<td>20003</td>
<td>1.85</td>
<td>$1.17 \times 10^2$</td>
<td>$1.0 \times 10^{-8}$</td>
<td>50</td>
</tr>
<tr>
<td>-9.9</td>
<td>HF</td>
<td>20002</td>
<td>1.826</td>
<td>$1.05 \times 10^4$</td>
<td>$4.0 \times 10^{-10}$</td>
<td>35</td>
</tr>
<tr>
<td>-10.1</td>
<td>$^{17}$O$_2$</td>
<td>33002</td>
<td>0.0186</td>
<td>$3.47 \times 10^2$</td>
<td>$1.5 \times 10^{-4}$</td>
<td>$\sim 90$</td>
</tr>
<tr>
<td>-10.2</td>
<td>H$<em>2$O$</em>{^{17}}$</td>
<td>19003</td>
<td>1.85</td>
<td>$1.16 \times 10^2$</td>
<td>$1.9 \times 10^{-9}$</td>
<td>50</td>
</tr>
<tr>
<td>-10.3</td>
<td>HDO</td>
<td>19002</td>
<td>1.732</td>
<td>$9.56 \times 10^1$</td>
<td>$1.5 \times 10^{-9}$</td>
<td>50</td>
</tr>
<tr>
<td>-10.3</td>
<td>OH</td>
<td>17001</td>
<td>1.667</td>
<td>$6.03 \times 10^1$</td>
<td>$1.0 \times 10^{-9}$</td>
<td>50</td>
</tr>
<tr>
<td>-10.5</td>
<td>H$^{35}$Cl</td>
<td>36001</td>
<td>1.109</td>
<td>$6.09 \times 10^1$</td>
<td>$1.5 \times 10^{-9}$</td>
<td>50</td>
</tr>
<tr>
<td>-10.7</td>
<td>O$_2$ ($\nu_1$)</td>
<td>32002</td>
<td>0.0186</td>
<td>$1.64 \times 10^2$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$\sim 90$</td>
</tr>
<tr>
<td>-10.8</td>
<td>CO</td>
<td>28001</td>
<td>0.1098</td>
<td>$8.17 \times 10^1$</td>
<td>$1.0 \times 10^{-7}$</td>
<td>50</td>
</tr>
<tr>
<td>-10.9</td>
<td>N$_2$O</td>
<td>44004</td>
<td>0.1608</td>
<td>$3.74 \times 10^2$</td>
<td>$2.0 \times 10^{-7}$</td>
<td>20</td>
</tr>
<tr>
<td>-11.0</td>
<td>O$_3$ ($\nu_2$)</td>
<td>48005</td>
<td>0.5261</td>
<td>$2.26 \times 10^3$</td>
<td>$7.9 \times 10^{-8}$</td>
<td>35</td>
</tr>
<tr>
<td>-11.0</td>
<td>H$^{37}$Cl</td>
<td>38001</td>
<td>1.109</td>
<td>$6.10 \times 10^1$</td>
<td>$0.5 \times 10^{-9}$</td>
<td>50</td>
</tr>
<tr>
<td>-11.0</td>
<td>O$_3$ ($\Delta$)</td>
<td>32005</td>
<td>0.0186</td>
<td>$1.13 \times 10^2$</td>
<td>$3.0 \times 10^{-6}$</td>
<td>70</td>
</tr>
<tr>
<td>-11.1</td>
<td>HCN</td>
<td>27001</td>
<td>2.984</td>
<td>$1.06 \times 10^2$</td>
<td>$1.0 \times 10^{-10}$</td>
<td>30</td>
</tr>
<tr>
<td>-11.3</td>
<td>$^{16}$O</td>
<td>16001</td>
<td>0.0186</td>
<td>$6.324$</td>
<td>$1.0 \times 10^{-7}$</td>
<td>50</td>
</tr>
<tr>
<td>-11.3</td>
<td>H$_2$O ($\nu_2$)</td>
<td>18005</td>
<td>1.855</td>
<td>$1.16 \times 10^2$</td>
<td>$1.9 \times 10^{-10}$</td>
<td>50</td>
</tr>
<tr>
<td>-11.7</td>
<td>$^{35}$ClO</td>
<td>51002</td>
<td>1.298</td>
<td>$2.85 \times 10^4$</td>
<td>$3.0 \times 10^{-10}$</td>
<td>35</td>
</tr>
<tr>
<td>-11.8</td>
<td>$^{18}$O$_2$</td>
<td>50004</td>
<td>0.532</td>
<td>$4.69 \times 10^3$</td>
<td>$2.9 \times 10^{-8}$</td>
<td>35</td>
</tr>
<tr>
<td>-11.8</td>
<td>O$_3$ ($\nu_3$)</td>
<td>50003</td>
<td>0.532</td>
<td>$2.29 \times 10^3$</td>
<td>$1.4 \times 10^{-8}$</td>
<td>35</td>
</tr>
<tr>
<td>-12.0</td>
<td>O$_3$ ($\nu_3$)</td>
<td>48006</td>
<td>0.532</td>
<td>$2.26 \times 10^3$</td>
<td>$9.0 \times 10^{-9}$</td>
<td>35</td>
</tr>
<tr>
<td>-12.0</td>
<td>HNO$_3$</td>
<td>63001</td>
<td>1.99</td>
<td>$1.82 \times 10^3$</td>
<td>$5.0 \times 10^{-9}$</td>
<td>25</td>
</tr>
<tr>
<td>-12.1</td>
<td>$^{37}$ClO</td>
<td>53002</td>
<td>1.239</td>
<td>$2.90 \times 10^1$</td>
<td>$1.0 \times 10^{-10}$</td>
<td>35</td>
</tr>
<tr>
<td>log$<em>{10}$ (f \mu^2/Q</em>{n0})</td>
<td>Molecule or Atom</td>
<td>JPL SPEC-Tag</td>
<td>(\mu) (D)</td>
<td>(Q_{n0}) at 225 K</td>
<td>Approx. Max. Stratospheric Mixing Ratio</td>
<td>Plot of (\log_{10}\left{f \mu^2/Q_{n0}\right})</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----------------</td>
<td>-------------</td>
<td>--------</td>
<td>-----------------</td>
<td>---------------------------------</td>
<td>------------------</td>
</tr>
<tr>
<td>-12.2</td>
<td>O$_3$ ((r_1))</td>
<td>48006</td>
<td>0.532</td>
<td>2.26 \times 10^3</td>
<td>9.0 \times 10^{-9}</td>
<td>35</td>
</tr>
<tr>
<td>-12.5</td>
<td>NO</td>
<td>30008</td>
<td>0.1587</td>
<td>8.17 \times 10^2</td>
<td>1.0 \times 10^{-8}</td>
<td>40</td>
</tr>
<tr>
<td>-12.5</td>
<td>H$_2$CO</td>
<td>30004</td>
<td>2.331</td>
<td>1.87 \times 10^1</td>
<td>1.0 \times 10^{-10}</td>
<td>35</td>
</tr>
<tr>
<td>-12.5</td>
<td>N$_2$O ((r_2))</td>
<td>44009</td>
<td>0.1608</td>
<td>3.74 \times 10^2</td>
<td>4.6 \times 10^{-9}</td>
<td>20</td>
</tr>
<tr>
<td>-12.6</td>
<td>HO$_2$</td>
<td>33001</td>
<td>1.541</td>
<td>2.84 \times 10^3</td>
<td>3.0 \times 10^{-10}</td>
<td>50</td>
</tr>
<tr>
<td>-12.7</td>
<td>OCS</td>
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<td>Plot of ( \log_{10} { f \mu^2 / Q_n } )</td>
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<td>( Q_n ) at 225 K</td>
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<td>Plot of log₁₀ ( fμ^2 / Q_n )</td>
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<td>1.06 \times 10³</td>
<td>1.1 \times 10⁻¹⁴</td>
<td>30</td>
<td>○</td>
</tr>
<tr>
<td>-15.1</td>
<td>HNO₃ ( (ν₆ + ν₉) )</td>
<td>~2.0</td>
<td>1.82 \times 10⁴</td>
<td>4.3 \times 10⁻¹²</td>
<td>25</td>
<td>○</td>
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<tr>
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<td>CHCIF₂ (CFC-22)</td>
<td>1.24</td>
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<tr>
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<td>N¹⁸O</td>
<td>~0.16</td>
<td>~8.2 \times 10³</td>
<td>2.0 \times 10⁻¹¹</td>
<td>35</td>
<td>○</td>
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<tr>
<td>-15.2</td>
<td>O₃ (2ν₁)</td>
<td>~0.52</td>
<td>2.26 \times 10³</td>
<td>5.6 \times 10⁻¹²</td>
<td>35</td>
<td>○</td>
</tr>
<tr>
<td>-15.2</td>
<td>HNO₃ (2ν₂)</td>
<td>~2.0</td>
<td>1.82 \times 10⁴</td>
<td>3.1 \times 10⁻¹²</td>
<td>25</td>
<td>○</td>
</tr>
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<td>-15.2</td>
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<td>~1.8</td>
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<td>1.96 \times 10³</td>
<td>2.0 \times 10⁻¹³</td>
<td>35</td>
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<tr>
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<td>NO¹⁸O</td>
<td>~0.32</td>
<td>~8.8 \times 10³</td>
<td>4.1 \times 10⁻¹¹</td>
<td>40</td>
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</tr>
<tr>
<td>-15.3</td>
<td>SO¹⁸O</td>
<td>~0.32</td>
<td>~8.8 \times 10³</td>
<td>3.7 \times 10⁻¹¹</td>
<td>40</td>
<td>○</td>
</tr>
<tr>
<td>-15.4</td>
<td>HNO₃ ( (ν₆ + ν₉) )</td>
<td>~2.0</td>
<td>1.82 \times 10⁴</td>
<td>2.1 \times 10⁻¹²</td>
<td>25</td>
<td>○</td>
</tr>
<tr>
<td>-15.4</td>
<td>HNO₃ ( (ν₆ + ν₉) )</td>
<td>~2.0</td>
<td>1.82 \times 10⁴</td>
<td>2.0 \times 10⁻¹²</td>
<td>25</td>
<td>○</td>
</tr>
<tr>
<td>-15.4</td>
<td>SO¹⁸O</td>
<td>~1.6</td>
<td>~3.8 \times 10⁴</td>
<td>4.0 \times 10⁻¹²</td>
<td>~30</td>
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<td>62002</td>
<td>0.715</td>
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<td>6.0 \times 10⁻¹³</td>
<td>20</td>
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<tr>
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<td>CCl₃F₂ (CFC-12)</td>
<td>~0.5</td>
<td>1.17 \times 10⁵</td>
<td>2.0 \times 10⁻¹⁰</td>
<td>20</td>
<td>○</td>
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<tr>
<td>-15.6</td>
<td>HNO₃ ( ν₆ )</td>
<td>~2.0</td>
<td>1.82 \times 10⁴</td>
<td>1.3 \times 10⁻¹²</td>
<td>25</td>
<td>○</td>
</tr>
<tr>
<td>-15.6</td>
<td>HNO₃ ( ν₇ )</td>
<td>~2.0</td>
<td>1.82 \times 10⁴</td>
<td>1.2 \times 10⁻¹²</td>
<td>25</td>
<td>○</td>
</tr>
<tr>
<td>-15.7</td>
<td>³³Cl</td>
<td>0.0186</td>
<td>16.01</td>
<td>9.0 \times 10⁻¹²</td>
<td>40</td>
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</tr>
<tr>
<td>-15.7</td>
<td>HNO₃ ( ν₄ )</td>
<td>~2.0</td>
<td>1.82 \times 10⁴</td>
<td>1.1 \times 10⁻¹²</td>
<td>25</td>
<td>○</td>
</tr>
<tr>
<td>-15.7</td>
<td>HNO₃ ( ν₅ + ν₉ )</td>
<td>~2.0</td>
<td>1.82 \times 10⁴</td>
<td>1.0 \times 10⁻¹²</td>
<td>25</td>
<td>○</td>
</tr>
<tr>
<td>-15.7</td>
<td>HNO₃ ( ν₇ + ν₉ )</td>
<td>~2.0</td>
<td>1.82 \times 10⁴</td>
<td>9.4 \times 10⁻¹３</td>
<td>25</td>
<td>○</td>
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<tr>
<td>-15.8</td>
<td>HNO₃ (3ν₀)</td>
<td>~2.0</td>
<td>1.82 \times 10⁴</td>
<td>8.0 \times 10⁻¹³</td>
<td>25</td>
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</table>
### TABLE 8.8 (Continued)

<table>
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<tr>
<th>( \log_{10} \frac{f \mu^2}{Q_{rs}} )</th>
<th>Molecule or Atom</th>
<th>JPL SPEC-TAG</th>
<th>( \mu )</th>
<th>( Q_{rs} ) at 225 K</th>
<th>Approx. Max. Stratospheric Mixing Ratio</th>
<th>Plot of ( \log_{10} \left{ \frac{f \mu^2}{Q_{rs}} \right} )</th>
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<tr>
<td>(-15.8)</td>
<td>( \text{CH}_3\text{C}^{13}\text{N} )</td>
<td>42001</td>
<td>3.919</td>
<td>( 3.39 \times 10^3 )</td>
<td>(&lt; 3.7 \times 10^{-14})</td>
<td>(\bullet)</td>
</tr>
<tr>
<td>(-15.9)</td>
<td>( \text{HNO}_3 ) ((\nu_6 + \nu_8))</td>
<td>(-2.0)</td>
<td>(1.82 \times 10^4)</td>
<td>(6.0 \times 10^{-13})</td>
<td>(25)</td>
<td></td>
</tr>
<tr>
<td>(-15.9)</td>
<td>( \text{N}^{17}\text{O} )</td>
<td>(-0.16)</td>
<td>(~8.2 \times 10^2)</td>
<td>(3.7 \times 10^{-12})</td>
<td>(40)</td>
<td></td>
</tr>
<tr>
<td>(-16.1)</td>
<td>( \text{N}_2\text{O}_5 )</td>
<td>(-0.1)</td>
<td>(1.13 \times 10^5)</td>
<td>(1.0 \times 10^{-9})</td>
<td>(35)</td>
<td></td>
</tr>
<tr>
<td>(-16.2)</td>
<td>( ^{37}\text{Cl} )</td>
<td>0.0186</td>
<td>16.01</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(-16.3)</td>
<td>( \text{SO}^{17}\text{O} )</td>
<td>(-1.6)</td>
<td>(~3.8 \times 10^4)</td>
<td>(7.5 \times 10^{-12})</td>
<td>(&lt; \sim 30)</td>
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<tr>
<td>(-16.4)</td>
<td>( \text{CCl}_3\text{F} ) ((\text{CFC-11}))</td>
<td>0.46</td>
<td>(1.77 \times 10^4)</td>
<td>(8.0 \times 10^{-11})</td>
<td>(20)</td>
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<tr>
<td>(-16.5)</td>
<td>( \text{CCl}_2\text{FCCl}_2 ) ((\text{CFC-113}))</td>
<td>(-0.8)</td>
<td>(4.40 \times 10^5)</td>
<td>(2.0 \times 10^{-11})</td>
<td>(20)</td>
<td></td>
</tr>
<tr>
<td>(-16.7)</td>
<td>( \text{HNO}_3 ) ((\nu_2))</td>
<td>(-2.0)</td>
<td>(1.82 \times 10^4)</td>
<td>(9.0 \times 10^{-14})</td>
<td>(25)</td>
<td></td>
</tr>
<tr>
<td>(-16.9)</td>
<td>( \text{CH}_3\text{Br} )</td>
<td>1.82</td>
<td>(2.54 \times 10^4)</td>
<td>(&lt; 1.0 \times 10^{-13})</td>
<td>(20)</td>
<td></td>
</tr>
<tr>
<td>(-17.2)</td>
<td>( \text{CCIF}_3 ) ((\text{CFC-13}))</td>
<td>(-0.5)</td>
<td>(7.19 \times 10^4)</td>
<td>(2.0 \times 10^{-12})</td>
<td>(35)</td>
<td></td>
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<tr>
<td>(-17.3)</td>
<td>( \text{CCIF}_2\text{CF}_3 ) ((\text{CFC-115}))</td>
<td>(-0.8)</td>
<td>(2.50 \times 10^5)</td>
<td>(1.0 \times 10^{-12})</td>
<td>(35)</td>
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</tr>
<tr>
<td>(-17.4)</td>
<td>( \text{CBrF}_3 ) ((\text{CFC-13B1}))</td>
<td>(-1)</td>
<td>(1.13 \times 10^5)</td>
<td>(5.0 \times 10^{-13})</td>
<td>(20)</td>
<td></td>
</tr>
<tr>
<td>(-17.5)</td>
<td>( \text{CCIF}_2\text{CClF}_2 ) ((\text{CFC-114}))</td>
<td>(&lt;0.5)</td>
<td>(3.40 \times 10^5)</td>
<td>(4.0 \times 10^{-12})</td>
<td>(20)</td>
<td></td>
</tr>
<tr>
<td>(-17.7)</td>
<td>( \text{CBrClF}_2 ) ((\text{CFC-12B1}))</td>
<td>(-1)</td>
<td>(1.81 \times 10^5)</td>
<td>(4.0 \times 10^{-13})</td>
<td>(20)</td>
<td></td>
</tr>
<tr>
<td>(-18.1)</td>
<td>( \text{NO}_3 )</td>
<td>0.0093</td>
<td>(1.05 \times 10^4)</td>
<td>(1.0 \times 10^{-10})</td>
<td>(35)</td>
<td></td>
</tr>
<tr>
<td>(-21.9)</td>
<td>( \text{HNO}_3 ) ((\nu_1))</td>
<td>(-2.0)</td>
<td>(1.82 \times 10^4)</td>
<td>(7.0 \times 10^{-19})</td>
<td>(25)</td>
<td></td>
</tr>
</tbody>
</table>

*Molecules in the JPL catalog are identified by an entry in the JPL SPECTAG column and by the symbol \(\bullet\) in the plot.*
For situations in which $h_0$ is also much less than $R_E$, which includes low-orbit satellites and balloons, Eqs. 8.4 and 8.5 can be approximated by

$$S = 113 \sqrt{h_0 - h_T} \text{ km}$$  \hspace{1cm} (8.6)

and

$$\frac{dh_T}{d\theta} = 113 \sqrt{h_0 - h_T} \text{ km/radian}$$  \hspace{1cm} (8.7)

$$= 2 \sqrt{h_0 - h_T} \text{ km/degree}$$  \hspace{1cm} (8.8)

where $R_E = 6371$ km has been used, and $h_0$ and $h_T$ have units of km. Integrating Eq. 8.8 gives

$$\theta = \sqrt{h_0 - h_T} \text{ degrees}$$  \hspace{1cm} (8.9)

which is easily remembered: the angle (in degrees) down to the tangent point approximately equals the square root of the difference (in kilometers) of the observation and tangent point heights.

As an example, the orbit height of the Upper Atmosphere Research Satellite (UARS) is $h_0 = 600$ km and, for $h_T = 20$ km, we have $S = 2780$ km, $\theta = 23.5^\circ$, and $dh_T/d\theta = 48$ km/degree. An FOV width of $\approx 0.06^\circ$ is thus required for UARS instruments to provide the $\approx 3$-km vertical resolution needed for profile measurements.* A balloon instrument at $h_0 = 40$ km observing $h_T = 20$ km has $S = 360$ km, $\theta = 4.5^\circ$, and $dh_T/d\theta = 9$ km/degree. Balloon instruments thus require FOV widths of $\approx 0.3^\circ$.

The limb-path distance $s(h_1, h_T)$ from the tangent point at height $h_T$ to a point at height $h_1$ is just that given by Eq. 8.3 with $h_0 = h_1$:

$$s(h_1, h_T) = \sqrt{(2R_E + h_1 + h_T)(h_1 - h_T)}$$  \hspace{1cm} (8.10)

$$\approx 113 \sqrt{h_1 - h_T} \text{ km}$$  \hspace{1cm} (8.11)

*Approximately one-half the 6-8-km atmospheric scale ("e-folding") height. Antenna beam widths providing vertical resolution as small as $\sim 1$ km can be useful, however, as radiative transfer through the atmospheric limb can allow such resolution to be achieved—see Table 8.9 and Figure 8.5 discussed later.
where \( h_T + h_1 \ll R_E \), and \( R_E = 6371 \) km have been used in Eq. 8.11. A limb path extending to heights 5 km above the tangent point on both sides has a length \( \approx 500 \) km.

Simple expressions giving approximate weighting functions appropriate to composition measurements by microwave limb sounding can be easily derived. For optically thin measurements, which can always be obtained by choosing spectral channels at appropriate locations on the spectral line, the measured radiance can be approximated by

\[
I_\nu = \overline{B_\nu(T)} \int \alpha_\nu(s) \, ds \tag{8.12}
\]

where the integral is along the limb path, \( s \) is a point on this path, \( \overline{B_\nu(T)} \) is a mean value of the Planck function along the path, and \( \alpha_\nu(s) \) is the absorption coefficient at \( s \), which is described in detail in Appendix 8B of this chapter. Because \( \alpha_\nu \) is proportional to the abundance of the molecule, the weighting function at \( s \) along the path is proportional to \( \alpha_\nu(s) \):

\[
W(s) \propto \alpha_\nu(s) \tag{8.13}
\]

The weighting function with respect to height \( h \) above the tangent height \( h_T \) is obtained from Eq. 8.13 by a coordinate transformation:

\[
W(h) \propto 2W(s(h)) \frac{ds}{dh} \tag{8.14}
\]

where the factor of 2 is due to a given height layer occurring twice along the path. The largest variation in \( \alpha_\nu \) is due to its dependence upon pressure \( p \); this can be approximated by

\[
\alpha_\nu \propto A(T)p^a \tag{8.15}
\]

\[
\propto A(T)e^{-ah/H} \tag{8.16}
\]

where \( a \) is a constant (generally, between 0 and 2), \( H \) is the pressure-scale height, and \( A(T) \) describes the temperature dependence of \( \alpha_\nu \). For heights of interest here \( h_T \) and \( h \) are much less than \( R_E \) so Eq. 8.10, with \( h = h_1 - h_T \), gives

\[
h = \frac{s^2}{2R_E} \tag{8.17}
\]

Equations 8.13 through 8.17 lead to
\[ W(s) = \left( \frac{a}{\sqrt{2\pi R_E H}} \right) \exp \left( -\frac{as^2}{2R_E H} \right) \]  

(8.18)

\[ W(h) = \left( \frac{a}{\sqrt{\pi hH}} \right) \exp \left( -\frac{ah}{H} \right) \]  

(8.19)

where the multiplicative constants have been chosen to give a unit area under \( W \) and dependence on temperature is ignored (dependence on temperature is generally weak; see Figure 12 of Waters [38]). Note that the weighting function along the path is a Gaussian centered at the tangent point having a width approximately equal to the geometric mean of the pressure-scale height and the diameter of Earth. \( W(h) = \infty \) at \( h = 0 \) because at the tangent point there is a finite contribution to the emission for no change in \( h \). The fraction of the total radiation that arises from the portion of the path between \( \pm s' \), or between \( h = 0 \) and \( h = h' \) is

\[
\int_{\pm s'} W(s) \, ds = \text{erf} \left\{ s' \frac{a}{\sqrt{2R_E H}} \right\} = \text{erf} \left\{ \frac{ah'}{H} \right\}
\]

(8.20)

where

\[
\text{erf} (x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} \, du
\]

(8.22)

is the error function. Half the contribution to the total emission arises from \( \text{erf} (x) = 0.5 \), given by \( x = 0.48 \). Using \( H = 7 \) km and \( R_E = 6371 \) km leads to the values in Table 8.9. Figure 8.5 shows \( W(h) \) calculated from Eq. 8.21 with \( a = 1 \); additional weighting functions are shown that have been calculated to include the effects of smearing by the FOV of a 1.6-m diameter antenna.

**TABLE 8.9**  Extent of Atmospheric Layers Giving Rise to Half the Total Limb Radiation for an Optically Thin Ray Path

<table>
<thead>
<tr>
<th>Variation in Absorption</th>
<th>( k_v \propto p^{1/2} )</th>
<th>( k_v \propto p )</th>
<th>( k_v \propto p^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height above tangent point (km)</td>
<td>3.2</td>
<td>1.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Distance along observation path (km)</td>
<td>404</td>
<td>286</td>
<td>202</td>
</tr>
</tbody>
</table>
Figure 8.5. Weighting functions indicating vertical resolution of microwave limb sounding of upper atmospheric composition. These are normalized to a unit area. The dashed curve labeled “single ray” is calculated from Eq. 8.19 and applies to a single-ray path through the atmospheric limb. Other curves, calculated by W. G. Read, include field-of-view (FOV) smearing effects. They are for measurements at the indicated frequencies from a 600 km orbit using a diffraction-limited 1.6 m diameter antenna with −30 dB edge taper. They have different widths because the diffraction-limited FOV width is inversely proportional to measurement frequency. The 1.6 m antenna FOV vertical half-power width at 640 GHz, for example, is 1.2 km at the observation path limb tangent point. All curves are for an absorption coefficient that is directly proportional to pressure ($a = 1$ in Eq. 8.15 and following).

Limb-sounding experiments need high-beam-efficiency* antennas to reject the relatively large values of thermal emission from the Earth’s surface or troposphere. This implies antenna edge tapers of at least $\sim 15 \text{ dB}$, for which the FOV width between half-power points is [39]

$$\Theta_{HP} = 1.2 \frac{\lambda}{D_a} \text{ radians} \quad (8.23)$$

where $\lambda$ is wavelength, and $D_a$ is the antenna diameter. The value of $\Theta_{HP}$ required for 3-km resolution at the limb is

$$\Theta_{3 \text{km}} = \frac{3 \text{ km}}{dh_T/d\theta} \quad (8.24)$$

*Beam efficiency is the fraction of the signal collected by an antenna from within a certain angular range, usually defined as $2.5 \times \Theta_{HP}$ (the FOV width between half-power points), relative to that collected from all angles, when the antenna is immersed in an isotropic radiation field.
Using Eqs. 8.5 and 8.23 in Eq. 8.24 gives the antenna diameter required for 3-km limb resolution:

\[ D_{a}^{3\text{km}} = 4.0 \times 10^{-4} \lambda_{\text{mm}} \sqrt{(2R_{E} + h_{0})(h_{0} - h_{T})} \text{ m} \]  
(8.25)

where \( \lambda_{\text{mm}} \) is the wavelength in mm, and \( h_{0}, h_{T}, \) and \( R_{E} \) are in km as before. For \( h_{0} \ll R_{E}, \) Eq. 8.25 becomes

\[ D_{a}^{3\text{km}} = (4.5 \times 10^{-2}) \lambda_{\text{mm}} \sqrt{h_{0} - h_{T}} \text{ m} \]  
(8.26)

Figure 8.6 shows \( D_{a}^{3\text{km}} \) as a function of wavelength (and frequency) for \( h_{T} = 20 \) km and various values of \( h_{0}. \)

The frequencies of spectral lines measured in orbit are Doppler shifted by the platform orbital motion, the Earth’s rotation, and wind. A satellite in circular orbit at height \( h_{0} \) has velocity of magnitude [40, Chapter 2]

\[ v_{0} = \frac{7.91}{\sqrt{1 + h_{0}/R_{E}}} \text{ km/s} \]  
(8.27)

The orbital motion Doppler shift \( \delta v_{0} \) is given by

\[ \frac{\delta v_{0}}{v_{0}} = \frac{v_{0}}{c} \cos \theta \cos \phi \]  
(8.28)

where \( \phi \) is the angle between the satellite velocity vector and the FOV direction projected into the local horizontal plane at the satellite. The spectral line rest fre-

---

**Figure 8.6.** Antenna diameter that gives 3 km vertical resolution at 20 km tangent height for various observation heights (\( h_{0} \)). Balloons have \( h_{0} \approx 40 \) km, low-orbit satellites have \( \sim 250 \text{ km} \leq h_{0} \leq \sim 1000 \) km, and geostationary satellites have \( h_{0} \approx 36,000 \) km.
frequency is $v_0$, and $c$ is the speed of light. Combining Eqs. 8.27 and 8.28, and using Eq. 8.1 for $\cos \theta$ and $3.00 \times 10^5 \text{ km/s}$ for $c$, gives

$$\frac{\delta v_0}{v_0} = (2.64 \times 10^{-5}) \frac{1 + h_T/R_e}{\sqrt{(1 + h_0/R_E)^3}} \cos \phi \quad (8.29)$$

$$\approx (2.3 \times 10^{-5}) \cos \phi \quad \text{for low-orbit satellites} \quad (8.30)$$

where $h_0 = 600 \text{ km}$, and $h_T \ll R_E$ have been used in Eq. 8.30.*

The ratio of orbital Doppler shift to the spectral line thermal half-width** $\Delta v_T = (4.3 \times 10^{-7}) v_0 \sqrt{T/M}$, where $M$ is the molecular weight in grams/mole, and $T$ is the temperature in Kelvins, is (for low-orbit Earth satellites)

$$\frac{\delta v_0}{\Delta v_T} = 53 \sqrt{\frac{M}{T}} \cos \phi \quad (8.31)$$

Upper-atmospheric molecules with sufficient abundance to produce measurable signals at high altitudes, where thermal broadening dominates, have $M$ ranging from 18 (H$_2$O) to 48 (O$_3$), and $T \approx 200 \text{ K}$ at these altitudes. The motion of a low-orbit satellite will thus shift a limb-emission (or absorption) spectral line by 15–30 times its thermal half-width if the FOV direction is in the orbital plane ($\phi = 0$). A 300-GHz ($\lambda = 1 \text{ mm}$) limb-emission spectral line would be shifted 7.5 MHz by the orbital motion.

Earth's rotation gives an East–West tangential velocity of 0.465 km/s at the equator. This causes a maximum Doppler shift (for an East–West FOV direction at the equator) of $1.55 \times 10^{-6} v_0$ that is 1–1.7 times thermal half-widths. A 300-GHz limb emission spectral line is shifted a maximum of 0.465 MHz by Earth’s rotation. Upper atmospheric winds are typically several tens of meters per second; a 30-m/s wind produces a Doppler shift of 0.03 MHz in a 300-GHz spectral line.

Global (or near-global) coverage of measurements is desirable. The tangent point for an instrument in low Earth orbit is $\sim 23^\circ$ great circle distance away from the suborbital track of the satellite. Therefore, in order to obtain global (or near-global) coverage with scanning in the vertical plane only, a limb-sounding instrument in low Earth polar orbit must observe in (or near to) the plane of the orbit. An interesting feature of this measurement geometry is that the vertical scan can be performed at a rate to give a vertical tangent point locus.† The tangent point

*Note that, although the maximum orbital Doppler shift occurs at $\phi = 0$ (i.e., FOV directions in the orbital plane), the change in the orbital shift per unit change in $\phi$ is maximum at $\phi = 90^\circ$ (i.e., FOV directions to the ‘side’ of the satellite). To infer atmospheric winds with an accuracy of $\approx 1 \text{ m/s}$ from their Doppler shift of spectral lines, the FOV direction on low-orbit satellites for instruments having $\phi = 90^\circ$ must be known to an accuracy of $\approx 0.01^\circ$. To accomplish this for $\phi = 0$, the FOV direction need be known to only $\approx 0.5^\circ$.

**See Chapter 2.

†This was suggested to the author by Dr. J. J. Barnett of Oxford University.
moves nearer the observer as the FOV is scanned upward and, for a "forward-
looking" instrument, the vertical scan rate can be chosen such that this effect
cancels that due to the forward orbital motion of the platform.* The required an-
gular scan rate, which can be deduced by inspection from Figure 8.4, is simply
the same as the great-circle angular rate of orbital motion, but in the opposite
direction. Consider, for example, an instrument in 600 km orbit with the need to
make a measurement every 2.5° along the orbit track. Say, measurements are
wanted over 0–100 km vertical range with 2.5 km vertical resolution. The period
for a 600 km Earth orbit is 97 minutes; the time for the satellite to move 2.5°
along the orbit is $\frac{1}{144}$ of the orbital period, 40 s. A scan every 40 s is thus needed
to produce a profile every 2.5°. A vertical scan of 0–100 km at the rate required
for a vertical tangent point locus, 0.062°/s, is implemented by moving the antenna
between angles of 21.83 and 23.95° in 34 s.** It could have 40 steps separated
by 0.053° (corresponding to 2.5-km vertical distance at the limb), each step dwell-
ing for 0.7 s with 0.15 s for movement between steps. The FOV retrace, when
radiometric calibration could also be performed, would be done in 6 s, during
which time the tangent point moves 2.5° along the orbit.

8.5 SENSITIVITY CONSIDERATIONS

The heterodyne radiometer systems used for microwave limb-sounding measure-
ments have the property that $\Delta \omega = \lambda^2$, where $\Delta$ is the antenna receiving area, $\omega$
is the field-of-view solid angle, and $\lambda$ is the wavelength of measurement. As the
diffraction-limited antenna receiving area $\Delta$ gets larger, the solid angle $\omega$ gets pro-
portionally smaller so that the received power for a signal that fills the antenna
beam remains constant. The spatial resolution improves with larger $\Delta$, of course,
as discussed in Section 8.4. The maximum thermal power per spectral interval that
can be coupled into these systems is then $\sim \frac{1}{2} \lambda^2 B_\nu(T)$, where $B_\nu(T)$ is the Planck
function at temperature $T$ and frequency $\nu$, and the factor of $\frac{1}{2}$ is due to a single
polarization being received. At atmospheric temperatures, $\frac{1}{2} \lambda^2 B_\nu(T) \approx 3 \times 10^{-15}$
W/MHz for frequencies up to $\sim 3000$ GHz (wavelengths down to $\sim 100 \mu$m) and
beyond $\sim 10,000$ GHz (30-µm wavelength), its value falls rapidly as shown in
Figure 8.7. This means that heterodyne systems can efficiently measure atmos-
pheric thermal emission up to $\sim 10,000$ GHz frequency.†

The rms noise on a measurement having integration time $\Delta t$ and spectral reso-

*The same effect can, of course, be accomplished by a "backward-looking" instrument: the FOV is
then scanned downward.

**The scan range given here is for the mean Earth radius of 6371 km, and would need to be varied
around the orbit to account for Earth's oblateness and nonunity eccentricity of the orbit.

†However, heterodyne measurements of solar absorption signals are efficient to much higher frequen-
cies because $T$ in $B_\nu(T)$ is then $\sim 6000$ K, as opposed to $\sim 200$–300 K for atmospheric thermal-emission measurements, and $\frac{1}{2} \lambda^2 B_\nu(T)$ is constant to much higher frequencies. This is the fundamental
reason that infrared laser heterodyne measurements have been made of atmospheric signals in solar
absorption, but not in thermal emission.
Figure 8.7. The function $\frac{1}{2} \lambda^2 B_v(T)$, which is the maximum thermal power per unit spectral interval available for measurement by a heterodyne radiometer system receiving a single polarization.

The noise power $\Delta P$ is $\sim kT_N \sqrt{\Delta \nu/\Delta t} W$, where $k = 1.3807 \times 10^{-23}$ J/K is Boltzmann’s constant, and $T_N$ is the overall radiometer “noise temperature,” including contributions from the scene being measured. A typical state-of-the-art value for $T_N$ is $\sim 2000$ K, although this can be $\sim 10 \times$ smaller at the lower frequencies considered to $\sim 10 \times$ larger at the higher frequencies.*

Integration times of a few seconds and spectral resolution of 25 MHz, typical of spectral line halfwidths at 30-km altitude, give noise of $\sim 10^{-16}$ W. When compared with the value of $\frac{1}{2} \lambda^2 B_v(T) \Delta \nu$ this indicates that midstratospheric spectral lines below $\sim 3000$ GHz having emissivities (optical depths) greater than $\sim 10^{-3}$ can be measured with integration times of less than 1 minute.

Signal-to-noise variation as a function of altitude (pressure) can be derived as follows for measurements that spectrally resolve the emission lines at all altitudes, as can be the case for microwave limb sounding. For pressure-broadened lines,

*Heterodyne radiometer technology is rapidly advancing to higher frequencies. Sensitivity adequate for very useful atmospheric measurements has now been demonstrated to at least 2500 GHz [41, 42] using gallium arsenide Schottky diodes specially developed for this purpose by the University of Virginia Semiconductor Device Laboratory [43]. A recent review by Carli and Carlotti [44] compares heterodyne and nonheterodyne techniques for atmospheric measurements. Figure 25 of Carli and Carlotti [44] indicates that, for 1985 technology [45], heterodyne techniques have better sensitivity for measurements of stratospheric spectral line emission up to $\sim 700$ GHz frequency, and nonheterodyne (photometric) techniques have better sensitivity above $\sim 700$ GHz. Technical advances since 1985 cause us to conclude that heterodyne techniques now (1992) have better sensitivities for such measurements up to $\sim 3000$ GHz frequency.
the measured line-center radiance is proportional to the molecule volume-mixing ratio (the signal at line center is proportional to the number density of the emitting gas divided by a line-width proportional to pressure, and is thus proportional to the volume-mixing ratio of the emitting gas). For Doppler-broadened lines, the signal at line center is proportional to the number density of the emitting gas and, therefore, to volume-mixing ratio times pressure. It follows that the volume-mixing ratio required for a given line-center radiance is independent of pressure for pressure-broadened lines, but is inversely proportional to pressure for Doppler-broadened lines. For spectral resolution matched to the line width (as is effectively done during data processing), instrument noise is given by the instrument-noise temperature divided by the square root of the product of line width and integration time. Because Doppler-broadened line widths are independent of pressure, but pressure-broadened line widths are proportional to pressure, it follows that the noise-equivalent volume-mixing ratio varies as $P^{-1/2}$ for pressure-broadened lines and as $P^{-1}$ for Doppler-broadened lines. There will be slight temperature corrections, but lines can be selected for measurement where these are very small [38, Figure 12, for example].

8.6 THE UARS MLS EXPERIMENT

The Upper Atmosphere Research Satellite (UARS) launched by the Space Shuttle on September 12, 1991 is a NASA mission dedicated to the comprehensive and integrated study of Earth's upper atmosphere [46]. The Microwave Limb Sounder (MLS) is one of ten UARS instruments. Its primary measurement objectives, shown in Figure 8.8, are ClO (~15-45 km), O$_3$ (~15-80 km), H$_2$O (~15-85 km), temperature (~30-60 km), and pressure (~30-60 km). Because ClO is the rate-limiting molecule in the chlorine destruction of O$_3$, the ClO abundance is a measure of the rate at which chlorine destroys ozone. ClO measurement on a global scale by MLS is important for understanding and monitoring chlorine depletion of ozone. Simultaneous MLS measurements of O$_3$ and H$_2$O provide additional information on stratospheric ozone chemistry.* The H$_2$O and O$_3$ measurements are to higher altitudes than previously explored on a global basis, and will provide new information on chemistry in the mesosphere. The pressure measurements (from O$_2$ lines) provide the vertical reference for composition measurements. Secondary MLS measurement goals include H$_2$O$_2$, HNO$_3$, and one component of wind in the mesosphere. The UARS MLS experiment is led by the Jet Propulsion Laboratory in the United States with collaboration from Heriot-Watt and Edinburgh Universities and Rutherford Appleton Laboratory in the UK. Prior development included aircraft [48, 49] and balloon [50-53] experiments.

The MLS "looks" in a direction that is 90° from the UARS orbital velocity.

*A somewhat similar experiment, the Millimeter-wave Atmospheric Sounder (MAS), has been developed for flights on the Space Shuttle Atmospheric Laboratory for Applications and Science (ATLAS) [47].
As discussed in Section IV, the tangent point of the observation path (where the signals mostly originate) is approximately 23° away from the suborbital track of the satellite. The 57° inclination of the UARS orbit thus allows MLS to perform measurements from 34° on one side of the equator to 80° on the other. UARS performs a 180° "yaw maneuver" ten times per year, allowing MLS and other instruments to alternately view northern and southern high latitudes with a periodicity of about ~36 days (this varies a few days through a yearly cycle). Local solar times at measurement locations do not vary appreciably with longitude on a given day, but can vary greatly with latitude. The UARS orbit plane processes so that all local times are covered at all latitudes during each ~36-day period.

A signal-flow block diagram of the UARS MLS is shown in Figure 8.9. An antenna receives radiation from the atmospheric limb and is mechanically scanned in the vertical. The optics are diffraction-limited and the 1.6-m vertical dimension of the antenna gives a 205-GHz FOV, having full width at half-maximum of 1.3 × 10⁻³ radians (0.07°), corresponding to 3.5-km vertical extent at the limb. The surface of the antenna primary mirror is parabolic to within 23 μm rms to keep scattering losses to no more than a few percent. A switching mirror accepts radiation either from the antenna or, for calibration, from an internal target or a space view. Space and target views with the switching mirror can be used in a manner to optimize radiometric calibration of the instrument [54]. A dichroic plate following the switching mirror separates a signal to the 63-GHz radiometer (for 62.998-
Figure 8.9. Signal-flow block diagram for the UARS MLS.
and 63.569-GHz O$_2$ lines). A polarization grid then separates signals to the 183-GHz radiometer (for 183.310-GHz H$_2$O and 184.378-GHz O$_3$) and 205-GHz radiometer (for 204.352-GHz ClO, 206.132-GHz O$_3$, 204.575-GHz H$_2$O$_2$, and several weak lines of HNO$_3$).

Ambient-temperature Schottky-diode mixer radiometers [55] down-convert the radiation to intermediate-frequency (IF) bands in the range of 0–3 GHz. Local oscillators are at frequencies of 63.283, 184.777, and 203.267 GHz. The radiometers have approximately equal response at IF frequencies above and below the local oscillator. The 183- and 205-GHz local oscillators are generated by frequency tripling from phase-locked Gunn oscillators, and are combined quasi-optically [56] with the signals. The intermediate-frequency signals, after amplification, are further frequency converted to six spectral bands, each centered at 400 MHz with a 500-MHz width. These bands are input to six filter banks that split the signal into 15 separate spectral channels, measure the power in each of these channels, and digitize the resulting signals for transmission to the ground for data processing.

All measurements are performed continuously, day and night. The instrument integration time is 2 s, and a vertical scan in discrete steps over the altitude range ~5–95 km is performed each minute. The scan “tracks” Earth’s limb by using “oblateness” signals generated by UARS to update the scan pattern (which can also be programmed from the ground). The measured in-orbit noise temperature for the most critical ClO band is 990 K double sideband. This provides zonal mean measurements of ClO profiles to ~0.1-ppbv (ppbv is 10$^{-9}$ volume-mixing ratio) sensitivity, and allows ClO greater than ~0.5 ppbv to be detected on each limb scan. Sensitivities to middle stratospheric O$_3$ and H$_2$O are a few percent on each limb scan.

The instrument has three assemblies: sensor, spectrometer, and power supply. Thermal control of the sensor and spectrometer is radiational by louvers, with in-orbit temperature stability of ~0.01°C per minute, allowing “total power” measurements that do not require fast chopping. The overall instrument mass is 280 kg, power consumption 163 W, and the output data rate is 1250 bits/s. A detailed description of the instrument is given in Barath et al. [57], and its calibration (including calibration of the radiometric, FOV, and spectral response of the instrument) is described in Jarnot and Cofield [58]. Figure 8.10 shows the MLS sensor and spectrometer in flight configuration. Figure 8.11 is a drawing of UARS showing the MLS and other instruments. A photograph of the UARS observatory, as it appeared in ground testing at completion of thermal vacuum tests, is given in Waters [59].

Some initial results from UARS MLS are shown in Figures 8.12 to 8.16. Figure 8.12 compares 205 GHz ClO emission measured by UARS MLS with previous measurements by the balloon MLS.* Figure 8.13 shows a map of ClO in the Antarctic ozone hole made from data for 1 day shortly after launch. Figure 8.14 shows ozone at the same time. Very high abundances of ClO in the northern hemi-

*In addition to its scientific value, the balloon MLS provided valuable experience in preparing for UARS MLS.
Figure 8.10. The UARS MLS sensor and spectrometer assemblies (flight units). The long (vertical) length of the antenna is 1.6 m. The spectrometer assembly is immediately above the antenna.

Figure 8.11. Drawing of UARS (from NASA). The MLS sensor assembly is on the near side and can be recognized by the antenna. The MLS spectrometer assembly is the rectangular box above the MLS antenna.
Figure 8.12. Measured 204 GHz CIO stratospheric emission. At left is a midstratospheric spectrum from the balloon MLS [51, 52] made near 34° north latitude on September 26, 1989 (R. A. Stachnik, private communication). Center is midstratospheric spectrum from a zonal average of UARS MLS data at midlatitudes on September 21, 1991. Right is lower-stratospheric emission, measured over the Antarctic Weddell Sea by UARS MLS on September 21, 1991. The Weddell Sea spectrum is the average of five individual 2-s integrations (at the point in the limb scan when the instrument FOV was at ~20-km tangent height) on consecutive limb scans of one orbit passing over Antarctica. The stronger and broader CIO line on the right is due to enhanced lower stratospheric CIO in the Antarctic “ozone hole” (see Figures 8.13 and 8.14). All spectra were measured during midday. The vertical scale is the double-sideband brightness temperature of the emission.

sphere were observed by UARS MLS starting in mid-December 1991. In mid-January 1992, the northern hemisphere CIO abundances were comparable to those measured in the Antarctic ozone hole. Figure 8.15 shows CIO measured on January 11, 1992. The high abundances of CIO decreased during February, presumably due to warming of the arctic lower stratosphere, and the extent to which ozone was depleted is under investigation at the time of this writing. Further analyses of these and future MLS data, and data from other UARS instruments, will improve our understanding of ozone depletion on a global scale. SO₂ from the Pinatubo volcano has also been measured from rotational SO₂ lines, which appear in the 205-GHz radiometer.* Figure 8.16 shows the SO₂ map of MLS data for September 21, 1991.

*The SO₂ lines, at 200.288 and 204.246 GHz, occur at locations that do not interfere significantly with the primary measurement objectives of UARS MLS.
Figure 8.13. The distribution of ClO measured by UARS MLS on September 21, 1991. This map is for a layer centered near 20 km with vertical thickness of approximately 3 km, and was made from data taken when the observation tangent point was on the “day” side of the orbit. Darkest shades indicate ClO in excess of 1 part per billion by volume. Measurement locations are indicated by “*”, and map contours were determined by linear interpolation of data between the measurement locations. The white area centered at the pole indicates the region of no measurements.

8.7 FUTURE POSSIBILITIES

An enhanced MLS experiment for the future NASA Earth Observing System (EOS) [60, for example] or an “Earth Probe” mission is being studied. This enhanced instrument will be here referred to as “EOS MLS” although, at the time of writing, the mission on which a future MLS will fly has not been determined. EOS MLS will take advantage of improved technology since UARS MLS and the current design includes radiometers operating at submillimeter wavelengths, broadband intermediate-frequency amplifiers, and miniature low-power acoustooptic spectrometers. Certain mixers and first-stage amplifiers can be radiationally cooled to $\sim 100$ K.

Radiometers covering bands centered near 637, 560, 268, 205, and 117 GHz were initially planned for EOS MLS [38]. Figure 8.17 shows “noise-equivalent volume-mixing ratio” sensitivity as a function of altitude for some of the initially planned measurements. A conservative instrument-noise temperature of 10,000 K was assumed for the 637 and 560 GHz radiometers. The sensitivities were deter-
Figure 8.14. Ozone measured by UARS MLS on September 21, 1991. This map is for a layer centered near 20 km with vertical thickness of approximately 3 km. Lightest shades indicate values of ozone less than approximately 0.5 parts per million by volume; darkest shades indicate values greater than approximately 3 parts per million. The "ozone hole" is clearly evident, and generally corresponds the region of high ClO shown in Figure 8.13. Low abundances of ozone are expected in the tropics (at the height for this map) due to upward motion of ozone-poor air. However, preliminary analyses indicate the tropical abundances seen here are significantly below climatological values, and possibly due to perturbations resulting from the Pinatubo volcano.

mined by first performing a radiative transfer calculation of line strength for an observation altitude of 36 km, and then by using the dependence of noise-equivalent volume-mixing ratio with pressure as described in Section 8.5. Line widths as a function of altitude are shown in Figure 8.18; the transition from pressure to Doppler broadening occurs at ~63 km for spectral lines near 600 GHz. Curves are given for a vertical scan covering 0-120 km heights—both for individual profile measurements (~1 s integration time) and for monthly 5° latitude zonal means (~10-min integration time). Expected atmospheric mixing-ratio vertical profiles are also given in Figure 8.17. Equinox profiles at 30°N from the California Institute of Technology model [19, 61; L. Froidevaux, private communication] for 1 p.m. local time are shown. The OClO profile is from the Cambridge 1-D model for 45° night [M. Chipperfield, private communication]—the original reference for this model is Fabian et al. [62], with updates to it described in Webster et al. [63] and Chipperfield and Gray [64]. The BrO profile is from the Lawrence Liv-
Figure 8.15. The distribution of CIO measured by UARS MLS on January 11, 1992. This map is for a layer centered near 20 km with vertical thickness of approximately 3 km. Darkest shades indicate CIO in excess of 1 part per billion by volume. Measurement locations are indicated by '*', and map contours were determined by linear interpolation of data between the measurement locations. The arctic winter vortex, containing sufficiently low temperatures for ice clouds on which heterogeneous reactions leading to formation of CIO can occur, was over Scandinavia and northern Russia at the time of this measurement. The CIO abundance decreases northward of approximately 70° latitude because measurements at those high latitudes occurred in darkness; CIO is expected to be quickly converted to dimer form (which is not observed by MLS) at night. The patch of high CIO northward of central Siberia was in darkness at the time, but in a region of relatively high temperatures where thermal dissociation of the CIO dimer might be expected to reform CIO.

Furthermore, Laboratorv midlatitude model [D. Wuebbles, private communication]. The NO profile above 60 km is close to the mean of observational and model results given in Solomon et al. [65]. The HCN profile is from [66], extrapolated above 60 km. Antarctic spring conditions for CIO [15, 67], OCIO inferred from Solomon et al. [68, 69], and BrO [70] are indicated, as are possible volcanic injections of SO₂ [71].

The measurements now being considered for EOS MLS are more "focused" to highest priority issues, and take advantage of recent technology developments. Radiometers are planned that operate near 2514 GHz (primarily for OH), 1230 GHz (for HF), 640 GHz (for several molecules including HCl, CIO and BrO),
440 GHz (for several molecules including H$_2$O, O$_3$, N$_2$O, HNO$_3$, NO), and 215 GHz (for continuity of the UARS MLS measurements and upper tropospheric H$_2$O and O$_3$). A simple bore-sighted infrared radiometer for measuring ice clouds and aerosols (valuable for identifying regions of potential heterogeneous chemistry) is also being considered, as is a high-precision gyroscope package mounted on the antenna to provide geometric heights of pressure surfaces (valuable for atmospheric dynamics studies).

Figure 8.19 summarizes primary measurement objectives for the EOS MLS currently being studied. The objectives include source gases, radicals, and reservoirs in all the chemical cycles thought to significantly affect stratospheric ozone. Upper tropospheric H$_2$O and O$_3$, important for their radiational forcing of surface temperature (global warming) will also be measured. Temperature and pressure can be measured over the full vertical range from the upper troposphere to the upper mesosphere, as can CO. Measurements of excited states of molecular oxygen, O$_2$ ($^3\Delta$) and O$_2$ ($^v = 1$), should provide needed insights into the production of O$_3$ in the upper stratosphere and mesosphere. Several additional isotopic and vibrationally excited states of certain molecules can also be measured. Some measurements (NO, CO, H$_2$O, OH, O$_3$, for example) can also be extended well above 80 km into the lower thermosphere simply by scanning the antenna to higher tangent heights. NO$_2$ could also be measured, as could atomic oxygen in the upper stratosphere through the lower thermosphere.

Figure 8.16. The distribution of SO$_2$ measured by UARS MLS on September 21, 1991. This map is for a layer centered near 26 km with vertical thickness of approximately 3 km. The dark band in the tropics shows remnants of SO$_2$ injected into the stratosphere approximately 3 months earlier by the massive eruption of the Pinatubo (Philippines) volcano on June 15, 1991. Darkest shades indicate SO$_2$ in excess of approximately 10 parts per billion by volume. The small patch of SO$_2$ south of Australia is thought to be from the very much smaller Cerro Hudson (Chile) volcano, which erupted in mid-August 1991. The map extends northward to only 34° N because, at the time of these measurements, MLS was “viewing to the south” (see discussion in text).
Figure 8.17. Expected noise-equivalent volume-mixing ratio of some measurements considered for EOS MLS. Bold solid lines give noise for individual profiles; long dashed lines give noise for monthly zonal means. Other lines show expected atmospheric abundances as discussed in the text. This figure was prepared by L. Froidevaux.
Figure 8.17 (Continued)

Figure 8.18. Variation of line-width parameter with altitude. This parameter is the line half-width at half-maximum. Shown are a pressure-broadened linewidth of $\Delta \nu_P = 2.5 \times P(T/300)^{-0.7}$ MHz, which is typical for many molecules, and a Doppler-broadened line width of $\Delta \nu_D = 3.6 \times 10^{-7} \sqrt{T/M}$, with $M = 48$ amu for ozone. The line frequency is $\nu$, $T$ is temperature in K, and $P$ is pressure in mbars. The pressure and Doppler line-shape functions must be convolved at altitudes where $\Delta \nu_P$ and $\Delta \nu_D$ have comparable values. This figure was prepared by W. G. Read.
EOS MLS can provide great improvement over UARS MLS for the important CIO measurement. Figure 8.20 shows the Antarctic CIO-O₃ anticorrelation measured on September 16, 1987, by Anderson et al. [15], together with the EOS MLS CIO sensitivity for 0.6-s integration time and the UARS MLS CIO sensitivity for 2-s integration time. Polar stratospheric clouds and volcanic aerosols have negligible effect on the signals.*

OH measurement can now be planned for EOS MLS because of recent technology advances mentioned in Section 8.5. OH is chemically active in all regions of Earth’s atmosphere, and its measurement is needed to both understand and monitor atmospheric chemistry. Spectral resolution of the heterodyne technique, combined with its sensitivity and instantaneous bandwidth of spectral coverage, allows remote measurements of OH (and other molecules) over the largest possible altitude range, including the lower stratosphere.**

*The largest effect on the 640 GHz radiometer signals, of worst-case polar stratospheric clouds measured [72] over Antarctica (ice particle number density of ~200 m⁻³ with maximum dimension of ~50 x 10⁻⁶ m), is calculated (using expressions in Gunn and East [73], an ice complex index of refraction at 600 GHz of n_r = 1.8 - 0.02i from Deirmendjian [74], and a path length of 500 km for a cloud of 5- km vertical extent all along the FOV limb path) to be ~0.1%.

**The spectral resolution allows emission by the more abundant high-altitude OH, which has a relatively narrow spectral feature due to fewer molecular collisions, to be distinguished from the broader spectral feature of lower-altitude OH emission, which, from space, must be observed while "looking through" the high-altitude OH.
Figure 8.20. Aircraft measurements by Anderson et al. [15] of ClO and O_3 at ~19-km altitude near Antarctica on September 16, 1987. Measurement sensitivities expected for EOS MLS have been added to the figure. UARS MLS ClO sensitivity is indicated on the right.

Strong OH rotational lines exist near 1.8, 2.5, 3.5 THz and higher frequencies (see Figure 8.1). Figure 8.21 shows calculated emission by the 1.8 and 2.5 THz OH lines for a limb path through the lower stratosphere. The 2.5 THz OH lines are currently considered best for the EOS MLS measurement of OH. These lines are particularly attractive because the instrument local oscillator can be generated by a laser operating on a nearby CH_3OH line. Such a laser can be space-qualified, and can provide sufficient local oscillator power to operate a radiometer containing mixers on both polarizations to provide both redundancy and improved sensitivity. Emission from the 2.5 THz OH line in the Orion nebula has been measured with an airborne heterodyne radiometer [75]. Figure 8.22 shows the estimated OH measurement sensitivity, which can be obtained using performance already demonstrated [41, 42] in temperature heterodyne radiometer systems at 2.5 THz.

Expected technology advances in the future, as well as cooling, can provide significantly improved precision for the important OH measurement, as well as for many others. The EOS MLS instrument is being designed in a modular fashion so that it can easily accommodate evolving measurement priorities and technology advances.
Figure 8.21. OH spectral-line emission near 1.8 and 2.5 THz calculated by W. G. Read. The upper panels show the two sets of Λ-type doublet transitions near 2510 and 2514 GHz. The bottom panels show similar transitions near 1835 and 1838 GHz. The calculation is for a limb path having 20-km tangent height. Noise levels for heterodyne measurements, with sensitivities that have been demonstrated with uncooled radiometers, are also indicated (they are the small crosses at the bottom of the downward-pointing arrows).
Figure 8.22. Measurement sensitivity for OH. The sensitivities shown here (dotted lines) are for measurement of the OH lines at 2.5 THz, with both Λ-type doublets and both polarizations simultaneously measured. A scan pattern is used that emphasizes the lower stratosphere (giving ~10 s integration time per measurement in the lower stratosphere) and allows profiles with 3 km vertical resolution and 15–80 km height range to be measured every 5° along the orbit. The curve labeled "zonal mean" applies to zonal means (with 5° latitude resolution) of daily data. A conservative noise temperature (30,000 K, which has been demonstrated with room-temperature radiometers at 2.5 THz [42]) was used. Technology improvements and radiational cooling are expected to give an EOS MLS sensitivity to OH, which is substantially better than shown here. The OH profile (solid line), from Figure 5.31 of [29], is for midday equinox conditions at middle latitudes.

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APPENDICES TO CHAPTER 8

**AA SUBMILLIMETER SPECTRA OF STRATOSPHERIC MOLECULES**

Figures 8A.1–8A.65 show plots of 0–3000 GHz spectra of stratospheric molecules (and atomic oxygen) made using data from the JPL catalog. The vertical axis in each figure is the logarithm (base 10) of the line-center optical depth, \( \tau_{nu}^{ul} \), calculated from Eq. 8B.148 of Appendix 8B with \( T = 225 \) K, \( L = 500 \) km, and \( Q_{ev}(T) = 1. \) Optical depths of lines within a 30-MHz interval—the approximate width of spectral lines in the middle stratosphere—have been summed.** The mixing ratio \( f \) used in the \( \tau_{nu}^{ul} \) calculation is the approximate maximum expected in the stratosphere for that molecule; this is stated in each figure.† Spectra are given for molecules, including all isotopes and excited vibrational states, with any 0–3000 GHz spectral line having calculated \( \tau_{nu}^{ul} \geq \sim 10^{-3} \). Weaker spectra are also included for certain molecules (e.g., ClONO\(_2\), OCIO, ClOOCI) that are of interest because of their roles in stratospheric chemistry.

*The approximation \( Q_{ev}(T) \approx 1 \) is good for the molecules considered, as can be seen from the values of \( e^{-E_i/kT} \) given in the notes to Tables 8.1–8.6 of this chapter: \( e^{-E_i/kT} \ll 1 \) for all excited vibrational states, which implies only the ground vibrational state contributes significantly to the partition function and, therefore, that \( Q_{ev}(T) = 1 \) (contributions from excited electronic states to \( Q_{ev}(T) \) are even more negligible—except for spin states that are already included in \( Q_{ev} \)).

**Boundaries of the 30 MHz interval sometimes occur in the midst of a group of spectral lines. This can lead to "artificial" features in the figures—the slightly ragged appearance of the envelope of the HNO\(_3\) spectra in Figures 8A.23 and 8A.24, for example.

†The mixing ratio given in each figure includes both the expected relative abundance of that molecule in the stratosphere and the fraction of that molecule that is in the excited and/or isotopic state. Users of the JPL catalog data should remember, however, that the line-intensity data in the catalog already accounts for the fraction of molecules in excited vibrational states (assuming thermal equilibrium). Optical depths for different values of \( L \) and \( f \) can be obtained by a simple scaling of the data in each figure. Optical depths for different temperatures can be calculated using Eq. 8B.132 of Appendix 8B of this chapter; only the excited vibrational states have a very strong temperature dependence.
Figure 8A.1. Spectrum of atomic O. The mixing ratio of atomic O increases rapidly with increasing height. The $10^{-7}$ mixing ratio used here is typical for 50 km (the "top" of the stratosphere); values are $\sim 10^{-4}$ at $\sim 70$ km and $\sim 10^{-1}$ at $\sim 105$ km.

Figure 8A.2. Spectrum of O$_2$.

Figure 8A.3. Spectrum of O$_2$($\nu_1$).
Figure 8A.4. Spectrum of $^{18}O$. The $3.0 \times 10^{-6}$ mixing ratio used here is that expected for O$_2$ ($^{1}\Delta$) in the mesosphere where it is not in local thermodynamic equilibrium.

Figure 8A.5. Spectrum of $^{17}O$.

Figure 8A.6. Spectrum of $^{17}O$. 
\[ \log_{10}\left(\tau_{\text{ul}}^{03}\right) \]
for
\[ f = 7.0 \times 10^{-6} \]
\[ T = 225 \text{ K} \]
\[ L = 500 \text{ km} \]

\[ \log_{10}\left(\tau_{\text{ul}}^{03}\right) \]
for
\[ f = 7.9 \times 10^{-8} \]
\[ T = 225 \text{ K} \]
\[ L = 500 \text{ km} \]

\[ \log_{10}\left(\tau_{\text{ul}}^{03}\right) \]
for
\[ f = 9.0 \times 10^{-9} \]
\[ T = 225 \text{ K} \]
\[ L = 500 \text{ km} \]

**Figure 8A.7.** Spectrum of \(03\).

**Figure 8A.8.** Spectrum of \(03(v_2)\). Note change in vertical scale from that in the preceding \(03\) spectrum.

**Figure 8A.9.** Spectrum of \(03(v_1)\) and \(03(v_3)\). The JPL catalog has a single entry covering these two states.
\log_{10} (\tau_{ul})

\text{for}
\begin{align*}
  f &= 9.1 \times 10^{-10} \\
  T &= 225 \text{ K} \\
  L &= 500 \text{ km}
\end{align*}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig8a10}
\caption{Spectrum of O$_3(2\nu_2)$.}
\end{figure}

\log_{10} (\tau_{ul})

\text{for}
\begin{align*}
  f &= 2.9 \times 10^{-8} \\
  T &= 225 \text{ K} \\
  L &= 500 \text{ km}
\end{align*}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig8a11}
\caption{Spectrum of $^{18}$OOO.}
\end{figure}

\log_{10} (\tau_{ul})

\text{for}
\begin{align*}
  f &= 3.5 \times 10^{-10} \\
  T &= 225 \text{ K} \\
  L &= 500 \text{ km}
\end{align*}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{fig8a12}
\caption{Spectrum of $^{18}$OOO($\nu_2$).}
\end{figure}
Figure 8A.13. Spectrum of O$^{18}$O.

Figure 8A.14. Spectrum of O$^{16}$O($v_2$).

Figure 8A.15. Spectrum of O$^{17}$O.
Figure 8A.16. Spectrum of O^{17}OO.

Figure 8A.17. Spectrum of NO. The $10^{-8}$ NO mixing ratio used here is the approximate maximum expected in the stratosphere. The mixing ratio is much larger at higher altitudes; typical values at $\sim 100$ km are $\sim 10^{-5}$.

Figure 8A.18. Spectrum of NO$_2$. 
Figure 8A.19. Spectrum of N₂O (NNO). N₂O lines up to ~1500 GHz were in the JPL catalog when this figure was made; lines extend higher, of course.

Figure 8A.20. Spectrum of NNO(ν₂). NNO(ν₂) lines up to ~1800 GHz were in the JPL catalog when this figure was made; lines extend higher, of course.

Figure 8A.21. Spectrum of N¹⁵NO. A similar spectrum, with essentially identical line strengths, exists for N¹⁵NO.
Figure 8A.22. Spectrum of N\textsuperscript{18}O.

Figure 8A.23. Spectrum of HNO\textsubscript{3} (HONO\textsubscript{2}). HNO\textsubscript{3} lines up to \sim 2100 GHz were in the JPL catalog when this figure was made; lines extend higher, of course.

Figure 8A.24. Spectrum of HNO\textsubscript{3}(v\textsubscript{9}). HNO\textsubscript{3}(v\textsubscript{9}) lines up to \sim 1000 GHz were in the JPL catalog when this figure was made; lines extend higher, of course.
Figure 8A.25. Spectrum of HNO$_3$($v_7$). HNO$_3$($v_7$) lines up to $\sim$ 1000 GHz were in the JPL catalog when this figure was made; lines extend higher, of course.

Figure 8A.26. Spectrum of HNO$_3$($v_6$). HNO$_3$($v_6$) lines up to $\sim$ 1000 GHz were in the JPL catalog when this figure was made; lines extend higher, of course.

Figure 8A.27. Spectrum of H$_2$O.
Figure 8A.28. Spectrum of $\text{H}_2\text{O}(v_2)$. Note the change in the vertical scale from that in the preceding $\text{H}_2\text{O}$ spectrum.

Figure 8A.29. Spectrum of $\text{H}_2^{18}\text{O}$. Note the change in the vertical scale from that in the preceding $\text{H}_2\text{O} (v_2)$ spectrum.

Figure 8A.30. Spectrum of $\text{H}_2^{17}\text{O}$. Note the change in the vertical scale from that in the preceding $\text{H}_2^{18}\text{O}$ spectrum.
Figure 8A.31. Spectrum of HDO.

Figure 8A.32. Spectrum of HD$^{18}$O.

Figure 8A.33. Spectrum of HО$_2$. The value of $3.0 \times 10^{-9}$ used here for the HО$_2$ mixing ratio is the approximate maximum expected in the stratosphere. HО$_2$ mixing ratios in the mesosphere are $\sim 10$ times larger.
Figure 8A.34. Spectrum of OH. OH mixing ratios in the mesosphere are larger than in the stratosphere; values at 75 km are \( \sim 10^{-8} \).

Figure 8A.35. Spectrum of \(^{18}\)OH.

Figure 8A.36. Spectrum of OD.
Figure 8A.37. Spectrum of H$_2$O$_2$.

Figure 8A.38. Spectrum of HNO$_4$ (HO$_2$NO$_3$). Due to uncertainties in the quantum-mechanical calculations for lines at frequencies above $\sim 700$ GHz, some "series" of HNO$_4$ lines were truncated at $\sim 700$ GHz in the JPL catalog when this plot was made. This causes the relative scarcity of lines above 700 GHz in this figure; in reality, of course, the density of lines does not change so abruptly.

Figure 8A.39. Spectrum of H$^{35}$Cl.
\[ \log_{10}(\tau_{\nu}) \]

for
\[ f = 0.5 \times 10^{-9} \]
\[ T = 225 \text{ K} \]
\[ L = 500 \text{ km} \]

**Figure 8A.40.** Spectrum of H\(^{37}\)Cl.

\[ \log_{10}(\tau_{\nu}) \]

for
\[ f = 3.7 \times 10^{-10} \]
\[ T = 225 \text{ K} \]
\[ L = 500 \text{ km} \]

**Figure 8A.41.** Spectrum of \(^{35}\)ClO.

\[ \log_{10}(\tau_{\nu}) \]

for
\[ f = 1.3 \times 10^{-10} \]
\[ T = 225 \text{ K} \]
\[ L = 500 \text{ km} \]

**Figure 8A.42.** Spectrum of \(^{37}\)ClO.
Figure 8A.43. Spectrum of HO\textsuperscript{35}Cl.

Figure 8A.44. Spectrum of HO\textsuperscript{37}Cl.

Figure 8A.45. Spectrum of CH\textsubscript{3}\textsuperscript{35}Cl.
\[ \log_{10} \left( \frac{\tau_{\nu_4}}{\nu_4} \right) \]

for

\( f = 1.0 \times 10^{-10} \)

\( T = 225 \text{ K} \)

\( L = 500 \text{ km} \)

**Figure 8A.46.** Spectrum of CH\(_3\)Cl.

\[ \log_{10} \left( \frac{\tau_{\nu_4}}{\nu_4} \right) \]

for

\( f = 3.0 \times 10^{-11} \)

\( T = 225 \text{ K} \)

\( L = 500 \text{ km} \)

**Figure 8A.47.** Spectrum of O\(^{35}\)ClO.

\[ \log_{10} \left( \frac{\tau_{\nu_4}}{\nu_4} \right) \]

for

\( f = 0.6 \times 10^{-8} \)

\( T = 225 \text{ K} \)

\( L = 500 \text{ km} \)

**Figure 8A.48.** Spectrum of \(^{35}\)ClOO\(^{35}\)Cl. ClOOCl lines up to 1000 GHz were in the JPL catalog when this figure was made; lines extend higher, of course.
Figure 8A.49. Spectrum of $^{35}$ClONO$_2$. Some "series" of ClONO$_2$ lines in the JPL catalog were truncated at $\sim$ 300 GHz, and other series at higher frequencies, when this plot was made. This causes the "breaks" seen here at $\sim$ 300 and $\sim$ 650 GHz, and the absence of lines above $\sim$ 800 GHz. In reality, of course, the density of lines does not change so abruptly.

Figure 8A.50. Spectrum of COF$_2$.

Figure 8A.51. Spectrum of HF.
Figure 8A.52. Spectrum of DF.

Figure 8A.53. Spectrum of H$^{81}$Br. H$^{79}$Br has a similar spectrum, with essentially identical line strengths, to that shown here.

Figure 8A.54. Spectrum of $^{81}$BrO. $^{79}$BrO has a similar spectrum, with essentially identical line strengths, to that shown here. BrO lines up to $\sim 1300$ GHz were in the JPL catalog when this figure was made; lines extend higher, of course.
Figure 8A.55. Spectrum of CO. The $10^{-7}$ CO mixing ratio used in calculating intensities shown here is the approximate maximum expected in the stratosphere. At higher altitudes the CO mixing ratio is much larger and spectral lines are much stronger; typical CO mixing ratios at ~90 km are ~$10^{-5}$.

Figure 8A.56. Spectrum of $^{13}$CO. At higher altitudes, the $^{13}$CO mixing ratio is much larger and spectral lines are much stronger than shown here.

Figure 8A.57. Spectrum of $^{18}$CO. At higher altitudes, the $^{18}$CO mixing ratio is much larger and spectral lines are much stronger than shown here.
Figure 8A.58. Spectrum of H$_2$CO. Due to uncertainties in the quantum-mechanical calculations for lines at frequencies above ~1300 GHz, some "series" of H$_2$CO lines were truncated at ~1300 GHz in the JPL catalog when this plot was made. This causes the relative scarcity shown here for lines above 1300 GHz; in reality, of course, the density of lines does not change so abruptly.

Figure 8A.59. Spectrum of HCN.

Figure 8A.60. Spectrum of HCN ($v_2$).
**Figure 8A.61.** Spectrum of $^{13}$HCN.

**Figure 8A.62.** Spectrum of HCN-15.

**Figure 8A.63.** Spectrum of SO$_2$. The $10^{-9}$ SO$_2$ mixing ratio used here is that expected to be injected into the stratosphere by a moderate-size volcano. The "background" SO$_2$ in the stratosphere is $< \sim 10^{-11}$, and stratospheric SO$_2$ lines will normally be at least 100 times weaker than shown here. A major volcano is expected to increase the local SO$_2$ mixing ratio to $\sim 10^{-8}$, which would produce lines $\sim 10$ times larger than shown here.
8B THEORETICAL EXPRESSIONS

This appendix gives theoretical expressions to calculate microwave limb-sounding signals and a self-contained reference for their derivation.* It, together with the other appendixes to this chapter, provides an update for the stratosphere of the

*Such a reference is needed because various approximations, assumptions, systems of units, and nomenclature exist throughout the literature on this subject. This can easily lead to unnecessary confusion, especially for new workers in the field. The derivations given here start from fundamental principles in order to document all approximations and assumptions. The state degeneracy factor is
In the 15 years since that article was written, the ability to calculate millimeter/submillimeter wavelength absorption and emission by stratospheric gases has been significantly advanced by development of the JPL Submillimeter, Millimeter, and Microwave Spectral Line Catalog [34, 35 of Chapter 8]. Expressions are included here that can be used with spectroscopic data from that catalog. Specifics for the line-shape function and examples of spectroscopy for individual molecules are not discussed here—they are in Chapter 2.

8B.1 Interaction of Radiation and Matter

Radiation can interact with matter when a molecule or atom absorbs or emits a photon. A description of this process is conveniently separated into (1) interaction dynamics and (2) interaction Hamiltonian.

(1) Interaction Dynamics.

Consider a molecule or atom having an electron that can be in quantum states \(|1\rangle\) or \(|2\rangle\) with different energies. These states are described by the probability amplitudes (wave functions)

\[
\Psi_n(r, t) = \psi_n(r) e^{-iE_n t / \hbar}
\]

where \(n = 1\) or \(2\), \(r = (x, y, z)\) is the spatial coordinate, \(t\) is time, \(E_n\) is the energy of state \(n\), \(i = \sqrt{-1}\), and \(\hbar = h / 2\pi\), \(h\) being Planck's constant. \(|\Psi_n(r, t)|^2 = |\psi_n(r)|^2\) is the probability density for an electron in state \(n\) being at position \(r\). The functions \(\psi_n\) are eigenfunctions (with eigenvalues \(E_n\)) of the time-independent Schrödinger equation

\[
H_0 \psi_n(r) = E_n \psi_n(r)
\]

where

\[
H_0 = -\frac{\hbar^2}{2m} \nabla^2 + V(r)
\]

is the Hamiltonian operator for the electron in the molecule, \(m\) is the mass of the electron, and \(V(r)\) is the potential it sees. The \(\psi_n(r)\) are orthonormal, [6, Volume III, §11, for example]

\[
\int \psi_m^*(r) \psi_n(r) \, d^3r = \delta_{mn}
\]

where \(^*\) denotes a complex conjugate, and \(\delta_{mn}\) is 1 if \(m = n\) and 0 if \(m \neq n\).
Let the interaction between the molecule and "external" radiation be described by the time-dependent Hamiltonian $\mathcal{H}'$. We assume this interaction is sufficiently small that it does not significantly change the form of the stationary states $\psi_n(r)$. The Hamiltonian can then be written

$$H = H_0 + \mathcal{H}'$$

(8B.5)

where Eq. 8B.2 still holds to an adequate approximation. Regardless of its state before the interaction, afterwards the electron/molecule can be considered to be in a quantum superposition of the two allowed states—a measurement could yield either state. The probability amplitude after the interaction can be written

$$\Psi = a_1(t)\Psi_1 + a_2(t)\Psi_2$$

(8B.6)

where $a_n(t)$ are time-dependent complex numbers, and $t$ is the time since the start of the interaction. We require

$$|a_1(t)|^2 + |a_2(t)|^2 = 1$$

(8B.7)

because at any time the probability is 1 that the electron is in either $|1\rangle$ or $|2\rangle$.

$\Psi$ must satisfy the time-dependent Schrödinger equation

$$i\hbar \frac{\partial \Psi}{\partial t} = H\Psi$$

(8B.8)

Putting Eqs. 8B.6 and 8B.5 in Eq. 8B.8 and using Eqs. 8B.1 and 8B.2 leads to

$$i\hbar \left( \frac{da_1}{dt} \Psi_1 + \frac{da_2}{dt} \Psi_2 \right) = a_1 \mathcal{H}' \Psi_1 + a_2 \mathcal{H}' \Psi_2$$

(8B.9)

Multiplying Eq. 8B.9 on the left by $\Psi_2^*$, integrating over position, and using Eqs. 8B.1 and 8B.4 gives

$$i\hbar \frac{da_2}{dt} = a_1 \mathcal{H}'_{21} e^{i2\pi\nu_2 t} + a_2 \mathcal{H}'_{22}$$

(8B.10)

where

$$\mathcal{H}'_{mn} = \int \psi_m^*(r) \mathcal{H}' \psi_n(r) \, d^3r$$

(8B.11)

and

$$\nu_{21} = \frac{E_2 - E_1}{\hbar}$$

(8B.12)
Suppose that the electron is in state $|1\rangle$ at $t = 0$: $a_1(0) = 1$ and $a_2(0) = 0$. Then for sufficiently small $t$, Eq. 8B.10 is

$$i\hbar \frac{da_2}{dt} = \mathcal{C}_{21} e^{i2\pi \nu_1 t} \quad (8B.13)$$

Now let $\mathcal{C}'$ have harmonic time dependence with frequency $\nu'$:

$$\mathcal{C}_{21}' = H_{21}(e^{i2\pi \nu' t} + e^{-i2\pi \nu' t}) \quad (8B.14)$$

where $H_{21}$ is independent of time. Then Eq. 8B.13 becomes

$$i\hbar \frac{da_2}{dt} = H_{21}[e^{i2\pi (\nu_2 + \nu') t} + e^{i2\pi (\nu_2 - \nu') t}] \quad (8B.15)$$

The $(\nu_2 + \nu')$ term oscillates rapidly compared to the $(\nu_2 - \nu')$ term, and will not contribute significantly when we integrate later over many periods of $\nu_2$. We neglect that term now, and have

$$i\hbar \frac{da_2}{dt} = H_{21} e^{i2\pi (\nu_2 - \nu') t} \quad (8B.16)$$

Integrating from 0 to $\Delta t$ gives

$$a_2(\Delta t) = \frac{H_{21}}{i\hbar} \int_0^{\Delta t} e^{i2\pi (\nu_2 - \nu') t} \, dt \quad (8B.17)$$

$$= \frac{1}{\hbar} \left[ 1 - \frac{e^{i2\pi (\nu_2 - \nu') \Delta t}}{2\pi (\nu_2 - \nu')} \right] H_{21} \quad (8B.18)$$

$$= \left( \frac{-i \Delta t}{\hbar} \right) \left[ \sin \left( \pi (\nu_2 - \nu') \frac{\Delta t}{\Delta t} \right) \right] H_{21} \quad (8B.19)$$

The probability that, after time $\Delta t$, the interaction has induced a transition from $|1\rangle$ to $|2\rangle$ is $|a_2(\Delta t)|^2$. If, however, state $|2\rangle$ has degeneracy $g_2$, the same probability exists for a transition to each of its degenerate "substates," and the total transition probability is increased by the factor $g_2$:*

$$P_{1 \to 2} = g_2 |a_2(\Delta t)|^2 = g_2 \left( \frac{\Delta t}{\hbar} \right)^2 \left[ \sin \left( \pi (\nu_2 - \nu') \frac{\Delta t}{\Delta t} \right) \right]^2 |H_{21}|^2 \quad (8B.20)$$

*This assumes $H_{21}$ is the same for each of the degenerate substates of $|2\rangle$. 
We are interested in describing situations where $\mathcal{E}'$ is not monochromatic, and define $H_{21}(v')$ such that

$$|H_{21}|^2 \overset{\text{def}}{=} |H_{21}(v')|^2 \Delta v' \quad (8B.21)$$

for a small frequency interval $\Delta v'$ around $v'$. We are also interested in situations where the interaction can occur at a range of frequencies and define $b(v, v_{21}) \, dv$ as the probability that the $1 \rightarrow 2$ transition is caused by that portion of the Hamiltonian within the interval $dv$ centered at $v$.* Because the transition must be due to the Hamiltonian in some frequency interval, we require

$$\int_0^\infty b(v, v_{21}) \, dv = 1 \quad (8B.22)$$

The probability of a transition being induced by the portion of the Hamiltonian within a frequency interval $\Delta v'$ is then obtained by using Eq. 8B.21 in Eq. 8B.20. Accounting for transitions at a range of frequencies $\Delta v$, we add the factor $b(v, v_{21}) \, dv$ and replace $v_{21}$ by $v$ in Eq. 8B.20.** Letting $\Delta v'$ become infinitesimal and integrating over $v'$ gives the probability for a transition within the frequency range $\Delta v$:

---

*Transitions can be induced at frequencies other than $v_{21}$ for two reasons. First, relative motion between the molecule and the observer causes the transition frequency as seen by the observer to be different from that "seen" by the molecule. This is the Doppler effect. Second, the energy levels may not be exactly $E_1$ and $E_2$. Quantum mechanics requires an uncertainty in energy of $\Delta E \sim \hbar / \Delta t$, where $\Delta t$ is the lifetime of the state; this leads to "natural" broadening, which is generally negligible for cases of interest here. Interactions of the molecule with "external" systems also perturb the energy levels; collisions with other molecules is the most important of these for atmospheric applications. The quantity $b(v, v_{21})$ is generally referred to as the "line-shape function," as it describes the shape of a spectral line. The form of $b(v, v_{21})$ is discussed in Chapter 2 of this book, and the interested reader is also referred to Armstrong and Nicholls [2] for a summary discussion of line shapes, Ben-Reuven [7] and references therein for a detailed review of collision broadening, and Pickett [8] for an analysis of the effects of "velocity averaging." The Voigt shape is usually adequate for upper-atmospheric calculations; algorithms for it are given in Drayson [9], Pierluissi et al. [10], and Cope et al. [11], and a numerically very accurate algorithm has recently been developed [12].

**This is needed because $b(v, v_{21})$ describes the probability that the transition occurs at $v$, not $v_{21}$. The "frequency" $v_{21}$, defined by Eq. 8B.12, merely describes the difference in energy of the two states when the molecule is an isolated system (unperturbed by collisions, for example). Integrating the probability, rather than the probability amplitude, over $v$ assumes that contributions to the transition probability from radiation at different frequencies add incoherently. Coherent effects can exist, for example, when collisional "broadening" of "individual" lines is sufficiently large to cause line overlap. The involved quantum states can then become merged and one should, in principle, solve the Schrödinger equation using a potential $V(r)$ that includes the effects of collisions. This will not be pursued further here, but a specific case of atmospheric importance is mentioned later in the footnote preceding Eq. 8B.105. By having separate factors for $|H_{21}(v')|^2$ and $b(v, v_{21})$, it is also implicitly assumed that the mechanisms that permit $1 \rightarrow 2$ transitions at frequencies other than $v_{21}$ do not affect the Hamiltonian $H_{21}(v')$, other than perhaps by phase.
\[ P_{1 \to 2}(\Delta \nu) = g_2 \left( \frac{\Delta t}{\hbar} \right)^2 \int_0^\infty b(\nu, \nu_{21}) \Delta \nu \left[ \frac{\sin \left[ \frac{\pi (\nu - \nu')}{\nu - \nu'} \Delta t \right]}{\pi (\nu - \nu') \Delta t} \right]^2 |H_{21}(\nu')|^2 d\nu' \]  

(8B.23)

Now we assume that \(|H_{21}(\nu')|^2\) varies much more slowly with \(\nu'\) than the \([(\sin x)/x]^2\) factor, which is peaked at \(\nu' = \nu\) with width \(\Delta \nu' \sim 1/\Delta t\). \(|H_{21}(\nu')|^2\) can then be replaced by its value at \(\nu\), and brought outside the integral:*

\[ P_{1 \to 2}(\Delta \nu) = g_2 |H_{21}(\nu)|^2 b(\nu, \nu_{21}) \Delta \nu \left( \frac{\Delta t}{\hbar} \right)^2 \int_0^\infty \left[ \frac{\sin \left[ \frac{\pi (\nu - \nu')}{\nu - \nu'} \Delta t \right]}{\pi (\nu - \nu') \Delta t} \right]^2 d\nu' \]  

(8B.24)

By using \(\int_{-\infty}^\infty [(\sin x)/x]^2 dx = \pi\), Eq. 8B.24 becomes (for \(\nu \Delta t \gg 1\)):

\[ P_{1 \to 2}(\Delta \nu) = \frac{g_2}{\hbar^2} |H_{21}(\nu)|^2 b(\nu, \nu_{21}) \Delta \nu \Delta t \]  

(8B.25)

The total probability for a \(1 \to 2\) transition occurring within \(\Delta t\) is obtained by letting \(\Delta \nu\) become infinitesimal and integrating Eq. 8B.25 over \(\nu\):

\[ P_{1 \to 2} = \frac{g_2}{\hbar^2} \Delta t \int_0^\infty |H_{21}(\nu)|^2 b(\nu, \nu_{21}) d\nu \]  

(8B.26)

where, it should be recalled, \(\Delta t\) is the elapsed time since the start of the interaction (when the electron was "definitely" in state \(|1\rangle\)). Equation 8B.26 is the general expression for the probability of an induced transition between two discrete stationary states of different energies. The assumptions that have been made in deriving it are (1) that \(\Delta t\) is much longer than \(1/\nu\) for values of \(\nu\), where \(b(\nu, \nu_{21})\) has appreciable value, but is sufficiently short that the probability for a transition is much less than unity; (2) that \(|H_{21}(\nu)|^2\) is constant over a frequency range \(\Delta \nu \sim 1/\Delta t\), and is sufficiently small to not significantly change the stationary states \(\psi_n(r)\); (3) that contributions to the transition probability from radiation at different frequencies add incoherently; (4) that the interaction Hamiltonian is negligibly affected by the mechanism that allows transitions to be induced by frequencies other than \(\nu_{21}\); and (5) that \(H_{21}\) is the same for all degenerate "substates" of \(|2\rangle\). No assumptions are necessary on whether \(E_2\) or \(E_1\) is the higher energy.**

*Note that this has not required any assumption about \(b(\nu, \nu_{21})\): the integration in Eq. 8B.23 is over \(\nu'\), not \(\nu\) or \(\nu_{21}\).

**The argument following Eq. 8B.15 implicitly assumes that \(\nu_{21}\) is positive and, hence, that \(E_2 > E_1\). However, for negative \(\nu_{21}\) and \(E_2 < E_1\), the \((\nu_{21} + \nu)\) term rather than the \((\nu_{21} - \nu)\) term contributes in the same manner, and Eq. 8B.26 is again obtained.
(2) Interaction Hamiltonian.

The Hamiltonian for the interaction of electromagnetic radiation with a particle having charge \( q \) and mass \( m \) is

\[
\mathcal{H}' = \frac{i\hbar}{m} A \cdot \nabla + \frac{i\hbar}{2m} \nabla \cdot A + \frac{q^2}{2m} |A|^2 + q\phi
\]  

(8B.27)

where the vector potential \( A \) and the scalar potential \( \phi \) describe the electro-magnetic radiation.** The electric and magnetic fields are given by

\[
E = -\nabla \phi - \frac{\partial A}{\partial t}
\]  

(8B.28)

\[
B = \nabla \times A
\]  

(8B.29)

In vacuum, one can choose \( \nabla \cdot A = 0 \) and \( \phi = 0 \) without loss of generality, and the Hamiltonian (Eq. 8B.27) becomes

\[
\mathcal{H}' = \frac{i\hbar}{m} A \cdot \nabla + \frac{q^2}{2m} |A|^2
\]  

(8B.30)

The second term on the right of Eq. 8B.30 can be shown to be negligible‡ compared to the first, and we are left with

\[
\mathcal{H}' = \frac{i\hbar}{m} A \cdot \nabla
\]  

(8B.31)

In terms of \( A \), Maxwell’s equations become

\[
\nabla^2 A - \frac{1}{c^2} \frac{\partial^2 A}{\partial t^2} = 0
\]  

(8B.32)

which has the solution

\[
A = A_0 [e^{i(k \cdot r - 2\pi \nu t)} + e^{-i(k \cdot r - 2\pi \nu t)}]
\]  

(8B.33)

where \( A_0 \) is a constant, and

\[
|k| = \frac{2\pi \nu}{c} = \frac{2\pi}{\lambda}
\]  

(8B.34)

*See Bransden and Joachain [13, §4.1]. Equation 8B.27 is also Eq. 44.1 of Schiff [14] converted from Gaussian to S.I. units [(\( 1/c \))\( A \) of [14]'s (44.1) is converted to \( A \)].

**The potentials are a more complete description of nature than are the fields [6, Volume II, §15-5].

‡See Schiff [14, §44]. This term describes the absorption (or emission) of two photons.
Equation 8B.33 describes a wave traveling in the direction $k$ with frequency $\nu$ and wavelength $\lambda$. *

Using Eq. 8B.33 in Eqs. 8B.28 and 8B.29 with $\phi = 0$ gives

$$E = i 2\pi \nu A$$ \hspace{1cm} (8B.35)
$$B = i k \times A$$ \hspace{1cm} (8B.36)

$E$ is parallel to $A$, and we can write Eq. 8B.31 as

$$3C' = \frac{ih}{m} |A| \nabla E$$ \hspace{1cm} (8B.37)

where $\nabla E$ is the gradient component in the direction of $E$. Using Eq. 8B.37 in Eq. 8B.11 with $A$ from Eq. 8B.33 gives

$$3C_{21} = \frac{ih}{m} |A_0| \left\{ e^{\frac{i2\pi vr}{m}} \int \psi^*_2 e^{ik' \cdot r} \nabla E \psi_1 \, d^3r 
+ e^{\frac{i2\pi vr}{m}} \int \psi^*_2 e^{-ik' \cdot r} \nabla E \psi_1 \, d^3r \right\}$$ \hspace{1cm} (8B.38)

which has, nearly, the form of Eq. 8B.14. For $E_2 > E_1$, only the coefficient of the $e^{-\frac{i2\pi nr}{m}}$ term of Eq. 8B.14 contributes to Eq. 8B.26, whereas for $E_2 < E_1$, only the $e^{\frac{i2\pi nr}{m}}$ coefficient contributes. ** By comparing Eqs. 8B.14 and 8B.38, we find for $E_1 > E_2$,

$$H_{21} = \frac{ih}{m} |A_0| \int \psi^*_2 e^{ik' \cdot r} \nabla E \psi_1 \, d^3r$$ \hspace{1cm} (8B.39)

and for $E_1 < E_2$,

$$H_{21} = \frac{ih}{m} |A_0| \int \psi^*_2 e^{-ik' \cdot r} \nabla E \psi_1 \, d^3r$$ \hspace{1cm} (8B.40)

It can be shown [14, §44, for example] that

$$\left| \int \psi^*_2 e^{ik' \cdot r} \nabla E \psi_1 \, d^3r \right|^2 = \left| \int \psi^*_2 e^{-ik' \cdot r} \nabla E \psi_1 \, d^3r \right|^2$$ \hspace{1cm} (8B.41)

*There is also a solution to Eq. 8B.33 having exponential arguments $(k \cdot r + 2\pi \nu t)$; this describes a wave traveling in the $-k$ direction.

**See discussion in the footnote following Eq. 8B.26.
which means the transition probability (Eq. 8B.26) is the same regardless of which state has higher energy. We then have in general

$$|H_{21}|^2 = \left( \frac{\hbar}{m} \right)^2 |A_0|^2 \left| \int \psi_2^* e^{i k \cdot r} \nabla_E \psi_1 \, d^3 r \right|^2$$

(8B.42)

$|A_0|^2$ can be related to radiation intensity. The power crossing unit area in unit time is given by the Poynting vector $S$. The average of $|S|$ over the observation time is just $I_\nu \Delta \nu \Delta \Omega$ for the observed frequency interval $\Delta \nu$ and solid angle interval $\Delta \Omega$, where $I_\nu$ (units: W Hz$^{-1}$ sr$^{-1}$ m$^{-2}$) is the specific intensity of the radiation. We then have

$$I_\nu \Delta \nu \Delta \Omega = \overline{|S|}$$

(8B.43)

where the overbar indicates a time average, and it has been assumed that $I_\nu$ is constant over the intervals $\Delta \nu$ and $\Delta \Omega$. The Poynting vector is

$$S = \epsilon_0 c^2 (E \times B)$$

(8B.44)

where $E$ is the electric field vector, $B$ is the magnetic field vector, and $\epsilon_0$ is the permittivity of vacuum [6, Volume II, §27, for example].

Using Eqs. 8B.35 and 8B.36 in Eq. 8B.44 gives

$$S = -\epsilon_0 c^2 2 \pi \nu A \times (k \times A)$$

(8B.45)

$$= 4 \pi \epsilon_0 c^2 \nu |A_0|^2 \{ 1 + \cos [2(k \cdot r - 2 \pi \nu t)] \}$$

(8B.46)

where Eq. 8B.33 has been used in Eq. 8B.46. The time-average of the cosine term in Eq. 8B.46 is zero; so using Eq. 8B.46 in Eq. 8B.43

$$I_\nu \Delta \nu \Delta \Omega = 4 \pi \epsilon_0 c^2 \nu |k| |A_0|^2 = 8 \pi^2 \epsilon_0 c \nu^2 |A_0|^2$$

(8B.47)

where Eq. 8B.34 has been used in Eq. 8B.47. We then have

$$|A_0|^2 = \frac{1}{8 \pi^2 \epsilon_0 c \nu^2} I_\nu \Delta \nu \Delta \Omega$$

(8B.48)

for radiation within the frequency interval $\Delta \nu$, and within the solid-angle interval $\Delta \Omega$ about the direction $k$. By using Eqs. 8B.21 and 8B.48 in Eq. 8B.42:

$$|H_{21}(\nu)|^2 = \left( \frac{\hbar}{m} \right)^2 \frac{1}{8 \pi^2 \epsilon_0 c \nu^2} I_\nu \Delta \Omega \left| \int \psi_2^* e^{i k \cdot r} \nabla_E \psi_1 \, d^3 r \right|^2$$

(8B.49)

The $\nu^2$ term in the denominator on the right side of Eq. 8B.49 is disturbing, as it would appear to imply infinite interaction at zero frequency. However, a can-
celing $\nu^2$ term arises from the square of the integral; this can be obtained as follows. Define a coordinate system such that $z$ is along $k$ and $x$ is along $E$. The integral in Eq. 8B.49 then becomes

$$\int \psi_2^* e^{ikz} \nabla_E \psi_1 \, d^3r = \int \psi_2^* e^{ikz} \frac{\partial \psi_1}{\partial x} \, d^3r$$  \hspace{1cm} (8B.50)

where $k = |k|$ should not be confused with Boltzmann’s constant.* Now consider the expression

$$\int \frac{\partial \psi_2^*}{\partial t} f(r) \, \psi_1 \, d^3r + \int \psi_2^* f(r) \frac{\partial \psi_1}{\partial t} \, d^3r$$  \hspace{1cm} (8B.51)

where $f(r)$ is any function of $r$. Then for small perturbations (i.e., $3\zeta' \ll H_0$, so that $H = H_0$ is an adequate approximation) putting $\partial \Psi / \partial t$ from Eq. 8B.8 in Eq. 8B.51 and equating the expressions obtained separately using Eqs. 8B.2 and 8B.3 with $H = H_0$, gives

$$\int \psi_2^* f(r) \nabla^2 \psi_1 \, d^3r - \int \psi_1 f(r) \nabla^2 \psi_2^* \, d^3r$$

$$= 4\pi \nu_2 \left( \frac{m}{\hbar} \right) \int \psi_2^* f(r) \psi_1 \, d^3r$$  \hspace{1cm} (8B.52)

where Eq. 8B.12 has been used. Now, putting $f(r) = xe^{ikz}$ in Eq. 8B.52 and performing several integrations by parts using the fact that the wave functions and their spatial derivatives are zero at infinite $r$ gives**

$$4\pi \nu_2 \left( \frac{m}{\hbar} \right) \int \psi_2^* xe^{ikz} \psi_1 \, d^3r = - 2 \int \psi_2^* e^{ikz} \frac{\partial \psi_1}{\partial x} \, d^3r$$

$$+ k^2 \int \psi_2^* xe^{ikz} \psi_1 \, d^3r$$

$$- i2k \int \psi_2^* xe^{ikz} \frac{\partial \psi_1}{\partial z} \, d^3r$$  \hspace{1cm} (8B.53)

As discussed following Eq. 8B.21, we are interested in situations where interactions can occur in a range of frequencies around $\nu_2$. We replace $\nu_2$ by $\nu$ to account for this; then using Eq. 8B.34 for $k$ in Eq. 8B.53 gives

$$\int \psi_2^* e^{ikz} \frac{\partial \psi_1}{\partial x} \, d^3r = - 2\pi \nu \left( \frac{m}{\hbar} \right) \left\{ \left( 1 + \frac{\hbar \nu}{2mc^2} \right) \int \psi_2^* xe^{ikz} \psi_1 \, d^3r$$

$$- i \frac{\hbar}{mc} \int \psi_2^* xe^{ikz} \frac{\partial \psi_1}{\partial z} \, d^3r \right\}$$  \hspace{1cm} (8B.54)

*It should be clear from the context whether $k$ refers to the magnitude of the ‘‘wave vector’’ defined by Eq. 8B.34, or whether it refers to Boltzmann’s constant.

**See, for example, Slater [15, §4-7] for a discussion and other example of this procedure.
Consider the relative magnitude of the terms in the braces on the right side of Eq. 8B.54. The quantity $\frac{hv}{2mc^2}$ is the ratio of the interacting photon energy to twice the electron rest-mass energy.* We are interested in radiation at submillimeter wavelengths (or longer) for which $\nu < 3 \times 10^{12}$ Hz; then $\frac{hv}{2mc^2} < 10^{-8}$ and this term can be neglected.** The quantity $h/mc$ is $(2\pi)^{-1}$ times the Compton wavelength of an electron, $3.9 \times 10^{-13}$ m. The integral multiplying it is $\sim 1/a$ times the value of the first integral, where $a \sim 2 \times 10^{-10}$ m, is a typical molecular dimension. So the size of the term involving the second integral is $\sim 2 \times 10^{-3}$ times the size of the term involving the first integral. We can, therefore, neglect all terms except the first on the right side of Eq. 8B.54 and obtain

$$\int \psi_2^* e^{ikz} \frac{\partial \psi_1}{\partial x} \, d^3r = -2\pi \nu \left( \frac{m}{\hbar} \right) \int \psi_2^* xe^{ikz} \psi_1 \, d^3r$$  \hspace{1cm} (8B.55)$$

Using Eq. 8B.55 in Eq. 8B.50 gives

$$\int \psi_2^* e^{ik\cdot r} \nabla E \psi_1 \, d^3r = -2\pi \nu \left( \frac{m}{\hbar} \right) \int \psi_2^* xe^{ikz} \psi_1 \, d^3r$$  \hspace{1cm} (8B.56)$$

$$= -2\pi \nu \left( \frac{m}{\hbar} \right) \int \psi_2^* r_E e^{ik\cdot r} \psi_1 \, d^3r$$  \hspace{1cm} (8B.57)$$

where the integral on the right side of Eq. 8B.57 has been written in vector form to make it independent of the coordinate system; $r_E$ is the component of $r$ in the direction of the electric field of the interacting radiation. Putting Eq. 8B.57 in Eq. 8B.49 gives

$$|H_{21}(\nu)|^2 = \frac{I_\nu \Delta \Omega}{2\epsilon_0 c} \left| \int \psi_2^* qr_E e^{ik\cdot r} \psi_1 \, d^3r \right|^2$$  \hspace{1cm} (8B.58)$$

Equation 8B.58 shows that the interaction Hamiltonian depends upon the intensity of the interacting radiation and the electron probability distribution in the two quantum states involved. Equation 8B.58 accounts for interactions of the electron with the radiation field except those involving two-photon interactions† and those involving the magnetic moment associated with the intrinsic spin of the electron. Interactions involving intrinsic spin are not described by Schrödinger’s equation or “geometrical” expressions such as the integral in Eq. 8B.58. The “Pauli spin matrices” have been developed to describe spin interactions [6, Volume III, §11, for example].

*A photon of this energy can produce an electron–positron pair, and Dirac’s relativistic equation for the electron [16, Eq. (11) of §67], rather than Schrödinger’s equation, is needed for an accurate description at these high energies. Dirac’s equation predicted positrons (before they were discovered experimentally) and showed that intrinsic electron spin is required by the theory of relativity.

**The quantity $\frac{hv}{2mc^2}$ is unity for $\nu = 2.5 \times 10^{20}$ Hz (gamma rays); it is also a negligible $2 \times 10^{-6}$ for visible light ($\nu = 5 \times 10^{14}$ Hz).

†See the footnote following Eq. 8B.30.
8B.2 Einstein Coefficients

Let $|u\rangle$ denote the "upper" state of a molecule (or atom) that has greater energy than a "lower" state denoted by $|l\rangle$: $E_u > E_l$. Combining Eqs. 8B.25 and 8B.58 gives the probability for radiation of intensity $I_p$ within solid-angle interval $\Delta \Omega$ and frequency interval $\Delta \nu$ to induce a transition from $|l\rangle$ to $|u\rangle$ in time $\Delta t$:

$$P^i_{l \rightarrow u}(\Delta \nu) = \beta_{lu} l_p b(\nu, \nu_{ul}) \Delta \nu \Delta \Omega$$  \hspace{1cm} (8B.59)

where the superscript $i$ in $P^i_{l \rightarrow u}(\Delta \nu)$ indicates this is an induced transition, and

$$\beta_{lu} \overset{\text{def}}{=} \frac{1}{2\epsilon_0 c \hbar^2} g_u \left| \int \left( \psi_u^* \mathbf{r} e^{i \mathbf{k} \cdot \mathbf{r}} \psi_l \right) d^3r \right|^2$$  \hspace{1cm} (8B.60)

is called the Einstein B-coefficient for the $l \rightarrow u$ transition. *

The expression for the reverse $u \rightarrow l$ transition is the same as Eq. 8B.59 except for interchange of the subscripts $u$ and $l$. The absolute square of the integral in Eq. 8B.60 is unchanged on interchange of $u$ and $l$, so it follows that

$$g_f \beta_{lu} = g_u \beta_{ul}$$  \hspace{1cm} (8B.61)

Transitions $l \rightarrow u$ result in the absorption of a photon from within $\Delta \nu$ and $\Delta \Omega$; transitions $u \rightarrow l$ result in the emission of a photon within the same $\Delta \nu$ and $\Delta \Omega$ (and with the same polarization) as the stimulating radiation.

Transitions $u \rightarrow l$ can also occur by spontaneous emission of a photon with no preferred direction. ** The probability of a photon being spontaneously emitted in time $\Delta t$ in a direction within $\Delta \Omega$ and at a frequency within $\Delta \nu$ can be written in

*Einstein postulated, prior to derivation of Eq. 8B.59 from first principles of the later developed quantum mechanics, that the probability per unit time of radiation inducing a transition is proportional to its energy density. The total probability per unit time of a transition is obtained by letting $\Delta \nu$ and $\Delta \Omega$ become infinitesimally small and integrating Eq. 8B.59 over frequency and solid angle; this can be shown to be proportional to the total radiation energy density. $\beta_{lu}$ is sometimes defined in terms of energy density, rather than in terms of intensity as done in Eq. 8B.59; these definitions of $\beta_{lu}$ differ from that given in Eq. 8B.60 by a factor of $c$ if the energy density is for isotropic radiation traveling in all directions. *Intensity* is used here (as in [6, Volume III, §9-6]) in the definition of $\beta_{lu}$ because the photon absorbed or emitted in the induced transition has the direction and polarization described by the inducing radiation intensity. Other potential confusions in the definition of the Einstein coefficients include (1) whether frequency is defined as radians per second (usually denoted by $\omega$) or revolutions per second (usually denoted by $\nu$) as done here, and (2) whether S.I. or Gaussian units are used. Much literature on this subject uses Gaussian units—some works using S.I., or at least mks, include the following references [6, 13, 17, 18].

**The reason that spontaneous emission goes "only" in one direction (from higher to lower energy states of the atom or molecule) has to do with entropy: "... in the most probable situation the field is excited with a photon, and the atom is de-excited. ... It isn't that it [the atom] "wants" to lose energy, because, in fact, when it radiates, the energy of the world is the same as it was before. Radiation or absorption goes in the direction of increasing entropy." [6, Volume III, §7].
terms of the Einstein A-coefficient $\mathcal{G}_{ul}$,

$$P_{u \rightarrow l}^s(\Delta \nu) = \mathcal{G}_{ul} b(\nu, \nu_{ul}) \Delta \nu \frac{\Delta \Omega}{4\pi} \Delta t \tag{8B.62}$$

where it has been assumed that the line-shape function is the same as for induced transitions. The total probability for a $u \rightarrow l$ spontaneous transition is obtained by integrating Eq. 8B.62 over solid angle and frequency:

$$P_{u \rightarrow l}^s = \mathcal{G}_{ul} \Delta t \frac{1}{4\pi} \int d\Omega \int b(\nu, \nu_{ul}) d\nu \tag{8B.63}$$

$$= \mathcal{G}_{ul} \Delta t \tag{8B.64}$$

where Eq. 8B.22 has been used. Derivation of $\mathcal{G}_{ul}$ from first principles requires quantum electrodynamics.* However, $\mathcal{G}_{ul}$ can be related to $\mathcal{B}_{ul}$ by thermodynamic arguments. Let a system have $n_l$ molecules per unit volume in state $|l\rangle$ and $n_u$ molecules per unit volume in state $|u\rangle$. Considering only the frequency interval $\Delta \nu$ and solid-angle interval $\Delta \Omega$, the average number of transitions per unit volume from $|l\rangle$ to $|u\rangle$ in time $\Delta t$ is

$$\overline{\Delta n_{l \rightarrow u}} = \overline{n_l P_{l \rightarrow u}^I(\Delta \nu)} \tag{8B.65}$$

and the average number from state $|u\rangle$ to $|l\rangle$ is

$$\overline{\Delta n_{u \rightarrow l}} = \overline{n_u [P_{u \rightarrow l}^I(\Delta \nu) + P_{u \rightarrow l}^s(\Delta \nu)]} \tag{8B.66}$$

where an overbar indicates a time average. Detailed balancing** at thermal equilibrium requires $\overline{\Delta n_{l \rightarrow u}} = \overline{\Delta n_{u \rightarrow l}}$. Equating Eqs. 8B.65 and 8B.66, using Eqs. 8B.59, 8B.61, and 8B.62 with the assumption† that the line-shape function is the same for emission and absorption: $b(\nu, \nu_{ul}) = b(\nu, \nu_{lu})$ gives

$$\mathcal{G}_{ul} = 4\pi \mathcal{B}_{ul} \left( \frac{n_l g_u}{n_u g_l} - 1 \right) I_\nu \tag{8B.67}$$

*See, for example, Schiff [14, §57] and Heitler [19, §17]. The probability for a transition which emits a photon in a particular state (direction, polarization, frequency) is proportional to $(n + 1)$, where $n$ is the number of photons already present in that state. This follows directly from the fact that photons are a system of Bose particles whose wave-function phase is unchanged upon interchange of two photons [6, Volume III, §4, for example]. The proportionality to $(n + 1)$ accounts for both induced transitions (through the term $n$) and spontaneous transitions (through the term $1$). The ratio of the induced transition probability to the spontaneous transition probability is always just the number of photons already present in the radiation field.

**This is the principle that power radiated and absorbed at thermal equilibrium must be equal for any frequency, direction, and polarization [20, §9-15, for example].

†This must be true if the incident radiation has constant intensity in the region of the line breadth [19, §18].
for \( n_u, n_l, \) and \( I_v \) in local thermal equilibrium. Statistical mechanics requires, for local thermal equilibrium at temperature \( T \),

\[
\frac{n_u}{n_l} = \frac{g_u}{g_l} e^{-(E_u - E_l)/kT} \quad (8B.68)
\]

\[
= \frac{g_u}{g_l} e^{-\hbar \nu_{ul}/kT} \quad (8B.69)
\]

where Eq. 8B.12 has been used in Eq. 8B.69. A system in thermal equilibrium has \( I_v \) equal to the Planck function \( B_v \):

\[
I_v = \frac{2\hbar \nu^3}{c^2} \frac{1}{e^{\hbar \nu/kT} - 1} = B_v \quad (8B.70)
\]

Using Eqs. 8B.70 and 8B.69 in Eq. 8B.67 gives

\[
\mathcal{G}_{ul} = \frac{8\pi \hbar \nu^3}{c^2} \left( \frac{e^{\hbar \nu/kT}}{e^{\hbar \nu/kT} - 1} \right) \mathcal{B}_{ul} \quad (8B.71)
\]

\[
= 4\pi B_v (e^{\hbar \nu_{ul}/kT} - 1) \mathcal{B}_{ul} \quad (8B.72)
\]

The term in parentheses on the right side of Eq. 8B.71 is unity for interaction occurring only at frequency \( \nu_{ul} \). It can generally be approximated by unity for cases of interest here: \( b(\nu, \nu_{ul}) \) is usually sharply peaked at \( \nu = \nu_{ul} \), so only frequencies near \( \nu_{ul} \) need be considered.

**8B.3 Electric-Dipole Transitions**

We are interested in radiation whose wavelength is much longer than the dimensions of the molecule. Then \( k \cdot r \ll 1 \) for values of \( r \) where the integrand in Eq. 8B.60 has appreciable value, and we can set \( e^{ik \cdot r} = 1 \) in Eq. 8B.60.** The integral in Eq. 8B.60 is over coordinates that are fixed with respect to the molecule, and we are interested in obtaining expressions for a coordinate system fixed with respect to the interacting field and the observer. We define the dipole moment-vector

*Keeping the term in parentheses in the expression for \( \mathcal{G}_{ul} \) shows, without requiring the approximation that all interaction occurs at \( \nu_{ul} \), that the radiative transfer "source function" at thermal equilibrium is the Planck function—see Eqs. 8B.99 and 8B.101.

**The next term in the series expansion of \( e^{ik \cdot r} \) represents electric quadrupole and electron orbital magnetic-moment interactions, and higher-order terms represent higher-order interactions. Contributions of successive terms generally decrease by the factor \( \sim (ka)^2 = (2\pi a/\lambda)^2 \), where \( a \) is the molecular dimension (which determines the extent of the region over which there is significant contribution to the integral in Eq. 8B.60), and \( \lambda \) is wavelength of the radiation.
matrix element

\[ \mu_{ul} \stackrel{\text{def}}{=} \int \psi_u^* q r \psi_l \, d^3 r \quad (8B.73) \]

where \( r = (x, y, z) \) are coordinates fixed with respect to the molecule. The absolute square of the integral in Eq. 8B.60 can then be written

\[ \left| \int \psi_u^* q r E \psi_1 \, d^3 r \right|^2 = \mu_{ul}^2 \cos^2 \theta \quad (8B.74) \]

where \( \theta \) is the angle between the interacting electric field and \( \mu_{ul} \), and \( \mu_{ul} \stackrel{\text{def}}{=} |\mu_{ul}|^2 \). The effective interaction of a collection of molecules is given by the expected value of Eq. 8B.74 over the collection. If all orientations of the molecule relative to the interacting field are equally likely, *this is

\[ \mu_{ul}^2 \int_0^\pi \cos^2 \theta \, 2\pi \, \sin \theta \, d\theta = \frac{1}{2} \mu_{ul}^2 \quad (8B.75) \]

\[ \mu_{ul}^2 \int_0^\pi \cos^2 \theta \, 2\pi \, \sin \theta \, d\theta = \frac{1}{2} \mu_{ul}^2 \quad (8B.76) \]

Equation 8B.76 also applies to a single molecule in a randomly polarized radiation field, because only the relative orientation between the molecule and the radiation polarization is important.

The effective Einstein A and B coefficients for electric-dipole transitions of a molecule immersed in isotropic radiation (or equivalently for a collection of molecules randomly aligned to the radiation field) are obtained by putting Eq. 8B.76 in Eq. 8B.60 with \( e^{ik \cdot r} = 1 \), and using Eqs. 8B.61 and 8B.71:

\[ \mathcal{Q}_{ul}^{ed} = \frac{1}{6\epsilon \omega c^3 h} \frac{\epsilon_1}{2} \mu_{ul}^2 \quad (8B.77) \]

\[ \mathcal{Q}_{ul}^{ed} = \frac{8\pi^2 \nu_3}{3\epsilon \omega c^3 h} \frac{\epsilon_1}{2} \mu_{ul}^2 \quad (8B.78) \]

where the approximation that \( \nu \approx \nu_{ul} \) has been made in Eq. 8B.78.

*An example when this is not true in Earth’s atmosphere is for \( \text{O}_2 \) molecules at heights above \( \sim 50 \) km. At these heights, the time between molecular collisions (which randomize the molecular orientations) is not much less than the time that the magnetic dipole of \( \text{O}_2 \) precesses about the terrestrial magnetic-field direction, and the \( \text{O}_2 \) molecules are “aligned” by the magnetic field. Theoretical expressions for this situation are given in Lenoir [21, 22] and Rosenkranz and Staelin [23].
It is, perhaps, worthwhile to rewrite Eqs. 8B.77 and 8B.78 in the form

\[ \mathcal{B}_{ul} = \left( \frac{1}{4\pi\epsilon_0} \right) \frac{8\pi^3}{3c^2} \frac{\delta_1^2}{g_{ul}} \tag{8B.79} \]

\[ G_{ul} = \left( \frac{1}{4\pi\epsilon_0} \right) \frac{64\pi^4}{3h^3} \frac{\delta_1^2}{g_{ul}} \tag{8B.80} \]

explicitly showing the \((1/4\pi\epsilon_0)\) factor, which is not present when Gaussian units are used. Expressions without this factor, and without the factor of \(c\) in the denominator of Eq. 8B.79—because of \(\mathcal{B}_{lu}\) being defined in terms of radiation energy density—are commonly found in the microwave literature.*

8B.4 Absorption Coefficient and Radiative Transfer

Consider a collection of molecules, each having quantum states \(|l\rangle\) and \(|u\rangle\), where \(E_u > E_l\). Let \(n_l\) be the number of molecules per unit volume in state \(|l\rangle\) and \(n_u\) be the number per unit volume in state \(|u\rangle\). The energy emitted by a \(u \rightarrow l\) transition in the time interval \(\Delta t\), the frequency interval \(\Delta \nu\), and the solid-angle interval \(\Delta \Omega\) by molecules in an elemental volume \(\Delta V\) is (average number of molecules in \(|u\rangle\) \times (probability of a \(u \rightarrow l\) transition in time \(\Delta t\) in the frequency range \(\Delta \nu\) and solid-angle range \(\Delta \Omega\)) \times (energy per emitted photon):

\[ \Delta E_{ul}^{emis} = (n_u \Delta \nu) [P_{ul}^{\text{in} \rightarrow l}(\Delta \nu) + P_{ul}^{\text{out} \rightarrow l}(\Delta \nu)] \Delta \nu \Delta \Omega \Delta t \tag{8B.81} \]

\[ = n_u \left( \mathcal{B}_{ul} I_v + \frac{G_{ul}}{4\pi} \right) h\nu b(\nu, \nu_{ul}) \Delta \nu \Delta \Omega \Delta t \tag{8B.82} \]

\[ = \eta_{ul}^v \Delta \nu \Delta \Omega \Delta t \Delta \nu \tag{8B.83} \]

where Eqs. 8B.59 (written for the \(u \rightarrow l\) transition) and 8B.62 have been used in Eq. 8B.82, it has again been assumed that \(b(\nu, \nu_{ul}) = b(\nu, \nu_{ul})\), and

\[ \eta_{ul}^v \overset{\text{def}}{=} n_u \left[ \mathcal{B}_{ul} I_v + \frac{G_{ul}}{4\pi} \right] h\nu b(\nu, \nu_{ul}) \tag{8B.84} \]

\[ = n_u \mathcal{B}_{ul} \left[ I_v + \frac{2h\nu^3}{c^2} \left( \frac{e^{h\nu_{ul}/kT} - 1}{e^{h\nu/kT} - 1} \right) \right] h\nu b(\nu, \nu_{ul}) \tag{8B.85} \]

\[ = n_u \mathcal{B}_{ul} \left[ I_v + (e^{h\nu_{ul}/kT} - 1) B_v \right] h\nu b(\nu, \nu_{ul}) \tag{8B.86} \]

is called the "volume emission coefficient"—the energy emitted per unit volume, per unit frequency interval, per unit solid angle, and per unit time. The first term in brackets is due to induced emission and the second term in brackets is due to

*For example, Eqs. 3.6 and 3.14 of Gordy and Cook [24]. The classic reference for derivation of these expressions is Pauling and Wilson [25, §40b]. The expressions in both [24] and [25], however, assume nondegenerate states so they do not explicitly contain the factor \(g_{ul}\).
spontaneous emission; Eq. 8B.71 has been used in Eq. 8B.85, and Eq. 8B.72 in Eq. 8B.86.

Likewise, the energy absorbed from the frequency interval $\Delta \nu$ and solid-angle interval $\Delta \Omega$ by the $l \to u$ transition is

$$\Delta E_{\nu}^{\text{abs}} = (\bar{n}_l \Delta \nu)[P_{l \to u}^{0} \Delta \nu]h\nu$$

$$= \bar{n}_l \mathcal{B}_{lu} I_{v} h\nu b(v, \nu_{ul}) \Delta \nu \Delta \Omega \Delta t \Delta \nu$$

$$= \alpha_{v}^{ul'} I_{v} \Delta \nu \Delta \Omega \Delta t \Delta \nu$$

where Eq. 8B.59 has been used, and

$$\alpha_{v}^{ul'} \overset{\text{def}}{=} \bar{n}_l \mathcal{B}_{lu} h\nu b(v, \nu_{ul})$$

The net energy change in the radiation field within $\Delta \nu$ and $\Delta \Omega$ in time $\Delta t$ due to the $l \leftrightarrow u$ interaction with molecules in volume $\Delta v$ is

$$\Delta E_{\nu}^{\text{abs}} = \Delta E_{\nu}^{\text{emiss}} - \Delta E_{\nu}^{\text{abs}}$$

$$= (\eta_{v}^{ul} - \alpha_{v}^{ul'} I_{v}) \Delta \nu \Delta \Omega \Delta t \Delta \nu$$

This change in energy can be written as the change in intensity $\Delta I_{\nu}$ as the radiation travels a distance $\Delta l$, where $\Delta \nu = \Delta A/\Delta l$, and $\Delta A$ is an element of area normal to the direction of travel:

$$\Delta E_{\nu}^{\text{abs}} = \Delta I_{\nu} \Delta \nu \Delta \Omega \Delta t \Delta A$$

Equating Eqs. 8B.92 and 8B.93, using $\Delta \nu = \Delta A/\Delta l$ and letting $\Delta l$ become infinitesimally small, yields the differential equation

$$\frac{dI_{\nu}}{dl}^{\text{ul}} = \eta_{v}^{ul} - \alpha_{v}^{ul'} I_{v}$$

Using Eqs. 8B.86 and 8B.90 in Eq. 8B.94, and again assuming $b(v, \nu_{ul}) = b(v, \nu_{lu})$, gives

$$\frac{dI_{\nu}}{dl}^{\text{ul}} = [\bar{n}_{u} \mathcal{B}_{ul}(e^{h\nu_{ul}/kT} - 1)B_{v}$$

$$- (\bar{n}_l \mathcal{B}_{lu} - \bar{n}_l \mathcal{B}_{ul})I_{v}]h\nu b(v, \nu_{ul})$$

$$= \bar{n}_l \mathcal{B}_{lu} \left(1 - \frac{\bar{n}_u \mathcal{B}_{ul}}{\bar{n}_l \mathcal{B}_{lu}}\right)h\nu b(v, \nu_{ul})$$

$$\times \left[ B_{v} \left(e^{h\nu_{ul}/kT} - 1\right) \left(\frac{\bar{n}_l \mathcal{B}_{lu}}{\bar{n}_u \mathcal{B}_{ul}} - 1\right)^{-1} - I_{v}\right]$$

$$= \alpha_{v}^{ul}(J_{\nu}^{ul} - I_{v})$$
where Eq. 8B.61 has been used in Eq. 8B.96, and

\[
\alpha_{\nu}^{ul} \overset{\text{def}}{=} \bar{n}_l \mathcal{B}_{lu} \left( 1 - \frac{n_u g_l}{n_l g_u} \right) h \nu b(\nu, \nu_{ul})
\]  

(8B.98)

\[
J_{\nu}^{ul} \overset{\text{def}}{=} B_\nu (e^{h \nu_{ul} / kT} - 1) \left( \frac{n_l g_u}{n_u g_l} - 1 \right)^{-1}
\]  

(8B.99)

Equation 8B.97 is the differential equation of radiative transfer for a two-state system. It is a statement of conservation of energy combined with the definitions of \( J_{\nu}^{ul} \) and \( \alpha_{\nu}^{ul} \). \( J_{\nu}^{ul} \) is generally called the "source function," and \( \alpha_{\nu}^{ul} \) is called the "absorption coefficient"—or "volume absorption coefficient" because it is a per volume quantity due to the \( \Delta \nu \) factor in Eq. 8B.92.*

For conditions of local thermodynamic equilibrium, we use Eq. 8B.69 in Eqs. 8B.98 and 8B.99 to obtain

\[
\alpha_{\nu}^{ul} = \bar{n}_l \mathcal{B}_{lu} (1 - e^{h \nu_{ul} / kT}) h \nu b(\nu, \nu_{ul})
\]  

(8B.100)

and

\[
J_{\nu}^{ul} = B_\nu
\]  

(8B.101)

where \( B_\nu \) is the Planck function given by Eq. 8B.70. The mean number density of molecules in state \( |l\rangle \) at thermal equilibrium is related to the total number density \( n \) by

\[
\bar{n}_l = \frac{g_l e^{-E_l / kT}}{Q} n
\]  

(8B.102)

where

\[
Q = \sum_j g_j e^{-E_j / kT}
\]  

(8B.103)

is the partition function. Using Eqs. 8B.102 and 8B.79 in Eq. 8B.100 gives the absorption coefficient for electric-dipole interactions under conditions of local thermal equilibrium:

\[
\alpha_{\nu}^{ul} = n \left( \frac{1}{4 \pi \epsilon_0} \right) \frac{8 \pi^3}{3 \hbar c Q} g_l g_u \mu_{lu}^2 (e^{-E_l / kT} - e^{-E_u / kT}) \nu b(\nu, \nu_{ul})
\]  

(8B.104)

*Note that \( \alpha_{\nu}^{ul} \) as given by Eq. 8B.98 includes the effects of stimulated emission, and the common practice of calling it the "absorption" coefficient is somewhat misleading—this is motivated because \( \alpha_{\nu}^{ul} \) gives the net decrease in the radiation intensity per unit distance. "Pure" absorption is described by what we have called \( \alpha_{\nu}^{ul} \) defined by Eq. 8B.90. "Mass" and "atomic" absorption coefficients are also sometimes defined [2, §2.1, for example] that give the absorption per unit mass and per atom (molecule), respectively.
where Eq. 8B.12 has been used and the first factor in parentheses is not present when Gaussian units are used. The factor $g_u$ in Eq. 8B.104 is often implicitly included* in the definition of $\mu_{lu}$; this must be done if $g_u$ has not been previously introduced in the probability of a $l \to u$ transition.

Molecular systems generally have more than two states, and Eq. 8B.97 must be extended to account for this. If there are no "coherent" effects between different transitions, then the probabilities for the various transitions add** and Eq. 8B.97 changes to

$$\frac{dI_v}{dl} = \sum_{\text{all transitions}} \alpha_v^{ul} (J_v^{ul} - I_v) \tag{8B.105}$$

For local thermodynamic equilibrium, using Eq. 8B.101 in Eq. 8B.105 gives

$$\frac{dI_v}{dl} = \alpha_v (B_v - I_v) \tag{8B.106}$$

where

$$\alpha_v = \sum_{\text{all transitions}} \alpha_v^{ul} \tag{8B.107}$$

The differential radiative transfer equation can be converted to an integral equation as follows. We define

$$d\tau_v^{\text{def}} = - \alpha_v \, dl \tag{8B.108}$$

and

$$\tau_v(l, L) \overset{\text{def}}{=} \int_l^L \alpha_v(l') \, dl' \tag{8B.109}$$

where $\tau_v$ is called the "optical depth." The integral in Eq. 8B.109 is along the radiation path described by $l'$; $l$ is an "arbitrary" point on this path, and $L$ is the

*For example, in Eq. 2.3.8 of Waters [5].

**Coherent effects can exist, for example, when collisional "broadening" of "individual" lines is sufficiently large to cause line overlap. The involved quantum states can then become merged and one should, in principle, solve the Schrödinger equation using a potential $V(r)$, which includes the effects of collisions. An important case of atmospheric absorption and emission of microwaves in which coherent overlapping effects must be included is the 60-GHz spin-rotation band of molecular oxygen at heights below ~ 20 km: Rosenkranz [26, 27] has developed expressions that account for this effect with good accuracy [28].
point at which $I_\nu$ is to be calculated. By using Eq. 8B.108, Eq. 8B.97 becomes*

$$\frac{dI_\nu}{d\tau_\nu} = I_\nu - J_\nu$$  \hspace{1cm} (8B.110)

Multiplying both sides of Eq. 8B.110 by the integrating factor $e^{-\nu(L)}$ gives

$$\frac{dI_\nu}{d\tau_\nu} e^{-\nu(L)} - I_\nu e^{-\nu(L)} = -J_\nu e^{-\nu(L)}$$  \hspace{1cm} (8B.111)

which is identical to

$$\frac{d}{d\tau_\nu} (I_\nu e^{-\nu(L)}) = -J_\nu e^{-\nu(L)}$$  \hspace{1cm} (8B.112)

Integrating Eq. 8B.112 from $\tau_\nu(L, L) = 0$ to $\tau_\nu(0, L)$ gives

$$I_\nu(0) e^{-\nu(0,L)} - I_\nu(L) = -\int_0^{\tau_\nu(0,L)} J_\nu e^{-\nu(L)} d\tau_\nu$$  \hspace{1cm} (8B.113)

or

$$I_\nu(L) = I_\nu(0) e^{-\nu(0,L)} + \int_0^{\tau_\nu(0,L)} J_\nu e^{-\nu(L)} d\tau_\nu$$  \hspace{1cm} (8B.114)

where $I_\nu(0)$ is the value of $I_\nu$ at $l = 0$. The first term on the right side of Eq. 8B.114 can be interpreted as the attenuation of the incident radiation by the factor** $e^{-\nu(0,L)}$ as it passes from $l = 0$ to $l = L$. The second term can be interpreted as the integral of an infinitesimal emission $J_\nu \, d\tau_\nu$ attenuated by $e^{-\nu(L)}$ as this "infinitesimal emission" passes from $l$ to $L$. Equation 8B.114 is the integral equation of radiative transfer. Figure 8B.1 sketches the geometry.

Equation 8B.114 can be written

$$I_\nu(L) = I_\nu(0) e^{-\nu(0,L)} + \bar{J}_\nu(1 - e^{-\nu(0,L)})$$  \hspace{1cm} (8B.115)

*Equation 8B.110 assumes that either (1) only a single transition is important at a given frequency $\nu$—as is the case for sufficiently isolated spectral lines, and/or (2) $J_\nu$ is the same for all transitions—as is the case for local thermodynamic equilibrium. Otherwise, the source function $J_\nu$ for individual transitions must be kept inside the summation given in Eq. 8B.105; Eq. 8B.110 must then be modified to include the appropriate summation.

**The factor $e^{-\nu(0,L)}$ is called the "transmittance" between 0 and $L$. Some authors use $\nu$ as a symbol for transmittance instead of for optical depth as done here—readers should be aware of potential confusion in notation between optical depth and transmittance.
Figure 8B.1. Radiative transfer geometry.

where $\overline{J}_\nu$ is the appropriately averaged source function:

$$
\overline{J}_\nu = \frac{\int_0^{\tau_\nu(0,L)} J_\nu e^{-\tau_\nu(l,L)} d\tau_\nu}{\int_0^{\tau_\nu(0,L)} e^{-\tau_\nu(l,L)} d\tau_\nu}
$$

(8B.116)

For "optically thick" cases (defined by $\tau_\nu(0,L) \gg 1$), Eq. 8B.115 gives

$$
I_\nu(L) = \overline{J}_\nu
$$

(8B.118)

In this case, the intensity at $L$ is simply the (appropriately averaged) source function: The incident radiation has no effect at $L$ because of the large attenuation.

For "optically thin" cases (defined by $\tau_\nu(0,L) \ll 1$), keeping the first-order term in the series expansion of the exponential in Eq. 8B.115 gives

$$
I_\nu(L) = \tau_\nu(0,L) (\overline{J}_\nu - I_\nu(0)) + I_\nu(0)
$$

(8B.119)

which shows that $I_\nu(L) \to I_\nu(0)$ when $\tau_\nu(0,L) \to 0$, as it must.

Often of interest is the difference between intensity at a spectral-line center and at a frequency sufficiently removed from the line center that $\tau_\nu(0,L) = 0$. By using Eq. 8B.115, this is

$$
\Delta I_\nu^{ul}(L) = (\overline{J}_\nu - I_\nu(0))(1 - \exp[-\tau_{\nu(0,L)}])
$$

(8B.120)
where it has been assumed that \( J_p \) and \( I_r(0) \) do not change between the spectral-line center and the "sufficiently removed" frequency. Equation 8B.120 shows:

1. \( \Delta I_{ul}^m(L) > 0 \) if \( J_p > I_r(0) \): the spectral line is "seen" in emission
2. \( \Delta I_{ul}^m(L) < 0 \) if \( J_p < I_r(0) \): the spectral line is "seen" in absorption
3. \( \Delta I_{ul}^m(L) = 0 \) if \( J_p = I_r(0) \): the spectral line emits exactly the amount that it absorbs from the incident radiation; it is not "seen" at all.

### 8B.5 Rotational Transitions

Consider a molecule that makes a transition between two rotational states \(|l\rangle\) and \(|u\rangle\). The component along a space-fixed axis \( F \) of the dipole-moment matrix element of the transition is given by [24, §2.6]

\[
\mu_{ul}^F = \mu_{ul}^x \int r \psi_u^* \cos \phi_F \psi_l \, d^3r
\]  

(8B.121)

where \( \mu_{ul}^x \) is the dipole-matrix-element component along a molecule-fixed axis \( x \), \( \psi_u \) is the rotational wave function of state \(|u\rangle\), and \( \phi_F \) is the angle between the fixed axis \( F \) and the rotating molecular axis \( x \). The square of the matrix element in space-fixed coordinates is

\[
|\mu_{ul}|^2 = |\mu_{ul}^x|^2 + |\mu_{ul}^y|^2 + |\mu_{ul}^z|^2
\]  

(8B.122)

where \( X, Y, \) and \( Z \) are space-fixed Cartesian coordinates. For rotational transitions \(|\mu_{ul}|^2\) given by Eq. 8B.122 should be used in Eq. 8B.76 and following equations. The factor of \( \frac{1}{3} \) is still needed in Eq. 8B.76—the space-fixed \( X, Y, Z \) coordinate system has equally likely orientation in any direction.

The vibration and electronic states of the molecule do not change in pure rotational transitions. Equation 8B.73 then contains the same electronic and vibrational wave functions for both states involved in the transition and, for the \( x \) component, becomes

\[
\mu_{ul}^x = \int \psi_{ev}^* q x \psi_{ev} \, d^3r \quad \text{def}
\]  

(8B.123)  

\[
\mu_{ul}^x = \mu_x
\]  

(8B.124)

where \( \psi_{ev} \) is the electronic-vibrational wave function, and \( \mu_x \) is the "permanent electric dipole moment" (along the molecular \( x \)-axis) for the molecular state denoted by \( \psi_{ev} \).

Using Eqs. 8B.121, 8B.122, and 8B.124 in Eq. 8B.104, we obtain

\[
\alpha_{ul}^v = n \left( \frac{1}{4\pi\epsilon_0} \right) \frac{3\pi^2 S_{ul} \mu_x^2}{3\hbar cQ} \left( e^{-E_v/kT} - e^{-E_u/kT} \right) \nu b(\nu, \nu_{ul})
\]  

(8B.125)
for the absorption coefficient of a $u \leftrightarrow l$ rotational transition, where

$$xS_{ul} \overset{\text{def}}{=} g_l g_u \sum_{F=X,Y,Z} \left| \int \psi_u^* \cos \phi_F \psi_l d^3r \right|^2$$  \hspace{1cm} (8B.126)

is sometimes [34, for example] called the “line strength.”

### 8B.6 JPL Catalog Data

The line intensity in the JPL Submillimeter, Millimeter and Microwave Spectral Line Catalog* is defined as

$$g_{ul} \overset{\text{def}}{=} 10^{12} \left( \frac{1}{4\pi\epsilon_0} \right) \frac{8\pi^3 xS_{ul} \hbar^2}{3hc} \exp \left( \frac{E_l}{kT} - \frac{E_u}{kT} \right) \frac{Q_{rs}}{300K}$$  \hspace{1cm} (8B.127)

where $Q_{rs}$ is the “rotation–spin” partition function, all temperature-dependent quantities are evaluated at $T = 300$ K, and other symbols are as previously defined. The “total” partition function $Q$ can be written as the product of “rotation–spin” and “electronic–vibration” factors. This follows from the overall degeneracy of a state being the product of the rotation–spin and electronic–vibration degeneracies, and from the total energy of the state being the sum of the energies. Equation 8B.103 then gives

$$Q = \sum_{i,j} g_i^{rs} g_j^{ev} \exp \left(-\left(\frac{E_i^{rs} + E_j^{ev}}{kT}\right)\right)$$  \hspace{1cm} (8B.128)

$$= \left[ \sum_i g_i^{rs} \exp \left(-\frac{E_i^{rs}}{kT}\right) \right] \left[ \sum_j g_j^{ev} \exp \left(-\frac{E_j^{ev}}{kT}\right) \right]$$  \hspace{1cm} (8B.129)

$$= Q_{rs} Q_{ev}$$  \hspace{1cm} (8B.130)

where $rs$ and $ev$ indicate rotation–spin and electronic–vibration, respectively. The electronic–vibration partition function can be further broken down into separate factors for the electronic and vibrational states. Usually, but not always, $Q_{ev}$ can be approximated by unity for atmospheric submillimeter, millimeter, and microwave spectral lines.

By using Eqs. 8B.127 and 8B.130, the absorption coefficient expression (Eq.

*This catalog [34, 35 of Chapter 8] contains spectroscopic data for submillimeter, millimeter and microwave spectral lines of molecules and atoms of atmospheric and astrophysical interest. There is a separate catalog entry (listing of data) for different isotopic and vibrational states of a molecule or atom. The data include line frequencies, intensities, quantum numbers, lower-state energies, upper-state degeneracies, and values of the rotation–spin partition function (the portion of the overall partition function for states contained within a catalog entry: Eq. 8B.103 with the summation extending over the states within each entry). The catalog rotation–spin partition function and rotational line intensities for $O_3$ and $H_2O$ include the (of order 1%) effects of vibrational states of these molecules. This was done to improve accuracy of atmospheric calculations for these.
8B.125) can be written*

\[ \alpha_{\nu}^{ul} = (10^{-12}) n \Sigma_{ul} \frac{\nu b(\nu, \nu_{ul})}{\nu_{ul}} \frac{r(T)}{Q_{e\nu}(T)} \text{ m}^{-1} \]  

(8B.131)

where

\[ r(T) \overset{\text{def}}{=} \left\{ \frac{[(1 - e^{-h\nu_{ul}/kT})e^{-E_{l}/kT}]}{[1 - e^{-h\nu_{ul}/kT})e^{-E_{l}/kT}]} \right\} \frac{Q_{r_{s}(300 \text{ K})}}{Q_{r_{s}(T)}} \]  

(8B.132)

and Eq. 8B.12 has been used in Eq. 8B.132.

The Einstein A coefficient for a transition can also be expressed in terms of data in the catalog. Using Eqs. 8B.61, 8B.71, 8B.100, 8B.102, 8B.130, and 8B.131 leads to

\[ G_{ul} = (10^{-12}) \frac{8\pi \nu_{ul}^2 \Sigma_{ul}}{c^2 g_{u}} \frac{Q_{r_{s}(300 \text{ K})}}{[(1 - e^{-h\nu_{ul}/kT})e^{-E_{l}/kT}]}_{300K} \]  

(8B.133)

where \( \nu = \nu_{ul} \) has been assumed.

The catalog lists the lower-state energy in units of wave numbers** \( \bar{E} = E/100ch \). Using \( \bar{E} \), we have

\[ \frac{E}{kT} = \frac{100 \text{ ch}\bar{E}}{kT} \]  

(8B.134)

\[ = \frac{1.4388\bar{E}}{T} \]  

(8B.135)

where \( T \) is in kelvin. Equations 8B.132 and 8B.133 can then be written

\[ r(T) = \left[ \frac{(1 - e^{-4.7992 \times 10^{-11} \nu_{ul}/T})e^{-1.4388\bar{E}_{l}/T}}{(1 - e^{-1.5998 \times 10^{-13} \nu_{ul}/T})e^{-0.0048\bar{E}_{l}}} \right] \frac{Q_{r_{s}(300 \text{ K})}}{Q_{r_{s}(T)}} \]  

(8B.136)

and\dagger

\[ G_{ul} = (2.7964 \times 10^{-28}) \frac{\nu_{ul}^2 \Sigma_{ul}}{g_{u}} \left[ \frac{Q_{r_{s}(300 \text{ K})}}{[(1 - e^{-1.5998 \times 10^{-13} \nu_{ul}/T})e^{-0.0048\bar{E}_{l}}]} \right] s^{-1} \]  

(8B.137)

*We have shown here only that the absorption coefficient for rotational transitions and electric-dipole interactions can be written in the form of Eq. 8B.131. However, Eq. 8B.131 very conveniently holds for all transitions whose data are listed in the catalog. This is due to the catalog definitions of \( \Sigma_{ul} \) and \( k_{l} \) for the other types of transitions and interactions.

**The inverse of the wavelength (in cm) of a photon having that amount of energy.

\dagger The constant in Eq. 8B.137 is \( 10^{12} \) smaller than in Eq. 1 of [34 of Chapter 8] because their equation is for \( \nu_{ul} \) in MHz (catalog units), whereas Eq. 8B.137 is for \( \nu_{ul} \) in Hz.
8B.7 Useful Approximations

We often need to estimate the strength of absorption or emission from a molecule whose relative abundance in the atmosphere is very small, and whose spectral lines are broadened by collisions with "air" molecules. Letting \( f \) be the volume mixing ratio* of such a molecule, we can write its number density as

\[
n = f n_{\text{air}} = \frac{f P_{\text{air}}}{kT} = (0.72429 \times 10^{25}) f \frac{[P_{\text{air}}]_{\text{mbar}}}{T}
\]

(8B.138) (8B.139) (8B.140)

where \( n_{\text{air}} \) is the total density of air molecules, \( P_{\text{air}} \) is total air pressure, and the gas law \( P_{\text{air}} = n_{\text{air}} kT \) has been used in Eq. 8B.139; \([P_{\text{air}}]_{\text{mbar}}\) is the total air pressure in millibars.**

The value of the line-shape function \( b(\nu,\nu_{ul}) \) on the center [i.e., at \( \nu = \nu_{ul} \)] of a narrow collisionally broadened line is

\[
b(\nu_{ul},\nu_{ul}) = \frac{1}{\pi \Delta \nu_c}
\]

(8B.141)

where \( \Delta \nu_c \) is the collisional line-width parameter.† Using Eqs. 8B.139 and 8B.141 in Eq. 8B.131 gives, at \( \nu = \nu_{ul} \),

\[
\alpha_{\nu_{ul}}^u = (10^{-12}) \frac{f \beta_{ul}}{\pi kT} \left[ \frac{r(T)}{Q_{ev}(T)} \right] \frac{\Delta \nu_c}{P_{\text{air}}} \text{ m}^{-1}
\]

(8B.142)

\[
= (2.3 \times 10^6) \frac{f \beta_{ul}}{T} \left[ \frac{r(T)}{Q_{ev}(T)} \right] \frac{\Delta \nu_c}{P_{\text{air}}} \text{ MHz/mbar} \text{ m}^{-1}
\]

(8B.143)

where in Eq. 8B.143, \( \Delta \nu_c / P_{\text{air}} \) is in the frequently used units of MHz/mbar, as indicated. A typical value of \( \Delta \nu_c / P_{\text{air}} \) is 2.3 MHz/mbar; using this in Eq. 8B.143 gives

\[
\alpha_{\nu_{ul}}^u \approx 10^6 \frac{f \beta_{ul}}{T} \left[ \frac{r(T)}{Q_{ev}(T)} \right] \text{ m}^{-1}
\]

(8B.144)

At \( T = 300 \) K, and making the approximation \( Q_{ev}(300 \) K) \( \approx 1 \), we have

\[
\alpha_{\nu_{ul}}^u \bigg|_{300K} \approx (3 \times 10^3) f \beta_{ul} \text{ m}^{-1}
\]

(8B.145)

*The relative abundance of the molecule on a *per volume* basis.

**The millibar (mbar) is the pressure unit commonly used in atmospheric work: 1 mbar = 100 Pascal (Pa), where Pascal (\( = J \text{ m}^{-3}) \) is the S.I. pressure unit.

†One-half of the width between the values of \( \nu \) at which \( b(\nu,\nu_{ul}) \) is half its maximum.
The line-center optical depth for a path having length $L$ meters is

$$\tau_{ul} = \alpha_{ul} L$$  \hspace{1cm} (8B.146)

$$= (2.3 \times 10^{6}) \frac{f g_{ul} L}{T} \left[ \frac{r(T)}{Q_{ev}(T)} \right] \left[ \frac{\Delta v_{c}}{P_{air \text{ MHz/mbar}}} \right]^{-1}$$  \hspace{1cm} (8B.147)

$$\approx 10^6 f g_{ul} L \frac{r(T)}{Q_{ev}(T)}$$  \hspace{1cm} (8B.148)

where Eqs. 8B.109, 8B.143, and 8B.144 have been used, and $T, f$ are assumed constant over the path. The length of a limb path through the atmosphere from a point 5 km above the tangent point on one side to 5 km above the tangent point on the other side is $L \approx 500$ km; for this length path, Eq. 8B.148 gives

$$\tau_{ul \text{ limb}} \approx (5 \times 10^{11}) \frac{f g_{ul}}{T} \frac{r(T)}{Q_{ev}(T)}$$  \hspace{1cm} (8B.149)

and at 300 K with the approximation that $Q_{ev}(300 \text{ K}) \approx 1$:

$$\tau_{ul \text{ limb, 300K}} \approx (1.6 \times 10^9) f g_{ul}$$  \hspace{1cm} (8B.150)

An easy way to remember Eq. 8B.150 is that a 1 ppbv* mixing ratio gives a line-center 500 km path optical depth that is numerically equal to approximately 1.6 times the catalog line intensity—an even easier way is to remember that the line-center optical depth is approximately equal numerically to the catalog line intensity for 1 ppbv of the molecule in a 300 km path. It should be noted that these only hold for collisionally broadened lines.

It is useful to have a single “figure of merit,” which indicates the expected strength of atmospheric signals for each catalog entry and for candidates to be added in the future. Ignoring all transition-dependent quantities and constants in Eq. 8B.127, we obtain the simple expression

$$f = \frac{f_{\mu^2}}{Q_{rs}}$$  \hspace{1cm} (8B.151)

as a figure of merit, where Eq. 8B.127 has been used and the subscript $x$ on $\mu$ has been deleted: $f$ accounts for atmospheric abundance, $\mu^2$ for the “overall” strength of the molecule interacting with radiation and $Q_{rs}$ for the approximate number of molecular states over which the total abundance is distributed. Using $M$ as a figure of merit has the attraction that the spectroscopic quantities involved can often be estimated without knowledge of the spectrum. This makes it useful for helping

*Parts per billion by volume, $\text{ppbv} = 10^{-9}$ per volume.
decide those molecules/atoms (and their excited/isotopic states) that need to be added to the JPL catalog for atmospheric studies and, equally important, those that do not. *M* has the disadvantage that additional factors, such as line frequency, that affect line strength are not included.*

**8C FORTRAN CODE FOR ABSORPTION COEFFICIENTS**

This appendix describes FORTRAN functions that use JPL catalog data to calculate absorption coefficient values according to Eq. 8B.131, and using Eq. 8B.140 to convert the absorbing molecule’s number density to the volume-mixing ratio. The CLO spectral “line” near 204 GHz is illustrated. This line is composed of several hyperfine components due to chlorine nuclear-spin transitions, and has small (~1%) population in an excited vibrational state. It thus illustrates some considerations that are not present in simpler situations.

Figures 8C.1 to 8C.3 give listings for the following FORTRAN functions:

1. **ABSX_CLO_204**, which returns absorption coefficient per unit mixing ratio**

2. **QLOG**, which returns the ratio of the (catalog) partition function value at temperature *T* to its value at 300 K.

3. **ABSX_CLO_MLS**, which is a “faster” version of **ABS_CLO_204**. Certain approximations are made to greatly increase speed at a small cost in accuracy.

These are briefly discussed in the following sections. **ABS_CLO_204** and **ABSX_CLO_MLS** call a function **VOIGT(X,Y)**, which returns the value of the Voigt line shape when given the input parameters

\[
X = \sqrt{\ln 2} \left( \frac{\nu - \nu_{dl}}{\Delta \nu_D} \right) \quad (8C.1)
\]

\[
Y = \sqrt{\ln 2} \left( \frac{\Delta \nu_C}{\Delta \nu_D} \right) \quad (8C.2)
\]

*Inclusion of such factors would require some knowledge of the molecular structure or spectrum. This may be available in some cases. An appropriately weighted “average frequency” for molecules with simple spectra (e.g., linear molecules) could probably be derived requiring only estimates of the rotational constants. However, a similar average frequency would also be required for other molecules in order to have the same comparison basis for all.

**The rationale for returning an absorption coefficient *per unit mixing ratio* is to easily obtain partial derivatives with respect to the mixing ratio, which can be used for “retrieving” atmospheric mixing ratios from atmospheric radiances.
PURPOSE: Returns quantity which, when multiplied by volume mixing ratio, gives absorption coefficient in units of 1/km.

INVOCATION METHOD:

ABS_COEFF = ABSX_CLO_204 (T, P, F, V)

ARGUMENTS:

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>I/O</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>R*4</td>
<td>I</td>
<td>temperature (Kelvin)</td>
</tr>
<tr>
<td>P</td>
<td>R*4</td>
<td>I</td>
<td>pressure (millibar)</td>
</tr>
<tr>
<td>F</td>
<td>R*4</td>
<td>I</td>
<td>frequency (MHz)</td>
</tr>
<tr>
<td>V</td>
<td>R*4</td>
<td>I</td>
<td>velocity toward observer (m/s)</td>
</tr>
</tbody>
</table>

EXTERNAL REFERENCES:

Subprogram | S/F | Purpose
------------|-----|------------------
QLOG        | F   | Gives base 10 logarithm of the ratio of partition function at temperature T to that at 300 K.
VOIGT       | F   | Gives Voigt shape having area DFD*SQR(pi/ln2).

HISTORY:

<table>
<thead>
<tr>
<th>Author</th>
<th>Date</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>J. Waters</td>
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<tr>
<td>J. Waters</td>
<td>05/03/90</td>
<td>added more lines, corrected for new ClO dipole</td>
</tr>
</tbody>
</table>

---

REAL*4 FUNCTION ABSX_CLO_204 (T, P, F, V)
IMPLICIT NONE

*** Arguments ---
REAL*4 T, P, F, V

*** External Functions ---
REAL*4 QLOG, VOIGT
EXTERN QLOG, VOIGT

*** Local Variables ---
INTEGER*2 N, NLINES
PARAMETER (NLINES = 25) !Number of spectral lines summed

REAL*4 ABSX, DF, DFC, DFD, EL(NLINES), Q0(3), F0(NLINES), FS, FV
&, SO(NLINES), SI(NLINES), TCOR, X, X1, Y

Figure 8C.1. The function ABSX_CLO_204.
Following data from JPL catalog 10 June 1986

[Except for S1(I) which is 10**(S0(I)). S1 is not used here, but is used by ABSX_CLO_MLS subroutine. It is here for reference.]

DATA Q0 /3.5149, 3.3578, 3.1485/ !Log partition fcn at 300,225,150K

DATA F0(1), S0(1), S1(1), EL(1)
& 204269.6293, -6.3348, 4.6259E-07, 14.2541/
DATA F0(2), S0(2), S1(2), EL(2)
& 204270.6105, -6.3348, 4.6259E-07, 14.2541/
DATA F0(3), S0(3), S1(3), EL(3)
& 204293.6695, -4.5223, 3.0040E-05, 14.2541/
DATA F0(4), S0(4), S1(4), EL(4)
& 204295.0431, -4.5223, 3.0040E-05, 14.2541/
DATA F0(5), S0(5), S1(5), EL(5)
DATA F0(6), S0(6), S1(6), EL(6)
DATA F0(7), S0(7), S1(7), EL(7)
& 204327.3583, -4.4016, 3.9664E-05, 14.2522/
DATA F0(8), S0(8), S1(8), EL(8)
DATA F0(9), S0(9), S1(9), EL(9)
& 204346.0000, -3.1176, 7.6278E-04, 14.2541/
DATA F0(10), S0(10), S1(10), EL(10)
& 204346.0000, -3.1176, 7.6278E-04, 14.2541/
DATA F0(11), S0(11), S1(11), EL(11)
& 204350.8482, -4.5235, 2.9957E-05, 14.2512/
DATA F0(12), S0(12), S1(12), EL(12)
& 204350.8928, -4.5235, 2.9957E-05, 14.2512/
DATA F0(13), S0(13), S1(13), EL(13)
DATA F0(14), S0(14), S1(14), EL(14)
DATA F0(15), S0(15), S1(15), EL(15)
& 204356.8600, -3.2847, 5.1916E-04, 14.2512/
DATA F0(16), S0(16), S1(16), EL(16)
& 204357.4800, -3.2847, 5.1916E-04, 14.2512/
DATA F0(17), S0(17), S1(17), EL(17)
& 204362.5570, -3.3695, 4.2707E-04, 14.2508/
DATA F0(18), S0(18), S1(18), EL(18)
& 204362.5570, -3.3695, 4.2707E-04, 14.2508/
DATA F0(19), S0(19), S1(19), EL(19)
& 204491.5160, -3.7568, 1.7507E-04, 335.7944/
DATA F0(20), S0(20), S1(20), EL(20)
& 204491.9455, -3.8392, 1.4481E-04, 335.7966/
DATA F0(21), S0(21), S1(21), EL(21)
& 204493.3373, -3.9238, 1.1918E-04, 335.7992/
DATA F0(22), S0(22), S1(22), EL(22)
& 204497.9724, -4.0886, 9.8039E-05, 335.8018/
DATA F0(23), S0(23), S1(23), EL(23)
& 204556.7491, -5.1614, 9.8039E-06, 335.7994/
DATA F0(24), S0(24), S1(24), EL(24)
& 204571.6555, -5.0408, 9.1033E-06, 335.7966/
DATA F0(25), S0(25), S1(25), EL(25)
& 204576.5400, -5.1627, 6.8754E-06, 335.7992/

Figure 8C.1. (Continued)
**APPENDICES TO CHAPTER 8**

*** Executable Code ---

```plaintext
DFD = 0.010247 * SQRT(T)  
\[ \text{Doppler width from Townes & Schawlow with } M=51 \text{ for } ^{35}\text{ClO} \]

DFC = 188.57 * P / (T**0.75)  
\[ \text{Collision width from Pickett, et al., JGR, 86, 7279 (1981)} \]

\[ X_1 = 0.83255 / DFD \]

\[ Y = DFC * X_1 \]

ABSX = 0.0

DO N = 1, NLINES

\[ \text{X} = X_1 * \text{ABS(F-F0(N) * (1. + 0.33356E-02*V)}) \]
\[ \text{Accounts for Doppler shift} \]

\[ \text{TCOR} = \text{EXP} (1.4388*EL(N) * (3.3333E-03 - 1./T)) \]
\[ \text{Exp}(E^*/300k - E^*/kT) \]

\&
\[ * \text{(1. - EXP (-4.7993E-05 * F0(N) / T))} \]
\[ 1-\text{EXP}(hv/kT) \]

\&
\[ / \text{(1. - EXP (-1.5998E-07 * F0(N)))} \]
\[ 1-\text{EXP}(hv/300k) \]

\[ \text{ABSX} = \text{ABSX} + \text{TCOR} * \text{VOIGT(X,Y)} * (10.*S0(N)) * (F / F0(N)) \]

ENDDO

\[ \text{ABSX} = \text{ABSX} * X_1 * 0.56419 \]
\[ \text{Accounts for VOIGT area equal to } \sqrt{\pi}/X_1 \]

\[ \text{ABSX} = \text{ABSX} / (10.*QLOG(Q0,T)) \]
\[ \text{IT-dependence of partition function} \]

\[ \text{ABSX} = 0.72435E10 * \text{ABSX} * P / T \]
\[ \text{When multiplied by volume mixing ratio of absorbing species this gives absorption coefficient in units of } 1/\text{km} \]

* 

* Some additional corrections specific to ^{35}\text{ClO}

\[ \text{FV} = 1. - \text{EXP} (-1215./T) \]
\[ \text{Fraction in ground vibrational state from Waters, et al., JGR,84,7034 (1979)} \]

\[ \text{ABSX} = 0.7553*\text{ABSX*FV} \]
\[ 10.7553 \]
\[ \text{is assumed isotopic fraction c}^* \]
\[ \text{ClO in } ^{35}\text{ClO [Leighton, 1959]} \]
\[ \text{Note that volume mixing to be multiplied for obtaining absorption coefficient must be total volume mixing ratio for both } ^{35} \text{and } ^{37} \text{ClO.} \]

\[ \text{ABSX_CLO_204= 1.0965*ABSX} \]
\[ \text{Corrects catalog intensities for new measurement of ClO dipole moment by Yaron et al. (1988) New value = 1.2974 D} \]
\[ \text{Catalog intensities are for 1.239 D} \]
\[ (1.2974/1.239)**2 = 1.0965 \text{ correction} \]

RETURN
END
```

Figure 8C.1. (Continued)
### PROLOGUE

PROLOGUE

```fortran
!*p

PROGRAM QLOG

Cabove 10 logarithm of the ratio of partition function at temperature T to that at 300 K
C
CARGUMENTS:
C  Q0 R*4(3) I base 10 logarithms of partition function at T=300, 225, 150K
C  T R*4 I temperature (Kelvin)
C
CNOTES: Linear interpolation in log(T) and log(Q) is used. JPL catalog accuracy is maintained over temperature range 150-300K.
C
CHISTORY:
C  Author    Date       Comments
C  J. Waters 06/02/86   initial release
C  V. Perun  04/30/90   edited to documentation and coding standards
C
C** Arguments ---
** REAL*4 Q0(1), T
C
** Local Variables ---
** REAL*4 SLOPE
**       TLOG
**       TLOGO(3) /2.47712, 2.35218, 2.17609/ !LOG(T) FOR T=300,225,150
C
** Executable Code ---

TLOG = ALOG10(T)
IF (TLOG .LT. TLOGO(2)) THEN
   SLOPE = 5.67891 * (Q0(2) - Q0(3)) !const is 1/[TLOGO(2)-TLOGO(3)]
   QLOG = Q0(2) - Q0(1) + SLOPE * (TLOG - TLOGO(2))
ELSE
   SLOPE = 8.00384 * (Q0(1) - Q0(2)) !const is 1/[TLOGO(1)-TLOGO(2)]
   QLOG = SLOPE * (TLOG - TLOGO(1))
ENDIF
END

Figure 8C.2. The function QLOG.
```
**APPENDICES TO CHAPTER 8**

---

**PROLOGUE**

ABSX_CLO_MLS

---

**PURPOSE:** This function returns quantity which, when multiplied by volume mixing ratio of absorbing species, gives absorption coefficient in units of 1/km.

**INVOCATION METHOD:** ABS_COEFF = ABSX_CLO_MLS (T, P, F, V)

**ARGUMENTS:**

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>I/O</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>R*4</td>
<td>I</td>
<td>temperature (Kelvin)</td>
</tr>
<tr>
<td>P</td>
<td>R*4</td>
<td>I</td>
<td>pressure (millibar)</td>
</tr>
<tr>
<td>F</td>
<td>R*4</td>
<td>I</td>
<td>frequency (MHz)</td>
</tr>
<tr>
<td>V</td>
<td>R*4</td>
<td>I</td>
<td>velocity toward observer (m/s)</td>
</tr>
</tbody>
</table>

**EXTERNAL REFERENCES:**

- QLOG: Subprogram
- VOIGT: Subprogram

**NOTES:**

- Uses same expressions as in FUNCTION ABSX_CLO_204(T,P,F,V) but with approximations to improve efficiency.

**HISTORY:**

<table>
<thead>
<tr>
<th>Author</th>
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<tr>
<td>J. Waters</td>
<td>05/03/90</td>
<td>added more lines, corrected for new ClO dipole</td>
</tr>
</tbody>
</table>

---

**REAL*4 FUNCTION ABSX_CLO_MLS (T, P, F, V)**

IMPLICIT NONE

*** Arguments ***

REAL*4 T, P, F, V

*** External Functions ***

REAL*4 QLOG, VOIGT

EXTERNAL QLOG, VOIGT

*** Local Variables ***

INTEGER*2 N, NLINES

---

**Figure 8C.3.** The function ABSX_CLO_MLS.
PARAMETER (NLINES = 7) !Number of spectral lines summed

REAL*4 ABSX, DF, DFC, DFD, EL(NLINES), QO(3), F0(NLINES), FS
& S0(NLINES), S1(NLINES), X, XI, Y

QO is from JPL catalog
DATA QO / 3.5149, 3.3578, 3.1485 / !Log partition fcn at 300,225,150K

Catalog data for 'nearby' lines have been combined into one as indicated below. Some weak lines have been deleted. See listing for ABSX_CLO_204 for reference.

DATA F0(1), S0(1), S1(1), EL(1)
& / 204294.4563, -4.2213, 6.0080E-05, 14.2541 / 12 lines 1.1 MHz apart
DATA F0(2), S0(2), S1(2), EL(2)
& / 204327.5844, -4.1006, 7.9328E-05, 14.2522 / 12 lines 0.5 MHz apart
DATA F0(3), S0(3), S1(3), EL(3)
& / 204346.0000, -2.8166, 1.5265E-03, 14.2541 / 12 lines 0.0 MHz apart
DATA F0(4), S0(4), S1(4), EL(4)
& / 204351.9000, -2.8780, 1.2556E-03, 14.2512 / 14 lines within 2 MHz
DATA F0(5), S0(5), S1(5), EL(5)
& / 204356.9500, -2.9837, 1.0385E-03, 14.2512 / 14 lines 0.6 MHz apart
DATA F0(6), S0(6), S1(6), EL(6)
& / 204362.5570, -3.0685, 8.5414E-04, 14.2508 / 14 lines 0.0 MHz apart
DATA F0(7), S0(7), S1(7), EL(7)
& / 204492., -3.2699, 5.3710E-04, 135.8 / 14 lines within 6 MHz

DFD = 0.010247 * SQRT(T) = 3.581E-07*F0(4)*SQRT(T/M), Doppler width with IM=51 for 35ClO [Townes & Schawlow, (1955)]

DFC = 188.57 * P / (T**0.75) = 2.51*P*(317./T)**0.75, Collision width !from Pickett, et al., JGR, 86, 7279 (1981)

X1 = 0.83255 / DFD
Y = DFC * X1
ABSX = 0.0
FS = F - 0.68164E-03*V !Accounts for Doppler shift [for f0=204352 MHz]

DO N = 1, NLINES !Sum over lines
IF ((DF/(DFD+DFC)) .LT. 10.) THEN !Only include lines within 10 wid!
   X = X1 * DF
   ABSX = ABSX + S1(N) * VOIGT(X,Y)
ENDIF
ENDDO

Following is expansion about T=230K.

ABSX_CLO_MLS = 9.15314E11 * ABSX * P
& * (1.0362 - 26.122 / T - 1.1797E-04*T)
& / (DFD * T * T * 10.*QLOG(QO,T))
RETURN
END

Figure 8C.3. (Continued)
where $\Delta \nu_D$ is the Doppler line-width parameter (half width at half maximum), and $\Delta \nu_C$ is the collisional line-width parameter. The FORTRAN code for VOIGT is given by Drayson [19]; it produces a line shape having an integrated area of $\Delta \nu_D \sqrt{\pi / \ln 2}$, and it must be remembered to account for this in expressions (like those in Appendix 8B of this chapter), which require a line shape with unity integrated area.

8C.1 ABSX_CLO_204

Inputs are temperature $T$ in kelvin, pressure $P$ in millibars, frequency $F$ in megahertz, and velocity $V$ toward the observer in meters/second (velocity is input so that the effects of any Doppler shifts—by atmospheric wind or instrument motion—can be calculated). JPL catalog data are "hard coded" via DATA statements. One DATA statement for three values of $Q_0$ gives catalog values of the logarithm of the partition function at 300, 225, and 150 K: these are used as inputs to QLOG. There is one data statement for each hyperfine transition $I$ giving (1) $F_0(I)$: the line frequency in MHz; (2) $SO(I)$: the catalog line-intensity logarithm; (3) $S1(I) = 10^{SO(I)}$, which is used in ABSX_CLO_MLS and included here only for traceability and cross-checks; (4) $EL(I)$: the lower state energy in cm$^{-1}$. Two ClO electronic spin states, $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$, have significant population at atmospheric temperatures. These are included in the JPL catalog data. The 204-GHz spectral lines occur from rotational (and nuclear-spin) transitions within these electronic spin states. $^2\Pi_{3/2}$ transitions can be recognized in the ABSX_CLO_204 DATA statements by their 14-cm$^{-1}$ EL values; $^2\Pi_{1/2}$ transitions can be recognized by their 335-cm$^{-1}$ EL values (not all $^2\Pi_{1/2}$ transitions are entered—because of their weakness and/or because their frequency is outside the range of interest).

The function first calculates line-width parameters: the Doppler line-width parameter is calculated using Eq. 13-2 of Townes and Schawlow [29], the collisional line-width parameter and its temperature dependence are from Pickett et al. [30]. It then sums over all lines the product of $\nu/nul$ [$= F/FO(I)$], temperature-correction factor for line intensities [$= TCOR$], line shape [$= VOIGT$], and line intensity [$= 10^{SO(I)}$]. It then corrects for (1) VOIGT not having unity area, (2) the temperature dependence of the partition function, and calculates the number density for unity mixing ratio from the input temperature and pressure values. The constants are chosen to give an absorption coefficient in units of km$^{-1}$ convenient for atmospheric calculations; this adds an additional factor of $10^3$ beyond those described in the text of this chapter. Another factor of $10^{-6}$ has been added because of the MHz$^{-1}$ units used for the line-shape function.$^*$

$^*$Up to this point, except for the data statement entries and line-width parameter expressions, this FORTRAN function is general for any molecule/transition—it can be transcribed to other cases simply by changing to other data from the catalog (not forgetting to set the N_LINES parameter to the total number of lines included) and using the appropriate line-width parameter expressions.
Additional "corrections" specific to CIO are then made. The first accounts for the fraction of molecules in the ground vibrational state—the factor $1/Q_{ev}$ in Eq. 8B.131—as described in Waters et al. [48 of Chapter 8]: at $T = 230$ K, this fraction is 0.9949. The second "correction" accounts for the fraction of CIO molecules in the $^{35}$ClO isotope—this allows the total CIO mixing ratio (i.e., the sum of ClO in both isotopes) to be used in determining the absorption coefficient. The third "correction" accounts for a new measurement [31] of 1.2974 Debye for the CIO dipole moment, whereas the catalog intensities at the time this function was written were calculated for an earlier value of 1.239 Debye—using the new value increases line intensities by $(1.2974/1.239)^2 = 1.0965.$

The returned value must be multiplied by the CIO mixing ratio to obtain the absorption coefficient. Table 8C.1 gives values obtained from ABSX_CLO_204 for a CIO mixing ratio of $10^{-9}$. The CPU time required by this function on a DEC Microvax II computer is $\sim 16$ milliseconds per call.**

8C.2 QLOG

Inputs are catalog values of $Q_{rs}$ at 300, 225, and 150 K, and $T$. QLOG interpolates linearly in $Q_{rs}$ versus logarithm of temperature to output the (base 10) logarithm of $Q_{rs}(T)/Q_{rs}(300)$. This interpolation method, suggested by H. M. Pickett, is exact in the classical limit, where $Q_{rs}$ goes as $T$ for linear molecules and $T^{3/2}$ for nonlinear molecules.

8C.3 ABSX_CLOMLS

This function makes approximations and coding efficiency improvements to ABSX_CLO_204. Intensities of $^2\Pi_{3/2}$ hyperfine lines separated by less than $\sim 2$ MHz and of weaker $^2\Pi_{1/2}$ hyperfine lines separated by less than $\sim 6$ MHz are summed and entered in a single DATA statement.† The catalog "log intensity" $S_0$ is manually converted to intensity $S_1$, which is entered in the DATA statements. $S_0$ is retained in the data statement for traceability only; it is not used. Weaker lines that have $< \sim 1\%$ effect are not included. The line summation is also restricted to lines within 10 line-width parameters from line center—this introduces an error of, at most, $\sim 1\%$. The factor $\nu/\nu_{ul}$ is also approximated as unity; this introduces an error of less than $\sim 0.2\%$ for the $< \pm 300$-MHz frequency range, which is usually needed for calculations.

The temperature-correction factor $TCOR$ is evaluated using $E_i = 14.252 \text{ cm}^{-1}$

*JPL catalog data, starting with version 3.0 released in 1992, now uses the new ClO dipole moment.

**This is the average time per call for 11,781 calls with 21 different values of pressure ($P = 10(m-1)/10$ for $m = 1, \cdots, 21$), 51 different values of temperature ($T = 200, 201, \cdots, 250$), and 11 values of frequencies ($-250$ to $+250$ MHz from 204352 MHz in steps of 50 MHz).

†This can be done because we are generally interested in stratospheric ClO where line widths are $\sim 10$ MHz or greater
and \( v_{ul} = 204352 \times 10^6 \text{ Hz} \) for all the hyperfine components:

\[
T_{\text{COR}} = \frac{(1 - e^{-4.7995 \times 10^{-11} v_{ul}/T}) e^{-1.4388 E_1/T}}{(1 - e^{-1.5998 \times 10^{-13} v_{ul}/T}) e^{-0.0048 E_1}}
\]  
(8C.3)

\[
= \frac{(1 - e^{-9.80787/T}) e^{-20.5058/T}}{(1 - e^{-0.032692}) e^{-0.06841}}
\]  
(8C.4)

\[
\approx \left( \frac{326.49}{T} \right) \left( 1.0061 - \frac{25.435}{T} \right)
\]  
(8C.5)

In going from Eq. 8C.4 to Eq. 8C.5, the exponentials containing \( 1/T \) are approximated by a series expansion—with significant terms of higher order than \( 1/T \) evaluated at 230 K, a typical temperature of the middle stratosphere. The errors in going from Eq. 8C.4 to Eq. 8C.5 are 0.2% at \( T = 300 \text{ K} \), 0.1% at \( T = 265 \text{ K} \), 0.0% at \( T = 230 \text{ K} \), −0.3% at \( T = 195 \text{ K} \), and −0.8% at \( T = 160 \text{ K} \).

The fraction in the excited vibrational state is also expanded in a series about its value at 230 K:

\[
F_{V} = 1 - e^{-1215/T}
\]  
(8C.6)

\[
\approx 0.99492 (1.0270 - 1.1725 \times 10^{-4} T)
\]  
(8C.7)

where the errors in going from Eq. 8C.6 to Eq. 8C.7 are 0.4% at \( T = 300 \text{ K} \), 0.1% at \( T = 265 \text{ K} \), 0.0% at \( T = 230 \text{ K} \), 0.1% at \( T = 195 \text{ K} \), and 0.4% at \( T = 160 \text{ K} \).

Taking the product of the previous approximations for \( T_{\text{COR}} \) and \( F_{V} \), accounting for the fraction in the \(^{35}\text{ClO}\) isotope, and correcting for the new ClO dipole-moment measurement as described before for \texttt{ABSX\_CLO\_204} yields the final expression in \texttt{ABSX\_CLO\_MLS}.

Table 8C.2 gives the relative (to "line-center" value) error between values obtained from \texttt{ABSX\_CLO\_MLS} and from \texttt{ABSX\_CLO\_204}. This error is usually less than 1% at 10-mbar pressure (the middle stratosphere, \( \sim 30\text{-km height} \)), less than a few percent at 1 mbar (the upper stratosphere, \( \sim 48\text{-km height} \)), and \( \sim 2-5\% \) at 100 mbars (the lower stratosphere, \( \sim 16\text{-km height} \)) for the expected range of atmospheric temperatures. The CPU time required by \texttt{ABSX\_CLO\_MLS} on the DEC Microvax II computer is \( \sim 0.8 \) milliseconds per call.* This is 20 times faster than \texttt{ABSX\_CLO\_204}.

*The same computer and range of calling parameters described before for timing \texttt{ABSX\_CLO\_204}. 
### TABLE 8C.1. Absorption Coefficient Values (in km\(^{-1}\)) Obtained from \textit{ABSX\_CLO\_204} and Using \(10^{-9}\) C\textit{L}O Volume-Mixing Ratio\(^a\)

<table>
<thead>
<tr>
<th>DFREQ</th>
<th>(T = 160.0)</th>
<th>(T = 195.0)</th>
<th>(T = 230.0)</th>
<th>(T = 265.0)</th>
<th>(T = 300.0)</th>
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<tr>
<td>-500.0</td>
<td>3.72198E-09</td>
<td>1.77536E-09</td>
<td>9.52770E-10</td>
<td>5.52059E-10</td>
<td>3.41162E-10</td>
</tr>
<tr>
<td>-100.0</td>
<td>9.74946E-08</td>
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*The Fractional Difference Given Here Is Defined as \((\text{ABSX_CLO_MLS} - \text{ABSX_CLO_204}) / (\text{ABSX_CLO_204 at DFREQ} = 0)\).*
REFERENCES


9

RETRIEVAL OF ATMOSPHERIC PARAMETERS IN PLANETARY ATMOSPHERES FROM MICROWAVE SPECTROSCOPY

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9.1 INTRODUCTION

The exploitation of microwave-spectroscopy techniques for the investigation of the planets is in its infancy compared to most of the other topics treated in this volume. Venus and Mars have been extensively studied from Earth observations using the first few rotational transitions of CO and its isotopes. Attempts to measure water lines have been fruitless until a recent Mars experiment at 22 GHz at the Very Large Array (VLA) and SO$_2$ lines have been seen in the tenuous and variable "atmosphere" of Io, which is apparently maintained by SO$_2$ volcanism. Only a few measurements have been made in the submillimeter part of the spectrum due to the high opacity of the Earth’s atmosphere in this wavelength region. However, it is clear that this spectral range will be rich in molecular lines for all of the...
planets. The field of planetary microwave spectroscopy will grow substantially with the development of the submillimeter and millimeter spectral range once we have instrumentation above the Earth's atmosphere and sufficiently near the various planets to achieve high spatial resolution for limb sounding. Currently, the highest spatial resolution of a few arc seconds can be achieved with millimeter wavelength arrays, as compared to observable planetary diameters, which range from less than an arc second (Titan) to 60 minutes for Venus. The ultimate goal of achieving atmosphere scale–height resolution on the limbs of planets requires spacecraft at the planets, or possibly, very large submillimeter arrays at high-altitude sites on the Earth or perhaps even on the Moon.

The goals of solar system microwave spectroscopy include (1) the identification of molecular species; (2) measurements of their abundance profiles as a function of altitude, longitude, and latitude; (3) measurements of the variations of these species as a function of the local time of day and the seasons; (4) determination of atmospheric temperature–pressure profiles; and (5) measurements of atmospheric wind fields that, in conjunction with temperature–pressure profiles and latitudinal variations in atmospheric chemistry, can be interpreted in terms of the coupled photochemistry and dynamics of planetary atmospheres. The physics, chemistry, and dynamics of the planetary atmospheres are for the most part similar to those of the Earth. For this reason, we rely heavily on Chapters 7 and 8 here. The topic of spectroscopic observations using arrays is a new one and is treated in what follows. It is reasonable to neglect scattering in this chapter because no problems faced to date have important effects. However, considerations of very short submillimeter wavelengths in an exotic atmosphere like Titan's may involve scattering. Probing the deep atmospheres of the major planets encounters water cloud particles, but not spectroscopy in the usual sense.

To first order, the atmospheres of the planets divide into two distinct groups: the terrestrial planets (Venus, Earth, and Mars) and the major planets (Jupiter, Saturn, Uranus, and Neptune). The oxygen-rich compositions of the terrestrial atmospheres are dominated by the volatiles N$_2$, CO$_2$, H$_2$O, O$_2$, CO, and SO$_2$, and O$_3$. The major planetary atmospheres are composed largely of H$_2$ and He with traces of volatiles such as NH$_3$, CH$_4$, and H$_2$O and small abundances of HCN, ethane, acetylene, and other hydrocarbons and nitriles. Although the major planetary atmospheres are oxygen-poor at pressures lower than about 100 bars, great quantities of water and related oxygen species must exist at higher pressures. The presence of oxygen species at these higher pressures is difficult to detect with microwave spectrographic techniques due to considerable pressure broadening. Infrared transitions of CO have been observed in Jupiter and Saturn, yet CO remains undetected in the microwave spectral region for all the major planets with the notable exception of Neptune.

Two major satellites are known to have ponderable atmospheres, Titan at Saturn and Triton at Uranus. The atmosphere of Titan is chemically "similar" to Earth's in that N$_2$ is the dominant species. However, the photochemistry of Titan is dominated by the reducing chemistry of hydrocarbons and nitriles, as found in the atmospheres of the major planets. Carbon monoxide and HCN have been detected
from ground-based observations in the microwave region. It is likely that the atmosphere of Triton has CO and HCN, but these lines will never be seen from Earth because the total pressure of Triton's atmosphere is a few microbars. As we will see, measurements from passing spacecraft are quite possible.

The spectroscopic study of even the terrestrial planets has been greatly inhibited by the very strong, broadband absorptions that arise from transitions of the same molecule to be investigated within the Earth's atmosphere. In most cases, the Doppler shifts due to the relative motion of the target planet are small compared to the line width in the terrestrial line. At the time of this writing, a single microwave spectrometer has been flown above the Earth's atmosphere (see Chapter 8), but not to the vicinity of another planet. Whereas sophisticated broadband receivers have been sent to the limits of the solar system, spectrometric devices have yet to fly on a planetary spacecraft. However, as we show in this chapter, the scientific questions and techniques are available for a new era in planetary investigations and for robotic microwave spectroscopy.

9.2 OBSERVATIONAL AND ANALYTICAL METHODS

Apart from broadband spectroscopic studies of NH₃ (due to a band of transitions around 23 GHz), the only true microwave spectroscopy of planetary atmospheres has been limited to observations of CO on Venus, Mars, Titan, and, most recently, Neptune; H₂O for Mars and Venus; HCN for Titan; and SO₂ for Io. Extensive searches have been made for other molecules, such as SO and SO₂ in Venus and CO in the major planetary atmospheres, without success due to well-understood reasons (e.g., excessively broadened line widths and low species abundances). Further progress in planetary microwave spectroscopy requires high spatial resolution on the order of an atmospheric scale height or better. Extremely low abundances of molecules can be detected in emission in the limb-sounding mode if high spatial resolution is achieved. Recently, the VLA has been employed to detect 22-GHz water vapor on the atmospheric emission limb of Mars and Venus, demonstrating an approximate form of planetary limb sounding with Earth-based observing. Millimeter arrays can currently achieve resolution of a few arc seconds with expectations of 1 arc second, which will make such limb searches for many molecules possible on most of the planets. Submillimeter arrays currently in the advanced planning stages will achieve sub-arc second resolution, and thus lead to true limb-sounding capabilities.

Carbon monoxide in Venus and Mars serves as a valuable trace species to measure the temperature-pressure profiles and the wind fields. CO in these planets, and the Earth, is primarily created from the photodissociation of CO₂, the primary constituent of the atmospheres of Venus and Mars. Fortunately, the abundance of CO in the Earth's stratosphere is low (order of 10¹² cm⁻²), which makes it possible for radio astronomers to observe this ubiquitous molecule throughout the universe. CO was first detected on Venus [1] and on Mars in 1976 and has been exploited as a tracer since then. We now consider the questions of spectroscopic detections,
line inversions, and interpretation of spectroscopic observations in geophysical terms.

The geometry of the radiative transfer problem is shown in Figure 9.1. The flux density observed from above the atmosphere with an infinitely narrow pencil beam can be thought of consisting of two components: (1) the blackbody thermal emission emitted by the deep continuum layer that is dispersively absorbed in passing through the atmosphere to the observer, and (2) the thermal emission in an infinitesimal cylinder from the layer defined by \( r, r + dr \), which in turn is absorbed by the layers between \( r \) and the observer. The deep continuum layer may be the planet's surface (e.g., Mars), a cloud of highly absorbing material (e.g., \( \text{NH}_3 \) on Jupiter), or a gradual increase of continuum absorption (e.g., Venus). The emission in the elementary cylinder consists of the resonant thermal emission from the gas under investigation (at frequency \( \nu \) from its line center), and any continuum emission from the remaining material in the cylinder. In general, the spherical shape of the atmosphere must be considered, as presented by Figure 9.1. The spectral-line flux density measured near the center of the planetary disk is usually seen in absorption because the temperature of the continuum layer is usually warmer than that of the upper atmosphere. Carbon monoxide and HCN in the Titan atmosphere are important exceptions, resulting from abundant CO and HCN in the warm Titan stratosphere. Stratospheric CO has also been detected as an emission feature for Neptune [2]. More generally, the flux from the pencil beam on the limb passing above the continuum layer will appear in emission. Furthermore, the limb contribution to the emitted line intensity is greatly increased relative to that from the planet's disk when the molecular line opacity is small. This results from the very long path length associated with the limb-sounding geometry (see Chapter 8). The integrated line intensity for an individual beam is given by Eq. 1.4 of Chapter 1, where the integration is performed over \( s = -\infty \) to \( +\infty \) for the coordinates of Figure 9.1. The Rayleigh–Jeans approximation, Eq. 1.13 of Chapter 1, is accurate.
for wavelengths longer than about 2 mm and provides insight into the simplicity of the radiative transfer problem. For example, in an isothermal planetary atmosphere at temperature $T_{a0}$, $T(s) = T_{a0}$, and Eq. (1.13) yields

$$T_b(\nu) = T_{b0} e^{-\tau} + T_{a0}(1 - e^{-\tau})$$

or

$$T_b(\nu) = T_{a0} + (T_{b0} - T_{a0}) e^{-\tau} \quad (9.1)$$

where $\tau$ is the frequency-dependent, total opacity along the ray path, and $T_{b0}$ is the surface or continuum temperature. For limb paths, $T_{b0} \equiv 0$. For other than limb paths, the brightness temperature at frequency $\nu_0$ is greater than $T_{b0}$ if the atmosphere is warmer than the surface, resulting in an emission line. An absorption line is generated if $T_{a0} < T_{b0}$, and no line is observed in the unlikely case that $T_{a0} = T_{b0}$.

Practical observations of a planet require the two-dimensional integration of Eq. 1.4 over a range of beam paths incorporated within the telescope beam, in the case of a single telescope observation, or the spatial resolution cell for observations with an array of telescopes. Even in the case of a telescope beam large compared the planet’s disk, the full spherical geometry must be used to avoid serious error in computing line emission near the planetary limb [3]. Examples of three measured classical line shapes are shown in Figure 9.2. The full-disk averaged spectrum is shown in each case where (a) is the CO (2-3) (345-GHz) emission of Titan [4] made at the Caltech Submillimeter Observatory (CSO) on Mauna Kea, (b) is a Venus [5] absorption spectrum for CO (0-1) (115-GHz) from the 12-meter telescope at Kitt Peak National Observatory (KPNO), and (c) is a Mars spectrum [6] made at KPNO that exhibits both emission and absorption. In the latter case, the CO emission shoulders are generated in the lowest level of the martian atmosphere, where the physical temperature of the atmosphere is greater than the brightness temperature of the surface, which is essentially the temperature of the atmosphere at the ground, reduced by the surface emissivity of about 0.9. The center absorption of the Mars spectrum results from less pressure-broadened CO line opacity originating in the cool atmosphere layer well above the surface. This aspect of the martian spectra is highly variable, depending on the climate. During dust storms, for example, the Mars atmosphere can be substantially heated. In such a case, the emission shoulders progress inward toward the line center and the line-center absorption becomes less pronounced. Clearly, information on the atmospheric temperature profile of Mars is contained in the spectra and can be retrieved with inversion techniques such as those discussed in previous chapters and in what follows. We consider in more detail the spectrum that would be observed in one of the pencil beams suggested in Figure 9.1. The integral of the contributions along a ray path must be done using the Planck function (see Chapter 1) at each local point, but we will use the Rayleigh–Jeans form here for conciseness. For a ray path that intersects the continuum level of the planet, the brightness-temperature
spectrum can be written

\[
T_B(\nu) = T_c \exp \left[ - \int_{s_c}^{\infty} \alpha(s)ds \right] + \int_{s_c}^{\infty} T[r(s)]\alpha(s) \exp \left[ - \int_{s_c}^{\infty} \alpha(s')ds' \right] ds
\]

(9.2)

where \(T_c\) is the brightness temperature of the continuum at the \(r(s_c)\) level, which may be a function of location on the planet, \(T[r(s)]\) is the physical temperature of
the \( r \)th layer and \( \alpha(s) \) is the absorption coefficient in the \( r \)th layer at frequency \( \nu \) from the spectral line center. \( T_b(\nu) \) is a vector with \( M \) elements, where \( M \) is the number of channels in the spectrometer. The absorption coefficient \( \alpha \) can be written in many forms (see Chapter 2 and Chapter 8, Eq. 8B.104), but for the purposes of demonstration, we consider the coefficient for the electric-dipole rotational transitions of CO [5, 6]. An expression sufficiently accurate for the first two transitions of CO is

\[
\alpha(\nu) \approx 9.2 \times 10^{-9} \left( \frac{\nu}{115} \right)^3 \frac{N_{\text{CO}}(r)}{T(r)^2} \left[ 1 - 0.048 \frac{\nu}{T(r)} \right] f(\nu) \quad (9.3)
\]

where \( N_{\text{CO}} \) is the number density of CO molecules, \( T(r) \) is the atmospheric temperature profile, \( f(\nu) \) is the normalized Voigt line-shape function given by Eq. (7.5) (see Chapter 2 for a more rigorous development), and \( \nu \) is the frequency in GHz. Inspection of Eqs. 9.2 and 9.3 indicates that the fundamental properties of a planetary atmosphere, \( N \) and \( T \), are incorporated in a very nonlinear fashion in the observed brightness-temperature spectrum, \( T_b(\nu) \). Furthermore, the Voigt function is the convolution of the Doppler line-spread function, a function of \( T(r) \), and the collisional spread function, which is a function of the total pressure in the \( r \)th layer. It is the Voigt function that encodes the pressure-altitude information on \( N \) and \( T \) into the observed spectral line, \( T_b(\nu) \). This pressure information comes into the spectrum in a complex way through the integrals in Eq. 9.2. Quite generally, the brightness at frequency \( \Delta \nu \) from the line center is contributed disproportionally by atmospheric emission layers at ambient pressures greater than some value determined by the pressure-broadening coefficient of the molecular specie in the ambient gas. The phenomenon can best be demonstrated by weighting func-
tions, such as shown in Figure 9.3 for a Mars standard atmosphere. The curves in Figure 3(a) are for normal incidence viewing. The contribution from the surface emission can be seen in the first five weighting functions, far from the line center. The half-power widths of the weighting functions in the middle altitudes are about 10 km, that is, about equal to the atmosphere-scale height. The optimum weighting functions for the limb-viewing ray paths are shown in Figure 9.3(b) before con-

![Diagram of weighting functions](image)

**Figure 9.3.** Optimum-temperature-sounding weighting functions for the CO (1-2) line on Mars: (a) is for normal incidence viewing and (b) for limb sounding. Channels with 1-MHz widths are indicated by the frequencies from line center. The limb functions have not been smoothed with a finite beam.
volution with an observing beam or a resolution cell. The improved vertical resolution afforded by limb sounding is primarily limited by the telescope diameter and the distance to the limb.

It should be clear that the interpretation of planetary spectra measured with a telescope beam whose size is the order of or larger than the planetary disk is extremely difficult. The information contained in such a measurement is a complex average of many such weighting functions, which depend strongly on the variable viewing geometry across the planetary disk. Nevertheless, disk-averaged spectra are the only planetary spectra that have been analyzed and appear in the literature at this time. We review current results from these single telescope observations before considering very recent millimeter array measurements of Mars and Venus.

The measurement of a brightness spectrum with a given spatial resolution contains information on the observed species abundance distribution as a function of altitude and the temperature distribution as a function of pressure-altitude. The measurement is, of course, sensitive to the averages of these quantities over the spatial resolution. The inversion problem for such measurements is reasonably straightforward when either the temperatures or the abundances of the species are known. It is practically impossible to invert the data for both profiles from the measurement of a single spectral line. If two or more lines are measured (different transitions of the same species or different isotopes if the isotope ratios are known), an inversion constraining both species abundance and atmospheric temperature becomes possible. The mathematical structure of the problem is revealed by constructing the set of \( N \) nonlinear, algebraic equations for a spectrum with \( N \) frequency channels. We divide the atmosphere into \( M \leq N \) layers of equal thickness \( dr \), the first layer being just above the continuum emission layer, for example, the planet's "surface." The brightness-temperature spectrum, \( T_B(\nu) = \nu_1, \nu_2, \cdots, \nu_M \), corresponding to observational ray paths that intersect the continuum lower boundary \( R_c, p < R_c \) in Figure 9.1, are given by

\[
T_B(\nu) = E(\theta)T_c \exp \left[ -\sum_{j=1}^{M} \alpha_j s_j \right] + \sum_{i=1}^{M} T_i (1 - e^{-\alpha_i s}) \exp \left[ -\sum_{q=1}^{M} \alpha_q s_q \right]
\]

(9.4)

where \( E(\theta) \) is the surface emissivity at incidence angle \( \theta \), and \( \alpha_i \) is the absorption coefficient in the \( i \)-th layer at frequency \( \nu \). The absorption coefficient is a function of atmospheric temperature \( T_i \), the number density \( N_i \) of the absorbing species, and \( s_i \), which is the distance along the ray path from \( r_i \) to \( r_i + dr_i \), that is,

\[
s_i = \sqrt{(r_i + dr)^2 - p^2} - \sqrt{r_i^2 - p^2}
\]

(9.5)

The emissivity function \( E(\theta) \) is a function of the dielectric constant of the surface materials and, in some cases, the surface roughness. Usually, the Fresnal reflection coefficients yield an adequate representation of \( E(\theta) \) for approximating the continuum emission of planetary surfaces. If the ray impact parameter \( p > R_c \), we must
treat the radiative transfer in the limb-sounding geometry and such that

\[
T_B(\nu) = \left[ 1 + \exp \left( -\sum_{q=1}^{M} \alpha_q s_q \right) \right] \times \sum_{i=p}^{M} T_i \left[ 1 - e^{-\alpha_i s_i} \right] \exp \left( -\sum_{q=i+1}^{M} \alpha_q s_q \right)
\]

(9.6)

where \( p \) is an integer label of the \( p \) in Eq. 9.5.

The equations are fundamentally of the form (for \( N \) discrete values of \( \nu \))

\[
T_B(\nu) = \sum_{i=1}^{M} T_i W_i(N_i, T_i, r_i)
\]

(9.7)

which are nonlinear because both \( N_i \) (the number density) and \( T_i \) appear in the weighting function and in exponents. Equation 9.7 is easily linearized in an iterative matrix-inversion procedure solving for the \( T_i \)'s if the \( N_i \)'s are known, but solving for \( N_i \)'s with known \( T_i \)'s is much more difficult. If spectra are available for more than one transition of the species, nearly independent equations, or at least much better-conditioned equations, are available and their simultaneous inversion will greatly improve the separation of the \( T \)'s and \( N \)'s as a function of the \( r_i \)'s. It should be clear that observations with poor spatial resolution, full-disk averaging in particular, greatly aggravate the inversion process. One must use poor physical assumptions such as requiring that the temperature and abundance profiles are the same over the entire planet at a given altitude. The full power of the inversion technique can only be exploited for high spatial resolution observations made with arrayed telescopes or with narrow-beam systems flown very near the planet. We treat the averaged disk measurements first and then discuss high-resolution observations, where the full power of Eq. 9.7 can be exploited.

9.3 OBSERVATIONS WITH SINGLE TELESCOPES

9.3.1 Mars

Mars CO has been systematically observed with single telescopes at the KPNO 12-meter [7], the 14-meter at the Five Colleges Radio Astronomy Observatory (FCRAO) [8] and with the Institut de Radio Astronomie Millimetrique (IRAM) 30-meter [9], where partial-disk resolution can be obtained in the (1–2) rotational transition. Clancy et al. [7] have published the most recent synthesis of Mars’ microwave spectroscopy work. Mars is the simplest case to treat because the CO distribution extends all the way down to the surface and the mixing ratio is nearly independent with altitude. The latter assertion is based partly on theoretical photochemical modeling and partly on detailed analysis of \(^{13}\text{C}O \) and \(^{12}\text{C}O \) microwave spectra [7]. Because Mars’ orbit lies beyond the Earth’s, it is always seen in full solar illumination with a small morning or evening dark terminator. This can sim-
plify the analysis of observations, but it means that diurnal variations in the atmosphere cannot be measured until equipment is flown in orbit about the planet.

A rather typical CO (0–1) Mars spectrum is shown in Figure 9.2(c), where the line brightness is expressed as a line-to-continuum ratio. A pseudo-continuum was obtained by averaging the outer few channels in the observed spectrum, which was then used as the divisor in the ratio. This procedure essentially removes the effects of uncertainties in the absolute flux calibration of the measurement, if the surface continuum emission cannot be modeled accurately (as is often the case). As long as identical procedures are adopted for comparison of model and observed spectra, the absorption method is self-calibrative. All observed spectra are treated this way, even narrow-band ones. The goal of the Mars' experiments was to search for atmospheric temperature variations on time scales of months. The temperature–CO abundance ambiguity in the radiative transfer problem is partially removed by simultaneously measuring $^{12}\text{C}^{16}\text{O}$, $^{12}\text{C}^{18}\text{O}$, and $^{13}\text{C}^{16}\text{O}$ spectra. The relative abundances of these isotopes have been determined from IR spectroscopy of $\text{CO}_2$ [10] and with mass-spectrometer in situ measurements on the Viking missions for the lower atmosphere.

Spectra of Mars CO made at two very different epochs are shown in the next few figures. Figure 9.4 shows three $^{12}\text{C}^{16}\text{O}$ spectra for the same epoch with frequency resolutions of (a) 250 KHz in a total band of 70 MHz, (b) 1 MHz in a band of 250 MHz, and (c) 100 KHz in a band of 28 MHz. In absolute units, the absorption line in Figure 9.4(c) is much deeper than the others before normalization with the outer channels. The epoch is identified with the season on Mars given by the martian longitude of the Sun, $L_s = 305^\circ$ (early winter in the North). In

![Figure 9.4](image-url)

**Figure 9.4.** Mars CO (1–2) spectra expressed as line-to-continuum ratios, that is, normalized by an average of the outer channels for (a) res = 250 KHz and a total width of 70 MHz.
Figure 9.4. (Continued) Mars CO (1–2) spectra expressed as line-to-continuum ratios, that is, normalized by an average of the outer channels for (b) res = 1 MHz with a total width of 250 MHz, and (c) res = 100 KHz with a total width of 28 MHz. The data were fit for a constant CO abundance vs. altitude profile with a ±10 K deviation around the temperature profile indicated by the dashed lines.

In each case, the observed line-to-continuum ratio is based on the continuum level within the outer channels and the model line-to-continuum ratios are determined in the same way. A best-fit CO volume mixing ratio of $6 \times 10^{-4}$ is determined from the optically thin $^{13}$CO spectrum. Atmospheric temperature profiles are determined from the optically thick $^{12}$CO line, which provides well-defined weight-
9.3 OBSERVATIONS WITH SINGLE TELESCOPES

The sensitivity of the $^{12}\text{CO}$ spectrum to variations in atmospheric temperatures is indicated by the dashed-line model spectra, Figure 9.4, calculated for $\pm 10$ K perturbations in atmospheric temperatures. Spectra for the (1–2) transition of $^{13}\text{CO}$ for the same epoch are shown in Figure 9.5. A convergence between model and observations is accomplished by iterative radiative transfer calculations of $^{13}\text{CO}$ and $^{12}\text{CO}$ spectra while adjusting the atmospheric temperature profile and the CO mixing ratio (constant in altitude) after each iteration. These procedures and results are crude relative to the promise of the foregoing retrieval equations and the discussion in

![Figure 9.5](image.png)

(a)

![Figure 9.5](image.png)

(b)

Figure 9.5. Same as Figure 9.4 for the $^{13}\text{CO}$ (1–2) isotope line of Mars at the same epoch.
Chapter 7, but they are the state of the art for disk-average spectra. Clancy et al. [7] presented the results for several martian epochs, which we summarize in Figure 6. The Viking Lander temperature profile model for its single epoch ($L_s \sim 100^\circ$ in 1976) is indicated by the circles in Figure 9.6, and a theoretical radiative-convective equilibrium profile is shown with crosses. The remaining curves are

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{mars_atmospheric_temperature_profiles.png}
\caption{Temperature profiles of the Mars atmosphere obtained by inverting CO (1-2) spectra for various epochs. The theoretical radiative-convective equilibrium profile is indicated by the crosses and the Viking reference profile estimated from the descent data of September 1976 by circles. Results in (a) tend to agree with the Viking profile when the atmosphere was "dusty" and results in (b) are in good agreement with radiative equilibrium that is expected when the Mars atmosphere is relatively dust-free. The temperature variations with epoch above 50 km are poorly constrained.}
\end{figure}
those estimated from the other microwave spectra, which show large variations with epoch. The single Viking profile is seen to be in poor agreement with the radiative-convective equilibrium model for the same season, a distinction that has been interpreted as a result of substantial heating of the Mars atmosphere by suspended dust [7]. On the other hand, one sees from Figure 9.6(b) that the microwave results for the same epochs agree well with the radiative equilibrium model. The authors have concluded that the martian atmosphere is typically much clearer than it was during the Viking mission in July-September 1976. The microwave data also indicate ~ 20 K seasonal variations in global Mars atmospheric temperatures (cf Figure 9.9), a result that is consistent with the high eccentricity of the Mars orbit about the Sun.

9.3.2 Venus

Carbon monoxide is the only microwave spectral line that has been observed in the Venus atmosphere, although several molecular species have been searched for without success. The CO₂ atmosphere is crowned with thick ubiquitous clouds of sulfuric acid/water mixtures that not only make the surface invisible from above, but facilitate a complex heterogeneous chemistry of SO₄ and Hₓₐ species. Water is highly depleted everywhere in the atmosphere, but in addition, the clouds act as a desiccant with very little water vapor expected to be in equilibrium above the clouds, that is, the vapor-pressure curve of H₂O above H₂SO₄ falls rapidly. The total pressure is about 1.3 atmospheres at the bottom of the cloud layer. Because a typical pressure-broadening coefficient is in the range of 3–5 GHz per bar, it is not feasible to detect spectral lines of molecular species below the clouds. Although it is likely that very low abundances of H₂O, O₂, O₃, SO₂, SO, CI₂, and HCl exist above the clouds where the lines would be reasonably narrow, (e.g., above the 50-mbar level), they have not been detected as yet because of the small Doppler shifts of interfering terrestrial lines and a lack of sufficient sensitivity with disk-averaged measurements.

Considerable effort was expended in the 1960s to detect the 22-GHz water-vapor line, without success. An appreciable water column resides in the clouds in solution with H₂SO₄, but at pressures that lead to excessively broadened line shapes. Water lines in the IR with variable intensity and reliability have been reported in the literature that suggest that total water above the clouds of between 10 to 100 precipital microns may exist at various latitudes and Sun angles. If this is the case, the emission flux density on the planet’s limbs should be detected with the VLA in the 22-GHz line. Many fundamental questions about the water distribution above the clouds could be answered with a 183-GHz system in Earth orbit, or much better, in orbit around Venus (see what follows).

Thus, we limit our discussion to CO spectroscopy of Venus, but emphasize that it is a very rich subject. Venus rotates in a direction retrograde to its orbit with a period of 243 Earth days. However, the atmosphere in and above the clouds superrotates with roughly a 4-day period, which corresponds to a zonal wind of about 100 m/s. This wind was measured up to an altitude of 70 km from the lateral motion of the Pioneer Venus entry probes [11] and cloud-tracking observations
from the Pioneer Venus orbiter. The altitude limit for the very high winds was recently extended to 100 km using measurements of the Doppler shifts of CO lines, which is discussed in what follows. CO is produced from the ultraviolet decomposition of CO$_2$ on the sunlit hemisphere at all altitudes above the clouds and flows to the antisolar region, where it is destroyed at lower altitudes in poorly understood chemical reactions probably involving OH and/or Cl [12]. These effects are manifest in the disk-averaged CO spectra measured as a function of planetary phase angle. Roughly, CO spectra observed at inferior conjunction (local midnight) are deep and narrow absorption lines due to the relative absence of CO at lower altitudes and higher pressures (~80–90 km) and relatively high abundances at altitudes above 90 km. Conversely, spectra measured at superior conjunction (local noon) are much broader due to increased CO mixing ratios at 80–90-km altitude, and decreased CO abundances above 90 km. Venus diurnal variations in CO spectra have been measured by a number of investigators [13], as summarized by Clancy and Muhleman [14] (which contains a complete list of references). The distinctive Venus absorption CO spectrum is shown in Figure 9.2(b).

More recently, nightside $^{12}$CO (0–1), $^{12}$CO (1–2), $^{13}$CO (1–2) and $^{18}$O (1–2) spectra were analyzed to estimate year-to-year variations in the nightside CO mixing ratio and temperature profiles as a function of epoch (1982, 1985, 1986, 1988, 1990) [14]. Temperature-weighting functions for the $^{12}$CO (1–2) line and a single, line-center weighting function for the isotope are shown in Figure 9.7. A Pioneer Venus nighttime temperature–pressure altitude profile is also shown. The investigators fit models to the optically thick $^{12}$CO and optically thin $^{13}$CO, $^{18}$O spectra with the iterative cut-and-try method. Large interannual variations in nightside CO and temperature profiles were inferred and are shown in Figure 9.8. Figure 9.9(a)

![Figure 9.7](image-url)
Figure 9.8. Retrieved venusian temperature profiles as a function of the local Sun time, based on full-disk-averaged spectra. (a) The late night and morning profiles when the morning terminator was seen from the Earth and (b) profiles showing the small variations observed when the evening terminator was in view.

contains CO profile results from the 1986 epoch when the sub-Earth point was near 3:00 A.M. (east limb at 9:00 A.M. and west limb at 9:00 P.M., showing the morning terminator to the Earth). The best fit to all of the spectra for this epoch required a strong variation of high-altitude CO abundance across the disk. This result was confirmed by interferometric mapping of the Venus $^{12}\text{CO}$ (0–1) line in 1986. The CO isotope observations also indicate substantial year-to-year variations in the nightside atmospheric temperatures near 90–100-km altitude (see Figure 9.9). Unfortunately, it has not been possible to get high-quality Venus spectra of CO isotopes near its superior conjunction corresponding to sub-Earth points near Venus noon. It is important to measure the mixing profile in the hemisphere of
maximum CO production. These data, combined with the data for the time of maximum CO destruction a few hours after midnight to a few hours after sunrise, would make it possible to develop a complete model of the upper-atmospheric circulation. As in the case of Mars, the problem requires observations from a close orbiter around the planet. Further progress has been made using millimeter wavelength arrays to achieve spatial resolution. We will return to Venus in Section 9.4.2.

9.3.3 Titan and Io

These two satellites both have microwave spectral lines in their atmospheres that can be detected, but present unique problems for the observer. The atmosphere of Titan is massive with a surface pressure of 1.5 bars and is very cold, 94 K. The high pressure near the surface of Titan means that very broad lines with collisional-broadening parameters up to 5 GHz are to be expected, leading to huge spectral lines that are wide compared to the useful widths of operational spectrometer back-ends. At the other extreme, Io has a tenuous atmosphere with a total surface pressure of a few nanobars caused by a combination of outgasing from volcanoes and sublimation from the SO2 surface frosts apparently laid down by the volcanoes. The only known neutral species is SO2, which was detected by Lellouch et al. [15] in the (11,1,11)–(10,0,10) transition at 221.965 GHz on the IRAM telescope. Io spectral lines contain no pressure information because the line shape is completely controlled by the Maxwellian Doppler line shape, proportional to the square root of the atmospheric temperature, which is expected to be higher than 200–300 K.
Carbon monoxide was first detected on Titan in IR lines [16] and in the (0–1) transition at 115 GHz using the Owens Valley Radio Observatory (OVRO) Millimeter array [17]. The microwave detection was confirmed at IRAM [18] and at the Caltech Submillimeter Observatory (CSO) [4] in the (2–3) transition at 346 GHz. A spectrum from the latter observations using the widest available backend (an acoustooptical spectrometer) is shown in Figure 9.2(a). It is clear that the continuum level was not reached and a unambiguous interpretation of the spectrum is not possible without excellent absolute calibration. A mixing ratio of $7 \times 10^{-5}$ for stratospheric CO (with assumed uniform mixing) was obtained with the fitted line. Although this result is consistent with the marginal OVRO result [17], it is inconsistent with the IRAM result, which reported $1 \times 10^{-6}$ based on their antenna calibration. The higher mixing ratio is consistent with Titan IR spectra, whereas the lower value is not. The distinction between these two microwave solutions is, in fact, highly significant in terms of the photochemistry of the Titan atmosphere. Hence, the resolution of the stratospheric distribution of CO in the Titan atmosphere is important for planetology (and the Cassini mission to Titan), but apparently cannot be resolved with the current state of the art!

The Io result [15] is equally interesting, but also ambiguous. The SO$_2$ line-center antenna temperature was about 0.2 K. The observed flux density expressed as a brightness temperature is shown in Figure 9.10. The brightness temperature of 18 K at line center would correspond to a very low temperature for the Io atmosphere if SO$_2$ were globally distributed and optically thick. The authors suggest that a more likely interpretation is that the line is thick, but the atmospheric emission comes from a relative small region of the disk, which is sufficiently warmed by the Sun to create a local atmosphere by SO$_2$ frost sublimation, for

**Figure 9.10.** The observed emission line for Io SO$_2$ at 221.965 GHz from Lellouch et al. [15]. The solid line is their best-fit model with a SO$_2$ surface pressure of 14 nbars, a surface temperature of 130 K, and an exospheric temperature of 700 K. The inner and outer dashed lines are for a surface partial pressure of 6 and 35 nbars, respectively.
example, a temperature above the surface temperature in the range from 125 K to, perhaps, 600 K. In any case, the measurement of the area under the spectrum does give a column abundance averaged over the surface of $4 \times 10^{16} \text{ molecules/cm}^2$, assuming that the atmosphere is optically thin. The ambiguities that arise in the Titan and Io observations can only be removed with high spatial resolution (for Titan and Io) and broad frequency resolution (for Titan). Both require measurements from spacecraft. Limb sounding of Titan from an orbiting spacecraft can be used to great effect because high spatial resolution can be achieved and the problem of great pressure broadening can be avoided.

### 9.4 Observations with Array Telescopes

The angular resolution of any telescope is approximately equal to the wavelength divided by the aperture diameter. Thus, if resolution on the order of an atmospheric scale–height is required, for example, <0.25 arc second, then synthetic apertures greater than 800 meters are required at a wavelength of 1 mm. It is not certain that a site can be found on the Earth with sufficient atmospheric stability to achieve this goal. The ultimate resolution of the VLA with its maximum aperture of 36 km operating at 23 GHz is 0.09 arc second. This resolution is degraded by more than a factor of 2 in practice. Two arrays fully operational at frequencies up to 115 GHz and marginally at 230 GHz are located at Caltech’s OVRO and the Berkeley–Illinois–Maryland Array (BIMA) at the University of California site in Hat Creek. The millimeter arrays currently use three telescopes each, but are being expanded to more than five elements. The VLA with 27 telescopes is a very different instrument that is able to employ all the modern image-processing and calibration techniques made possible by the redundancies of the large number of elements.

The basic principles of phase-coherent arrays have been worked out over the last 30 years by many people, led by Martin Ryle, resulting in very successful centimeter wavelength instruments in Cambridge University, OVRO, and in the Netherlands. The marvelous details of such instruments can be found in a recent text [19], but we only need the basic ideas here. The circular aperture of the array is only slightly filled by the physical area of the telescopes at any instance of time. However, as seen from a radio source at declinations other than zero, the rotation of the Earth tends to fill the aperture with time. The telescopes for the small arrays are physically moved as often as once a day to further fill the aperture. The vector voltage outputs of each antenna, which are proportional to the detected electric field strengths, are multiplied or correlated for each measurement record after heterodyning by a stable central oscillator. Thus, an $m$-element array measures $m(m - 1)/2$ complex visibilities for each record: 351 for the VLA and 3 for BIMA and OVRO. A nearby unresolved radio source of precisely known position on the sky is observed at regular intervals (as often as 15 min) to calibrate the phase and amplitude variations of each of the receivers and all the associated circuitry. It is vital that the quality of the master frequency reference and all RF
circuitry be such that the phase of each receiver drifts less than a turn between phase calibrations. Only then can aperture synthesis be achieved.

The positions of the telescopes are known relative to the array center to a small fraction of a wavelength. Consequently, after precise phase calibration, the instantaneous effective beam that was convolved with the target source is known. The true beam synthesized in a record, or an hour, or during the entire tract is perfectly known in the limit of zero-phase errors and it can be mathematically deconvolved from the "dirty" image to obtain a "clean" image. In practice, the phase errors are not zero due to short term variations in the atmosphere over each telescope, the small errors in the telescope position, etc. If more than three baselines are available (preferably many more), the redundancy relationships among the telescopes can be used to further reduce the phase error and improve the dynamic range of the image, that is, reduce noise in the image plane. For example, if the source has a spatial structure known in the form of a model, the output of the jth antenna is contained in all the visibility pairs correlated with it, usually yielding redundant measurements of the errors in the jth receiver system and the sky above it. The technique is called self-calibration or the phase-closure relationship technique. A uniformly bright, circular disk is an adequate source model for planetary observations, yielding improvements in dynamic range as large as a factor of 100 at the VLA. The technique must be applied with great care for a three-element array, which is the primary reason for increasing the number of elements at OVRO and BIMA.

There have been four successful applications of planetary microwave spectrometry with the arrays, which we will now briefly discuss.

### 9.4.1 Water Vapor in Mars' Atmosphere

Recently, the VLA was used for the first spectroscopic measurements of a planetary atmosphere, although OH in comets had been studied. Mars was observed in the 22-GHz water line during the 1991 opposition in the 3-km array configuration at the VLA [20]. The visibilities in 16 spectral channels of 1.5-MHz resolution were measured over a 10-hour track to produce 16 images of the planet. All images contain the Mars continuum flux-density distribution, but the effects of the H$_2$O absorption and emission reside in the center 5–10 MHz. Each map was calibrated and cleaned by using the phase- and amplitude-error matrix generated by self-calibration of the flux from the sum of the 16 channels, the "continuum," which is a source very well represented by a uniformly bright, circular disk. Water vapor in the cool atmosphere above the warm surface appears as a weak absorption over the solid surface. It appears much more strongly in emission on the limb of the planet, where it was easy to detect. The resolution in the 3-km array was about 400 km on Mars, such that any pixel on the limb spans the entire atmosphere. The average of the spectra over the limb pixels on the morning and evening limbs is shown in Figure 9.11. The continuum level of this spectrum arises from the fraction of the 400-km pixel, which was on the martian surface. The H$_2$O emission line of 2 K is easily seen. The vertical or martian altitude resolution that can be
Figure 9.11. Water-vapor emission spectra from the Mars limbs, deduced from VLA spectral line maps with res ~ 1.5 MHz about the 22-GHz line for (a) the equatorial regions, (b) the midlatitude regions, and (c) the morning and evening limbs. The observing epoch was December 1990.
achieved from the spectra is independent of the pixel size because it is coded in the pressure-broadened line shape.

Water vapor in the Mars' atmosphere has been studied using near IR spectroscopy from the Earth and on the Mariner 9 and Viking Orbiters [21]. Whereas the IR measurements are difficult to interpret due to scattering by dust in the atmosphere and difficulties in removing surface-emission effects, we have a good general picture of the column abundances of water vapor over the globe and as a function of seasons. The abundances nearly vanish over winter poles and summer values at high latitudes reach as high as 100 precipitable microns. However, the emission line shown in Figure 9.11 yields an average abundance that is about a factor of 5 smaller than that observed for the same season (northern late winter) by the collection of IR spectroscopic results. Because the microwave method is unaffected by the martian dust, an important question remains about the interpretation of the more comprehensive IR measurements. It is also possible that very large interannual variations in Mars atmospheric water exist.

A similar experiment was successfully carried out on Venus in fall 1991, which will be the first reliable measure of water lines in that planet. No details are available at this time.

### 9.4.2 Venus CO Abundances

Supersynthesis mapping of Venus in CO (0-1) was carried out at OVRO at the inferior conjunctions of 1986 and 1988 [22, 23] and at BIMA in 1988 [24]. The
OVRO maps are of sufficiently high quality that CO mixing-ratio profiles as a function of venusian longitude and latitude were mapped in both years and wind maps were obtained in 1988 [23]. The visibilities were measured in four antenna configurations in 9 days. Periods away from the epoch of inferior conjunction were selected to see the morning terminator in 1986 and the evening terminator in 1988 at OVRO. After all the visibilities were adjusted to a common Venus distance, 32 channel maps (centered on 115.27120 GHz) with 1.0-MHz resolution were made in both years and 32 channel maps with 0.050 MHz in 1988 for wind measurements and to sample higher in the venusian atmosphere. All maps were cleaned (beam deconvolution) and "mildly" self-calibrated using the 32-MHz continua. A dynamic range of order 25 was achieved in 5 arc-second synthesized beams on the 40 arc-second planet (3 arc-second beam in 1988). A map of 1986 Venus CO spectra is shown in Figure 9.12, where the entire absorption spectrum for each pixel (1.4" × 1.4") is plotted at the coordinates of the pixel. Each point plotted is the amplitude from a given channel map for the corresponding pixel in which the spectrum is plotted in Figure 9.12. The rotational axis of Venus is indicated and the morning terminator is shown corresponding to 6:00 A.M. local time with the sunlit crescent on the left (East). Significant variations appear in the map, some of which are true Venus effects and others are defects in the supersynthesis technique. Obviously, several absorption spectra appear off the limb. This occurs because the phase errors were not zero and some beam effects were not removed, a problem aggravated by the limited number of telescopes in the OVRO array. The

**Figure 9.12.** CO (0–1) spectra for individual 2 × 2 arc second cells are shown plotted on an outline of the venusian disk. The morning terminator is indicated with the dashed-line ellipse relative to the projection of the planet’s spin axis. The spectra were normalized to line-to-continuum ratios.
flux mapped off Venus was put there by residual beam sidelobes. Real and important effects are the diminution of the absorption depths on the sunlit part of the planet, nearly vanishing on the morning limb. These occur because the CO abundance is significantly lower there relative to the dead of night. The deepest lines are near the sub-Earth point (∼ 3:00 A.M.). Absorption depths also diminish toward the poles for reasons not completely understood, for example, possibly lower CO abundance, but limb-viewing effects and latitudinal temperature variations have not been worked out as yet.

Each of the spectra in Figure 9.12 is equivalent to the spectrum that would have been measured with a Gaussian pencil beam of FWHM 5", except for the processing effects inherent in the limitations of the supersynthesis technique. Equations 9.4 to 9.6 are directly applicable for the analysis of these spectra. These spectra have been inverted [22] for the CO abundance profile in each beam (4 pixels) with a Twomey–Chahine-type technique in an iterative, least-squares procedure (see Chapter 7, Eq. 7.40). It was necessary to adopt and hold fixed, temperature-altitude profiles in order to obtain solutions for CO-mixing-ratio profiles. A model of each spectrum was computed with an initial guess of a constant mixing ratio and the residuals were formed as observed minus model $T_b(\nu)$ (the following development was taken from Gurwell et al. [22]):

$$ R(\nu) = T_b(\nu) - T_b(\nu)_{\text{mod}} = \sum_{i=1}^{M} \frac{\partial T_b(\nu)}{\partial \mu_i} \Delta \mu_i $$

(9.8)

where $\mu_i$ is the CO-mixing ratio in the $i$th layer. Because the number density of CO (or $\mu_i$ if normalized by the local total density) only appears in the absorption coefficient $\alpha_i$, the partial derivatives are

$$ \frac{\partial T_b(\nu)}{\partial \mu_i} = \frac{\partial T_b(\nu)}{\partial \alpha_i} \frac{\partial \alpha_i}{\partial \mu_i} $$

because $\mu_i = N_i/N_0$.

$$ \frac{\partial T_b(\nu)}{\partial \mu_i} = N_0 \frac{\partial T_b(\nu)}{\partial \alpha_i} \frac{\partial \alpha_i}{\partial N_i} $$

(9.9)

and from Eq. 9.4,

$$ \frac{\partial T_b(\nu)}{\partial \alpha_i} = -s_i E(\theta) T_c \exp \left( -\sum_{q=1}^{M} \alpha_q s_q \right) $$

$$ -s_i \sum_{i=1}^{M-1} T_i \exp \left( -\sum_{q=1}^{M} \alpha_q s_q \right) $$

$$ + s_i \sum_{i=1}^{M} T_i \exp \left( -\sum_{q=1}^{M} \alpha_q s_q \right) $$

(9.10)
The atmosphere was divided into the same number of layers as the number of spectral channels, \( M = 16 \). There were 32 channels measured, but because the Voigt line is symmetric at the pressures considered here, only 16 are "independent." However, even these are not independent in the sense that each channel contains information that would allow us to solve for the \( \mu \)'s in the 16 selected atmospheric layers. Hence, the inversion of Eq. 9.8 for iterative corrections to the \( \mu \)'s is not possible due to the ill condition of the matrix of partial derivatives. An altitude smoothness constraint on the mixing profile was used to condition the matrix effectively requiring the mixing ratio of the \((i + 1)\)st layer to be constrained by

\[
\mu_{i+1} = \mu_i \pm \sigma \quad \quad (9.11)
\]

By writing \( P_{nm} \) for the partial derivative of \( T_b(\nu_m) \) with respect to \( \mu_M \), the equations to be inverted become

\[
\begin{bmatrix}
T_b(1) \\
. \\
. \\
. \\
. \\
. \\
. \\
. \\
. \\
. \\
0
\end{bmatrix} =
\begin{bmatrix}
P_{1,1} & . & . & . & P_{1M} \\
. & . & . & . & . \\
. & . & . & . & . \\
. & . & . & . & . \\
. & . & . & . & . \\
0 & 1/\sigma & -1/\sigma & . & 0 \\
. & 0 & 1/\sigma & -1/\sigma & 0 \\
. & . & . & . & . \\
. & . & . & . & . \\
. & . & . & . & . \\
0 & 0 & 0 & 1/\sigma & -1/\sigma
\end{bmatrix}
\begin{bmatrix}
N_1 \\
. \\
. \\
. \\
. \\
. \\
. \\
. \\
. \\
. \\
N_M
\end{bmatrix}
\]

where the value of the tolerance \( \sigma \) is found by the art of trial and error. This constraint has the property of yielding a constant mixing ratio in a group of layers for which no information is contained in the spectrum, such as above and below the region where the weighting function is significant.

Some results of the technique applied in the Venus work to the 1-MHz resolution data from 1986 are shown in Figure 9.13. While mixing ratio profiles are available for all the pixel cells in Figure 9.12, it is sufficient here to show some averaged profiles. The three curves in Figure 9.13 show the average values of the mixing ratios in the latitude range from \(+45\) to \(-45\) deg for three local time intervals: 10 P.M. to 6 A.M., 6 A.M. to 8:30 A.M. and 8:30 A.M. to 10 A.M. The late morning or daytime distribution is nearly constant, whereas the late night
9.4 OBSERVATIONS WITH ARRAY TELESCOPES

Average Profiles of Iterated Solutions for CO

Figure 9.13. CO mixing-ratio profiles from Venus obtained from inversions of the spectra from Figure 9.12. They confirm and improve on the results from disk-averaged spectra from Figure 9.8.

distribution varies by over an order of magnitude! The strong CO bulge during the night is still clearly evident. Whereas the general properties of this bulge have been known for many years, its precise origin remains a mystery. The CO is both produced in the daytime and destroyed in the daytime by chemical reactions with radicals such as OH, which vanish at sunset. Apparently, the winds convect the CO molecules upward and across to the nightside. CO is destroyed below about 70 km by OH on the dayside, but that effect is more evident on the stable nightside.

9.4.3 Venus Winds

The use of the Doppler shifts of CO lines to directly measure the winds in the Earth’s mesosphere was discussed in Chapter 7 and the results are shown in its Figure 7.28. Clearly the same technique can be used to measure the winds in the atmospheres of Venus and Mars when sufficient spatial resolution is achieved with millimeter wavelength arrays. Such experiments were carried out at OVRO on Venus in 1988 and on Mars in 1990 using the CO (0–1) transition and a filterbank spectrometer with a resolution of 50 KHz.

The wind field of Venus near an altitude of 100 km was developed from mea-
measurements by Kathryn Pierce Shah in her Ph.D. dissertation [23, 25]. A mean motion of a parcel of CO gas moving with speed $v$ along the line of sight toward the observer will create a CO (0–1) absorption or emission-line Doppler shifted toward the blue by $0.384v$ kHz with $v$ in m/s. Thus, a mean wind over the line-formation region with a component of 100 m/s toward the observer causes a Doppler shift of 38 kHz, which is easily seen in the 50-kHz channels used in 1988.

The spectrum in a given resolution cell such as those shown in Figure 9.12 is shifted by the component of wind along the line of sight. Spectra along the rotational equator from the 50-kHz system are shown in Figure 9.14. The strong variations in the line cores as a function of local time is immediately obvious in the figure, but one can also see that mean spectra are Doppler shifted toward the red at 11:40 P.M. to toward the blue by 3:00 P.M. The actual line shifts were obtained for all the resolution cells by cross-correlating model spectra with the observed spectra. All of the results have been published [23], but just the winds on the limbs are shown here in Figure 9.15 (recall that Venus rotates from right to left). The winds coming over the West limb cause a blue shift corresponding to a speed of about 100 m/s and at the East limb, a similar red shift of about 100 m/s. Because the $^{12}$CO (0–1) weighting functions on the limb peak at about 100-km altitude, the investigators have shown that the 4-day superrotating atmosphere continued upward to at least an altitude of 100 km in 1988. This has many consequences for our understanding of the dynamics of the Venus atmosphere, which are discussed in detail in Shah et al. [23]. The noise seen in the wind values in Figure 9.15 is caused by the incomplete removal of the true dirty beam. That is, the uncorrected sidelobes of the beam have transferred Doppler-shifted flux around the map, creating a noise in the wind map similar to the flux in the dirty beam. These effects can be minimized with a millimeter array with more than three telescopes for which the full power of the phase-closure technique can be exploited.

It is clear that the wind field of Venus continues with speeds as great as 100 m/s to altitudes of at least 100 km. This result is at variance with IR observations by Pioneer Venus, which, coupled with theoretical studies of the general circulation on the planet, show winds that decrease at or above 70 km, the altitude limit for the direct Pioneer Venus measurements of the Venus winds. Limited thermal IR sounding in the northern hemisphere from the Pioneer Venus orbiter were interpreted in terms of thermal winds that fell off above the cloud tops. The strong differences in the 1979 Pioneer Venus and 1988 microwave results remain to be explained.

9.5 SPECTROSCOPY FROM SPACECRAFT

Many difficulties must be overcome in order to send microwave spectrometers to close encounters with the planets other than the Earth. Planetary spacecraft instruments have rigid limits on size, mass, and power consumption. Nearly all designs of such planetary instruments have been much smaller than 0.2 m$^3$, less massive
Figure 9.14. High-resolution (50-kHz) spectra of Venus obtained from supersynthesis imaging of the planet near the CO (0-1) line [23]. The panels show spectra at various local Sun angles on Venus from the East to the West limbs, which are Doppler shifted by winds near 100-km altitude.
Figure 9.15. Estimates of the 100-km-altitude winds across the receding East limb and the approaching West limb of Venus. The units are m/s.

The power of microwave spectroscopic techniques for planetary research is very easily demonstrated, particularly in the short millimeter and submillimeter wavelength ranges. Most of the fundamental atmospheric species such as H₂O, O₂, O₃, CO, HCl, H₂SO₄, SO, and SO₂ for the terrestrial planets, and HCN, HC₃N, NH₃, PH₃, and many other hydrocarbons and nitriles in the outer solar system have strong transitions in this spectral region. Essentially, all of these species have transitions in the IR and, consequently, IR spectroscopy forms the backbone of planetary atmospheric observations. However, there are many clear advantages for microwave spectroscopy, which include the immunity to scattering by dust and aerosol particles, the use of heterodyne techniques that allow the detailed mea-
ured. Measurements of individual transitions without blending, the ability to measure precise Doppler shifts, and to see more deeply into material due to the longer wavelengths. There is also an advantage in many planetary problems to be working on the Rayleigh–Jeans side of the thermal spectrum of the objects where the observed flux depends nearly linearly on the physical temperature of the emitting region, that is, where the weighting functions are sensitive to the first power of the temperatures.

Observational techniques for orbiting instruments about planets are, of course, very similar to Earth observations from above the atmosphere. The techniques were thoroughly treated in Chapter 8 and need not be repeated here. Practical limits on planetary instruments are very important and include the spacecraft themselves, which must orbit completely above the sensible atmosphere to avoid drag or, in some cases, planetary ring systems and dust particles. Practical orbits for Venus and Mars, for example, would be above an altitude of about 150 km, which would create limb distances of 1300 km and 1010 km, respectively. If a scale-height resolution of about 5 km on the limb is needed, an aperture of about 30 cm is required at a wavelength of 1 mm for Mars. Thus, a small telescope is required for a complete study of the atmospheres of Mars and Venus with similar requirements for Titan (and other satellites like Io and Triton). Unfortunately, orbits and flybys of the major planets are limited to distances above their "surfaces" of more than a tenth of a planetary radius for many reasons. The 30-cm telescope would have resolution of about 300 km on the limb of Saturn, which is many atmospheric scale heights. Capability beyond that will not occur for decades. Nevertheless, such measurements would be powerful tools for planetary science in the outer solar system because many molecular species can be best studied in emission on planetary limbs and, even without adequate limb resolution, vertical information is encoded in the measured line shapes.

We limit the discussion here to a few design studies that have been developed in complete detail by the authors [26]. These include experiments for Venus, Mars, and Titan at wavelengths from 1 mm longward. Although planetary spectra become increasingly rich in information in the submillimeter region, practical spaceworthy devices such as backends do not exist to exploit this capability. Ultimately, perhaps, sensitive receivers and interferometric spectrometers will be developed that achieve sufficiently large bandwidths with high-frequency resolution in the wavelength range from 0.5 to 1 mm to bridge the gap between the IR and the microwave region. Given the current limits on deep-space investigations outlined before, consideration of submillimeter experiments is not appropriate for this volume.

Weighting functions for sounding the martian atmosphere in the CO (1-2) line at 230 GHz are shown in Figures 9.3(a) and 9.3(b) for nadir and limb viewing, respectively. This transition is ideal because the opacities of the atmosphere are such that it can be sounded at nadir or on the limb in each scale height from the surface to about 70 km. This region of the Mars atmosphere contains many of the phenomena that are of planetological interest, including the surface–atmosphere interactions, troposphere dynamics, and the region of gravity wave activity. The limb-sounding mode extends the coverage to about 100 km, adding a region of the
Mars atmosphere never before studied. Doppler winds can be measured from about 30 km to a height of 100 km if a reasonably stable oscillator is used in the instrument (\( \sim 1 \times 10^8 \)). Thus, a powerful data base can be obtained for a study of the planet’s general circulation. A limb-sounding instrument dedicated to wind measurements would require a simple backend with about 20 channels and channel resolution of about 100 KHz. Such a device is nearly an “off-the-shelf” instrument.

The capability of such an instrument for atmospheric temperature sounding is illustrated in Figure 9.16. The standard temperature–altitude profile measured on the Viking II descent spacecraft is indicated by the crosses in Figure 9.16(a). The dashed lines are the results of six independent retrievals made from synthetic spectra generated from the Viking profile with the assumption of a constant CO mixing-ratio profile. Random noise with a standard deviation of 2 K was added to each channel synthesized; channel selections correspond to the weighting functions in Figure 9.3(b). The random-noise standard deviation is what one would expect from a receiver with a system temperature of 1200 K, feeding into a 250-KHz channel in an integration time of 1.4 s. Because the required integration time is so short, it is clear that random receiver noise is not the problem with such an instrument, but, rather, the baseline stability and calibration. Figure 9.16(a) shows that

![Figure 9.16](image-url)

**Figure 9.16.** Monte Carlo tests of the inversions of noisy synthetic spectra for the martian atmosphere into the temperature–pressure profiles. Normal-incidence sounding was assumed for an atmosphere consistent with equatorial latitudes (upper panel) and over a winter pole (lower panel).
the temperatures would be retrieved to an accuracy equal to the real system stability or calibration across the spectrum from the lowest scale height to 70 or 80 km. This is sufficient for dynamical studies such as detailed measurements of tidal, gravity, and planetary waves in the Mars atmosphere. The temperature-altitude profiles over the poles of Mars were measured with the radio occultation technique on Viking and Mariner 9. An example of the temperature inversion over a winter pole of Mars is shown in Figure 9.16(b) and was used for a similar synthetic spectral inversion exercise with the results shown in the figure. Any physical temperature profile on Mars can be sampled and retrieved with an accuracy of 1 or 2 K with the CO spectrometer technique.

The water-vapor distribution on Mars can be mapped in three dimensions by utilizing the very sensitive transition at 183 GHz [26]. Whereas column abundances have been mapped during the Viking mission, no empirical information is available regarding the distribution of water with altitude. Synthetic 183-GHz spectra for the martian temperate zone and over a winter pole are shown in Figure 9.17. The upper panel presents line-to-continuum ratio $H_2O$ spectra that would be seen in temperate latitudes for a total column abundance of 10 precipitable microns, uniformly mixed to altitudes of 5, 10, 25, and 80 km, respectively. Given independent measurements of the atmospheric temperature profile from CO lines, the area under the $H_2O$ spectrum in Kelvin units determines the $H_2O$ column abundance and the detailed shape of the 183-GHz line can be analyzed to measure the height of the water distribution. The “measurement accuracy” indicated on the figure corresponds to an instrument similar to the one described before for CO measurements. Whereas the water line appears in absorption (with emission wings) over midlatitudes in the summer, the line will appear in emission over a winter pole. That circumstance is illustrated in Figure 9.17(a) for a total water abundance of 1 precipitable micron. Our analysis shows that the line could be measured even if the abundance is as low as 0.1 precipitable microns. Measurements such as these would bring the study of the martian atmosphere to a new scientific level that cannot be reached otherwise.

Equally sensitive spectra of $O_2$, $O_3$, and $HO_x$ molecules can be measured on Mars near 1-mm wavelength with currently available equipment. We and our colleagues have shown that a practical instrument can be built to simultaneously measure the fundamental constituents of the martian photochemistry: $H_2O$, $CO$, $O_2$, and $O_3$. However, the measurement of the missing element, OH, is a formidable task, but $H_2O_2$ and $HO_2$ lines do exist in the millimeter spectrum.

The results for Venus are quite similar to those for Mars because the spectroscopy in both cases is restricted to atmospheric regions at pressure levels lower than about 10 mbars. Although that region includes the entire martian atmosphere, it lies above about 70 km on Venus. The pressure limits are caused by the relatively narrow total bandwidths of currently available spectrometers and the difficulties in obtaining baseline stability over bandwidths of a few 100 MHz with heterodyne receivers. Winds, temperature profiles, and abundances of $H_2O$, $CO$, $SO$, $SO_2$, etc., can be mapped above the clouds on Venus as on Mars.

Titan is an object of great fascination and is of central importance in planetol-
The atmosphere’s basic constituent is molecular nitrogen like that of the Earth. However, the atmosphere is so cold none of the HO\textsubscript{x} and O\textsubscript{x} trace species found on Earth can remain as gases. The surface temperature is about 94 K with an adiabatic lapse to a cold trap at an altitude of 45 km of about 70 K. Above that, the atmosphere warms to about 160 to 180 K and remains essentially isothermal to hundreds of kilometers. The surface pressure is about 1.4 bars such that the atmosphere is very massive compared to Earth’s. The high surface pressure causes large pressure broadening relative to the bandwidths of currently available spectrometers and molecular spectroscopy is limited to altitudes above the cold trap. The Voyager spacecraft has detected many hydrocarbons and nitriles, methane, and carbon dioxide, all in the warmer layers of the atmosphere. For example, HCN and HC\textsubscript{3}N are found above the cold trap, but thermodynamical arguments show...
that these species must rain or snow out below the cold trap and fall to the surface. It is nearly certain that the basic structure of the surface is water ice, but other ices of CO₂, NH₃, etc., may be present and the hydrocarbons probably exist in liquid form such as ethane and methane—see Lunine et al. [27] for a recent review.

Because the lower atmosphere is opaque at visible and IR wavelengths and the major continuum absorber is N₂, the lower atmosphere and surface is best studied in the microwave range. Carbon monoxide has been detected as a trace species of the Titan atmosphere from the Earth, as shown in Figure 9.2(a). It offers an excellent trace gas to sound the atmosphere for temperature–pressure profiles and to measure the winds. Limb weighting functions for the CO (1–2) line and the N₂ continuum near 1.7 mm are shown in Figure 9.18. It can be seen that the entire atmosphere up to 600 km can be sounded with this technique. A careful analysis of the inversion of synthetic spectra corresponding to these weighting functions shows that the retrieved temperature profile over this altitude range would be accurate to the stability of the measurements, that is, ~2 to 3 K. Titan is an excellent example where the millimeter spectroscopy has clear advantages over the IR spectroscopy. Most of the visual opacity is caused by hydrocarbon aerosol layers, which may cause serious correction and interpretation problems for IR spectroscopy, depending on the particle size. The satellite is surrounded by a warm stratosphere over a cold troposphere. IR weighting functions, which depend on a higher power of temperature, contain significant weighting contributions from the stratosphere that make tropospheric sounding difficult. Finally, whereas strict local thermodynamical equilibrium holds for the populations of the lower rotational states of CO, important non-LTE effects obtain above about 200 km at IR wavelengths.

The techniques of submillimeter and millimeter spectroscopy will form the

![Figure 9.18](image-url)

**Figure 9.18.** Weighting functions for limb sounding on Titan for the CO (1–2) are indicated by the dashed lines and for the molecular nitrogen continuum by the solid lines. The functions were computed for optimum frequencies from the CO line center and are indicated on the figure. The CO lines are optically thick in limb sounding below the Titan cold trap near 50-km altitude, but the lower atmosphere can be sounded longward of 1.7 mm in the N₂ continuum.
future of planetary exploration by spacecraft. Strides in instrumental reliability and acceptability by the scientific community should occur for the next generation of deep-space missions. Microwave heterodyne techniques will be very important for the most obvious targets such as Mars, Venus, and Titan. They will offer unique capabilities for the study of incredibly thin atmospheres, such as those on Io, Triton, and Pluto, and the transient "atmospheres" of comets where the lines are only Doppler broadened and are as narrow as a few kilohertz. It is likely that the technology (and confidence) will come from Earth-orbiting instruments built to study the Earth and for astrophysical problems. A second edition of this chapter written after a couple of decades will be far more interesting.

REFERENCES

REFERENCES


PROPERTIES OF THE DEEP ATMOSPHERES OF THE PLANETS FROM RADIOASTRONOMICAL OBSERVATIONS

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10.1 INTRODUCTION

Our knowledge of the composition and physical properties of planetary atmospheres is important for the understanding of the origin and evolution of the planets themselves, as well as for providing a comparative basis for understanding the Earth’s atmosphere. The physical conditions of planetary atmospheres vary widely from place to place within a given atmosphere and from planet to planet. Consequently, a variety of experimental techniques is required to explore the atmospheres fully. Remote sensing using microwave techniques has been particularly productive in exploring the deep atmospheres of the giant planets, Jupiter, Saturn, Uranus, and Neptune, as well as our nearest neighboring planet, Venus, whose atmospheric pressure at its surface is nearly 100 times that of the Earth’s. We refer in this chapter to the planets Venus, Jupiter, Saturn, Uranus, and Neptune as the deep atmosphere planets.

The deep atmosphere planets are continuously or nearly continuously shrouded by thick cloud layers that obscure all but their upper atmospheres from external viewing at infrared and optical wavelengths. Remote sensing of these atmospheres using infrared and optical wavelengths is limited by gaseous absorption and scat-
tering to pressures less than a few atmospheres. Radio measurements carried out from ground-based observatories have provided the first, and with the exception of Venus, the only measurements of the deep atmosphere properties of these planets. In the case of Venus, its deep atmosphere was first sensed remotely using radio techniques and later measured directly by in situ atmospheric probes. The history of the high-temperature atmosphere measurements of Venus by microwaves and the subsequent confirmation by spacecraft are well-documented and discussed later in this chapter.

The general problem of the recovery of temperature, pressure, and composition (altitude) profiles in a planetary atmosphere from measurements of its outgoing radiation has been discussed extensively [1-5]. A principal result of these studies is the conclusion that solutions are not unique; there are a variety of temperature-pressure-altitude profiles and absorbing gas profiles that will satisfy a finite set of observed radiances within the experimental errors. The general solution to the problem, sometimes referred to as the inverse solution of the radiative transfer equation, will not be discussed in detail in this chapter. Rather, it is our aim to discuss the current status of the radio observations of the deep atmosphere planets and to discuss specific inverse solutions that satisfy the observational data and place constraints on the deep atmosphere models.

Clearly, in situ measurements carried out by entry probes will ultimately be required to unambiguously determine temperature structure and composition. Nevertheless, microwave remote sensing has important roles to play in the exploration of the deep atmosphere planets. For those planets not yet explored with probes, microwave remote sensing provides important engineering and scientific data for spacecraft engineering and instrument design. For those planets already explored with probes (only Venus at the present time), remote microwave sensing is necessary to extend the in situ measurements to the entire planet. Still another use of microwave remote sensing arises when the atmosphere is variable. Atmospheric variability cannot be studied conveniently with in situ probes, but can be monitored using remote techniques.

The physical characteristics of the deep atmosphere planets are given in Tables 10.1-10.3. The last column in the Table 10.1 gives the ranges of the angular diameters of the planets as seen from Earth. It can be noted that all of the planets in the table, with the exception of Venus, have a maximum angular diameter of

<table>
<thead>
<tr>
<th>Table 10.1</th>
<th>Properties of Deep Atmosphere Planets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planet</td>
<td>Mean Distance (AU)</td>
</tr>
<tr>
<td>Venus</td>
<td>0.723</td>
</tr>
<tr>
<td>Jupiter</td>
<td>5.203</td>
</tr>
<tr>
<td>Saturn</td>
<td>9.523</td>
</tr>
<tr>
<td>Uranus</td>
<td>19.164</td>
</tr>
<tr>
<td>Neptune</td>
<td>29.987</td>
</tr>
</tbody>
</table>
### Table 10.2 Composition of the Venus Lower Atmosphere

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Altitude (km)</th>
<th>Mixing Ratio</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>0–60</td>
<td>96 ± 2 %</td>
<td>LNMS</td>
</tr>
<tr>
<td>N₂</td>
<td>0–60</td>
<td>4 ± 2 %</td>
<td>LNMS</td>
</tr>
<tr>
<td>He</td>
<td>&gt;130</td>
<td>12 ±24/−6 ppm</td>
<td>BNMS</td>
</tr>
<tr>
<td>Ne</td>
<td>2–23</td>
<td>4.3 ± 0.7 ppm</td>
<td>LGC</td>
</tr>
<tr>
<td>Ar</td>
<td>2–23</td>
<td>67.2 ± 2.3 ppm</td>
<td>LGC</td>
</tr>
<tr>
<td>Kr</td>
<td>2–23</td>
<td>0.4 ± 0.2 ppm</td>
<td>VNMS</td>
</tr>
<tr>
<td>O₂</td>
<td>52</td>
<td>43 ± 25 ppm</td>
<td>LGC</td>
</tr>
<tr>
<td></td>
<td>42</td>
<td>16 ± 8 ppm</td>
<td>LGC</td>
</tr>
<tr>
<td>SO₂</td>
<td>70</td>
<td>0.1 ppm</td>
<td>OUVS</td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>10 ppm</td>
<td>LNMS</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>185 ± 43 ppm</td>
<td>LGC</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>130 ± 35 ppm</td>
<td>VGC</td>
</tr>
<tr>
<td>H₂O</td>
<td>0–42</td>
<td>&lt;100 ppm</td>
<td>VGC</td>
</tr>
<tr>
<td></td>
<td>52</td>
<td>200 ppm</td>
<td>VSP</td>
</tr>
<tr>
<td></td>
<td>22</td>
<td>60 ppm</td>
<td>VSP</td>
</tr>
</tbody>
</table>


### Table 10.3 Composition of the Major Planet Atmospheres

<table>
<thead>
<tr>
<th></th>
<th>Jupiter</th>
<th>Saturn</th>
<th>Uranus</th>
<th>Neptune</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>0.88 ± 0.036</td>
<td>0.963 ± 0.024</td>
<td>0.85</td>
<td>0.85</td>
</tr>
<tr>
<td>He</td>
<td>0.136 ± 0.04</td>
<td>0.034 ± 0.028</td>
<td>0.18 ± 0.07</td>
<td>0.15</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.002</td>
<td>0.0045</td>
<td>0.02 – 0.046</td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>1.78E − 4</td>
<td>(0.5 − 2.)E − 4</td>
<td>Less than solar</td>
<td>Less than solar</td>
</tr>
<tr>
<td>H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

less than 1 arc minute. For Venus, the maximum angular diameter is only slightly larger than 1 arc minute, and this occurs at closest approach when Venus is in conjunction with the Sun and difficult to observe.

#### 10.2 BASIC CONCEPTS

##### 10.2.1 Disk Temperature and Weighting Functions

The power per unit bandwidth delivered to a radio receiver from a planet can be obtained from Eq. 1.28 for the antenna temperature:

$$T_A = \frac{1}{4\pi} \int \int T_P(\theta, \phi, \nu) G(\theta, \phi, \nu) \sin \theta \ d\theta \ d\phi$$

(10.1)
where \( T_p \) is the frequency-dependent brightness temperature of the planet across its disk and is weighted by the directive gain \( G \) over \( 4\pi \) steradians.

The angular diameters of the planets are smaller than the beamwidths of most existing single-aperture radio telescopes used to observe them. Consequently, most (single-aperture) radio-astronomical observations of the planets are of the total radiated power emitted in the direction of the Earth by the entire planet in some spectral interval. When the planet is unresolved by the main beam of the telescope, the received power, expressed as an antenna temperature, is given by the approximate expression

\[
T_a = T_p \left(1 - e^{-\ln 2(D/HPBW)^2}\right)
\]  

(10.2)

where \( D \) is the planetary diameter, \( HPBW \) is the antenna beamwidth at half power, and \( T_p \) is the average planetary-disk brightness temperature. When the exponential term in Eq. 10.2 is close to unity, the expression can be further simplified to give

\[
T_a \approx \frac{\Omega_p}{\Omega_a} T_p
\]  

(10.3)

where \( \Omega_p \) is the solid angle of the planet, and \( \Omega_a = \lambda^2 / A_e \), see Eq. 1.31) is the beam solid angle of the telescope. Because the planetary solid angle and the beam solid angle are known approximately, a measurement of the antenna temperature can be used to estimate the disk-average brightness temperature using Eq. 10.2 or Eq. 10.3. This average temperature can be defined as the disk temperature:

\[
T_D = \frac{1}{\Omega_p} \int \frac{T_b(\theta, \phi)}{d\Omega}
\]  

(10.4)

where \( \Omega_p \) is not intrinsically well-defined because the atmosphere does not have a sharp edge. However, by convention, it is usually taken as that of an ellipsoid with polar and equatorial semidiameters given by the American Ephemeris and Nautical Almanac and adjusted for the tilt of its polar axis as viewed from the Earth, and the integral over \( T_b \) is not constrained by this otherwise arbitrary assumption.

The central problem of remote sensing is to convert the measured values of the antenna temperature as a function of wavelength into estimates of atmospheric parameters with the smallest possible errors. The equation of radiative transfer gives the mathematical description that relates the brightness temperature to the atmospheric composition and temperature along the line of site. Neglecting scattering and variations in the index of refraction, the radiative transfer equation, Eq. 1.13 can be written as

\[
T_b(\mu, \nu) = \int_0^\infty T(z) \alpha(\nu, z) \exp \left[ -\int_0^\infty \alpha(\nu, z) \frac{dz}{\mu} \right] \frac{dz}{\mu}
\]  

(10.5)
where $\mu = \cos \theta$, and $\theta$ is the angle between the local vertical and the direction of the emission. Equation 10.5 can be rewritten as

$$T_b(\mu, \nu) = \int_0^\infty T(z) W(\mu, \nu, z) \, dz / \mu \quad (10.6)$$

where $W$, defined as

$$W(z, \mu, \nu) = \alpha(\nu, z) \exp \left[ -\int_z^\infty \alpha(\nu, z) \, dz / \mu \right] / \mu \quad (10.7)$$

can be thought of as a weighting function for the model. Figure 10.1 shows a weighting function at 2 cm (long dash) and 6 cm (dot) superimposed on a model atmosphere of Saturn. The 2-cm weighting function is seen to be sharply peaked near 1-bar pressure. The 6-cm weighting function peaks near 2 bars and is considerably wider than the weighting function at 2 cm.

In practice, Eq. 10.5 (or Eq. 10.6) is evaluated by assuming that the atmosphere of a planet can be approximated by many thin, horizontal layers. The layer thick-
ness is assumed to be sufficiently thin such that the temperature, pressure, and composition are essentially constant in each layer, and have an opacity much less than unity. As a consequence, each layer can be characterized at a specified frequency with a single temperature and opacity. This approximation is sometimes called the "thin-layer approximation." Equation 10.6, written as a discrete sum, expresses the mathematical representation of the thin-layer approximation:

\[
T_B(\mu, \nu) = \sum_{z_0}^{z_1} T(z) W(\mu, \nu) \Delta z + T(z_0) e^{-\tau(z_0)}
\]  

(10.8)

In this expression, the summation runs from the surface (in the case of Venus) or from a depth where the atmospheric opacity is very large (\(>> 1\)) up to a sufficiently high level \(z_1\) that the atmospheric layers no longer contribute significantly to the summation. This level varies with frequency and emission angle. The last term in Eq. 10.8 accounts for emission either from a surface or from levels deeper than \(z_0\), attenuated by the overlying atmosphere. The coefficient of the exponential term is the total opacity of the atmosphere from \(z_0\) to \(z_1\) defined as follows:

\[
\tau(z_0) = \int_{z_0}^{z_1} \alpha(\nu, z) \, dz / \mu
\]

(10.9)

The value of microwave remote sensing is greatly enhanced if the brightness distribution across the disk can be measured. High-quality radio images have already been obtained for Venus, Jupiter, and Saturn using the technique of radio interferometry. Somewhat lower resolution but useful images of Uranus and Neptune have also been obtained. Such measurements allow one to measure spatial variations of composition and temperature, and to study the variations of brightness with emission angle, especially near the limb of the planet. The rapidly changing path length through the atmosphere near the limb provides a sensitive technique for studying the temperature and compositional structure. The brightness drops off sharply near the limb for an atmosphere whose temperature decreases with increasing altitude. This so-called limb darkening has been widely used to study the atmospheres of Venus and the giant planets [6].

If the measurements have insufficient resolution to determine the distribution across the planetary disk, then the mean-disk brightness temperature can be calculated from Eq. 10.4 and compared directly with the observations. Alternatively, the following equation

\[
T(\nu) = 2 \int_{0}^{1} T_B(\nu, \mu) \, d\mu
\]

(10.10)

is sometimes used if it can be assumed that the planet is spherical and has a brightness temperature (at a specified frequency) that depends solely on the emission angle. In reality, neither of these assumptions is strictly valid.
10.2.2 Model Atmospheres

The solution to Eq. 10.5 requires a knowledge of (1) the atmospheric temperature as a function of depth, (2) the absorption coefficient of the atmosphere as a function of frequency and depth, and (3) the emission angle \( \theta \) \((\mu = \cos \theta)\) at every point in the atmosphere. Of these three parameters, the emission angle is the easiest to estimate. By neglecting winds, the normal to each layer in the model is assumed to coalign itself with the direction of the acceleration of gravity at every point. Because the planets are axially symmetric but not perfect spheres, the direction of the acceleration of gravity varies with latitude, thereby causing the quantity \( \mu \) to vary in a complicated, but predictable, fashion. The variation in the acceleration of gravity with latitude due to the oblateness of a planet is given to first order by Hubbard and Marley [7]. DePater and Massie [8] discuss the calculation of \( \mu \) for an oblate spheroid. As an example, they show that the theoretical brightness temperature of Saturn at a wavelength of 20 cm is 14% larger for an oblate spheroid model than for a spherical model, assuming the same atmospheric composition. At 6.0 cm and 1.0 cm, the percentage increases are 7% and 3%, respectively.

The general procedure used to solve Eq. 10.8 is to ascribe a composition, pressure, and temperature to each layer in the model. Once defined, an absorption coefficient is calculated for each layer, and the brightness temperature is calculated by performing the summation over each layer and over the appropriate range of emission angles. The calculated brightness temperatures are then compared directly with the observed brightness temperatures. It is usually possible to bring the calculated values into agreement with the observed values by varying the model parameters in each layer.

Each layer in the model atmosphere is assumed to be homogeneous and in hydrostatic equilibrium. The lower troposphere is assumed to be in convective equilibrium, whereas the upper-atmosphere thermal distribution is determined from (a) theoretical considerations of the thermal structure, (b) in situ and spacecraft occultation data, or (c) remote-sounding IR and optical data.

In the convective region beneath the clouds, the dry-temperature lapse rate \( dT/dz \) is determined by the local gravity \( g \) and the specific heat \( c_p \) of the atmosphere through the relation

\[
\frac{dT}{dz} = -\frac{g}{c_p}
\]  

Both \( g \) and \( c_p \) may vary in general. The average dry adiabatic lapse rates relevant for the midlatitudes of Venus, Jupiter, Saturn, Uranus, and Neptune are, respectively, 10.1, 1.91, 0.8, 0.7, and 0.85 K km\(^{-1}\). Despite its lower gravity, the lapse rate for Venus is considerably larger (absolute value) than those of the other deep atmosphere planets. The larger lapse rate is due primarily to the low specific heat of CO\(_2\), the primary atmospheric constituent of Venus. For the other deep atmosphere planets, H\(_2\) is the primary atmospheric constituent and its specific heat is approximately 15 times larger than that of CO\(_2\).
In the region of cloud formation, the latent heat of condensation changes the local lapse rate from a dry adiabat to a wet adiabat. The wet adiabatic lapse rates for Jupiter, Saturn, Uranus, and Neptune have been discussed by Weidenschilling and Lewis [9] and Atreya and Romani [10].

10.3 VENUS

The planet Venus has an atmosphere that is two orders of magnitude more dense at its surface than that of the Earth. Illustrated in Figure 10.2, this massive atmosphere has a broken cloud layer at a relatively high altitude (0.1–1 bar) that is impervious at optical and infrared frequencies, and is therefore a prime candidate for microwave remote sensing. Indeed, the first evidence for the existence of this atmosphere was obtained in 1958 when the microwave emission from Venus was

Figure 10.2. The atmosphere of Venus. A solid deck of H$_2$SO$_4$ clouds extends from 50–70-km altitude and prevents the observation of the lower atmosphere at infrared and optical wavelengths. The pressure, temperature, and composition of the lower atmosphere have been determined from spacecraft radio occultations and from several descent probes.
measured for the first time [11], giving the unexpectedly high disk brightness temperature of 600 K at a wavelength near 3 cm. This discovery and its implications brought the attention of the rapidly developing science of radio astronomy to the problem, and by 1964, a disk temperature spectrum was established through most of the microwave region. A recent version of this spectrum is given in Figure 10.3 [12]. The spectrum is characterized by a gradual increase in disk brightness temperature from about 300 K at millimeter wavelengths to a maximum near 700 K in the centimeter region, followed by decreasing temperatures at longer wavelengths.

Barrett offered an early interpretation of the spectrum as thermal emission from a deep, near-adiabatic atmosphere with a source of absorption, which increases with frequency [13]. This interpretation is now well substantiated by abundant microwave, radar, and spacecraft measurements. In particular, the mean pressure and temperature profiles are now established from several descent probes launched from spacecraft [14]. The bulk composition has also been determined in situ by descent probes, as shown in Table 10.2 [15], although there is still considerable uncertainty in the concentration and vertical distribution of several of the minor constituents. The bulk constituent CO$_2$ is known to be a major contributor to the microwave opacity. This nonpolar gas possesses a nonresonant pressure-induced absorption with a frequency-squared pressure dependence that extends into the submillimeter region (see the discussion in Section 2.5 of Chapter 2). The absorption due to this source was measured in the laboratory by Ho, Kaufman, and Thaddeus [16] for a range of pressures and temperatures relevant to the Venus atmosphere, and gave a basis for subsequent analysis of the Venus microwave emission.

Additional opacity is expected from SO$_2$, H$_2$O, sulfuric acid clouds, and pos-

![Venus Microwave Spectrum](image-url)
sibly from other trace constituents such as H$_2$SO$_4$ vapor, which is anticipated to be present but that has not been specifically detected [17–19]. The high pressures of the lower atmosphere tend to broaden the absorption by all molecules into a nonresonant spectrum similar to that of CO$_2$, as illustrated by the spectrum of SO$_2$ versus pressure in Figure 10.4. H$_2$O [20] and possibly H$_2$SO$_4$ [21] retain distinct spectral features in the roughly 1–10-bar region just beneath the clouds, however.

The major success of the radioastronomical investigation of Venus was the detection of the existence of the hot, lower atmosphere. Once the various possibilities for the nonthermal origin of the high disk temperatures were discounted on the basis of other evidence, this result followed directly from the comparison of the disk temperatures with the cloud top pressure and 240 K temperature from infrared observations. Subsequent attempts to interpret the disk temperature spectrum in terms of the details of atmospheric composition and structure were largely fruitless, however. The difficulty arises because it is possible to construct a variety of atmospheric models that produce the same overall disk temperature spectrum when both the source of the absorption and the pressure–temperature structure are unknown, as is apparent from the radiative transfer equation. Boundary conditions on the composition, pressure and temperature in the vicinity of the cloud tops were used to narrow down the choices [16, 22]. Unfortunately, the interpretation of the infrared data to give these boundary conditions was also ambiguous because of the difficulty of treating the cloud scattering problem, and the then prevalent interpre-

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**Figure 10.4.** Pressure-broadened spectrum of SO$_2$ at pressures and temperatures representative of the Venus atmosphere. The assumed concentration of SO$_2$ is 180 ppm.
arnation of the CO₂ infrared lines as formed in a highly multiply-scattering atmosphere with a low CO₂ mixing ratio led to deep atmosphere models that tended to be well wide of the mark.

The Mariner V and Venera 4 spacecraft reached Venus on consecutive days in October 1967. The results from these historic missions relieved the microwave data from the burden of having to determine too much about the atmosphere. These and subsequent spacecraft missions have provided a different focus for the retrieval problem: with the physical structure of the atmosphere and the concentration of a major source of the opacity now known, the microwave disk temperature spectrum can be unambiguously computed with the assumption that there is no additional source of opacity; consequently, the magnitude of the additional absorption that might be present can be determined by comparison of this spectrum with the observational data. This approach was used following the 1967 spacecraft missions to call into question the Venera 4 detection of significant amounts of water vapor (0.5–2.5%) [20], and has been used more recently to bound the rather loose limits on the microwave-absorbing gas SO₂ detected by the Pioneer Venus probes [21].

The general procedure that has been used to infer atmospheric properties from the microwave data has been to fit the parameters of a detailed atmospheric model by direct comparison of computed observables with the data. The required computational model is more complicated for Venus than for the giant planets because (1) surface emission and downward-propagating atmospheric emission that is reflected from the surface must be considered, (2) refraction is significant at the high densities of the lower atmosphere, and (3) the atmosphere is not thin with respect to the planetary radius. These details are particularly important when interferometric data that depend on limb darkening are interpreted.

The observational data to which such a model has been applied include disk temperature measurements, interferometric data containing information on limb darkening, cloud-region absorption measured during spacecraft radio occultations, and radar reflectivity data. A simultaneous least-squares fit of all such data to a single model was carried out by Muhleman et al. [12]. The data are shown in Figures 10.5 through 10.7 and include the respective spectra computed for the best-fitting model. The principal atmospheric unknown that was determined in the fitting procedure was a constant factor G, which multiplies the CO₂ absorption coefficient at all altitudes. Surface quantities were also determined such as the dielectric constant, radar directivity, and the mean surface level.

The measured first zero crossing of the visibility function β₁ in Figure 10.5 shows a significant variation as the wavelength varies through the range where the total atmospheric opacity changes from <<1 to >>1. The quantity β₁ is the ratio of the disk radius to the interferometer fringe spacing at which the interferometer signal disappears. If the disk is uniformly bright, then it can be shown that β₁ is the first zero of the Bessel function J₁(2πβ₁), or β₁ ≈ 0.610. Limb darkening on the disk will increase this value. The fringe spacing at which the interferometric signal disappears is a null measurement, making it possible to measure β₁ with high accuracy. The moderate limb darkening seen in the figure at long wavelengths is expected due to emission from a dielectric surface at a uniform temperature,
whereas the stronger limb darkening at short wavelengths is caused by emission from an atmosphere with a negative-temperature lapse rate. The tendency to limb brightening seen at intermediate wavelengths is because the surface, seen toward the center of the disk, has a lower emissivity than the atmosphere that dominates toward the limbs (this also explains, in part, the decrease in disk temperature seen at longer wavelengths in Figure 10.3).

The data in Figure 10.5 represent measurements of circularly polarized radiation. If thermal emission from a dielectric sphere is observed in linear polarization,
however, then the apparent brightness is strongly asymmetric because of the dependence of emissivity on both incidence angle and polarization. Hence, the result depends strongly on the orientation of the received polarization with respect to the interferometer fringes when $\beta_1$ is measured. Figure 10.6 shows the measured difference between zero crossings when the polarization is perpendicular and parallel respectively to the fringe pattern, and clearly demonstrates the transition from atmospheric to surface emission as the wavelength increases. Finally, the wavelength dependence of the signal from Earth-based radar transmitters reflected from Venus also shows a sharp decrease as the atmospheric opacity becomes significant (Figure 10.7).

The best-fitting value for the absorption coefficient multiplier $G$ was $1.83 \pm 0.22$, and the principal conclusion was that a source of opacity is present in the atmosphere in addition to that provided by CO$_2$. The source of this additional opacity is not known, although the highly absorbing constituents, SO$_2$ and H$_2$O, as well as the sulfuric acid clouds are capable of providing more than enough opacity to explain this excess. Muhleman et al. [12] note that the determination is insensitive to the vertical distribution of the opacity, and that only the total opacity of the atmosphere is well-constrained. Information on the vertical distribution of opacity is contained in the disk temperature spectrum in the 1–3-cm wavelength range, but the apparent 20% scatter of supposedly well-calibrated measurements in this region has made the task of interpretation difficult. Also, the frequency dependence of the absorption may deviate in an unknown way from a square law, particularly at the upper altitudes. Janssen and Klein [23] have attempted to obtain a careful absolute disk temperature determination from observations made near 1-cm wavelength in order to set a tighter limit on the excess opacity in the region of the atmosphere above about 30 bars. They find a value for $G$ that is somewhat less than that of Muhleman et al., which implies that the excess opacity is concentrated toward the surface. This contradicts the spacecraft results, however, that indicate that the concentrations of potential contributors are larger at higher altitudes. The issue remains unresolved.
CHAPTER 10: DEEP ATMOSPHERES OF PLANETS

10.4 THE GIANT PLANETS

10.4.1 Introduction

The atmospheres of the giant planets constitute a significant fraction of their total mass, in contrast with the atmospheres of other planets in the solar system. The mean density and sizes of Jupiter and Saturn imply that these two planets are composed primarily of hydrogen and helium with only trace amounts of heavier elements. Uranus and Neptune are believed to contain a slightly higher percentage of heavier elements. It is believed that the giant-planet atmospheres are composed primarily of the primordial material from which the solar system was formed, a point noted by Wildt as early as 1934 [24, 25]. This situation is in contrast to the atmospheres of the terrestrial planets, which have undergone extensive evolution in the 4.5 billion years since planetary formation. Table 10.3 gives estimates of the atmospheric composition of the giant planets based on observational data.

As in the case of Venus, the giant planets all contain complex cloud structures that limit the remote-sensing possibilities in the infrared and optical. Microwave remote sensing has provided the first quantitative measures of the atmospheres in and beneath the clouds. Figures 10.8 through 10.11, taken from dePater [26] and dePater and Massie [8], show the observed disk microwave spectra for Jupiter, Saturn, Uranus, and Neptune. A component of synchrotron radiation has been

![Figure 10.8. The spectrum of Jupiter with superimposed model calculations. The dashed curve is for a solar-composition model atmosphere. The solid curve is based on an ammonia abundance as follows: $3 \times 10^{-5}$ at $P < 1$ bar, $2.5 \times 10^{-4}$ at $P > 2$ bars, subsaturated at $P \leq 0.6$ bar. The figure is taken from dePater [26].]
Figure 10.9. The spectrum of Saturn with superimposed model calculations. The figure is taken from dePater and Massie [8].

Figure 10.10. The spectrum of Uranus with superimposed model calculations. The figure is taken from dePater and Massie [8].
subtracted from the total observed emission from Jupiter at wavelengths $\geq 1.5$ cm, leaving the thermal emission from the atmosphere. Berge and Gulkis [27] discuss the various techniques that allow this separation to be performed. The data for Saturn are corrected for the contribution of Saturn’s rings according to the model by Klein et al. [28]. The data for Uranus and Neptune have not been altered.)

The disk temperature spectra for these four planets are quite similar, although the data for Uranus and Neptune show considerably more scatter than those for Jupiter and Saturn. (The scatter is partly due to the lower signal-to-noise ratio of the measurements, and for Uranus to an intrinsic variability.) The principal features of the spectra are (1) a rise in the disk brightness temperatures at wavelengths greater than a few centimeters (eventually reaching temperatures in excess of 300 K at the longest wavelengths for Jupiter and Saturn) and (2) disk brightness temperatures of $\sim 140$ K that occur near 1.5 cm. The spectra for Jupiter and Saturn show slightly warmer temperatures at millimeter wavelengths, whereas Uranus and Neptune temperatures are colder. The increasing temperature with increasing wavelength suggests that the longer wavelength radio emission originates from levels in the atmosphere below the clouds, which are warmer and denser.

In situ probes have not yet penetrated the atmospheres of the giant planets, making it necessary to calculate the thermal profile according to theoretical models. By neglecting the potential effects of dynamics on the cloud structure, the temperature profiles can be calculated using either dry or wet adiabatic lapse rates,
depending on whether the partial pressure of a constituent is less than or greater than its saturated vapor pressure. It is necessary to use the wet adiabatic lapse rate \[ [29] \] where the partial pressure of a constituent exceeds its vapor saturation pressure. On Jupiter, for example, clouds containing ammonia ice, ammonium hydro­
sulfide crystals, and water ice are expected to form. In addition to these, aqueous ammonia (NH\(_3\) and H\(_2\)O mixture) is likely to form on Saturn, Uranus, and Neptune. Clouds of methane ice are also likely on Uranus and Neptune. Weidenschilling and Lewis [9] and Atreya and Romani [10] have discussed the cloud structures on the giant planets. Figure 10.12 shows theoretical cloud masses and calculated lapse rates for clouds on Jupiter. Similar calculations have been carried out for Saturn, Uranus, and Neptune as well.

Theoretical temperature–pressure profiles have thus far formed the primary ba­
sis for interpreting the microwave data, leaving the opacity profile as a free param­
eter to be matched by solving Eq. 10.5 and comparing the result with the observa­tional data. The combined absorption due to the gases and the scattering that takes place within the clouds determines the outgoing radiance of these planets. The polarizable gases, ammonia and water vapor, and collision-induced absorption by hydrogen and helium are believed to be the most important sources of opacity in the giant planet atmospheres. Absorption due to gaseous ammonia, even though present as a minor constituent, dominates the long-wavelength spectra of the giant planets because of its large microwave opacity. Collision-induced absorption of hydrogen and helium dominates the short-wavelength spectra of Uranus and Neptune. Many other gases, either known or suspected to be present in the atmospheres, have strong rotational absorption lines (e.g., H\(_2\)S, PH\(_3\), CO, and HCN) that might influence the millimeter and submillimeter spectra, but their contribu­tion to the opacity is uncertain at this time. Scattering by cloud particles such as ammonia crystals or water droplets may also influence the spectra, especially at short wavelengths.

\[ \text{Figure 10.12. A model of the low-latitude cloud structure at Jupiter. Altitudes shown are relative to the 1-bar pressure level. Solar elemental abundance ratios are assumed for He, N, S, and C. The figure is taken from Atreya [29].} \]
Because of its dominant role in the interpretation of the giant-planet spectra, the absorptivity of gaseous ammonia under the conditions found in these atmospheres has received considerable attention over the last two decades [7, 30]. Currently, there is no agreed-upon single model of the absorption coefficient that fits the laboratory data over the full range of conditions found in the giant-planet atmospheres. Recent laboratory data taken by Spilker [30] suggest that the derived mixing ratios of ammonia in the giant-planet atmospheres may need to be increased by a few percent to as much as 50% as a result of inaccuracies in our current model of the absorption coefficient. The problem is complicated by the large pressure range over which the absorption takes place, and by the foreign-gas collisional broadening of hydrogen and helium that dominates the pressure broadening. The microwave spectrum of pure ammonia arises from a class of transitions known as “inversion” transitions, as discussed in Chapter 2. In the ammonia molecule, these are produced by the periodic transversal (inversions) of the nitrogen atom through the plane formed by the three hydrogen atoms. The inversion frequencies range from approximately 16 to 40 GHz with the strongest absorption occurring near 24 GHz. At low pressures (< ~1.6 atm in Jupiter’s atmosphere), the spectrum consists of a series of individual lines with line shapes well represented by the Van Vleck–Weisskopf line-shape factor. At higher pressures, the individual lines are pressure broadened so that individual lines overlap, thereby forming a broad continuous absorption feature centered near 24 GHz.

Townes and Schawlow [31] have given a good discussion of the classical theory of absorption of ammonia. Ben-Reuven [32] presented a quantum-mechanical formulation of the problem that greatly improved the agreement between experiment and theory, especially at high pressures. Gulkis and Poynter [33] (details reported in Berge and Gulkis [27]) compared the Ben-Reuven theoretical absorption coefficients with the laboratory absorption coefficient data of Morris and Parsons [34], and derived an empirical correction factor. The ammonia absorption coefficient used by Gulkis and Poynter [33] has been the most widely used absorption coefficient despite its shortcomings. Spilker [30] shows that errors exist in the temperature, pressure, and frequency dependencies, and that the dependences of line widths on pressure are not linear as generally assumed. Much work needs to be done to understand the absorption coefficient of ammonia. The absorption coefficient derived by Gulkis and Poynter [33] is given by

\[
a(\nu) = C \sum_{J=0}^{\infty} \sum_{K=1}^{\infty} A(J, K) F(J, K, \gamma, \delta, \xi, \nu) \text{ cm}^{-1} \tag{10.12}
\]

where \(C = 1.0075 + (0.0308 + 0.0552 P_{\text{H}_2}/T) P_{\text{H}_2}/T\) is an empirical correction factor derived from fitting the theoretical absorption coefficient to the data of Morris and Parsons [34]. The factor \(A(J, K)\) gives the line strength for the \((J, K)\) transition and \(F(J, K, \gamma, \delta, \xi, \nu)\) is the Ben-Reuven frequency-dependent line-shape factor derived in Chapter 2 (Equation 2.65):

\[
A(J, K) = (1.23 \times 10^3) \frac{(2J + 1) K^2 \nu_0^2(J, K) P_{\text{NH}_3}}{J(J + 1) \gamma T^{7/2}} \times \exp - \{[2.98 J(J + 1) - 1.09 K^2]/4.8/T\} \tag{10.13}
\]
and

\[ F(J, K, \gamma, \delta, \xi, \nu) = 2.0\gamma \frac{\nu^2}{\nu_0^2} (\gamma - \xi) \nu^2 + (\gamma + \xi)(\nu_0^2 + \delta^2 + \gamma^2 - \xi^2) \frac{\nu^2}{\nu^2 - (\nu_0^2 + \delta^2 - \gamma^2 + \xi^2)^2 + 4.0\nu^2\gamma^2} \]  

(10.14)

The center frequency for the \((J, K)\) transition \(\nu_0(J, K)\) is taken from the tabulation of measured frequencies given in Poynter and Kakar [35]. The pressure-broadened line widths are given by

\[ \gamma(J, K) = 2.318 \left( \frac{300}{T} \right)^{2/3} P_{H_2} + 0.79 \left( \frac{300}{T} \right)^{2/3} P_{He} + 0.75 \left( \frac{300}{T} \right) \gamma_0(J, K) P_{NH_3} \text{GHz} \]  

(10.15)

The coupling element and pressure-shift terms in the Ben-Reuven line-shape factor are given by \(\xi\) and \(\delta\), respectively.

\[ \xi(J, K) = 1.92 P_{H_2} \left( \frac{300}{T} \right)^{2/3} + 0.49 \left( \frac{300}{T} \right) P_{NH_3} \gamma_0(J, K) \]  

\[ + 0.3 \left( \frac{300}{T} \right)^{2/3} P_{He} \text{GHz} \]  

(10.16)

\[ \delta = -0.45 P_{NH_3} \text{GHz} \]  

(10.17)

In these expressions, \(P_x\) is the partial pressure of the species \(x(\text{NH}_3, \text{He}, \text{H}_2)\) in atmospheres, \(T\) is the temperature of the mixture, \(S(K) = 3\) for \(K\) a multiple of 3 and \(S(K) = 1.5\) otherwise, and \(\gamma_0(J, K)\) are the self-broadened line widths in MHz/torr as given by Poynter and Kakar [35]. In addition to the absorption due to the inversion transitions, the ground-state rotational transition of ammonia that occurs at a frequency of 572.5 GHz also contributes to the absorption especially in the submillimeter and millimeter spectral regions.

The water molecule has a somewhat smaller dipole moment than the ammonia molecule, and it produces considerably less absorption. Although present in nearly the same abundance as ammonia deep in the atmosphere, it is depleted in the upper atmosphere because it freezes out at a higher temperature. At a wavelength of 2.5 cm and a pressure of 8.55 atm, Berge and Gulkis estimated that the absorption coefficient is approximately 100 times smaller than that of ammonia. The water-absorption coefficient is composed of two terms [36]: an electric dipole resonance centered near 22.2 GHz, and a strong resonance in the infrared. The skirt of the infrared line dominates the water absorption at high pressures.

Hydrogen, helium, and methane have no permanent dipole moment; however, they have a small absorption coefficient due to a collision-induced dipole moment that varies as the frequency squared. The absorption due to methane is negligible.
The absorption due to hydrogen and helium is significant at millimeter wavelengths, especially in the atmospheres of Uranus and Neptune. This is due to their large abundances above the ammonia clouds.

10.4.2 Jupiter and Saturn

Early work aimed at understanding the brightness-temperature spectra of Jupiter and Saturn [33, 37-39] focused on simple hydrogen–helium model atmospheres containing ammonia as a trace constituent and the only source of microwave opacity. These models were motivated by the observation that the disk brightness temperatures of Jupiter and Saturn near 1-cm wavelength are approximately 140 K, close to the temperature where ammonia freezes and clouds form in the atmospheres of Jupiter and Saturn. Gulkis and Poynter [33] investigated the sensitivity of the brightness temperature to ammonia abundance by assuming a wide range of mixing ratios for ammonia for a different number mixing ratio of He to H₂ ranging from 0 to 0.2 (Figure 10.13). Their simple model predicted a brightness-temperature spectrum that is nearly constant for short centimeter wavelengths, but increases rapidly for longer wavelengths in agreement with the observations. They found good agreement between the observed data and the theoretical spectra with an ammonia mixing ratio of $\approx 1.5 \times 10^{-4}$. Based on solar cosmic abundance ratio data compiled by Cameron [40] and others, the expected ammonia abundance is $1.5 \times 10^{-4}$. These early results gave support to the idea that both Jupiter and Saturn have compositions similar to the primitive solar nebula, and established ammonia gas as the principal source of microwave opacity.

Recently, dePater and Massie [8, 26] investigated the radio-emission spectrum from Jupiter, Saturn, Uranus, and Neptune. For Jupiter, they assume a “solar composition” atmospheric model composed of 89% H₂ and 11% He for the primary constituents, and \( \text{CH}_4/\text{H}_2 = 8.35 \times 10^{-4} \), \( \text{H}_2\text{O}/\text{H}_2 = 1.38.0 \times 10^{-3} \), \( \text{NH}_3/\text{H}_2 = 1.7 \times 10^{-4} \), and \( \text{H}_2\text{S}/\text{H}_2 = 3.76 \times 10^{-5} \) for the minor constituents. A typical temperature-pressure profile is shown in Figure 10.14. The dashed curve

![Figure 10.13. Theoretical brightness-temperature spectra for Saturn showing the sensitivity to the ammonia mixing ratio and the helium to hydrogen mixing ratio. The figure is taken from Gulkis and Poynter [33].](image)
in Figure 10.8 shows the results of a model calculation for the “solar-composition” model. The overall agreement between the simple model and the observations is quite good; however, systematic differences are clearly noticeable. The model is too cold at millimeter wavelengths and somewhat too warm at centimeter wavelengths. The solid curve is for a model atmosphere in which ammonia is depleted by a factor of $\sim 5$ at $P < 1$ bar and is enhanced by a factor of 1.5 at $P > 2$ bars. Ammonia gas is allowed to be subsaturated at $P < 0.6$ bars to provide a better fit to the data in the vicinity of the strong ammonia inversion lines near 1.3 cm. It is not known at this time if the systematic differences are due to our inadequate knowledge of the absorption coefficient of ammonia, horizontal and vertical variations in the distribution of ammonia, additional absorbers, or some other mechanism.

High-resolution radio images of Jupiter and Saturn have been obtained at wavelengths of 2 cm and 6 cm with the VLA [26, 41]. The radio images show a considerable amount of structure across the disks as well as limb darkening. A 2-cm contour brightness image of Jupiter is shown in Figure 10.15. Bright (higher-temperature) horizontal (constant-latitude) bands appear on both planets, suggesting a variation in the ammonia abundance with latitude. On Jupiter, the bright bands correspond with the brown belts seen at visible and IR wavelengths [26]. DePater interprets the brighter regions as regions in which the ammonia abundance is depleted relative to the surrounding regions. Grossman et al. [41] report that their images of Saturn at 2 cm and 6 cm show an increase in brightness temperature of about 3 K from equator to pole at both wavelengths. Their 6-cm map shows a
Figure 10.15. A contour plot of the brightness temperature of Jupiter at a wavelength of 2 cm. Contour values in Kelvin are 1.8, 5, 9, 18, 44, 71, 98, 124, 151, 160, 168, and 174. The figure is taken from dePater [26].

bright band at northern midlatitudes. Model studies carried out by Grossman et al. imply a 25% relative decrease of NH$_3$ in northern midlatitudes, with a global mixing ratio of NH$_3$ equal to $1.2 \times 10^{-4}$ in the region below the NH$_3$ clouds to a level of a few bars.

10.4.3 Uranus and Neptune

Although Uranus and Neptune are similar to Jupiter and Saturn in many respects, they also show important differences. Their atmospheres are significantly colder than those of Jupiter and Saturn. One result of this is that the condensation threshold for methane lies within the atmosphere, making it possible for a methane cloud to form near the 70 K level. Jupiter and Saturn are too warm for a methane cloud to form. Because of the cold atmosphere, the condensation threshold pressure for ammonia clouds is considerably greater for Uranus and Neptune than it is for Jupiter and Saturn. The pressure at which condensation begins ranges from about 1 atmosphere at Jupiter to about 10 atmospheres at Neptune. A consequence of this is that there is considerably more hydrogen and helium above the ammonia cloud layers of Uranus and Neptune than there is on Jupiter and Saturn. At millimeter wavelengths, the dominant source of opacity is the pressure-induced dipole moment of hydrogen. This opacity source plays only a minor role on Jupiter and Saturn.
Unresolved disk brightness-temperature measurements of Uranus and Neptune have revealed the somewhat surprising result that these planets are too warm to be matched by a simple solar-composition model atmosphere [7, 42, 43]. Both planets show the characteristic increase in brightness temperature with increasing wavelength; however, the rate of increase of the temperature with wavelength is much greater at centimeter wavelengths than is predicted by radiative transfer calculations assuming an atmosphere model similar to those that explain the observations of Jupiter and Saturn. Ammonia needs to be depleted by two orders of magnitude or more relative to the solar abundance in order to explain the observations. Gulkis et al. [43] suggested that the depletion might be the result of the formation of a cloud of NH$_4$SH. This requires that the atmosphere have a ratio of S to N that is enhanced relative to the solar abundance value. The depletion of ammonia and the possible explanation in terms of the composition of the planet are of fundamental importance. DePater [26] has discussed a number of model atmospheres that contain enhanced concentrations of H$_2$S and H$_2$O. These species may remove NH$_3$ from the atmosphere and may also be additional sources of opacity. The specific absorbers in the atmosphere are hard to identify by their pressure-broadened spectra.

Another unusual property of the radio emission from Uranus, not yet observed on the other three giant planets, is that the radio emission is variable. Klein and Turegano [44] first discovered this variability in the 2- to 3.6-cm data. Subsequent measurements have shown that this variability extends to longer wavelengths as well. Most recently, Hofstadter [42] has made high-resolution images of Uranus with the VLA at 2 and 6 cm. He finds strong horizontal and vertical gradients in the atmospheric properties. Polar regions are much brighter than lower latitudes, and the deep troposphere appears less bright than would be expected based on the upper troposphere. Hofstadter proposes that the observed brightness temperatures are due to the general circulation and chemical processes in the atmosphere. He proposes that the Southern Hemisphere of Uranus is dominated by a single me-
ridional circulation cell, with an upwelling centered near $-25^\circ$ latitude that brings absorbers up from the 50-bar level to the 0.1-bar level. A schematic of his model is shown in Figure 10.16. While this model has yet to be confirmed, it nevertheless serves to illustrate how remote sensing at radio wavelengths provides important constraints and ideas on the most fundamental properties of the planets.

10.5 CONCLUSION

Microwave remote sensing of the deep atmosphere planets has allowed these planets to be probed beneath the clouds, into regions not yet sensed by remote probes or other remote-sounding techniques. The results to date have provided some answers about the horizontal and vertical profiles of temperature and composition, and they have raised a number of questions about the most fundamental properties of the planets. What was the composition of the original solar nebula? How did it vary with distance from the sun? What are the dominant circulation patterns on the planets and how deep do they extend?

Despite the progress that has been made to date, the field must still be considered to be very young, especially on the experimental side. Future progress in the field is expected to center around (1) improved laboratory measurements and theoretical understanding of the absorption properties of gases under high pressures and with foreign-gas broadening, and (2) additional observations with improved signal-to-noise ratios, better angular resolution, and over longer time intervals. Some of these data will undoubtedly require the use of orbiting spacecraft. From these data, it may be possible to infer additional atmospheric absorbers, and to get a much better understanding of atmospheric circulation, dynamics, and chemistry. Working with the data gathered by remote-sensing experiments at other wavelengths and with orbital and in situ instruments, it is expected that many additional properties of the deep atmosphere planets will be discovered by microwave remote-sensing observations.

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SYNTHETIC APERTURE RADAR
Systems and Signal Processing
John C. Curlander and Robert N. McDonough

Synthetic aperture radar (SAR) is a valuable tool for measuring characteristics of the Earth’s surface and its subsurface. A full understanding of the characteristics of the SAR imagery requires some knowledge of the sensor design, the mission operations, and the ground signal processing. This book specifically addresses these items, as applied to the design and implementation of the space borne SAR system with a strong emphasis on signal processing techniques. It presents a complete picture of SAR from a theoretical perspective by deriving from basic principles the SAR signal processing algorithms. Readers will be provided with some insight into the practical aspects of the sensor and ground system design and implementation. The book also analyzes the system performance given the common error sources and demonstrates their effect on the output image products. Radar engineers and applications scientists will value this single-source guide to the information required both for SAR system design as well as image data analysis.

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