

CHAPTER 9

Absorption by Atmospheric Gases[†]

In the previous chapter, we developed the mathematical tools for describing monochromatic radiative transfer, including both absorption and thermal emission, in a nonscattering atmosphere. Specifically, given the absorption profile $\beta_a(z)$ and temperature profile $T(z)$ in a plane parallel atmosphere, we can use (8.27) through (8.30) to compute the atmospheric contribution to the radiant intensity, as seen from the surface looking up or from a satellite looking down. With only slight modifications, they may be used to compute monochromatic intensities at *any* level z between the surface and the top of the atmosphere.

In these equations, it is the absorption coefficient β_a that directly links absorption and emission at any specific wavelength to the material composition of the atmosphere. In Section 7.4.1, we saw that a relatively small number of constituents, such as water vapor, carbon dioxide, and a few other trace gases, are responsible for almost all of the important features in the observed absorption/emission spectrum of the atmosphere. However, we have not yet examined *why* certain gases strongly absorb radiation at certain wavelengths nor *how* their absorption properties are influenced by temperature and pressure.

Is it really necessary, you ask, for the nonspecialist to know

the whys and hows of atmospheric absorption? Even without that insight, does anything prevent you from computing broadband fluxes (for example), simply by integrating monochromatic intensities over both solid angle and wavelength? No, of course not. All you need is a reasonably accurate specification of $\beta_a(\lambda, p, T, \dots)$ for each relevant constituent. Such models are already available “off the shelf.”

But while it is technically possible to learn to fly and land an airplane by rote without ever actually mastering the physical principles of flight, most of us would prefer to entrust our lives to a pilot with a deeper understanding of his/her job. When it comes to atmospheric radiation, the consequences of ignorance are less grave, but the argument is basically the same: the more you know, the less likely you are to do something embarrassing, even when working with someone else’s well-tested models.

Note, by the way, that even though I conceded the possibility of blindly applying the equations cited above to the problem of computing broadband fluxes (as required for general circulation models, weather forecast models and the like), this “brute force” approach is rarely attractive for routine calculations. Quite often, we need to obtain fluxes of modest accuracy *with the least possible expenditure of computational effort*. That requires us to take advantage of highly simplified *parameterizations* of radiative absorption and emission. If you’re going to stake your reputation on the results of such methods (as many atmospheric scientists do without even realizing it!), it’s certainly in your interest to know where they come from and how far they can be trusted.

Atmospheric remote sensing methods typically rely on calculations of quasi-monochromatic radiant intensity. This is admittedly a far simpler computational problem than that of broadband fluxes. Nevertheless, it is the detailed absorption behavior of various atmospheric molecules that largely determine optimal channel wavelengths, spectral widths, and other instrument characteristics. Those who work with remote sensing data and/or instrumentation, as many of us can expect to do at some point in our careers, should have at least a basic understanding of these issues.

9.1 Basis for Molecular Absorption/Emission

In Chapter 2, I pointed out that EM radiation has both wavelike and particle-like properties. Recall that there are times when radiation must be viewed as waves, times when it must be viewed as a shower of quantized particles having energy $E = h\nu$, and, finally, times when it doesn't matter which view you take.

The absorption of radiation by gases turns out to be one of those cases in which the quantized (particle) nature of radiation comes to the forefront. Simply stated, interactions between radiation and individual gas molecules — whether absorption or emission — are possible only for photons having energies satisfying certain criteria. Those criteria are largely determined by the arcane, and sometimes counterintuitive, laws of quantum mechanics. But don't despair: the *consequences* of those laws aren't difficult to grasp at the level targeted by this book.

When a photon is absorbed by a system, the energy originally carried by that photon must contribute to a corresponding increase in the internal energy of the system. Likewise, when a photon is emitted, the system must give up an equivalent amount of its internal energy. There are many different ways in which internal energy may increase or decrease. Examples include:

- Changes in the translational kinetic energy of molecules (i.e., temperature).
- Changes in the rotational kinetic energy of polyatomic molecules.
- Changes in the vibrational energy of polyatomic molecules.
- Changes in the distribution of electric charge within a molecule, possibly including the complete separation (or re-unification) of two components previously bound by electrostatic forces.

Collisions between molecules tend to equalize the distribution of the total internal energy in a gas among the various "storage" mechanisms listed above. Imagine, for example, that you were able to put a diatomic gas like oxygen into a unusual state in which

all of its molecules had translational kinetic energy but no rotational or vibrational kinetic energy. Subsequent collisions between the molecules would quickly set many of them to spinning and vibrating again. Before long, the total internal energy would be distributed between all available storage modes, reestablishing a condition known as *local thermodynamic equilibrium* (LTE; see also Section 6.2.3).

LTE can be taken as a given for most problems in the lower and middle atmosphere, where atmospheric density is comparatively high and collisions are therefore quite frequent. This assures us that knowledge of the physical temperature of the medium is sufficient to accurately predict the distribution of the total internal energy among *all* possible modes. It also ensures that any radiative energy absorbed or emitted by a medium will quickly give rise to a commensurate change in the physical temperature of that medium.

Note, however, that the *immediate* consequence of the absorption or emission of any particular photon is usually a change in the internal energy of a single molecule. For example, the emission by a gas of a single photon might entail a reduction in the rotational energy of one molecule of the gas. For another photon, the immediate consequence of an absorption event might be a simultaneous increase in the vibrational and rotational energy of the molecule. For yet another, the response might be an increase in the electrostatic potential energy of one of the electrons in the molecule. Yet all of these energy changes eventually get redistributed, via collisions, between all of the molecules in the vicinity, so that there is always a predictable distribution of the total internal energy in a gas among all available storage modes.

Now here is the kicker: most modes of energy storage at the molecular level and smaller are *quantized*. That is to say, a given molecule cannot have just *any* vibrational energy, but rather *only one of a discrete set of energy levels* $E_0, E_1, \dots, E_\infty$ permitted by the laws of quantum mechanics applied to that particular molecule. The same principle applies to other modes of energy storage, such as that associated with molecular rotation and electron excitation. Only the translational kinetic energy of molecules and other unbound particles is unquantized.

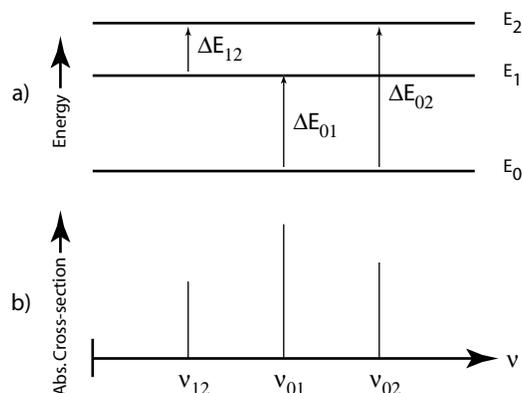


Fig. 9.1: Relationship between energy level transitions and the absorption/emission line spectrum for a hypothetical molecule with only three allowed energy levels. Panel (a) depicts the allowed transitions; panel (b) shows the corresponding positions of the lines in the spectrum, where $\nu_{ij} = \Delta E_{ij}/h$.

9.2 Absorption/Emission Lines

The consequences of the quantization of energy states are far-reaching. Basically, it implies that a photon can be absorbed or emitted by a molecule *only if the interaction leads to a transition from the molecule's original state to one of its other allowed states*. Thus, if a molecule is in energy state E_0 , then it can absorb a photon whose energy $\Delta E = E_n - E_0$ but not one whose energy is some other value. Furthermore, a molecule in energy state E_1 can only emit a photon with energy $\Delta E = E_1 - E_0$, since there is no other allowed transition that results in a decrease in the molecule's energy. A molecule in its base state E_0 cannot emit anything. However, the condition of LTE ensures that, for any given temperature above absolute zero, a predictable percentage of the molecules in a gas may be found in any given energy state. This ensures that a predictable set of allowed transitions (for both absorption and emission) is always available within any macroscopic sample of the gas in question.

Consider a hypothetical molecule with only three allowed energy states E_0 , E_1 , and E_2 (Fig. 9.1a). There are then three transitions available for the absorption of an incoming photon: $E_0 \rightarrow E_1$, $E_0 \rightarrow E_2$, and $E_1 \rightarrow E_2$. Each of these transitions corresponds to a specific photon energy ΔE and therefore, according to (2.41), to

a specific wavelength $\lambda = c/\nu = hc/\Delta E$ at which absorption may occur. For all other wavelengths, the molecule is nonabsorbing.

If we plot the absorption cross-section as a function of wavelength for our hypothetical molecule, we get an absorption *line spectrum* similar to Fig. 9.1b. The *positions* of the lines are determined by energy changes associated with the allowed transitions. The *relative strengths* of the lines are determined by a) the fraction of molecules that are in the particular initial state required for the transition and b) the intrinsic likelihood that a photon having the right energy and encountering a molecule in the required energy state will actually produce the relevant transition.¹

It is possible for more than one transition to contribute to a single absorption line, if they correspond to the same change of energy. For example, if the energy levels for the above hypothetical molecule were equally spaced, then both the $E_0 \rightarrow E_1$ and $E_1 \rightarrow E_2$ transitions would correspond to the same photon wavelength. The absorption spectrum would then consist of only two lines rather than three, with one occurring at half the wavelength of the other one. The latter, in this example, would be called *degenerate*, in that it is really two lines collapsed into one. Multiple degeneracies occur in some real gases; the associated absorption lines are often quite strong in comparison to their nondegenerate neighbors.

Problem 9.1: Consider a hypothetical molecule with N allowed energy levels E_i .

(a) Determine the total number of possible transitions that could lead to the absorption of a photon.

(b) If the energy levels happen to be equally spaced, then how many *distinct* absorption lines result from the above transitions?

¹Although the existence of absorption lines is justified here by invoking the quantized nature of radiation and of energy transitions in molecules, it turns out that there is a close analogy as well to the absorption of energy by a classical damped harmonic oscillator. If the frequency of the external wave coincides with the resonant frequency of the oscillator, absorption occurs, otherwise it does not. Some features of line absorption can be explained in classical terms using this analogy (see for example Thomas and Stamnes, 1999, Section 3.3). For this reason, you will sometimes hear the term *resonant absorption* used to describe line spectra of the type discussed above, as contrasted with *nonresonant* (or continuum) absorption spectra that do not exhibit line structure.

The energies carried by the photons of interest to atmospheric scientists cover a wide range — five orders of magnitude from $\sim 10^{-23}$ J for microwaves to $\sim 10^{-18}$ J for the far UV band. Because the quantization of energy states in atoms and molecules is quite different for the different modes of energy storage, different wavelength bands tend to be associated with different types of transitions.

For example, the allowed rotational energy states of most molecules are rather closely spaced; hence transitions between rotational states tend to involve low-energy photons, such as those in the far IR and microwave bands. On the other extreme, the tightly bound electrons in the inner shell of an atom require large amounts of energy in order to be “kicked up” to a higher level of excitation; consequently, this kind of transition is important primarily for the absorption and emission of X-rays. Intermediate energies are associated with transitions in the outer electronic shells, and with vibrational transitions. The following table gives the dominant transition type within the wavelength bands of interest to us:

Wavelengths	Band	Dominant transition
$>20 \mu\text{m}$	Far IR, microwave	Rotation
$1 \mu\text{m} - 20 \mu\text{m}$	Near IR, thermal IR	Vibration
$<1 \mu\text{m}$	Visible, UV	Electronic

As we shall see later, low-energy transitions, such as those associated with rotation, often occur simultaneously with high-energy transitions due to vibration and/or electronic excitation. The total energy change is the sum of the individual changes. The effect of such combinations is to add fine-scale structure to the absorption line spectrum that would result from “pure” vibrational or electronic transitions alone.

This book assumes that the reader has had little if any prior instruction in quantum physics. The following discussion of quantized energy transitions is therefore intentionally simplistic and largely descriptive, though mathematical relationships are derived for a few simple cases.² My purpose here is to give you a qualitative understanding of why atmospheric absorption spectra look the way

²More detailed treatments may be found in S94 (Section 3.2), TS02 (Section 4.5), and GY89 (Chapter 3).

they do, and why certain trace constituents, like CO₂, are far more important for radiation than are other far more prevalent species, like nitrogen. We will begin by examining the physical basis for the absorption line spectra associated with rotational, vibrational, and electronic transitions separately and in combination. This will be followed by a discussion of absorption line shape and width and, finally, by a survey of principal atmospheric absorbers.

9.2.1 Rotational Transitions

Moments of Inertia of Molecules

Let's first begin with a quick review of some familiar relationships from freshman physics. All physical objects, including molecules, have mass. According to Newton's law the mass m is a measure of the object's resistance to linear acceleration, i.e.,

$$F = ma \quad (9.1)$$

where F is the applied force and a is the resulting acceleration. Also, the mass figures prominently in the object's translational kinetic energy product, which is given by

$$E_{kt} = \frac{1}{2}mv^2, \quad (9.2)$$

where v is the speed. In the case of molecules in a gas, their average translational kinetic energy is proportional to the absolute temperature of the gas. Also, the linear *momentum* is given by

$$p = mv. \quad (9.3)$$

The above relationships all apply to linear motion by a mass; completely analogous relationships also exist for rotational motion. In particular, all physical objects that are not point masses have *moments of inertia*. Analogous to the role of mass in linear acceleration, the moment of inertia I is a measure of the object's resistance to *rotational* acceleration when subjected to a torque T :

$$T = I \frac{d\omega}{dt}. \quad (9.4)$$

Similarly, the *rotational kinetic energy* is given by

$$E_{kr} = \frac{1}{2} I \omega^2 . \quad (9.5)$$

Finally, the *angular momentum* is given by

$$L = I \omega . \quad (9.6)$$

The moment of inertia I depends not only on the mass m but also on how that mass is distributed in space about the object's center of gravity. Specifically, it is the sum of the products of the masses δm_i of each volume element in the object with the squares of their respective distance r_i from the axis of rotation:

$$I = \sum_i r_i^2 \delta m_i . \quad (9.7)$$

Thus, for two objects of equal mass, the more compact object will have the smaller moment of inertia. A hula hoop has about the same mass as a softball, but a hula hoop spinning about its axis at the rate of one revolution per second stores much more energy and angular momentum than does a softball spinning at the same rate.

In one sense, the analogy between rotational and translational measures of energy and momentum is very close — indeed, the respective equations for linear and rotational acceleration, kinetic energy, and momentum all have similar algebraic forms. In two respects, however, the picture is slightly more complicated for rotational motion than it is for translational motion.

First of all, translational motion is not quantized — a molecule is allowed to have any speed (how could this *not* be the case, since there is no absolute frame of reference for translational motion?). Rotational motion at the molecular level, on the other hand, *is* quantized according to the laws of quantum mechanics, and this discretization of energy/angular momentum states is responsible for the existence absorption/emission lines in connection with rotational transitions.

Secondly, any object has only one mass m , but it has *three* principal moments of inertia I_1, I_2, I_3 . Each of these corresponds to one of three perpendicular axes of rotation whose overall orientation is determined by the particular mass distribution (i.e., shape) of the

object. Although the actual axis of rotation of an object is not constrained to coincide with one of the principal axes, the overall angular momentum and/or rotational kinetic energy can nevertheless be analyzed in terms of the projection of the angular velocity vector on each of the three principal axes.

For objects having simple symmetry, it is often easy to guess the alignment of the principal axes and to judge the relative size of the corresponding moments of inertia. A rectangular brick, for example, has principal axes passing at right angles through each face and through the center of mass. The corresponding moments of inertia will be different for each axis: smallest for rotation about the longest axis of the brick (because the mass is most compactly distributed about that axis) and largest for rotation about the axis passing through the shortest dimension of the brick (because more of the mass is found at a greater distance from that axis).

For many common shapes, one or more of the moments of inertia have the same value. For example, a pencil has one very small moment of inertia corresponding to rotation about its lengthwise axis and two much larger, identical moments of inertia corresponding to rotation about any pair of axes at right angles to the first. A flat circular disk has one large moment of inertia about its radial axis and two smaller and equal moments of inertia about any pair of perpendicular axes that pass edgewise through the disk. A uniform sphere or a cube has three identical moments of inertia; moreover, it is irrelevant in these cases how you define the principal axes, because rotation about *any* axis is equivalent.

We are now ready to see how the above concepts apply to molecules. Let us start by considering an isolated atom. Virtually the entire mass of any atom is confined to its nucleus which, on a molecular scale, has a vanishingly small radius. For all practical purposes relevant to atmospheric radiation, a single atom has effectively zero moment of inertia for any axis of rotation; i.e., $I_1 = I_2 = I_3 \approx 0$. It follows that *isolated atoms exhibit no rotational transitions of interest to us.*

A diatomic molecule, on the other hand, consists of two or more bound atoms, each with finite mass, separated by a finite distance. Moreover, the distance separating the two atoms is quite large compared with the radius of the individual nuclei. One of the axes of

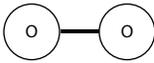
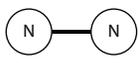
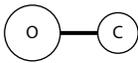
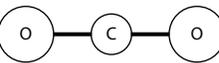
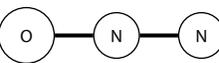
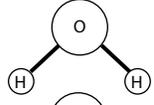
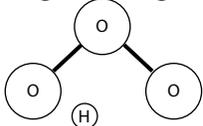
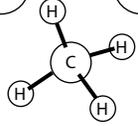
Molecule	Structure	Permanent Electric Dipole Moment?
Oxygen	 linear	No (magnetic dipole)
Nitrogen	 linear	No
Carbon Monoxide	 linear	Yes
Carbon Dioxide	 linear	No
Nitrous Oxide	 linear	Yes
Water	 asymmetric top	Yes
Ozone	 asymmetric top	Yes
Methane	 spherical top	Yes

Fig. 9.2: Molecular structure of several key atmospheric constituents. Also indicated is whether the molecule has a permanent electric dipole moment (note that oxygen has a permanent magnetic dipole moment).

rotation can be taken to pass through the two nuclei. For this axis, the moment of inertia $I_1 = 0$. The remaining two axes are perpendicular to each other and to the first; for them the moments of inertia are nonzero and $I_2 = I_3$. These properties also apply more generally to a *linear* polyatomic molecule — i.e., any molecule with all of its constituent atoms lying in a straight line.

Finally, we come to nonlinear polyatomic molecules, which have three nonzero moments of inertia. Depending on the symmetry of

the molecule, there are three possible cases: 1) all moments of inertia equal, corresponding to a *spherical symmetric top* molecule, 2) two equal and one different in the case of a *symmetric top* molecule, and 3) all three different — the so-called *asymmetric top*.

The significance of the above distinctions lies in the number of mechanically dissimilar modes of rotation available to a given molecule. There can be no rotational energy, and therefore no absorption or emission of radiation, in connection with a principal axis for which $I = 0$. Furthermore, axes of rotation for which the moments of inertia are equal are energetically indistinguishable and therefore give rise to identical absorption spectra. Thus, linear and spherical symmetric top molecules have the fewest distinct modes of rotation, and therefore the simplest absorption spectra due to rotational transitions, while asymmetric top molecules have the richest set of possible transitions, and therefore the most complex rotation spectra.

The following table summarizes the different types of rotational symmetry, in order of increasing complexity, and lists the most important atmospheric molecules in each category (see also Fig. 9.2).

Description	Moments of Inertia	Examples
Monoatomic	$I_1 = I_2 = I_3 = 0$	Ar
Linear	$I_1 = 0; I_2 = I_3 > 0$	N_2, O_2, CO_2, N_2O
Spherical symmetric top	$I_1 = I_2 = I_3 > 0$	CH_4
Symmetric top	$I_1 \neq 0; I_2 = I_3 > 0$	NH_3, CH_3Cl, CF_3Cl
Asymmetric top	$I_1 \neq I_2 \neq I_3$	H_2O, O_3

Quantization of Angular Momentum

A diatomic molecule may be regarded as a two-body rigid rotator consisting of two masses m_1 and m_2 separated by distance $r = r_1 + r_2$, where r_i is the distance of each mass m_i from the axis of rotation. For any freely rotating body, the axis of rotation coincides with the *center of mass* which, in this example, satisfies $m_1 r_1 = m_2 r_2$. It can be shown from (9.7) that the moment of inertia $I_2 = I_3 = I$ (recall that $I_1 = 0$ for a linear molecule) is given by

$$I = m' r^2, \quad (9.8)$$

where we introduce the so-called *reduced mass*

$$m' \equiv \frac{m_1 m_2}{m_1 + m_2} . \quad (9.9)$$

If the molecule is rotating with angular velocity ω , then its kinetic energy of rotation is

$$E = \frac{1}{2} I \omega^2 = \frac{L^2}{2I} , \quad (9.10)$$

where

$$L = I \omega \quad (9.11)$$

is the angular momentum. Quantum mechanics tells us (via Schrödinger's equation), that the angular momentum of our rigid molecule is restricted to discrete values given by

$$L = \frac{h}{2\pi} \sqrt{J(J+1)} , \quad (9.12)$$

where $J = 0, 1, 2, \dots$ is the *rotational quantum number*. Combining the above with (9.10) yields a set of discrete energy levels

$$E_J = \frac{1}{2} I \omega^2 = \frac{J(J+1)h^2}{8\pi^2 I} . \quad (9.13)$$

Problem 9.2: Equations (9.11) and (9.12) imply that the angular velocity ω of an object can only take on discrete (quantized) values. Explain why this quantization is not observable for macroscopic objects like frisbees and hula hoops.

Rotational Absorption Spectrum

If we now consider transitions between adjacent rotational states J and $J+1$ (it turns out that none other are allowed by quantum mechanics), we find that the associated energy change is

$$\Delta E = E_{J+1} - E_J = \frac{h^2}{8\pi^2 I} [(J+1)(J+2) - J(J+1)] , \quad (9.14)$$

or

$$\Delta E = \frac{h^2}{4\pi^2 I} (J + 1). \quad (9.15)$$

The corresponding photon frequency ν is then

$$\nu = \Delta E/h = \frac{h}{4\pi^2 I} (J + 1), \quad (9.16)$$

or

$$\nu = 2B(J + 1), \quad (9.17)$$

where B is the *rotational constant* defined as

$$B = \frac{h}{8\pi^2 I}. \quad (9.18)$$

From (9.17), we see that the rotational absorption line spectrum of our simple diatomic molecule consists of a series of equally spaced lines separated by $\Delta\nu = 2B$.

Problem 9.3: Oxygen (O_2 ; molecular mass 32.0 kg/kmole) is a diatomic molecule whose lowest-frequency rotational absorption band is found at a frequency of 60 GHz. From the relationships given in this section, find the distance r separating the two oxygen atoms in the molecule.

We have just discussed the quantization of rotational energy, and the associated line spectrum, for the simplest case: that of a diatomic molecule with only one nonzero moment of inertia I and rotational quantum number J . Analogous relationships exist for nonlinear molecules possessing up to three different moments of inertia I_n and associated rotational quantum numbers J_n . Each quantum number J_n has its own distinct set of energy levels, the spacing of which is determined by the value of I_n . In this case, however, the absorption or emission of a photon often entails a *simultaneous* change in two or more of the rotational quantum numbers. Because of the likelihood of simultaneous transitions, the rotation line spectrum of a nonlinear molecule is considerably more complex and irregular than that of a linear molecule.

There are additional complications that I will mention but not dwell on. For example, both vibrational and rotational motions can

perturb the moments of inertia I_n from their static values — e.g., by slightly stretching the mean interatomic distance r . These interactions can give rise to slight shifts in the positions of lines relative to the “pure” case. Since the perturbing influence is itself quantized, the usual result is the splitting of what would otherwise be a single line into family of closely spaced lines.

Dipole Moments

The above discussion hopefully gives you some insight into the basic nature of rotational line spectra, but there is one final issue that we have not yet considered. In order for a molecule to interact with an electromagnetic wave via rotational transitions, it must possess either a magnetic or electric *dipole moment*. That is to say, an externally applied magnetic or electric field, respectively, must have the capacity to exert a torque on the molecule.

For example, the needle in a compass has a magnetic dipole moment. The earth’s magnetic field exerts a torque on the needle that causes it to rotate until it is aligned with the field. Likewise, a molecule with no *net* electric charge but with an asymmetric internal distribution of positive and negative charge can have an electric dipole moment that allows it respond to an external electric field by changing its orientation.

A diatomic molecule that is also *homonuclear* — i.e., consisting of two identical atoms (e.g, N₂ or O₂) — has no permanent electric dipole moment because of the symmetry of the distribution of positive and negative charge within the molecule. The same applies to a symmetric linear triatomic molecule at rest, such as CO₂. A *heteronuclear* diatomic molecule, such as carbon monoxide (CO), will generally have a permanent electric dipole. Also, with the exception of CO₂, all triatomic (and larger) molecules of interest to us for atmospheric radiation, such as H₂O, N₂O, O₃, and CH₄, have permanent electric dipole moments due to various asymmetries in their structure.

Here is the “bottom line” for rotational absorption by atmospheric constituents:

- As noted previously, monoatomic constituents such as argon (Ar) and other noble gases have effectively zero moment of

inertia I and therefore no rotational transitions.

- Molecular nitrogen (N_2), the most abundant atmospheric constituent, has neither electric nor magnetic dipole moment and therefore has no rotational absorption spectrum.
- Oxygen (O_2) also has no electric dipole moment but, unlike most other diatomic gases, it does have a permanent magnetic dipole moment. This property is what permits it to have rotational absorption bands at 60 and 118 GHz.
- Carbon dioxide (CO_2) has no permanent electric or magnetic dipole moment and is therefore radiatively inactive with respect to pure rotational transitions. However, bending vibrational motions can break the linear symmetry of the molecule and introduce an oscillating dipole moment whose presence permits combined vibration-rotation transitions at shorter wavelengths (see Section 9.2.2).
- All other major molecules found in the atmosphere exhibit permanent electric dipole moments and therefore also major rotational absorption bands.

9.2.2 Vibrational Transitions

The covalent bonds between two atoms in a molecule arise from a balance of attractive and repulsive electrostatic forces. The former dominates when the two atoms are relatively widely separated; the latter, due to mutual repulsion of the positively charged nuclei, takes over when the atoms get pushed too close together. The arrangement of atoms in a molecule at rest corresponds to the positions for which all attractive and repulsive forces exactly cancel.

Diatomic Molecules

The molecular bond is thus not rigid but behaves like a spring. In particular, for sufficiently small displacements, the force between two atoms in a diatomic molecule is given by

$$F = -k(r' - r), \quad (9.19)$$

where k is analogous to a spring constant, and F is thus the restoring force when the separation r is smaller or greater than the equilibrium separation r' . Because the atoms have mass, the molecule would, in the classical limit, behave like a simple harmonic oscillator with resonant frequency

$$\nu' = \frac{1}{2\pi} \sqrt{\frac{k}{m'}}, \quad (9.20)$$

where m' is the reduced mass defined by (9.9).

In the quantum mechanical limit, however, the actual vibrational frequency ν of the oscillator is quantized according to

$$\nu = \left(v + \frac{1}{2}\right) \nu', \quad (9.21)$$

where v (letter 'V', not Greek 'nu') is the *vibrational quantum number* and, like the rotational quantum number J , can only take on non-negative integer values.

The energy associated with each frequency ν is the same as it is for a photon with the same frequency:

$$E_v = h\nu = \left(v + \frac{1}{2}\right) h\nu'. \quad (9.22)$$

A vibrational transition $\Delta v = \pm N$ therefore entails a change of energy

$$|\Delta E_v| = N h\nu', \quad (9.23)$$

and we see, somewhat to our amazement, that the photon frequency associated with the transition is just an integer multiple of the classical resonant frequency of the harmonic oscillator.

Vibration/Rotation Spectra

There are two important points to note:

- Vibrational transitions tend to be associated with considerably larger energies than rotational transitions. Therefore vibrational transitions give rise to absorption/emission lines at much shorter wavelengths — e.g., in the thermal and near IR bands — than those due to pure rotational transitions, which are generally associated with the far IR and microwave bands.

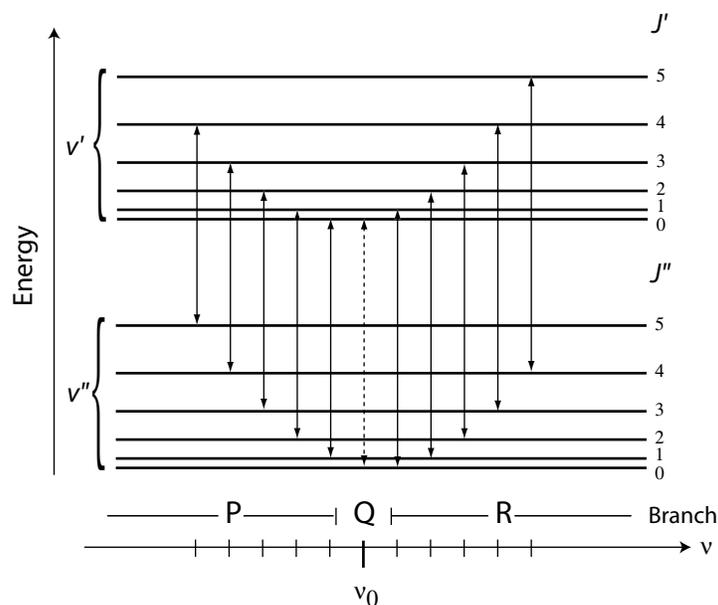


Fig. 9.3: Vibrational-rotational transitions for $\Delta v = \pm 1, \Delta J = [-1, 0, +1]$, showing the relative positions of the transitions in the spectrum. The P-branch corresponds to transitions involving $\Delta J = -1$, while the R-branch corresponds to $\Delta J = +1$. The Q-branch, when present, represents a superposition of all possible transitions involving $\Delta J = 0$ and occurs close to frequency $\nu_0 = \Delta E/h$, where ΔE is the energy associated with pure vibrational transitions.

- Vibrational and rotational transitions may, and usually do, occur simultaneously. It follows from the previous point that the energy (and photon wavelength) of combined vibration/rotation transition is slightly greater or less than that of a pure vibrational transition, depending on whether the rotational quantum number J increased or decreased during the transition. The effect of rotational transitions is therefore to split up vibrational absorption lines into a series of rather closely spaced separate lines.

The second of the above points is illustrated by Fig. 9.3, which depicts the positions of lines associated with various combinations of $\Delta v = \pm 1$ and $\Delta J = [-1, 0, 1]$. The nominal frequency of a pure vibrational transition ($\Delta J = 0$) is indicated in this figure as ν_0 and is approximately the same regardless of the value of J in force when

the transition occurs. The associated absorption/emission lines, when present (see below), belong to what spectroscopists refer to as the *Q branch* of the vibration/rotation spectrum.³

For transitions involving $\Delta J = -1$ and $\Delta J = +1$, respectively, the absorption lines associated with $\Delta v = 1$ are spread out slightly below or above ν_0 . These lines do not overlap because of the uneven spacing of the rotational energy levels. The lines associated with $\Delta J = -1$ belong to the so-called *P branch*; the $\Delta J = +1$ transitions are known as the *R branch*.

Note that for certain molecular configurations, quantum mechanics *requires* a vibrational transition of $\Delta v = \pm 1$ to be accompanied by a nonzero rotational transition (typically $\Delta J = \pm 1$). In such cases, the central Q branch is absent and the absorption spectrum consists of the P and R branches alone.

Polyatomic Molecules

When an molecule consists of more than two atoms, the variety of possible vibrational motions increases substantially and, in general, consist of combinations of bending and stretching of interatomic bonds. It turns out that, for a given molecular structure, any physically admissible vibrational motion can be expressed as the superposition of a finite set of *normal modes*, each of which can be considered independently of the others, and each of which is associated with its own set of vibrational energy levels. The situation is analogous to the existence of three distinct rotational quantum numbers for aspherical top molecules, but the number of possible vibrational modes is a function of the structure of the molecule.

For the diatomic molecule considered earlier, the sole possible vibrational mode consisted of stretching and compression along the axis of the molecule. Its vibrational energy levels can therefore be expressed in terms of only one vibrational quantum number v .

For triatomic molecules, there are three energetically distinct modes: (1) symmetric stretching, (2) asymmetric stretching, and (3)

³In actuality, the rate of rotation of the molecule has a weak influence on vibrational energy levels, so that the Q branch is very finely split into a number of nearly overlapping lines (not pictured in Fig. 9.3).

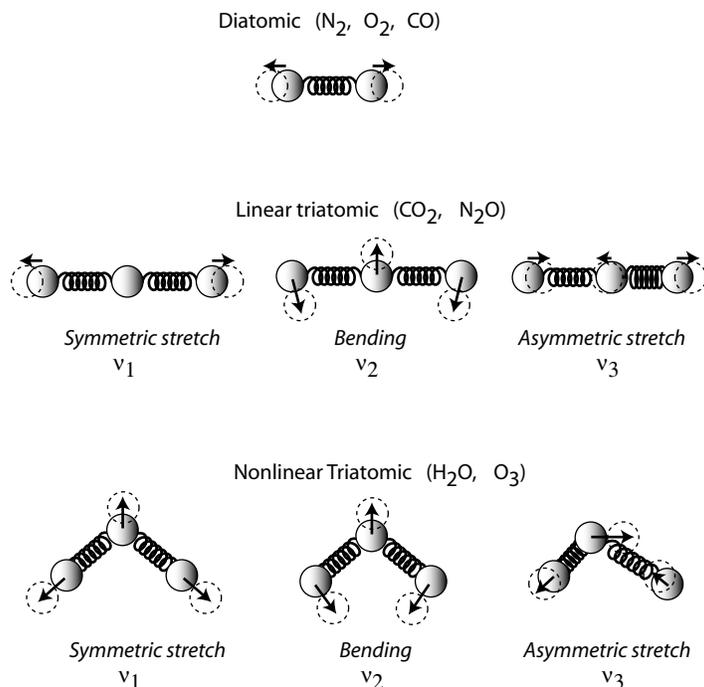


Fig. 9.4: Illustration of normal modes of vibration for simple molecules.

bending.⁴ The nature of these vibrational motions is illustrated in Fig. 9.4. For this case, three vibrational quantum numbers v_1 , v_2 , v_3 are required to describe all possible vibrational energy levels. During the absorption or emission of a photon, simultaneous transitions may occur in one, two, or three of these quantum numbers. It follows that the vibrational absorption spectra of triatomic molecules is considerably more complex than those of diatomic molecules.

For molecules consisting of four or more atoms — e.g., methane (CH_4), chlorofluorocarbons, etc., the number of normal modes multiplies very rapidly, and the associated absorption spectrum becomes very rich indeed. In general, a molecule consisting of $n > 1$

⁴For a linear molecule such as CO_2 , there are actually two normal modes associated with bending - one lying in each of two orthogonal planes. However, these two modes are energetically equivalent and therefore needn't be considered separately.

atoms has $N = 3n - 6$ normal modes if it is nonlinear, or $N = 3n - 5$ if it is linear.

Problem 9.4: Chlorofluorocarbons (CFCs) are synthetic compounds that have strong absorption bands in the IR band. One of the simplest CFCs has the formula CFCl_3 . Given that it is a nonlinear molecule, how many vibrational normal modes does it have?

Problem 9.5: Assume that a molecule has N distinct vibrational quantum numbers v_i . How many possible simultaneous (nonzero) energy transitions of the form $\Delta v_i = \{-1, 0, 1\}$ exist?

9.2.3 Electronic Transitions

Having discussed rotational and vibrational transitions, we now briefly consider a third transition type, which involves the energy levels of the electrons orbiting an atomic nucleus. Just as energy has to be added to a satellite in order to raise it to a higher orbit above the earth's surface, the energy associated with an electron increases with its mean distance from the nucleus. As before, the allowed energy levels of electronic orbits are quantized. Also, the more tightly bound an electron is to a nucleus, the larger the magnitude of the energy steps ΔE between levels.

In general, a photon can be absorbed when its energy corresponds to the excitation of an electron to a more energetic state; a photon of an appropriate wavelength can be emitted when an excited electron drops back to a lower state.

For the purposes of this book, it is principally the outermost electrons that are of interest, since transitions between their ground state and the first excited state are associated with photon wavelengths in the near IR, visible and ultraviolet bands. Inner electrons, which are more strongly bound by attractive forces to the nucleus, tend to have energy transitions corresponding to very short wavelengths.

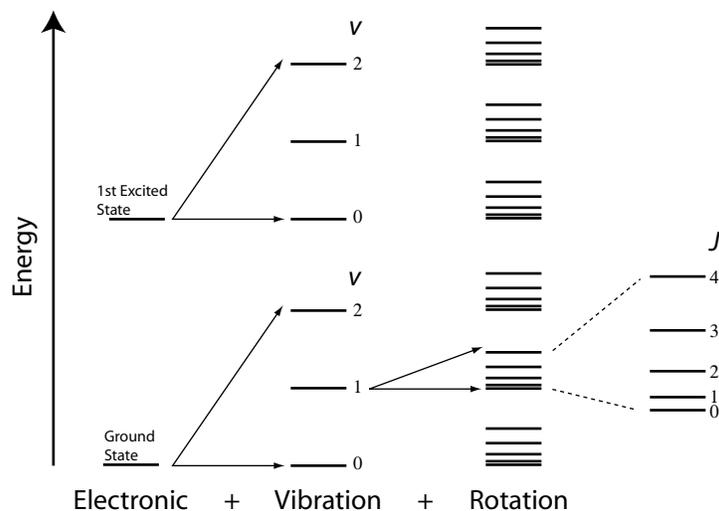


Fig. 9.5: Schematic depiction of the superposition of electronic, vibrational and rotational energy levels. The absorption spectrum of a molecule is determined by all nonforbidden transitions between pairs of levels in the righthand column.

At ordinary atmospheric temperatures, collisions between molecules are very rarely energetic enough to kick electrons into excited states. Those few that do briefly find themselves in an excited state, for whatever reason, usually give up their energy again in the course of subsequent collisions without emitting a photon. There are therefore extremely few electrons found *naturally* in excited states and even fewer opportunities for the spontaneous emission of photons due to electronic transitions back to the ground state. This fact is of course consistent with the sharp fall-off in thermal emission at the short wavelength end of the Planck function.

When electron orbits in atmospheric molecules *are* found in an excited state, it is usually because of the absorption of an incoming photon with the right energy, usually one of solar origin. As for rotational and vibrational transitions, we therefore expect to find discrete absorption lines associated with each allowed transition to higher electronic orbital states.

9.2.4 Combined Energy Transitions and Associated Spectra

As noted in the previous subsections, each atmospheric molecule has associated with it a number of discrete energy levels associated with electronic, vibrational, and rotational quantum states. Electronic energy states are the most widely separated and therefore correspond to photon absorption/emission at the shortest wavelengths; vibrational and rotational transitions, respectively, are associated with intermediate- and low-energy transitions.

The combination of all three modes of excitations leads to a set of discrete energy levels that are depicted schematically in Fig. 9.5. The total absorption line spectrum of the molecule is determined by all *allowed* transitions between pairs of energy levels (recall that not all transitions are allowed by quantum mechanics) and by whether the molecule exhibits a sufficiently strong electric or magnetic dipole moment (either permanent or otherwise) to be able to interact with the radiation field.

9.3 Line Shapes

The above introduction of absorption line spectra might have understandably left you with the impression that absorption by molecules can occur only at the precise wavelengths determined by the permitted energy transitions. If this were indeed the case, line absorption would be completely unimportant. Why? Recall that, for natural radiation, the energy (or flux) associated with exactly one wavelength is zero. In order to account for a finite percentage of the total radiation field, it is necessary to consider a finite interval of wavelength. That being the case, if absorption lines had zero width, then no matter how strong they were and no matter how many of them were scattered through the spectrum, their practical impact on atmospheric radiative transfer would be zilch. The observed *broadening* of absorption lines is therefore of tremendous practical importance for radiative transfer, as it permits a given atmospheric constituent to absorb radiation not only at the nominal wavelength associated with a transition but also at nearby wavelengths as well (Fig. 9.6). Where absorption lines are closely spaced, as they are in

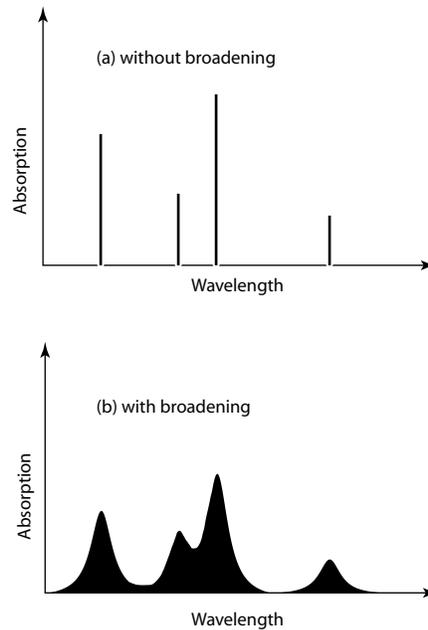


Fig. 9.6: Schematic depiction of the effect of broadening on a hypothetical line spectrum.

much of the thermal IR band, line broadening can completely close the gaps between neighboring lines so that the atmosphere becomes effectively opaque over a continuous range of wavelength.

There are three distinct processes responsible for line broadening. Their relative importance depends on local environmental conditions.

Natural broadening: The Heisenberg uncertainty principle, which is one of the most fundamental and far-reaching early findings of quantum physics, ensures that an absorption line must have finite (though very small) width, even in the absence of other factors. Throughout most of the atmosphere, natural broadening is entirely negligible compared with the other two broadening mechanisms. We will not consider it further in this book.

Doppler broadening: Because of the random translational motions of individual molecules in any gas, absorption and emission

occurs at wavelengths that are Doppler-shifted relative to the natural line position. This is the primary broadening mechanism in the mesosphere and above.

Pressure broadening: Collisions between molecules randomly disrupt natural transitions between energy states, so that emission and absorption occurs at wavelengths that deviate from the natural line position. This is the primary broadening mechanism in the troposphere and lower stratosphere.

9.3.1 Generic Description of Lines

Before going into the details of the line shapes associated with the above broadening mechanisms, it is convenient to introduce a generic framework for describing *any* individual absorption line. Specifically, there are three pieces of information that one needs to know about a line under a given set of environmental conditions:

Line position: Where does the line fall in the EM spectrum?

Line strength: How much total absorption is associated with the line?

Line shape: How is the above absorption distributed about the center of the line?

All of the above characteristics are captured succinctly in the following formulation:

$$\sigma_\nu = S f(\nu - \nu_0) , \quad (9.24)$$

where σ_ν is the absorption cross-section per molecule (or some other equivalent description, such as cross-section per unit mass) at frequency ν . ν_0 is the *center frequency* of the absorption line, S is the *line strength*, and $f(\nu - \nu_0)$ is the *line shape* function. In order that the strength and the shape be completely decoupled in the above description, the shape function is normalized to unit area:

$$\int_0^\infty f(\nu - \nu_0) d\nu = 1 , \quad (9.25)$$

so that the line strength is given by

$$\int_0^\infty \sigma_\nu d\nu = \int_0^\infty S f(\nu - \nu_0) d\nu = S . \quad (9.26)$$

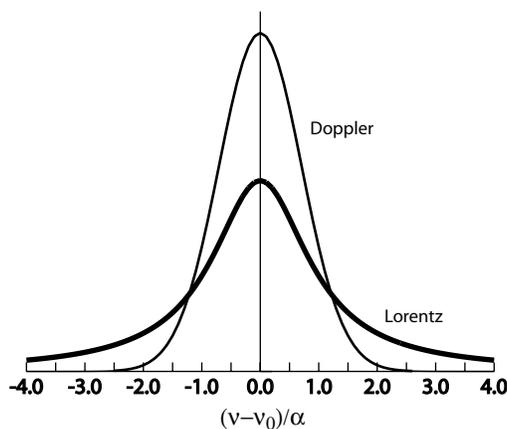


Fig. 9.7: Comparison of the Doppler and Lorentz line shapes for equal widths and strengths.

Although the shape of $f(\nu - \nu_0)$ depends on the broadening mechanism, one feature common to all shape functions is that the maximum occurs at the line center $\nu = \nu_0$, and the function falls sharply and monotonically with increasing $|\nu - \nu_0|$. Moreover, the line shape is usually symmetric about ν_0 (except in the microwave band); therefore it is common to succinctly characterize the overall width of the line via a parameter $\alpha_{1/2}$ known as the *half width at half-maximum*. That is to say, $\alpha_{1/2}$ represents the value of $|\nu - \nu_0|$ for which the absorption cross-section falls to half of its maximum value at the line center; i.e. $f(\alpha_{1/2}) = f(0)/2$.

Let us now consider the two major line broadening mechanisms and their implications for the shape function $f(\nu - \nu_0)$.

9.3.2 Doppler Broadening

In any gas, individual molecules are in constant motion, following random ballistic trajectories interrupted only by collisions with other molecules. The average kinetic energy of all of the molecules is proportional to the temperature. From the perspective of a stationary observer, each molecule has a random velocity component v_s toward or away from the observer. The statistical probability of any particular velocity component v_s along the line-of-sight s is

given by the Maxwell-Boltzmann distribution

$$p(v_s) = \frac{1}{v_0 \sqrt{\pi}} e^{-(v_s/v_0)^2}, \quad (9.27)$$

where $v_0 = \sqrt{2k_B T/m}$ represents the standard deviation (or root-mean-squared value) of v_s , m is the mass per molecule ($= M/N_0$, where M is the molar mass and $N_0 = 6.02 \times 10^{23}$), T is the temperature, and k_B is the Boltzmann constant.

The motion of each molecule along a particular line-of-sight introduces a Doppler shift into the frequency of the photons it emits and absorbs, as measured from the perspective of a stationary observer. In Problem 2.2, you were asked to show that, in the case of an EM wave traveling at the speed of light c , the Doppler-shifted frequency is given by

$$\nu' = \nu(1 - v/c), \quad (9.28)$$

where ν is the frequency as measured by an observer who is stationary relative to the source, and ν' is the frequency measured by an observer moving with a velocity component v *away* from the source.

Because of the Doppler effect, EM frequencies that would appear not to coincide with the nominal position ν_0 of an absorption line can be absorbed, nevertheless, by any molecule having the right relative velocity. Conversely, radiation whose frequency *is* equal to ν_0 can only be absorbed by those relatively few molecules whose relative velocity is close to zero. The net effect, therefore, is a decrease in the likelihood of absorption by a molecule at ν_0 and an increase at nearby frequencies.

Combining (9.27) with (9.28) yields the line shape for Doppler broadening:

$$f_D(\nu - \nu_0) = \frac{1}{\alpha_D \sqrt{\pi}} \exp \left[-\frac{(\nu - \nu_0)^2}{\alpha_D^2} \right], \quad (9.29)$$

where

$$\alpha_D = \nu_0 \sqrt{\frac{2k_B T}{mc^2}}. \quad (9.30)$$

We can find the line halfwidth at half max $\alpha_{1/2}$ by setting

$$\frac{f_D(\alpha_{1/2})}{f_D(0)} = \frac{1}{2} \quad (9.31)$$

and solving for $\alpha_{1/2}$. We find that

$$\alpha_{1/2} = \alpha_D \sqrt{\ln 2}. \quad (9.32)$$

The interpretation of (9.29) is straightforward. This Maxwell-Boltzmann distribution of line-of-sight velocities (9.27) is Gaussian; therefore the Doppler-broadened shape of an initially narrow line is also Gaussian. The mean speed of the molecules, and therefore the line width, increases with temperature and decreases with molecular mass. The shape of the Doppler profile is depicted in Fig. 9.7.

9.3.3 Pressure Broadening

In Section 9.2, the occurrence and position of absorption lines was justified under the implicit assumption that molecules were free to make transitions between their various energy states without external interference. For gases in the tenuous upper atmosphere, this is a reasonable assumption. In the denser portions of the atmosphere (i.e., in the stratosphere and troposphere), collisions occur between molecules with very high frequency. The effect of a collision is to “shock” the molecule at a time when it might just be in the process of emitting or absorbing a photon. Not surprisingly, this adds a significant new level of complexity to the problem of predicting which wavelengths might be most readily absorbed or emitted during a particular transition. In fact, no exact theory has yet been developed to describe the so-called *pressure broadening* of absorption/emission lines that results.

It is beyond the scope of this book to go through the heuristic arguments that have been used to derive an approximate expression for the shape of pressure broadened lines. Suffice it to say that one common model invokes collision-induced random phase shifts imposed on an otherwise “pure” sinusoidal oscillation to explain the resulting “smearing” of emitted (and absorbed) frequencies about the nominal frequency ν_0 . The interested student is referred to Section 3.3.1 of S94 and Section 3.3 of GY89 for details.

The bottom line, for our purposes, is that pressure broadening is usually described adequately, though by no means perfectly, by the

Lorentz line shape

$$f(\nu - \nu_0) = \frac{\alpha_L / \pi}{(\nu - \nu_0)^2 + \alpha_L^2}, \quad (9.33)$$

where α_L is the Lorentz halfwidth at half max and is roughly proportional to the number of collisions per unit time. Thus, to first order

$$\alpha_L \propto pT^{-1/2}, \quad (9.34)$$

where p is the pressure and T is the temperature. As a practical matter, α_L for any particular line is usually modeled as

$$\alpha_L = \alpha_0 \left(\frac{p}{p_0} \right) \left(\frac{T_0}{T} \right)^n, \quad (9.35)$$

where α_0 is the laboratory-measured line width at reference pressure p_0 and temperature T_0 , and n is an empirically determined exponent. When measured in units of wavenumber, typical values of α_0 lie in the range 0.01–0.1 cm^{-1} , for $T_0 = 273 \text{ K}$ and $p_0 = 1000 \text{ mb}$. The corresponding range in units of frequency is 3×10^8 to $3 \times 10^9 \text{ Hz}$.

The Lorentz line shape has two notable deficiencies. One is that the *far wings* of actual absorption lines have been found to be poorly represented by this line shape. It might strike you as unimportant whether a line shape model does well in the far wings, where absorption due to a single line is very small anyway. However, recall that the absorption coefficient at any particular frequency ν is due to the combined contributions of *all* lines, near and far. And there are of course many more distant lines than nearby lines! In particular, at any frequency located in a spectral window where there *are* no nearby lines, *all* of the absorption is due to the accumulated far wings of countless thousands of distant lines. In general, it has been found that the Lorentz model underestimates this contribution.

Another limitation of the Lorentz model is that it is only valid when $\alpha_L \ll \nu_0$; that is, when the line width is very small compared to the center frequency. When this condition doesn't hold, then the Lorentz model is invalid, because it fails to account for the fact that line wings cannot extend down to zero frequency. This is primarily a problem in the microwave band, where ν_0 is quite small. In

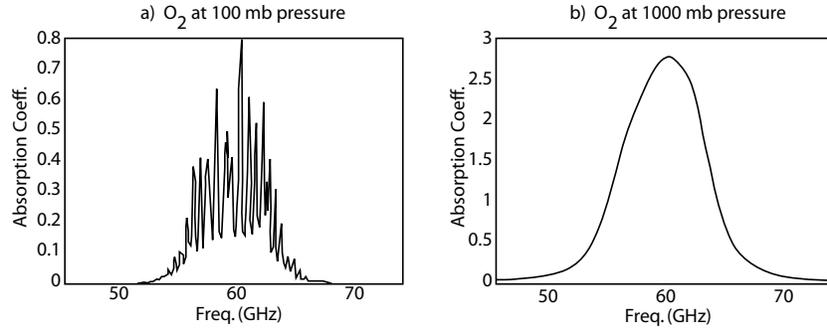


Fig. 9.8: Absorption coefficient of oxygen in the microwave band near 60 GHz, (a) at 100 mb pressure, revealing the individual lines making up the absorption band; (b) at 1000 mb, for which pressure broadening obliterates the line structure.

this case, the preferred line shape model is the *van Vleck-Weisskopf* function

$$f_{VW}(\nu - \nu_0) = \frac{1}{\pi} \left(\frac{\nu}{\nu_0} \right)^2 \left[\frac{\alpha_L}{(\nu - \nu_0)^2 + \alpha_L^2} + \frac{\alpha_L}{(\nu + \nu_0)^2 + \alpha_L^2} \right]. \quad (9.36)$$

Note that the van Vleck-Weisskopf line shape is asymmetric about ν_0 and, more importantly, is constrained to go obediently to zero as $\nu \rightarrow 0$.

An example of the how pressure broadening affects absorption line spectra is shown in Fig. 9.8. At high altitudes, individual lines are narrow enough to be clearly separated. At lower altitudes, pressure broadening often completely obliterates the individual lines, leading to the appearance of one single broad absorption feature. Note that the careful positioning of a satellite sounding channel between lines can lead to a sharpening of the absorption/emission weighting function $W(z)$, because the mass extinction coefficient at that wavelength then sharply increases toward the surface, rather than being constant, as we assumed in the previous chapter.

9.3.4 Comparing Doppler and Pressure Broadening

The shape of the Lorentz profile is compared with the Doppler profile in Fig. 9.7 for equal values of the width parameters α_L and α_D . The most important difference is that the Lorentz shape puts much

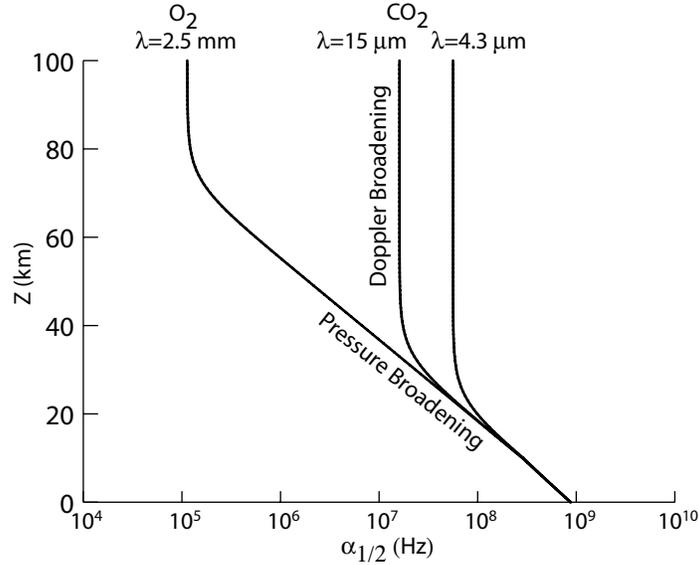


Fig. 9.9: Approximate linewidth as a function of altitude for three prominent absorption bands.

more absorption out in the far wings of the line.

Both Doppler and pressure broadening occur at all levels of the atmosphere. However, if the degree of broadening by one mechanism is substantially greater than that due to the other, then the latter may be neglected. The relative importance of each may therefore be assessed by way of the ratio of α_D to α_L , using (9.30) and (9.35):

$$\frac{\alpha_D}{\alpha_L} \approx \left[\frac{p_0}{\alpha_0 c} \sqrt{\frac{2k_B}{T_0}} \right] \frac{T\nu_0}{p\sqrt{m}} \sim [5 \times 10^{-13} \text{ mb Hz}^{-1}] \left(\frac{\nu_0}{p} \right), \quad (9.37)$$

where we have assumed that $n \approx 1/2$ and, in the far righthand terms, used "typical" values for m , T , α_0 . Because pressure varies by several orders of magnitude through the atmosphere, whereas all other variables (except ν_0) typically vary by less than a factor of two, we conclude that p is the principal factor determining whether Doppler broadening or pressure broadening prevails in any given case. If we choose $\nu_0 = 2 \times 10^{13}$ Hz, corresponding to a wavelength

of 15 μm , we find that $\alpha_D \approx \alpha_L$ at $p \sim 10$ mb. At this altitude, the two broadening processes are of roughly equal importance. For lines in the microwave band, we have $\nu_0 \sim 10^{11}$ Hz, so that the pressure level at which parity occurs is in the vicinity of 0.1 mb or less. Fig. 9.9 depicts the transition from predominantly pressure broadening at low altitudes to primarily Doppler broadening at higher altitudes for the two cases discussed above.

When α_D is of the same order of magnitude as α_L , both Doppler and pressure broadening must be considered simultaneously. In this case, it is necessary to use the hybrid *Voigt* line shape, which accounts for both mechanisms. Near the center of the line, it behaves like a Doppler profile; in the wings, it has the characteristics of the Lorentz profile. The interested student should consult p. 112 of GY89 for further details.

9.4 Continuum Absorption

The most important absorption features in the IR and microwave bands are due to bands of discrete absorption lines, as discussed above. However, outside the major resonant absorption bands, one generally finds some level of atmospheric absorption that does not exhibit line-like structure. This is known as *continuum* (or *nonresonant*) absorption, because it tends to vary smoothly with frequency.

There are at least three causes of continuum absorption, two of which, *photoionization* and *photodissociation* are well-understood and affect primarily the very short wavelength end of the solar spectrum. The third, affecting spectral windows throughout the infrared and microwave bands, is significant both for remote sensing and for thermal radiative transfer in the atmosphere but is, unfortunately, less well understood.

9.4.1 Photoionization

Photoionization occurs when a photon has enough energy not only to excite an electron in an atom to a higher level but to actually strip it completely from the atom, creating a positively charged ion and a free electron. We saw earlier that ordinary electron excitation was constrained to discrete energy levels, leading to absorp-

tion/emission lines in the visible and UV bands. A fixed amount of energy is also required to ionize an atom. However, any photon *exceeding* that ionization energy can be absorbed in the course of an ionization event; the excess energy appears in the form of kinetic energy of the ion and/or the free electron. Recall that translational kinetic energy is not quantized; hence there is no constraint on the exact energy level of the photon.

The ionization of atoms requires very energetic photons. It is observed primarily in connection with X-ray and gamma radiation from extraterrestrial sources. It is therefore a phenomenon that is of relatively little interest from an atmospheric radiation point of view. However, it is responsible for the existence of the *ionosphere*, a highly conductive region of the atmosphere that has important implications for the propagation of radio waves.

9.4.2 Photodissociation

A second cause of continuum absorption is photodissociation. Just as photoionization is electronic excitation carried to the extreme that the electron completely separates from the atom, photodissociation is molecular vibration carried to the extreme that the molecule breaks into two pieces. Thus, any photon whose energy E exceeds the chemical binding energy E_{bond} between two components of a molecule can induce photodissociation, with the excess energy $\Delta E = E - E_{\text{bond}}$ appearing as unquantized kinetic (thermal) energy.⁵ At the molecular level, of course, a gain in kinetic energy is synonymous with an increase in temperature.

The binding energies in the diatomic molecules of gases like O_2 , N_2 , etc., tend to be large. Therefore, only very short wavelengths can dissociate them (see Section 3.4.1).

⁵Again, to return to the refrigerator magnet analogy: imagine that only 0.01 J of energy is necessary to separate a 20 g magnet from the door, but that, by whatever means, you supply 1 J of mechanical energy to the magnet (e.g., by snapping a wet dish towel at it). The magnet will acquire 0.99 J of kinetic energy, corresponding to a speed of almost 10 m/sec.

9.4.3 Continuum Absorption by Water Vapor

In addition to the above well-understood modes of continuum absorption, which are primarily active at UV wavelengths, there is also significant continuum absorption by water vapor between the major absorption bands in the infrared and microwave bands. The physical mechanism behind the water vapor continuum remains a matter of some controversy. There are basically two competing theories:

Far wings of lines - As noted earlier in this chapter, the Lorentz line shape doesn't do a good job of describing the intensity of absorption in the far wings of collision-broadened absorption lines. Therefore, one possible explanation of continuum absorption is that it is simply that portion of the accumulated contribution of the far wings of countless distant lines that is not accounted for by the Lorentz model.

H₂O clusters - Water molecules exert a significant attractive force on one another (it is for this reason that water condenses readily at relatively low temperature and pressure combinations). Therefore, molecules that encounter one another at low relative speeds tend to stick to each other, forming temporary clusters of two or more molecules that are subsequently broken up again by other collisions. Such *dimers* (two molecules), *trimers* (three) and *polymers* (many molecules) would naturally be expected to exhibit far more complex vibrational and rotational transitions than an isolated molecule. Furthermore, the range of structural configurations that these loose clusters might exhibit at various points in their formation and disintegration is almost infinitely variable. There is therefore no reason to expect absorption to be limited to a finite set of discrete photon energies. Instead, we expect absorption to be smoothly distributed over a broad range of wavelengths, as is in fact observed with the water vapor continuum.

It is possible that the ultimate explanation of water vapor continuum will be found to combine elements of both theories. Regardless of the explanation, there are two points that are worth noting: (1) the strength of the continuum tends to increase steadily with frequency through the microwave and far IR bands but is weak again in the

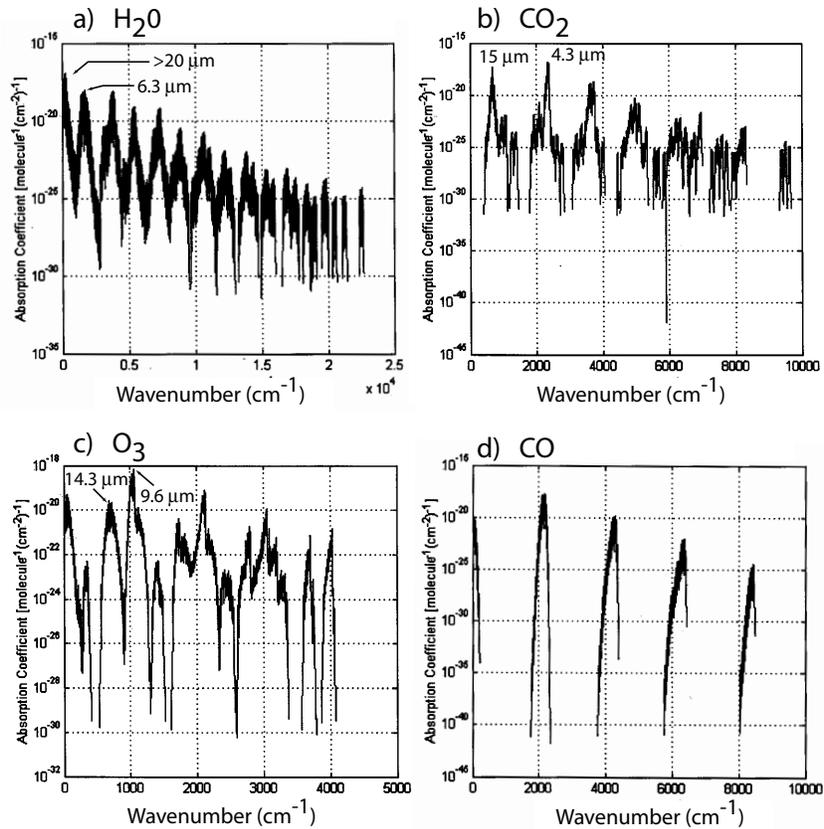


Fig. 9.10: Spectra of absorption cross-sections for several molecules encountered in the atmosphere. Absorption bands of particular significance for thermal radiative transfer in the atmosphere are labeled with the center wavelength. (a) Water vapor. (b) Carbon dioxide. (c) Ozone. (d) Carbon monoxide.

thermal and near IR bands, and (2) the volume extinction coefficient β_a is not proportional to the water vapor density ρ_v (as would be expected if the mass absorption coefficient k_a were approximately constant) but rather something closer to the *square* of that density. Therefore, continuum absorption is generally significant mainly in the lower troposphere, where water vapor density is the highest.

9.5 Applications to Meteorology, Climatology, and Remote Sensing

The main focus in this chapter has been on the following questions: (1) *how* does absorption by gases in the atmosphere occur, (2) what physical properties of molecules determine *where* in the EM spectrum absorption lines or bands will occur, and (3) by what processes are absorption lines broadened about their nominal wavelengths, and what is the shape of the resulting broadened line? I will now put some of the above ideas into a practical context with a survey of those constituents responsible for most absorption and emission in the cloud-free atmosphere.

9.5.1 Atmospheric Absorbers in the IR Band

From the perspective of most mainstream atmospheric scientists, absorption by gases in the atmosphere is mainly a feature (or defect, depending on your point of view) of the IR bands. While not discounting the importance of absorption in other bands to a handful of overachievers (e.g., atmospheric chemists, stratospheric dynamicists, and microwave remote sensing specialists), it is safe to say that those individuals are not relying on this book alone for their education in atmospheric radiation.

Within the IR band (including near-, thermal-, and far-IR), the most important absorbers are carbon dioxide (CO₂), water vapor (H₂O), ozone (O₃), methane (CH₄), and nitrous oxide (N₂O). The major absorption features associated with each of these constituents was depicted in Fig. 7.6, which you may wish to refer back to occasionally while reading this section. It is perhaps no surprise that all of the above absorbers are (at least) triatomic, owing to the wealth of both rotational and vibrational transitions available in such molecules.

A broad-spectrum view of absorption by several representative molecules is depicted in Fig. 9.10. Included in this figure is a molecule of lesser importance, carbon monoxide (CO), which (fortunately for our health) is not usually present in the atmosphere in concentrations high enough to contribute much to atmospheric opacity. The reason for including CO here is to illustrate how much

simpler the absorption spectrum is for a diatomic molecule, which (as discussed earlier) has just one vibration quantum number v and one rotational quantum number J .

The most obvious feature of Fig. 9.10d is the evenly spaced series of major absorption bands of CO. Although it is less apparent in this figure, each band is actually a cluster of numerous closely spaced lines, most of which overlap strongly due to pressure broadening.

The first band on the far left (near zero wavenumber) is a pure rotation band with $\Delta v = 0$, each line corresponding to a transition from a particular initial J to the next higher value. Subsequent bands, moving from left to right, are associated with vibrational transitions $\Delta v = 1, 2, \dots$; their central positions are predicted by (9.23). The occurrence of simultaneous J transitions (both positive and negative) again splits each band into a cluster of closely spaced lines. In fact, it is not too much of a stretch to consider each major vibration-rotation band a near-clone of the one before it, since the fine-scale structure imposed by rotational transitions is similar in each case.

Turning our attention to the three triatomic molecules in Fig. 9.10(a–c), we see that the possibility of simultaneous transitions between multiple rotational and vibrational quantum numbers (up to three each) adds a fair amount of complexity to the absorption spectra. In particular, the “windows” between adjacent vibration bands are not nearly as broad and clear as they were for CO.

Note that CO₂ is the only molecule in Fig. 9.10 exhibiting no pure rotation band on the far left edge of the plot. As pointed out earlier, this is because CO₂ lacks a permanent electric dipole moment and can interact with radiation only via combined rotation-vibration transitions.

Let’s now take a closer look at absorption by selected atmospheric molecules.

Water Vapor

Globally speaking, water vapor (H₂O) is the single most important atmospheric absorber in the IR band. Fig. 9.11 gives a moderate-resolution depiction of the zenith transmittance due to water vapor alone under the conditions of temperature and humidity found in

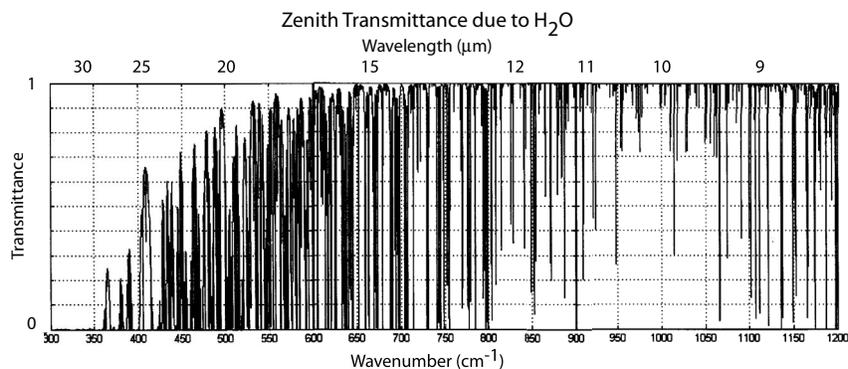


Fig. 9.11: Zenith transmittance of the atmosphere in a portion of the thermal IR band due to water vapor in a U.S. Standard atmosphere.

the U.S. Standard Atmosphere. The enormous complexity, and apparent randomness, of the line structure is readily apparent. This randomness is characteristic of a nonlinear molecule, owing to the wide range of rotational transitions that are available to it.

The most transparent region of the H₂O spectrum in the thermal IR band lies between about 8 and 12 μm . At longer wavelengths (smaller wavenumbers), the spectrum is increasingly dominated by the numerous lines due to pure rotational transitions. In fact, beyond about 25 μm , the atmosphere is effectively opaque and doesn't begin to open up again until well into the microwave band (not shown).

Not shown in Fig. 9.11 but visible in Fig. 9.10 are vibration-rotation bands centered around 6.3 μm and 2.7 μm , the latter falling solidly in the near-IR band. The 6.3 μm band is due to the ν_2 (bending mode) fundamental ($\Delta v = 1$), while both the ν_1 (symmetric stretch) and ν_3 (asymmetric stretch) fundamental modes contribute to absorption in the vicinity of 2.7 μm . Higher-order vibrational transitions ($\Delta v > 1$) contribute weak absorption bands at shorter wavelengths throughout the solar part of the spectrum. Also, as discussed earlier, not all of H₂O absorption is due to lines; there is also a significant continuum contribution throughout the IR band, though its overall intensity varies somewhat with wavelength.

An additional factor contributing to the complexity of the H₂O absorption band is the existence in the atmosphere of multiple iso-

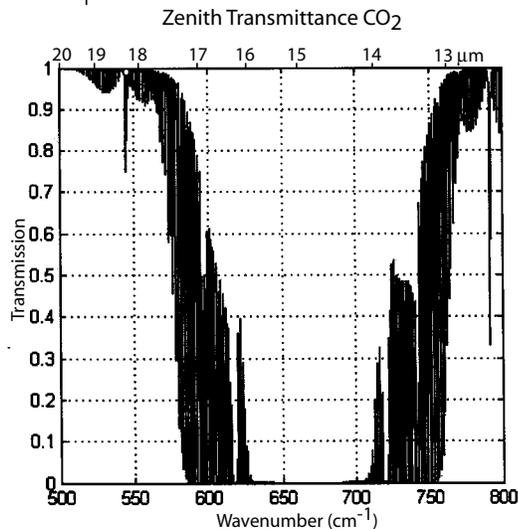


Fig. 9.12: Zenith transmittance of the atmosphere due to CO₂ in the vicinity of 15 μm.

topes of the constituent elements. In addition to the common hydrogen isotope ¹H, a small fraction (about 0.03%) of water molecules include at least one ²H, or deuterium (D) atom. Also, oxygen exists both as the ¹⁶O isotope and also the less common ¹⁸O isotope, found in about 0.2% of water vapor molecules. Naturally, changing the nuclear masses of one or more of the constituent atoms in a molecule alters both the rotational and vibrational spectra of the molecule, adding numerous new lines to those already contributed by the most common form. However, because isotopic variations of the water molecule comprise such a small fraction of the total, most of these added lines are relatively weak.

An important property of water vapor that is not shared with other radiatively important atmospheric gases is of course its enormous variability in both time and space. There are significant ranges of the IR spectrum for which the atmosphere may be virtually opaque under conditions of high humidity but relatively transparent (or at least translucent) in a dry arctic atmosphere.

CO₂ Transmission in air over 1 m path

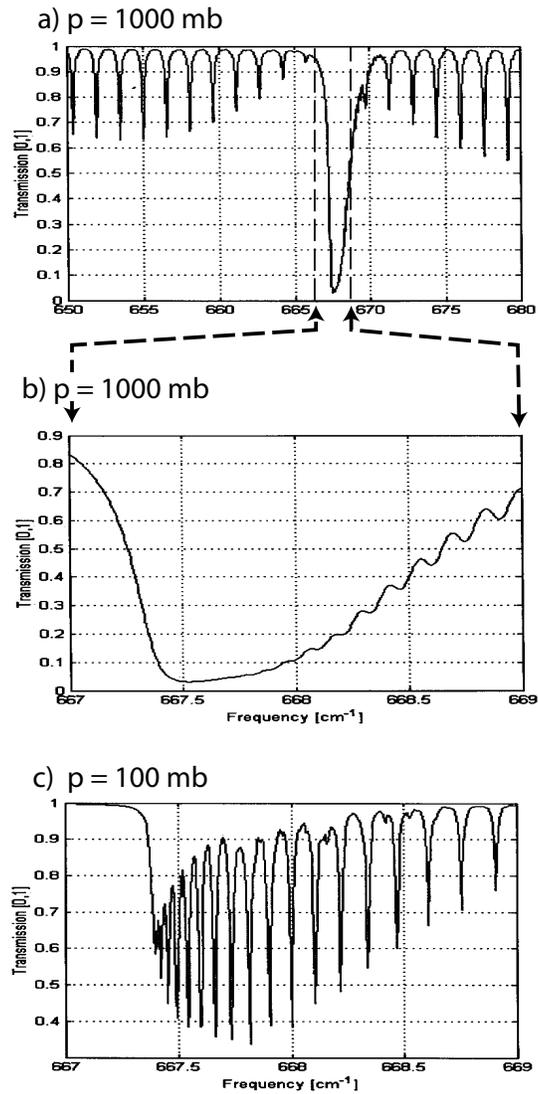


Fig. 9.13: (a) High resolution depiction of the transmission spectrum of a one-meter path through air with typical CO₂ concentration, at 1000 mb pressure. (b) Same as (a), but “zoomed in” on the central Q-branch. (c) Same as (b), but at reduced atmospheric pressure of 100 mb, revealing that what previously appeared as a single absorption line is actually a cluster of closely spaced but distinct lines.

Carbon Dioxide

No other atmospheric constituent is better known to the general public as a “greenhouse gas” than carbon dioxide (CO_2). In actuality, water vapor has a larger overall impact on the radiative energy budget of the atmosphere. But CO_2 is of particular concern from a public policy point of view owing to its steadily increasing abundance in the atmosphere due to fossil fuel use (see Fig. 7.5).

CO_2 possesses two very strong rotation-vibration bands in the IR band, one centered on $4.3 \mu\text{m}$ (v_3 fundamental), the other at $15 \mu\text{m}$ (v_2 fundamental). The $4.3 \mu\text{m}$ band is actually the stronger of the two, but because it’s located out on the edge of both the solar and longwave bands, it isn’t terribly important for broadband radiative fluxes in either band.

The $15 \mu\text{m}$ band is very important for longwave radiative transfer in the atmosphere, because it is positioned near the peak of the Planck emission function for terrestrial temperatures and renders the atmosphere completely opaque between 14 and $16 \mu\text{m}$ (Fig. 9.12). Moreover, the atmosphere is at least partly absorbing for several micrometers more to either side of the above wavelengths.

Problem 9.6: The effect of the CO_2 $15 \mu\text{m}$ band on atmospheric transmission to space of surface emission can be crudely approximated by assuming total opacity between 13.5 and $17 \mu\text{m}$, and total transparency outside these limits. Use Fig. 6.4 to estimate the fraction of surface longwave emission that is reabsorbed by the CO_2 in the atmosphere (ignoring other absorbers). Assume a surface temperature of 288 K .

Examining the center of the $15 \mu\text{m}$ band closely (Fig. 9.13), we find that it looks much like the idealized vibration-rotation band associated with a diatomic molecule — that is, it exhibits a strong central Q branch associated with pure vibration transitions ($\Delta v = 1$; $\Delta J = 0$), as well as the usual P branch ($\Delta v = 1$; $\Delta J = -1$) and R branch ($\Delta v = 1$; $\Delta J = +1$). Unlike the random-appearing H_2O rotation spectrum, the P and R branches for CO_2 consist of very regularly spaced lines, again as predicted for a diatomic molecule (Fig. 9.3).

Why does CO₂, which is triatomic, yield a spectrum so unlike that of another triatomic molecule, H₂O? The reason is that CO₂ is a linear molecule with effectively only one rotation mode (similar to a diatomic molecule), as compared with three for H₂O, which is an asymmetric top. This seemingly minor difference eliminates the whole universe of lines that would arise from transitions involving J_2 or J_3 .

As noted also for water vapor, isotopic variations of the constituent atoms multiply the total number of lines found in the CO₂ absorption spectrum. Here we have not only the two most common oxygen isotopes ¹⁶O and ¹⁸O, but also two major carbon isotopes ¹²C and ¹³C, the latter comprising about 1% of total carbon in the atmosphere.

We conclude our discussion of CO₂ by noting that the central lines of the 15 μm band are really quite strong. Despite the diluteness of CO₂ in air (about 370 parts per million by volume), the strongest part of the central Q branch (Fig. 9.13b) absorbs all but 5% of radiation over just a 1-meter path in air at 1000 mb pressure! Also, we see that, at reduced pressure (Fig. 9.13c), the Q branch resolves into a series of very closely spaced but separate lines. Each of these is associated with a ($\Delta v = 1$; $\Delta J = 0$) transition, but depending on the rate of rotation of the molecule (i.e., value of J), there are slight differences in the energy associated with a pure $\Delta v = 1$ transition.

Ozone

Ozone (O₃), which (except in urban pollution) is confined primarily to the stratosphere, is another nonlinear triatomic molecule, like water vapor. Therefore, it possesses many of the same general absorption features as water vapor, such as a relatively strong rotation spectrum consisting of numerous quasi-randomly spaced lines, as well as three fundamental vibrational bands ν_1 , ν_2 , and ν_3 . These bands, respectively, are found at 9.066, 14.27, and 9.597 μm. In the atmosphere, the 14.3 μm band is essentially masked by CO₂'s 15 μm band — that is, the presence or absence of ozone doesn't change much in this band, because absorption by CO₂ is already overwhelmingly strong.

The moderately strong ν_1 and very strong ν_3 bands are close

enough to each other that they are commonly viewed as a single entity known as the $9.6 \mu\text{m}$ band of ozone. Note that this band sits squarely in the middle of the $8\text{--}12 \mu\text{m}$ “window” of H_2O as well as falling not far from the peak of the Planck function for terrestrial emission. For both reasons, ozone is an important player in the atmospheric radiation budget, especially in the stratosphere.

Ozone also has a strong band at $4.7 \mu\text{m}$, but this is at the edge of the Planck functions for both solar and terrestrial emission (as was also the case for the CO_2 $4.3 \mu\text{m}$ band) and therefore is of very limited relevance for broadband radiative fluxes. Additional vibration-rotation absorption bands can be found in the near-IR regions of the spectrum down to about $2.5 \mu\text{m}$ (see Fig. 9.10c), but these are weak and therefore of only minor importance.

Also, as is well-known to the many specialists and laypeople alike concerned about recent observed declines in stratospheric ozone concentrations, ozone exhibits very strong absorption in the UV band below $0.28 \mu\text{m}$ due to electronic rather than vibrational excitations. As was discussed in Section 3.4.1, this absorption is exceedingly important for life on earth, because of the biologically damaging effects of UV-B radiation. A near-steady-state balance between absorption of solar UV-B and re-emission of longwave IR in the $9.6 \mu\text{m}$ band is largely responsible for the temperature structure of the stratosphere and lower mesosphere.

Methane

Methane (CH_4) is a spherical top molecule with five atoms and therefore $3(5) - 6 = 9$ fundamental modes of vibration. However, because of the symmetry of the molecule (four hydrogen atoms all bound to one central carbon atom), five of the modes are equivalent, leaving only four distinct modes v_1 , v_2 , v_3 , and v_4 . The most important of these are the v_3 and v_4 fundamentals at approximately $3.3 \mu\text{m}$ and $7.6 \mu\text{m}$, respectively. In addition, there are a few weak overtone ($\Delta v_i > 1$) and combination bands scattered through the near-IR.

Although methane is present in the atmosphere in relatively low concentrations, its $7.6 \mu\text{m}$ absorption band is strong enough, and is placed in an otherwise relatively transparent part of the atmo-

spheric spectrum (especially in a dry atmosphere) to have a measurable impact on longwave fluxes. In addition, it is now known that methane concentrations are increasing as a direct or indirect consequence of human activities.⁶

Nitrous Oxide

Nitrous oxide (N₂O) is another minor atmospheric constituent that nevertheless has a measurable radiative impact, primarily owing to its absorption band at 7.8 μm , which acts to broaden and strengthen the absorption band already present at 7.6 μm due to methane. In addition, there is a strong 4.5 μm band which, however, is less significant for the same reasons as given for the CO₂ 4.3 μm band and the ozone 4.7 μm band.

⁶To give just one example, widespread clearing of tropical forests has led to a marked increase in the number of methane-producing termite colonies, which thrive in the resulting open spaces!