

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 :

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