

# AT622 Section 8

## Elementary Molecular Spectroscopy

The aim of this section is to build up some understanding of how gases absorb, why only certain gases absorb and what dictates where they absorb in the atmospheric absorption spectrum.

### References

Chapter 3: Remote Sensing Notes  
Chapters 3, 4, and 5: Goody and Yung  
Selected reference cited in notes.

## 8.1 Atomic Absorption

In 1752 Thomas Melville studied the color of flames using a prism and found that the spectrum is not continuous like the spectrum of the sun or the radiation emitted by a blackbody. From this historical perspective we learned that the interaction of radiation with certain gases produce not a continuous spectrum like the emission spectrum but a discrete spectrum.

The realization that the bright line spectra of vaporized elements match the dark lines in the solar spectra (Fig. 8.1) was the key to understanding the quantum nature of matter. The basic explanation was forwarded by Bohr who perceived an orbital model of atoms (Fig. 8.2). Electrons falling from one level to a lower level give rise to emission of photons

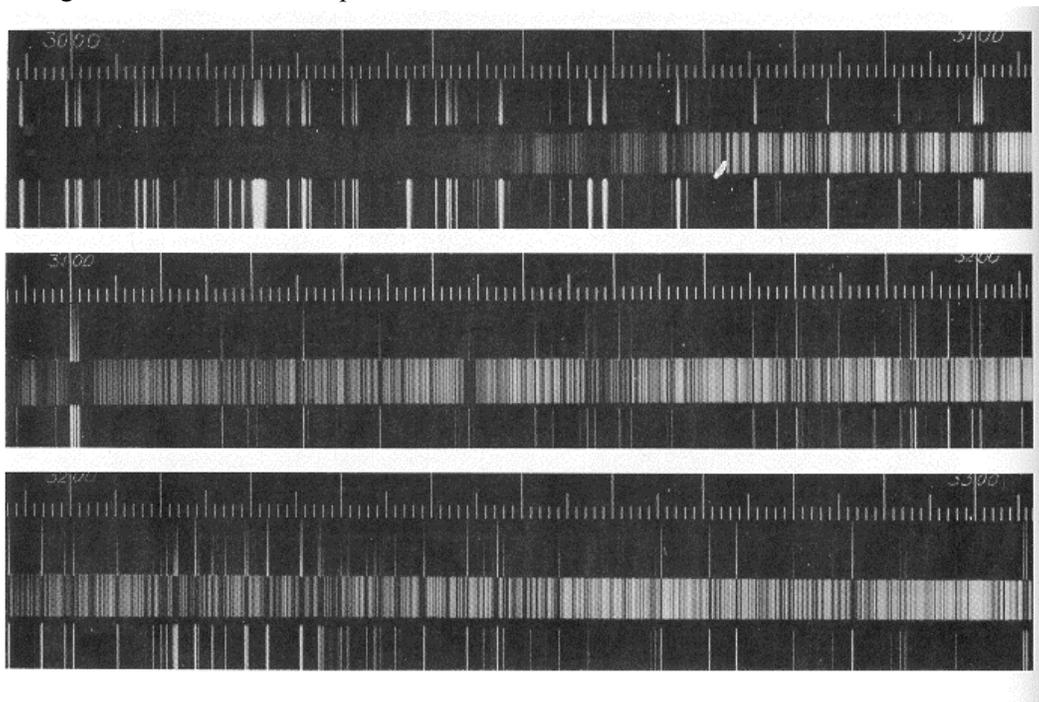


Fig. 8.1 The bright line spectrum of the vaporized element iron is shown with the spectrum of the sun. The wavelength regions are from  $300 \mu\text{m}$  to  $330 \mu\text{m}$ , in the ultraviolet. The solar spectrum is in the center of each strip, and the iron spectrum is above and below it. The bright lines of iron occur at the same wavelengths as some of the dark lines in the solar spectrum.

$$h\nu = E_2 - E_1 = \Delta E \quad (8.1)$$

- Thus absorption occurs when an electron jumps from level 1→2 (line absorption spectrum).
- Emission occurs when an electron falls from level 2→1 (emission spectrum).

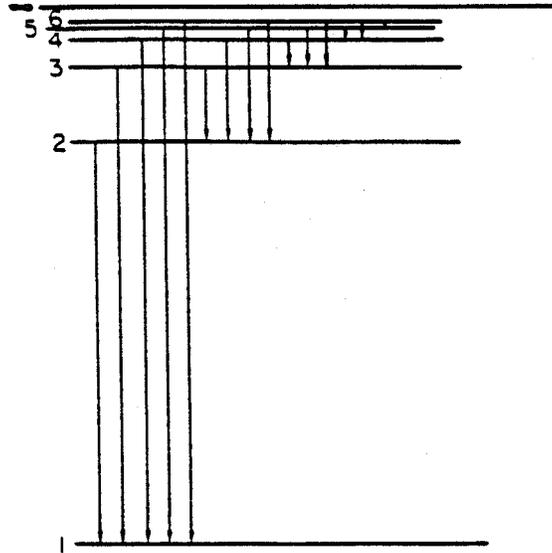
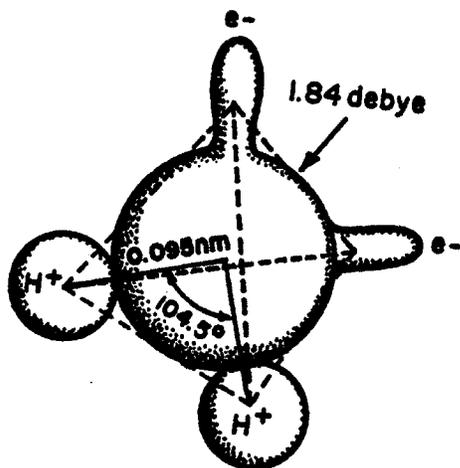


Fig. 8.2 Energy levels of the hydrogen atoms according to the Bohr theory. The first six levels are shown and drawn to scale. Level 1 is the atoms' ground state. Light is emitted whenever the atoms make a transition from a higher state to a lower one, and the frequency of light is proportional to the energy difference. Higher levels are closer together. The line labeled infinity ( $\infty$ ) represents the energy the electron would have if it became barely free; that is, just able to escape from the nucleus.

The atomic line spectrum is defined by internal energy states of atoms. The molecular line spectra are defined by the same plus the dynamic properties of the internal motions (such as vibrations and rotations). What determines whether a particular molecule absorbs radiation depends on, among other things, the way atoms are bonded and the geometry of the molecule.

The prevalent type of bonding is the covalent bond—viewed as a sharing of electrons. Certain molecules, like  $\text{H}_2\text{O}$  (Fig. 8.3) have a structure that naturally produces a dipole moment owing to the geometric configuration of the molecule that creates an asymmetry in the charge distribution that arises through this bonding. Molecules, like  $\text{H}_2\text{O}$ , that possess a permanent dipole moment are called polar molecules. Homonuclear molecules like  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{H}_2$  are homopolar as they do not possess a permanent  $\vec{p}$ . So too is  $\text{CO}_2$ . Homonuclear and homopolar molecules are not active absorbers in the IR region. An exception is pressure-induced absorption (e.g., in the atmosphere of Saturn). Polar molecules are radiatively active—the charge separation leads to oscillating charges, which according to EM theory produces an EM wave.



Molecule	$\mu$ , m C
HCl	$3.43 \times 10^{-30}$
HBr	$2.60 \times 10^{-30}$
HI	$1.26 \times 10^{-30}$
CO	$0.40 \times 10^{-30}$
H <sub>2</sub> O	$6.20 \times 10^{-30}$
H <sub>2</sub> S	$5.30 \times 10^{-30}$
SO <sub>2</sub>	$5.30 \times 10^{-30}$
NH <sub>3</sub>	$5.00 \times 10^{-30}$
C <sub>2</sub> H <sub>3</sub> OH	$3.66 \times 10^{-30}$

Molecules with zero dipole moment include: CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> (methane), C<sub>2</sub>H<sub>4</sub> (ethane), and CCl<sub>4</sub> (carbon tetrachloride).

Fig. 8.3 Schematic of atomic configuration and electronic orbitals for water molecule, with oxygen atom at center and hydrogen atoms at an angle of 105°. Dipolar character comes from protons at H<sup>+</sup> positions and unshared electrons at e<sup>-</sup> locations; the direction of the dipole moment is along the symmetry axis. The atoms and the electronic orbitals have tetrahedral symmetry. The table to the right lists the dipole moment for selected molecules.

## 8.2 Molecular Absorption Spectra

The absorption spectrum of a molecule is substantially more complex than that of an atom. Not only are transitions possible between the energy states of the atoms that make up the molecule, but also transitions occur between energy states associated with movements of the atoms themselves.

Since the energy required to induce a transition from a lower to a higher state is inversely proportional to the wavelength of the photon, the types of mechanisms that induce absorption also depend on the wavelength of the absorbed photon. These mechanisms must induce either a magnetic or an electric effect, which can be influenced by electromagnetic radiation. Mechanisms responding fastest occur at the shortest wavelengths whereas the more sluggish mechanisms produce absorption at longer wavelengths. We can use this wavelength dependence as a convenient classification of the absorption mechanisms as shown in Fig. 8.4, although the dividing boundaries are by no means precise.

- In the radio frequency regime, the absorption is associated with the nucleons and electrons, which we consider to be tiny charged particles that spin, producing tiny magnetic dipoles. The reversal of this dipole due to spin reversal interacts with the magnetic field at frequencies in the range  $3 \times 10^6$  to  $3 \times 10^{10}$  Hz.
- In the visible and ultraviolet region excitation of valence electrons results in moving electric charges in the molecule. Changes in the electric dipole give rise to a spectrum by its interaction with the oscillating electric field of radiation. These electronic transitions occur within the individual atoms of molecules and dominate the visible and ultraviolet portions of the electromagnetic spectrum. At even shorter wavelengths, photons can actually disrupt the absorbing molecule by *photodissociation* or even produce *photoionization* of individual atoms.
- Absorption by molecules in the mid and near infrared occur by vibration (although a mixture of vibrations and rotations are usually induced at these frequencies). Induction of vibrations requires

more energy than rotations and thus takes place at higher frequencies of infrared wavelengths between about 0.7  $\mu\text{m}$  and about 20  $\mu\text{m}$ .

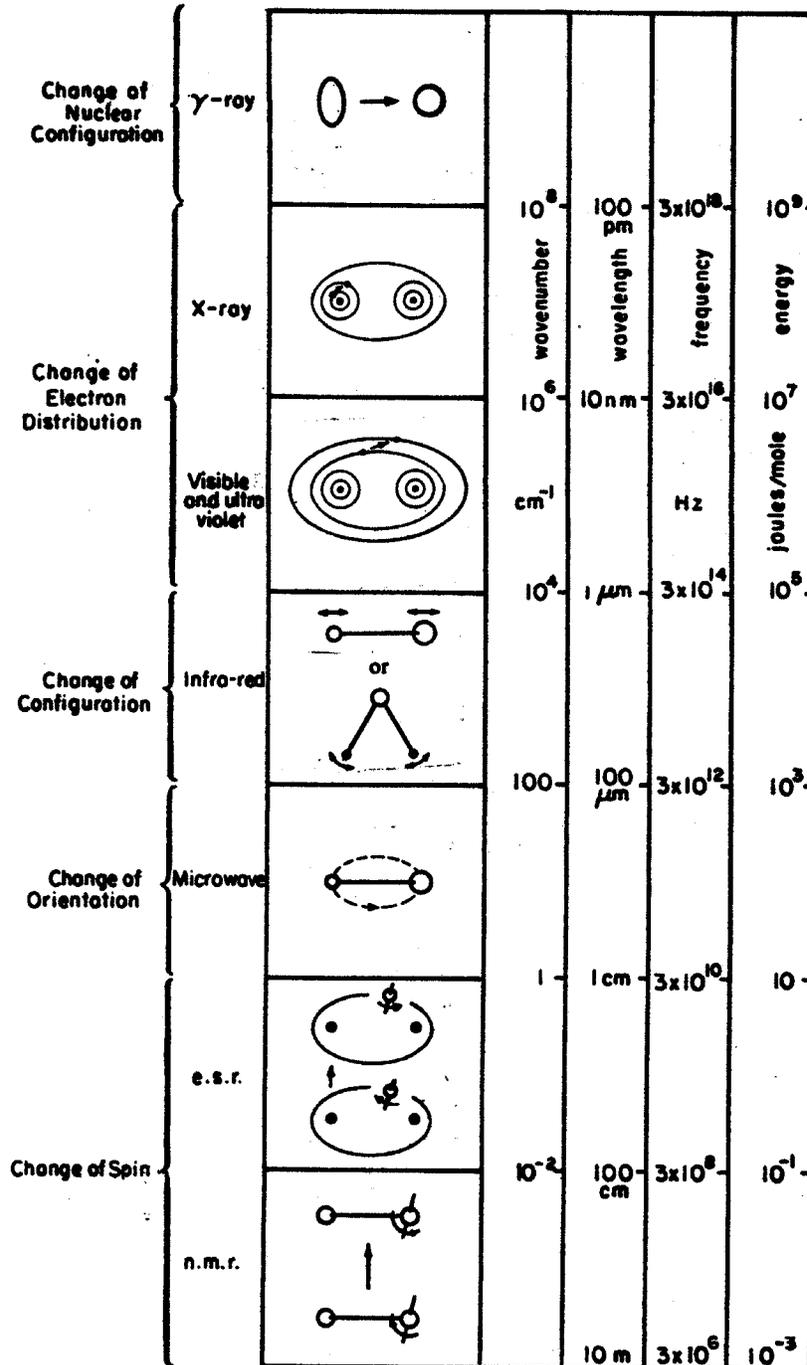


Fig. 8.4 The electromagnetic spectrum and the possible types of interactions between photons and a molecule or atom (Bandwell, 1983).

- In the microwave and far infrared, the molecule undergoes a rotation like that depicted in Fig. 8.5a and the component of the dipole in a given direction fluctuates in a regular fashion as shown in the lower part of Fig. 8.5a. These fluctuations are more sluggish than are the fluctuations associated with vibrations or the fluctuations associated with electronic transitions. Rotational lines generally occur in bands at the longer infrared wavelengths beyond about  $20\ \mu\text{m}$  extending into the microwave spectral region where individual rotational lines can be resolved.

As a consequence of the vibrational-rotational transitions, absorption lines are spread into bands containing many lines (as illustrated in Fig. 8.5b), which are used, either individually or as a group, to fingerprint molecules in the same way that atomic spectral lines fingerprint atoms. It is the vibrational-rotational absorption spectrum of molecules that is largely of interest to topics discussed in these notes.

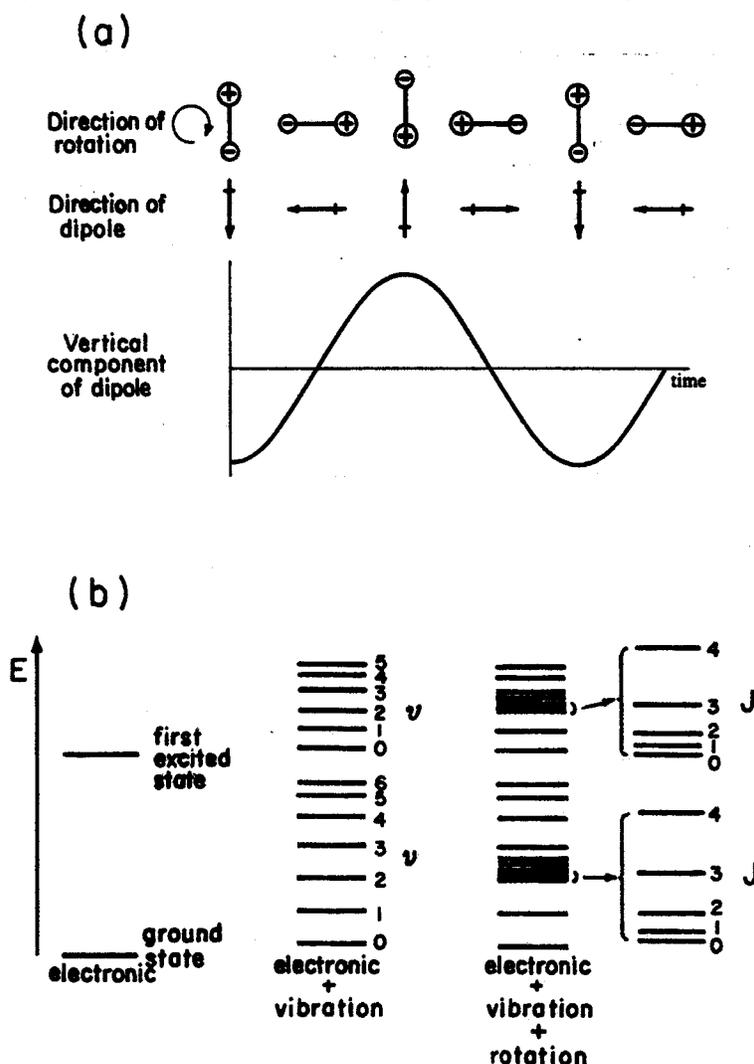


Fig. 8.5 (a) The rotation of a simple diatomic molecule showing the fluctuation in the dipole moment measured in a particular direction (Bandwell, 1983). (b) Molecular absorption spectra actually consist of closely spaced lines due to rotational and vibrational transitions.  $J$  and  $v$  refer to the quantum numbers associated with the rotational and vibrational transitions, respectively. This diagram shows how these transitions are superimposed on electronic states.

### 8.3 Simple Model Analogs of Vibrating and Rotating Molecules

Despite the complexity of the absorption processes within molecules, we can begin to understand their spectra by drawing on results from simple mechanical analogs to vibrating and rotating molecules.

(a) *Simple Model of Rigid Rotators*

Consider a simple diatomic molecule (Fig. 8.6), with the moment of inertia

$$I = m_1 r_1^2 + m_2 r_2^2 ,$$

and the center of mass

$$m_1 r_1 = m_2 r_2 .$$

Thus

$$I = \frac{m_1 m_2}{m_1 + m_2} (r_1 + r_2)^2$$

or

$$I = m' r^2$$

where  $m'$  is the reduced mass of the molecule and  $r$  is the distance between the two atoms. Quantum mechanics tells us that the angular momentum is  $L = I\omega = \sqrt{K(K+1)}\hbar$  where  $K$  is the rotational quantum number ( $K = 0, 1, 2, \dots$ ). As noted above, only molecules with electric dipole moments (e.g., HCL) can interact with electromagnetic photons. The energy of a rigid rotator is

$$E = \frac{1}{2} I \omega^2 = \frac{L^2}{2I} = \frac{K(K+1)}{2I} \hbar^2 .$$

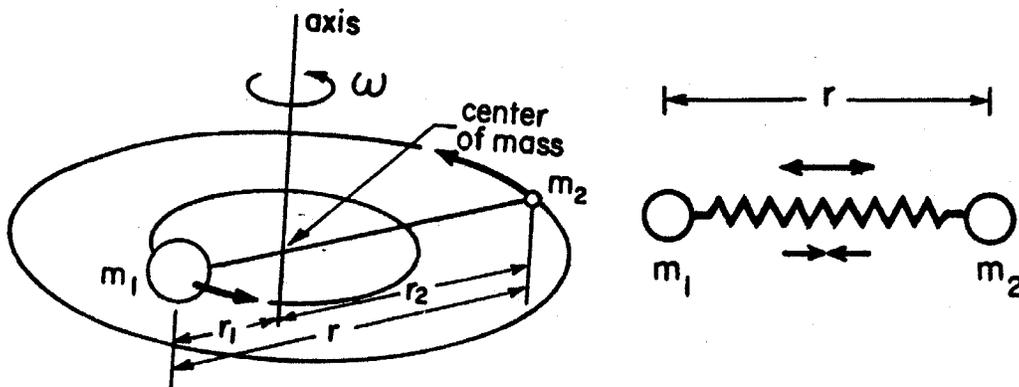


Fig. 8.6 A diatomic molecule that rotates and vibrates about its center of mass.

Thus, since

$$\begin{aligned}\Delta E &= E_{K+1} - E_K = h\nu \\ \nu &= \frac{\hbar}{2\pi I}(K+1) \\ \Delta\nu &= \nu_K - \nu_{K-1} = \frac{\hbar}{2\pi I}(K+1 - K)\end{aligned}\tag{8.2}$$

Thus, the energy levels predicted for a diatomic molecule give rise to equally spaced absorption lines spaced  $\Delta\nu \approx \frac{\hbar}{2\pi I}$  apart (Fig. 8.7).  $B = \frac{\hbar}{2\pi I}$  is a basic quantity of the molecule known as the rotational constant.

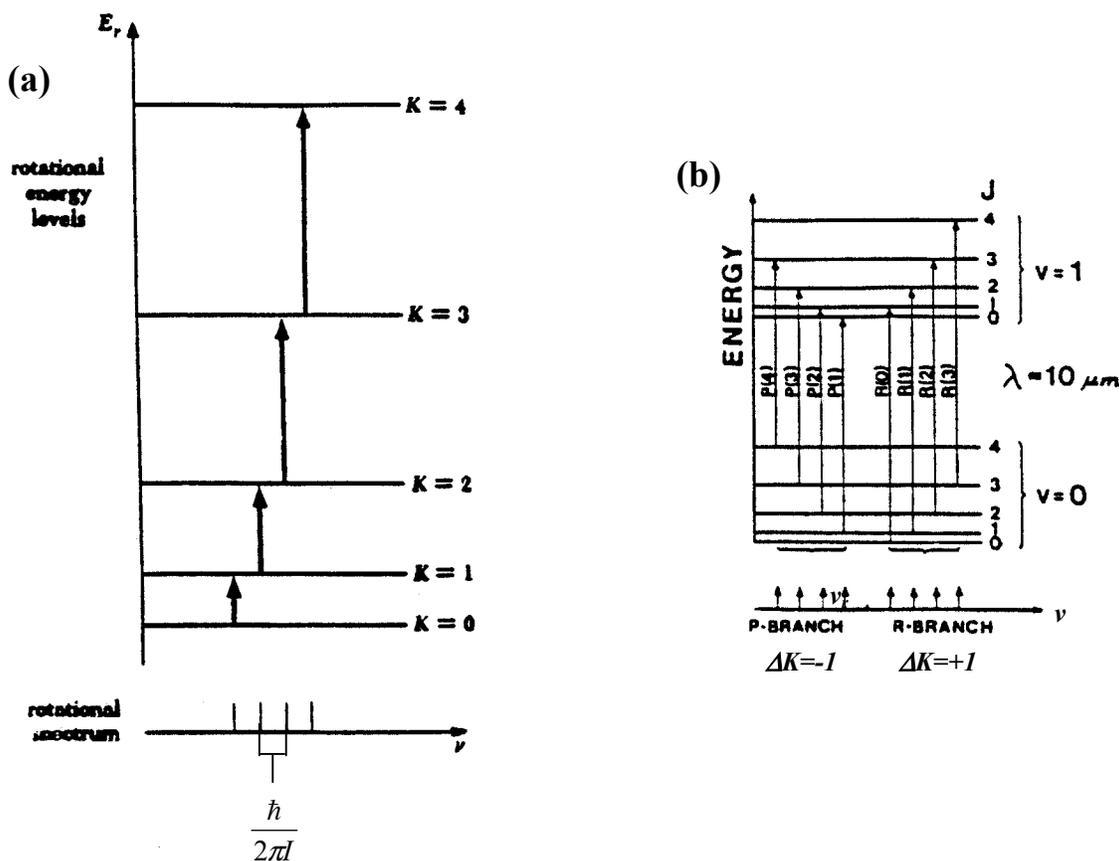


Fig. 8.7 (a) Energy levels and rotation spectrum of diatomic molecule. (b) Vibration-rotation spectra of a hypothetical diatomic molecule.

Note that:

- $\nu \rightarrow (I)^{-1}$ . If we assume a value of  $r$  that is similar for all diatomic molecules, then the  $\nu$  spectra is largely determined by the mass distribution within molecules. For typical molecules ( $H_2O$ ),  $\nu_{\text{rotation}} \geq 20 \mu m$ .

From Eqn. (8.2) the moment of inertia of a molecule can be deduced from its rotational spectra and, since the masses of its constituent atoms are known, the interatomic separation  $r$  can be calculated.

Rotational molecules are generally specified in terms of its three principal moments of inertia

- Linear molecules:  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ ,  $\text{C}_2\text{H}_2$ ...
- Symmetric to  $p$  molecules:  $\text{NH}_3$ ,  $\text{CH}_3\text{Cl}$ ,  $\text{CF}_3\text{Cl}$ , nonlinear with  $I_1 = I_2$ ,  $I_3$  different
- Spherical symmetric top: (methane)  $I_1 = I_2 = I_3$
- Asymmetric top:  $\text{H}_2\text{O}$ ,  $\text{O}_3$  - all three moments of inertia are different. Absorption spectra defined by three rotational constants  $= \frac{\hbar}{2\pi I}$  and three sets of rotational quantum numbers.

### (b) Elementary Discussion of Vibrating Molecules

Excitation energy required to vibrate molecules is greater than that of rotation—so rotation always accompanies vibration. Vibration can be treated as a simple analogy to two masses attached to a spring, for which the restoring force related to some displacement about equilibrium is

$$F = -k(r - r_e)$$

For a harmonic oscillator, the frequency of the vibrating body is

$$\nu' = \frac{1}{2\pi} \sqrt{\frac{k}{m'}}$$

Quantum theory predicts that the frequency of a harmonic oscillator is quantized such that

$$\nu = \left( \nu_i + \frac{1}{2} \right) \frac{1}{2\pi} \sqrt{\frac{k}{m'}} = \left( \nu_i + \frac{1}{2} \right) \nu'$$

where  $\nu$  is the vibrational quantum number.

The energy required for a vibrational transition is larger than that required for a rotational transition. Vibrations, however, are typically accompanied by rotations so the rotating molecule is not exactly like a rigid rotator. We learn from quantum mechanics however, that only certain types of vibrations and rotations are permitted together. These are defined by selection rules, which for the diatomic molecule (or a longitudinal polyatomic molecule like the carbon dioxide molecule), the transition  $\Delta\nu = \pm 1$  occurs simultaneously with a  $\Delta K = \pm 1$  transition. This selection rule produces pairs of transitions of the form shown in Fig. 8.7b. As a rule, each vibrational transition frequency is split up into a series of spectral lines with mutual separations that approximately correspond to the respective rotational constant. In Fig. 8.7b, the vibrational transition from  $\nu = 0$  to  $\nu = 1$  is shown. Two branches of rotation lines result for this vibrational transition: one for  $\Delta K = +1$ , which is referred to as the *R branch* and the other for  $\Delta K = -1$ , the *P branch*.

### (c) Triatomic Molecules

The rotational and vibrational absorption spectra of polyatomic molecules are much more complex than are the spectra of diatomic molecules owing to the higher degrees of freedom of both vibrational and rotational motions. The absorption spectra of the  $\text{CO}_2$  molecule are highly relevant to atmospheric remote sensing. The  $\text{CO}_2$  molecule vibrates in four different modes, two of which are energetically equivalent.

These modes are referred to as the *symmetric stretch mode*, the *asymmetric stretch mode*, and the *bending mode*, which has two equivalent modes of vibration. The dipole moment of the symmetric stretch mode is plainly zero throughout the whole motion (Fig. 8.8a) and this vibration is radiatively inactive. The asymmetric stretch produces a periodic alteration of the dipole moment and this mode is 'infrared active' as is the bending mode (Figs. 8.8b and c). The bending mode actually permits  $\Delta v = \pm 1$ ,  $\Delta K = 0$  transitions. These transitions then produce a large absorption peak centered on the fundamental frequency of the oscillator. The absorption is strong at these frequencies due to the superposition of all  $\Delta v = 1$  transitions between all available  $J$ -levels. This absorption is referred to as the *Q branch*.

Another molecule of considerable importance to the study of the Earth's atmosphere is the  $\text{H}_2\text{O}$  molecule. Since this molecule is not linearly arranged like the  $\text{CO}_2$  molecule, geometrically different modes of vibration and rotation occur. Figure 8.8d indicates the three modes of vibration of the water molecule. Superimposed on these three modes are the rotational modes around three axes of rotation. The spectra arising from the multiplicity of vibration-rotation transitions are accordingly complex producing absorption spectra that are more irregular in appearance.

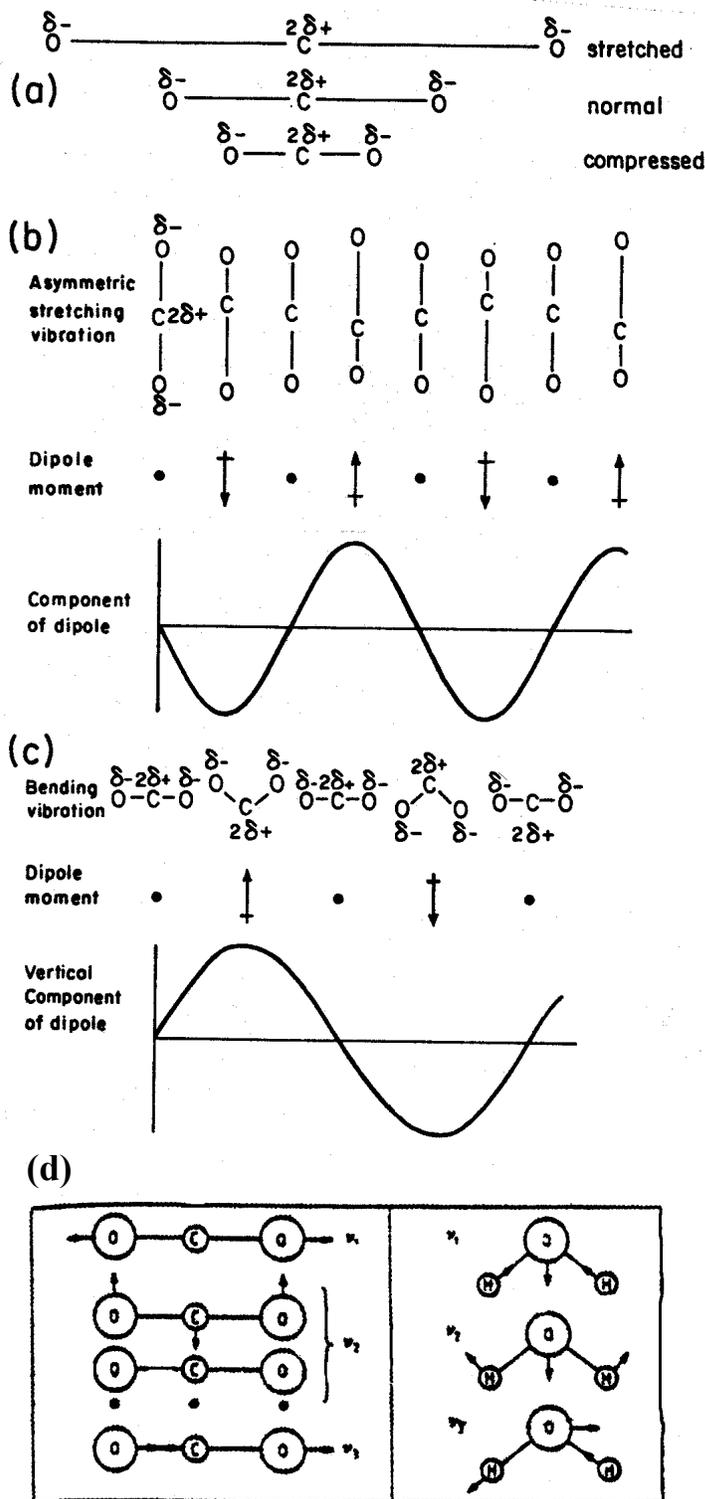


Fig. 8.8 (a) The symmetric stretching of a vibrating  $\text{CO}_2$  molecule. (b) The asymmetric stretching of the  $\text{CO}_2$  molecule showing the fluctuating dipole moment. (c) The bending motion of the carbon dioxide molecules and its associated dipole fluctuation (Bandwell, 1983). (d) Vibrational modes of a water-vapor molecule.

## 8.4 The Absorption Coefficient

Energy states of a molecule are more complicated in structure than of individual atoms. This arises from complicated motions of the atomic nuclei that make up the molecule. The electronic excitation to higher energy levels within the atoms of the molecule require much more energy and involve radiation in the shorter visible and UV. Superimposed on these electronic transitions are the vibration and rotation effects (Fig. 8.9 and Table 8.1).

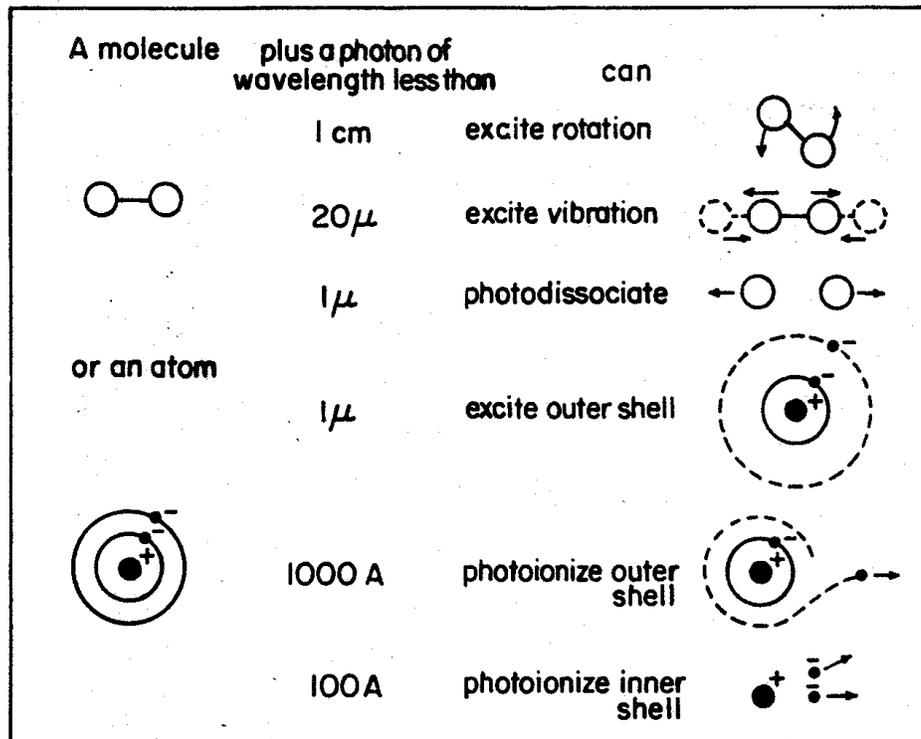


Fig. 8.9 Possible interactions between a molecule or atom and a photon. The longer wavelength events, which involve less energy, are at the top. Bands in molecular spectra actually consist of closely spaced lines due to rotational and vibrational transitions.

Table 8.1 Typical energy differences and spectral ranges in electronic, vibrational, and rotational transitions.

Transition	$\Delta W$ [eV]	$\nu = \Delta W/h$ [Hz]	Spectral range
Electronic	10	$2.4 \times 10^{15}$	Ultraviolet and visible
Vibration	$10^{-1}$	$2.4 \times 10^{13}$	Infrared
Rotation	$10^{-3}$	$2.4 \times 10^{11}$	Millimeter waves

The absorption spectra are characterized in terms of the absorption coefficient  $k_\nu$ . For an absorption line,  $k_\nu$  is characterized by its

- spectral position  $\nu_0$ , (and is determined by the factors already considered)

- strength  $S$  (or effectiveness of absorber)
- shape  $f(\nu - \nu_o)$  (spectral "fine structure").

That is

$$k_\nu = Sf(\nu - \nu_o) \quad (8.3)$$

where the shape factor

$$\int_{-\infty}^{\infty} f(\nu - \nu_o) d\nu = 1$$

by definition. We now consider the latter two factors in more detail.

(a) *Line Strength*

This is a product of two distinct factors

- probability that a single isolated molecule in its lower state will absorb a photon (cross section  $\sigma$ )
- relative population of lower and upper states

Thus

$$S = \sigma (n - n_u)/n_{total}$$

The relative populations are determined by Boltzman's distribution (and hence are a function of temperature) according to  $e^{-\Delta E/KT}$ . (This is not true in the mesosphere where a "breakdown" of local thermodynamic equilibrium occurs). Here,  $\Delta E$  is the energy associated with a particular  $\nu$  and  $K$  transition. The effect of this factor on the absorption spectrum occurs in the following way:

- Since  $\Delta E$  is proportional to  $K + 1$  for rotational lines, the line intensities are largest (i.e., absorption strongest) near the shortest wavelengths of each band. The important feature is the absorption line strength is temperature dependent owing to the temperature effects on population.

(b) *Line Shape*

Lines are not sharp but "fuzzy". Three main mechanisms for broadening lines are

- Natural broadening

The energy level can only be defined within the uncertainty  $\Delta E$  defined according to

$$\Delta E \Delta t \leq h/2\pi$$

$$\frac{\nu}{2} = \frac{1}{4\pi\Delta t} = \sigma_N \quad (8.4a)$$

If we take the mean lifetime in the upper state of molecules as indicative of  $\Delta t$ , then we can derive an estimate of  $\sigma_N$  typically ( $\sim 3 \times 10^{11} \text{ cm}^{-1}$ ), which is negligible for absorptions in the troposphere and stratosphere.

- Doppler broadening

Line broadening can occur through the motion of the molecules in the earth's atmosphere as they move about in random directions. The probability that molecules in a gas at temperature  $T$  possesses a velocity  $v$  is given by the Maxwellian distribution  $\exp[-m_m v^2/2kT]$  where  $m_m$  is the molecular mass.

The shift in frequency due to such motion is

$$v - v_o = \Delta v = \pm \frac{v}{c} v_o$$

and the distribution of Doppler shifts follows as

$$f_D(v - v_o) = \frac{1}{\alpha_D \sqrt{\pi}} \exp(-(v - v_o)^2 / \alpha_D^2) \quad (8.4b)$$

where  $\alpha_D$  is the Doppler half width  $\left( \alpha_D = v_o \sqrt{\frac{2KT}{mc^2}} \right)$ . This derivation assumes the distribution

$$p(v)dv = \left( \frac{m}{2\pi kT} \right)^{1/2} \exp\left( \frac{-mv^2}{2kT} \right) dv$$

$$f(v - v_o) = \int_{-\infty}^{\infty} p(v) \Delta v dv = \int_{-\infty}^{\infty} p(v) \frac{v v_o}{c} dv$$

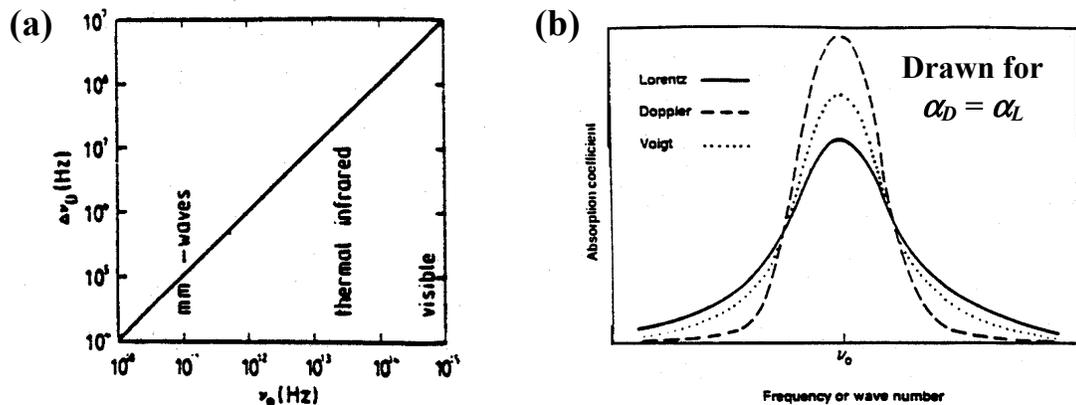
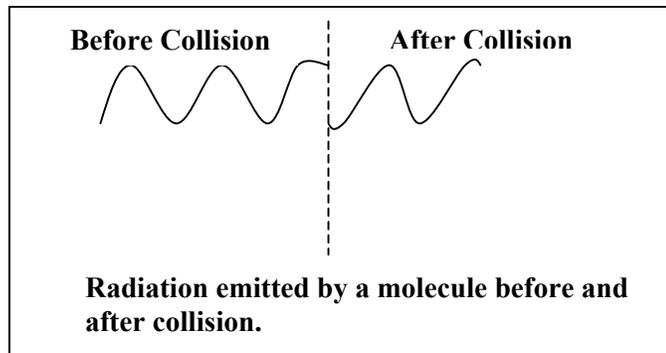


Fig. 8.10 (a) Typical width of Doppler broadened lines of light molecules at room temperature as a function of the respective center frequency. (b) Lorentz and Doppler line shapes from approximately equal half-widths and intensities. The corresponding Voigt profile is also shown.

For  $\text{CO}_2$  and IR wavelengths,  $\alpha_D \sim 7 \times 10^{-4} \text{ cm}^{-1}$ . Doppler broadening is mainly important in the stratosphere and above. Accurate measurements of line width at low pressures allow deduction of  $T$  (through  $T^{1/2}$  dependence).

- Pressure broadening

The third line broadening mechanism, and the one most relevant to our interests is through the effects of collisions (collision/pressure broadening). No precise model of this collision exists (the 'many' bodied problem). So simple conceptual models of collisions are employed. One model is to treat the collision as a discontinuity in the phase of the EM wave. These phase shifts are modeled as randomly occurring between 0,  $2\pi$  and the period of collision is considered small compared to the period associated with passage of one wavelength.



The simplest and most successful treatment of this broadening is that of Lorentz

$$f_L(\nu - \nu_o) = \frac{\alpha_L / \pi}{(\nu - \nu_o)^2 + \alpha_L^2} \quad (8.4c)$$

for which  $\alpha_L = \frac{1}{2} \pi \bar{t}$  ( $\bar{t}$  = mean time between collisions, i.e., the more the collisions the broader the line). It follows that

$$\alpha_L \sim \alpha_{Lo} \left( \frac{P}{P_s} \right) \left( \frac{T_s}{T} \right)^{1/2} \approx 0.07 \left( \frac{P}{P_s} \right) \left( \frac{T_s}{T} \right)^{1/2} \text{ cm}^{-1}$$

For example  $P_s = 1000 \text{ mb}$ ,  $T_s = 273$ ,  $\alpha_L$  ranges between  $0.005 - 0.11 \text{ cm}^{-1}$ .

Lorentz width is proportional to pressure (this is well confirmed by measurements). Dependence on  $T$  is less important and less well understood. Pressure dependence of absorption is of fundamental importance.

Some issues are:

- Line width is a function of type of colliding molecule (mostly  $N_2$ ). Self-broadened lines (e.g.,  $H_2O \rightarrow H_2O$ ) are broader than foreign-broadened lines ( $N_2 \rightarrow H_2O$ )
- A fundamental problem is in the wings of Lorentz lines—extended wings are important to transparent regions of the spectrum (windows). Departures from Lorentz line shapes (super and sub Lorentzian) in the extended wings are virtually impossible to measure and a major source of uncertainty. In the far wings  $\nu - \nu_o \gg \alpha_L$  and

$$f_L(v-v_o) \approx \frac{\alpha_L \left(\frac{P}{P_s}\right) \left(\frac{T_s}{T}\right)^{1/2}}{(v-v_o)^2} \quad (8.5)$$

- Example of the significance of  $p$  effect on line shape: intuitive description of weighting functions that are relevant to topics of remote sensing profiles of temperature and certain species.

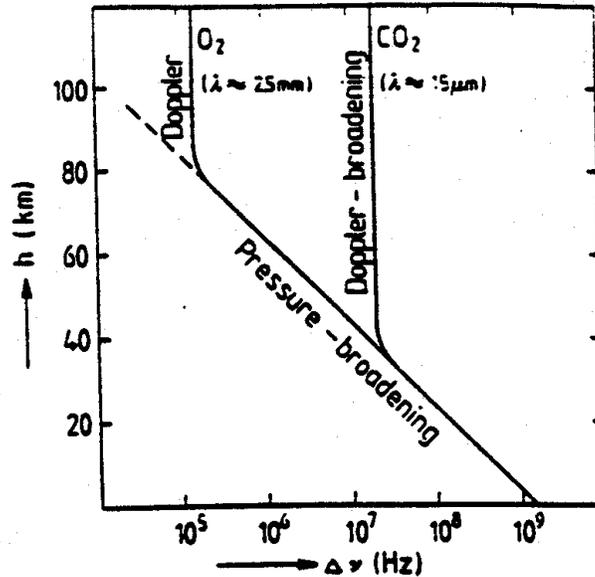


Fig. 8.11 Approximate relationship between atmospheric height  $h$  and line width for a microwave line of  $O_2$  and an infrared line of  $CO_2$  (idealized isothermal atmosphere and equal  $\Delta\nu_o$  values for  $O_2$  and  $CO_2$  are assumed).

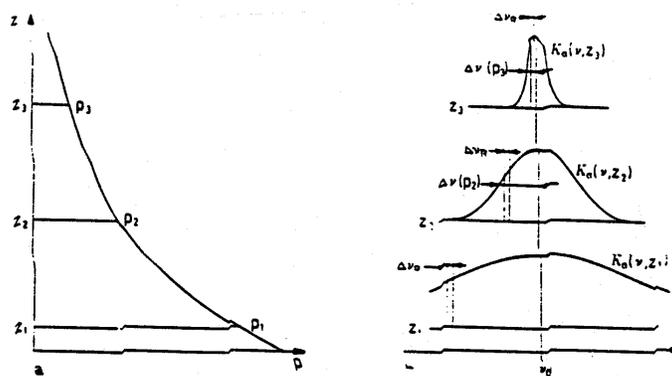


Fig. 8.12 (a) The atmospheric pressure as a function of the height. (b) The line shapes at three different height levels and filter positions.

## 8.5 Problems

### Problem 8.1

The wavelength of radiation absorbed during a particular spectroscopic transition is observed to be 10  $\mu\text{m}$ . Express this in frequency (Hz) and in wavenumber ( $\text{cm}^{-1}$ ) and calculate the energy change during the transition in both joules per molecule and joules per mole. If the energy were twice as large, what would be the wavelength of the corresponding radiation? Hint: Planck's constant has the value  $h = 6.63 \times 10^{-24}$  joules $\cdot$ s $\cdot$ molecule $^{-1}$ . Avagadro's number  $N = 6.02 \times 10^{23}$  mol $^{-1}$ .

### Problem 8.2

The rotational spectrum of  $^{79}\text{Br}^{19}\text{F}$  shows a series of equidistant lines spaced  $0.71433 \text{ cm}^{-1}$  apart. Calculate the rotational constant  $B$  and hence the moment of inertia and the bond length of the molecule. Determine the wavenumber of the  $J = 9 \rightarrow J = 10$  transition.

### Problem 8.3

Using your answers to Problem 8.2, calculate the number of revolutions per second that a BrF molecule undergoes when in (a) the  $J = 0$  state, (b) the  $J = 1$  state. [Hint: Use (3.9) but remember that  $\omega$  is in radians per second.]

### Problem 8.4

The masses of the H, Cl, C, and O atoms are  $1.6 \times 10^{-27}$  kg,  $58.8 \times 10^{-27}$  kg,  $20 \times 10^{-27}$  kg, and  $26.5 \times 10^{-27}$  kg, respectively.

- Calculate the reduced masses of the HCl and CO molecule.
- If the spring constants of the HCl and CO molecules are  $4.78$  and  $1907 \text{ kgs}^{-2}$ , respectively, determine the wavelength of the vibrational transition  $0 \rightarrow 1$ .

### Problem 8.5

Derive a relationship between the central frequency  $\nu_o$  of a line and the pressure (in atmospheres) at which the half-widths of a Lorenz line and a Doppler line are the same. Estimate this pressure for a  $\text{CO}_2$  and  $\text{O}_2$  molecule for the frequencies and temperature used to produce the curves shown in Fig. 8.11b. Assume the reference value of the Lorenz half-width at the ground is that given in Fig. 8.11b.