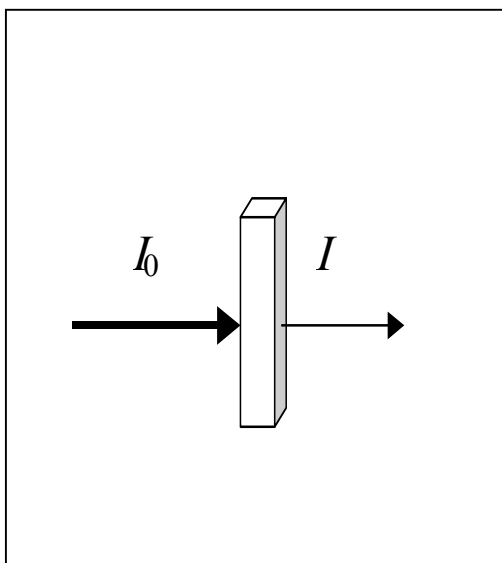


## CHAPTER 13 LECTURE NOTES

Spectroscopy is concerned with the measurement of (a) the wavelengths (or frequencies) at which molecules absorb/emit energy, and (b) the amount of radiation absorbed at these various wavelengths (or frequencies). A plot of the amount of radiation absorbed (or emitted) as a function of wavelengths or frequencies is called a spectrum. The basis for measuring the amount of radiation absorbed is the Lambert-Beer law.

### 13.1. Lambert-Beer Law



Consider a light source that produces light of intensity  $I_0$ . This light is allowed to pass through a cell containing a sample, say a solution of concentration  $c$ . The path length of the beam of light is  $l$ . Let the intensity of the transmitted light beam be  $I$ .

Then, the Lambert-Beer law states that the variation of the intensity of the incident beam as it passes through the cell is proportional to the concentration and the path length:

$$-\frac{dI}{I} = \kappa c dx,$$

where the negative sign indicates that the intensity decreases with length  $dx$ , and  $\kappa$  is the proportionality constant. Integrating both sides, we get

$$-\int_{I_0}^I \frac{dI'}{I'} = \kappa c \int_0^l dx,$$

which gives

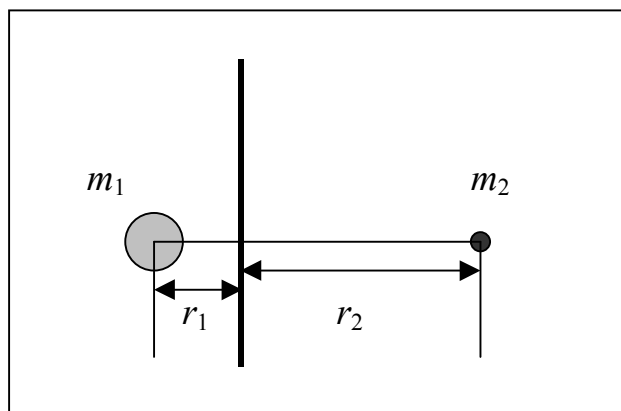
$$A = \log_{10} \frac{I_0}{I} = \epsilon c l. \quad (13.16)$$

Note that we have switched from natural logarithms to  $\log_{10}$ . This also requires a re-definition of the proportionality constant, which is now called the **molar absorption coefficient**. The left hand side is called the **absorbance** of the sample. This equation, Eq. (13.16) in the text, is the statement of the Lambert-Beer law.

**Example 13.2, Problems: 13.4–13.6, 13.10.**

### 13.3. Pure Rotational Spectrum of Molecules

Recall that a molecule, which is a quantum system, can only absorb or emit radiation in discrete amounts, given by  $h\nu$ . The magnitude of the frequency depends on the energy difference between the initial and final states. In the case of rotational spectra, these frequencies typically correspond to the **microwave region** of the electromagnetic spectrum.



The quantum mechanical model we will adopt for studying the rotational spectra of diatomic and linear triatomic molecules is the rigid rotor model. The distance to the two masses from the center of mass defines the moment of inertia  $I$ :

$$I = m_1 r_1^2 + m_2 r_2^2 = \mu r_0^2,$$

where the interatomic distance (or bond length)  $r_0 = r_1 + r_2$  and the reduced mass  $\mu = m_1 m_2 / (m_1 + m_2)$ . Thus, the rotation of the two masses  $m_1$  and  $m_2$  of a diatomic molecule about the axis of rotation is equivalent to the rotation of a single mass  $\mu$  at a distance of  $r_0$  from the origin. From our earlier treatment of the particle on a sphere problem, the energy of such a system is well-known:

$$E_J = J(J+1) \frac{\hbar^2}{2I}, \quad J = 0, 1, 2, \dots$$

where we used the letter  $J$  rather than  $l$  for the quantum number, in order to conform to common convention.

In the case of the rigid rotor, it is possible to show that the most probable rotational transitions are those for which  $\Delta J = \pm 1$ . This is known as the **selection rule** in rotational spectroscopy.

Consider the energy difference between a given energy level labeled by  $J$  and the next higher energy level, labeled by  $J+1$ :

$$\begin{aligned} \Delta E = E_{J+1} - E_J &= [(J+1)(J+2) - J(J+1)] \frac{\hbar^2}{2I} \\ &= 2(J+1) \frac{\hbar^2}{2I}. \end{aligned}$$

Now,  $\Delta E = h\nu$ . In rotational spectroscopy, the traditional units of energy is the wave number,  $\text{cm}^{-1}$ , defined as  $\Delta E/(hc)$  and denoted as  $\tilde{\nu}$ , where the velocity of light is in units of  $\text{cm s}^{-1}$ . Therefore, we get

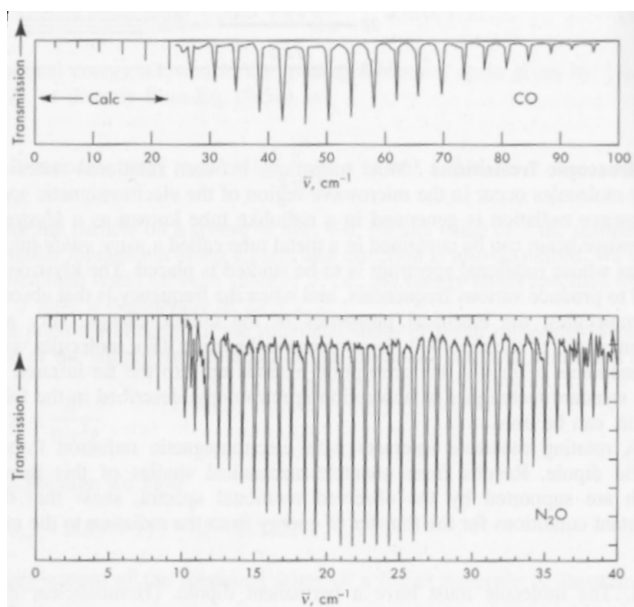
$$\begin{aligned}\tilde{\nu}(\text{cm}^{-1}) &= \frac{\Delta E}{hc} = 2(J+1) \frac{h}{8\pi^2 I c} \\ &= 2(J+1)\tilde{B}.\end{aligned}\tag{13.62}$$

The constant  $B$  is called the **rotational constant**, and its definition is obvious from the first equation above.

The figures below show the pure rotational (or microwave) spectrum of CO and the linear triatomic molecule  $\text{N}_2\text{O}$ . The spectra show transmittance, defined as  $I/I_0$  or

$$\log_{10}(1/T) = A.\tag{13.11}$$

So, the amount of transmitted light decreases sharply at regular intervals along the frequency axis, indicating that the molecules absorb radiation at these frequencies.



According to Eq. (13.62), the absorption of radiation occur at frequencies  $2B, 4B, 6B, 8B, \dots$  corresponding to transitions  $0 \rightarrow 1, 1 \rightarrow 2, 2 \rightarrow 3, 3 \rightarrow 4, \dots$ . The spacing between adjacent lines is constant, at  $2B$ , a characteristic pattern of a rigid rotor. [To the extent that real molecules are not “rigid,” the observed patterns do not exhibit a truly constant spacing over broad frequency ranges.]

The observed line spacings in microwave spectra for almost all known diatomic and linear triatomic

molecules can be readily matched with existing databases so that the compound can be identified. Since, from a microwave spectrum, we can get the (average) value of the rotational constant,  $B$ , the definition of  $B$  above can be used to calculate the moment of inertia and thus the interatomic distance  $r_0$ .

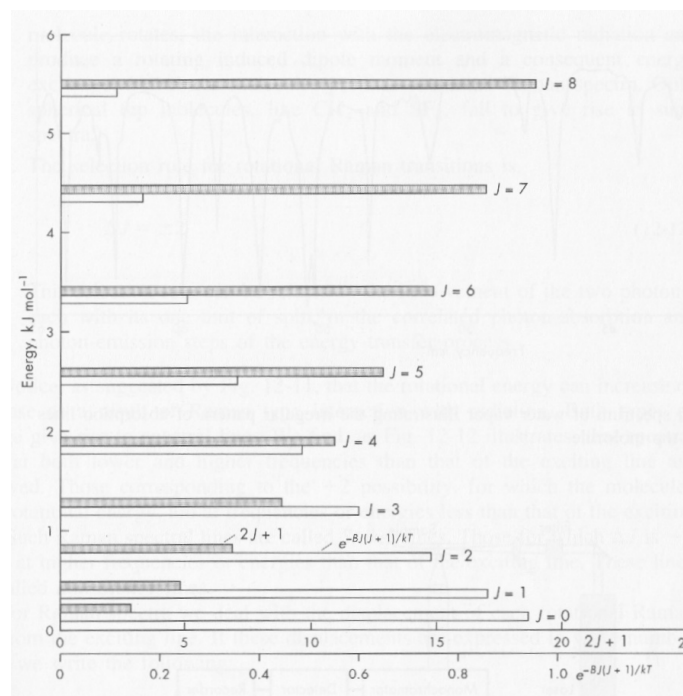
### Example 13.7, Problems 3.18–20.

## The factors affecting the intensity of absorption lines

The spectra shown above do not consist of lines of equal intensities. The variation of the intensities of the lines is, of course, due to the variation of the absorbance. Since the path length,  $l$ , through the sample is a constant and the molar absorption coefficient,  $\epsilon$ , does not vary with rotational state, we are led to the conclusion that the variation must be due to the changes in the concentration,  $c$ , from one rotational state to another.

This variation can be attributed to two factors, namely, the degeneracy factor and the energy factor.

The degeneracy factor is due to the fact that rigid rotor states are described by spherical harmonics  $Y_J^M(\theta, \phi)$ . At each energy level  $E_J$ , there are  $(2J+1)$  states, corresponding to the allowed values of  $M$ . The larger the degeneracy, the greater the availability of states for the molecules to occupy. So, this factor causes the concentration of molecules at a given energy level to increase with  $J$ .



The energy factor is essentially the same as the Boltzmann distribution discussed in Chapter 1, which states that beyond the most probable energy, the fraction of molecules decreases with increasing energy (see Fig. 1.11). The competition between these two factors are shown in the figure to the left (shaded bars represent the degeneracy factor and the empty bars represent the energy factor). This can also be expressed as

$$c_J \sim (2J+1)e^{-J(J+1)h^2/(2Ik_B T)},$$

where  $c_J$  is the concentration of molecules in the energy level  $J$ .

These factors will be present in all forms of spectra that we examine.

### 13.4. Vibrational-rotational spectra of molecules

It is impossible to put energy into a molecule's vibrational modes without affecting the rotational modes because, as we shall see below, vibrations and rotations are strongly coupled. So, there is no such thing as "pure vibrational" spectroscopy. The terms "vibrational spectroscopy" refers to vibrational-rotational spectroscopy. The frequency range for vibrational transitions occurs in the infrared region of the spectrum. So, another term for it is "infrared spectroscopy."

The quantum mechanical model for vibrations is the harmonic oscillator. From Chapter 11, the frequency of a harmonic oscillator is given by

$$\nu_0(\text{s}^{-1}) = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}.$$

The energy levels of the harmonic oscillator are given by

$$E_v = (v + \frac{1}{2})h\nu_0; \quad v = 0, 1, 2, \dots$$

where we have used the letter  $v$  for the quantum number in keeping with convention. The selection rule for transitions in harmonic oscillators is  $\Delta v = \pm 1$ .

The energy difference for a  $v \rightarrow v+1$  transition is given by

$$\tilde{\nu}(\text{cm}^{-1}) = \frac{\Delta E}{hc} = \left[ \left( v + \frac{3}{2} \right) - \left( v + \frac{1}{2} \right) \right] \frac{\nu_0}{c} = \frac{\nu_0}{c}.$$

For the remainder of our discussion, in keeping with the convention in vibrational spectroscopy, the quantity  $\nu_0$  will be re-labeled as  $\nu_e$ , where the subscript refers to the equilibrium bond length of the molecule, which will be referred to as  $r_e$ . Also, we will denote the transition frequencies in wave numbers by  $\omega_e$  to avoid confusing it with the fundamental frequency of the oscillator,  $\nu_e$ .

We will use the lab handout (**Lecture Notes Part A**) for the analysis of the infrared spectrum of HCl for the rest of our discussion of vibrational-rotational spectroscopy.

#### Problems 13.23, 13.25–13.28, 13.33

A simple function that approximates the behavior of potential energy with bond-length in diatomic molecules is the Morse potential function:

$$E_p(r) = D_e [1 - e^{-\alpha(r-r_e)}]^2,$$

where  $r_e$  is the equilibrium bond distance and  $D_e$  and  $\alpha$  are constants whose significance we will discuss.

### 13.5. Electronic Spectrum of Molecules

We examined the electronic configuration of homonuclear diatomic molecules in Chapter 12. For example, from Fig. 12.21(a), the electronic configuration of N<sub>2</sub> is

$$(1s \sigma_g)^2 (1s \sigma_u^*)^2 (2s \sigma_g)^2 (2s \sigma_u^*)^2 (2p\pi_u)^4 (2p\sigma_g)^2.$$

This corresponds to the ground state of the molecule, and is denoted as the  $^1\Sigma_g^+$  state (see the handout, Fig. 14.1 from *Physical Chemistry*, by Silbey and Alberty 3<sup>rd</sup> Ed.).

The convention in electronic spectroscopy is to label electronic states with their spin multiplicity (left superscript), the total angular momentum (the upper case Greek letter) and the symmetry of the wavefunction (right super- and sub-scripts). In addition, ground states are usually designated as the X-state, and the excited states are labeled A, B, C, etc., in the order of increasing energy.

Now imagine that one of the electrons in the  $2p\sigma_g$  molecular orbital of N<sub>2</sub> is provided with sufficient energy to excite it to the  $2p\pi_g^*$  state. The electronic configuration of the excited state will be

$$(1s \sigma_g)^2 (1s \sigma_u^*)^2 (2s \sigma_g)^2 (2s \sigma_u^*)^2 (2p\pi_u)^4 (2p\sigma_g)^1 (2p\pi_g^*)^1.$$

This state is designated as the  $^3\Pi_g$  state. If the electron had been excited to the  $2p\sigma_u^*$  orbital, we would get an excited state with the electronic configuration

$$(1s \sigma_g)^2 (1s \sigma_u^*)^2 (2s \sigma_g)^2 (2s \sigma_u^*)^2 (2p\pi_u)^4 (2p\sigma_g)^1 (2p\sigma_u^*)^1,$$

which would be designated as the  $^3\Sigma_u^+$  state.

From the handout (Fig. 14.1) it is clear that the  $^3\Sigma_u^+$  state is lower in energy than the  $^3\Pi_g$  state. This indicates that in the nitrogen molecule, the  $2p\sigma_u^*$  must be lower in energy than the  $2p\pi_g^*$  orbital. The energy ordering shown in Fig. 12.21 is purely schematic and so we must not attach too much significance to this.

The process by which molecules absorb energy so that electrons are excited from the ground electronic state to various excited electronic states is the basis for electronic absorption spectroscopy. The frequency of the radiation required is typically in the visible to ultraviolet wavelength range (700-200 nm).

We will use the lab handout (**Lecture Notes Part B**) for the analysis of the UV-Visible spectrum of Iodine for the rest of our discussion of electronic spectroscopy.