

## 7.6: Rotational Spectroscopy of Diatomic Molecules

The permanent electric dipole moments of polar molecules can couple to the electric field of electromagnetic radiation. This coupling induces transitions between the rotational states of the molecules. The energies that are associated with these transitions are detected in the far infrared and microwave regions of the spectrum. For example, the microwave spectrum for carbon monoxide shown at the beginning of the chapter in [Figure 7.6.1.1](#) spans a frequency range of 100 to 1200 GHz, which corresponds to 3 - 40  $\text{cm}^{-1}$ .

The selection rules for the rotational transitions are derived from the [transition moment integral](#) by using the spherical harmonic functions and the appropriate dipole moment operator,  $\hat{\mu}$ .

$$\mu_T = \int Y_{J_f}^{m_f*} \hat{\mu} Y_{J_i}^{m_i} \sin \theta d\theta d\varphi \quad (7.6.1)$$

Evaluating the transition moment integral involves a bit of mathematical effort. This evaluation reveals that the transition moment depends on the square of the dipole moment of the molecule,  $\mu^2$  and the rotational quantum number,  $J$ , of the initial state in the transition,

$$\mu_T = \mu^2 \frac{J+1}{2J+1} \quad (7.6.2)$$

and that the selection rules for rotational transitions are

$$\Delta J = \pm 1 \quad (7.6.3)$$

$$\Delta m_J = 0, \pm 1 \quad (7.6.4)$$

For  $\Delta J = +1$ , a photon is absorbed; for  $\Delta J = -1$  a photon is emitted.

### Exercise 7.6.1

Explain why your microwave oven heats water but not air. Hint: draw and compare Lewis structures for components of air and for water.

The energies of the rotational levels are given by Equation [7.6.5](#),

$$E = J(J+1) \frac{\hbar^2}{2I} \quad (7.6.5)$$

and each energy level has a degeneracy of  $2J+1$  due to the different  $m_J$  values.

### Exercise 7.6.2

Use the rotational energy level diagram for  $J = 0$ ,  $J = 1$ , and  $J = 2$  that you produced in Exercise 7.6.9, and add arrows to show all the allowed transitions between states that cause electromagnetic radiation to be absorbed or emitted.

## Transition Energies

The transition energies for absorption of radiation are given by

$$E_{\text{photon}} = \Delta E_{\text{states}} \quad (7.6.6)$$

$$= E_f - E_i \quad (7.6.7)$$

$$= h\nu \quad (7.6.8)$$

$$= hc\bar{\nu} \quad (7.6.9)$$

Substituted Equation [7.6.5](#) into Equation [7.6.9](#)

$$h\nu = hc\bar{\nu} \quad (7.6.10)$$

$$= J_f(J_f+1) \frac{\hbar^2}{2I} - J_i(J_i+1) \frac{\hbar^2}{2I} \quad (7.6.11)$$

Since microwave spectroscopists use frequency, and infrared spectroscopists use wavenumber units when describing rotational spectra and energy levels, both  $\nu$  and  $\bar{\nu}$  are included in Equation 7.6.11, and  $J_i$  and  $J_f$  are the rotational quantum numbers of the initial (lower) and final (upper) levels involved in the absorption transition. When we add in the constraints imposed by the selection rules,  $J_f$  is replaced by  $J_i + 1$ , because the selection rule requires  $J_f - J_i = 1$  for absorption. The equation for absorption transitions then can be written in terms of the quantum number  $J_i$  of the initial level alone.

$$h\nu = hc\bar{\nu} = 2(J_i + 1) \frac{\hbar^2}{2I} \quad (7.6.12)$$

Divide Equation 7.6.12 by  $h$  to obtain the frequency of the allowed transitions,

$$\nu = 2B(J_i + 1) \quad (7.6.13)$$

where  $B$ , the rotational constant for the molecule, is defined as

$$B = \frac{\hbar^2}{2hI} \quad (7.6.14)$$

### Exercise 7.6.3

Complete the steps going from Equation 7.6.11 to Equation 7.6.14 and identify the units of  $B$  at the end.

### Exercise 7.6.4

Infrared spectroscopists use units of wave numbers. Rewrite the steps going from Equation 7.6.11 to Equation 7.6.14 to obtain expressions for  $\hbar\nu$  and  $B$  in units of wave numbers. Note that to convert  $B$  in Hz to  $B$  in  $\text{cm}^{-1}$ , you simply divide the former by  $c$ .

Figure 7.6.1 shows the rotational spectrum of  $^{12}\text{C}^{16}\text{O}$  as a series of nearly equally spaced lines. The line positions  $\nu_J$ , line spacings, and the maximum absorption coefficients ( $\gamma_{\text{max}}$ ), the absorption coefficients associated with the specified line position) for each line in this spectrum are given here in Table 7.6.1.

Table 7.6.1: Rotational Transitions in  $^{12}\text{C}^{16}\text{O}$  at 40 K

J	$\nu_J$ (MHz)	Spacing from previous line(MHz)	$\gamma_{\text{max}}$
0	115,271.21	0	0.0082
1	230,538.01	115,266.80	0.0533
2	345,795.99	115,257.99	0.1278
3	461,040.76	115,244.77	0.1878
4	576,267.91	115,227.15	0.1983
5	691,473.03	115,205.12	0.1618
6	806,651.78	115,178.68	0.1064
7	921,799.55	115,147.84	0.0576
8	1,036,912.14	115,112.59	0.0262
9	1,151,985.08	115,072.94	0.0103

Let's try to reproduce Figure 7.6.1 from the data in Table 7.6.1 by using the quantum theory that we have developed so far. Equation 7.6.13 predicts a pattern of exactly equally spaced lines. The lowest energy transition is between  $J_i = 0$  and  $J_f = 1$  so the first line in the spectrum appears at a frequency of  $2B$ . The next transition is from  $J_i = 1$  to  $J_f = 2$  so the second line appears at  $4B$ . The spacing of these two lines is  $2B$ . In fact the spacing of all the lines is  $2B$  according to this equation, which is consistent

with the data in Table 7.6.1 showing that the lines are very nearly equally spaced. The difference between the first spacing and the last spacing is less than 0.2%.

### Exercise 7.6.5

Use Equation 7.6.13 to prove that the spacing of any two lines in a rotational spectrum is  $2B$ . That is, derive  $\nu_{J_i+1} - \nu_{J_i} = 2B$ .

## Non-Rigid Rotor Effects

*Centrifugal stretching* of the bond as  $J$  increases causes the decrease in the spacing between the lines in an observed spectrum. This decrease shows that the molecule is not really a rigid rotor. As the rotational angular momentum increases with increasing  $J$ , the bond stretches. This stretching increases the moment of inertia and decreases the rotational constant. Centrifugal stretching is exactly what you see if you swing a ball on a rubber band in a circle (Figure 7.6.1).



Figure 7.6.1: In the absence of the spring, the particles would fly apart. However, the force exerted by the extended spring pulls the particles onto a periodic, oscillatory path. (CC BY-SA 3.0; Cleonis).

The effect of centrifugal stretching is smallest at low  $J$  values, so a good estimate for  $B$  can be obtained from the  $J = 0$  to  $J = 1$  transition. From  $B$ , a value for the bond length of the molecule can be obtained since the moment of inertia that appears in the definition of  $B$ , Equation 7.6.14, is the reduced mass times the bond length squared.

### Exercise 7.6.6

Use the frequency of the  $J = 0$  to  $J = 1$  transition observed for carbon monoxide to determine a bond length for carbon monoxide.

When the centrifugal stretching is taken into account quantitatively, the development of which is beyond the scope of the discussion here, a very accurate and precise value for  $B$  can be obtained from the observed transition frequencies because of their high precision. Rotational transition frequencies are routinely reported to 8 and 9 significant figures.

As we have just seen, quantum theory successfully predicts the line spacing in a rotational spectrum. An additional feature of the spectrum is the line intensities. The lines in a rotational spectrum do not all have the same intensity, as can be seen in Figure 7.6.1.1 and Table 7.6.1. The maximum absorption coefficient for each line,  $\gamma_{max}$ , is proportional to the magnitude of the transition moment,  $\mu_T$  which is given by Equation 7.6.2, and to the population difference between the initial and final states,  $\Delta n$ . Since  $\Delta n$  is the difference in the number of molecules present in the two states per unit volume, it is actually a difference in number density.

$$\gamma_{max} = C_{\mu T} \cdot \Delta n \quad (7.6.15)$$

where  $C_{\mu T}$  includes constants obtained from a more complete derivation of the interaction of radiation with matter.

The dependence on the number of molecules in the initial state is easy to understand. For example, if no molecules were in the  $J = 7, m_J = 0$  state, no radiation could be absorbed to produce a  $J = 7, m_J = 0$  to  $J = 8, m_J = 0$  transition. The dependence of the line intensity on the population of the final state is explained in the following paragraphs.

When molecules interact with an electromagnetic field (i.e., a photon), they can be driven from one state to another with the absorption or emission of energy. Usually there are more molecules in the lower energy state and the absorption of radiation is observed as molecules go from the lower state to the upper state. This situation is the one we have encountered up to now. In some situations, there are more molecules in the upper state and the emission of radiation is observed as molecules are driven from the

upper state to the lower state by the electromagnetic field. This situation is called population inversion, and the process is called stimulated emission. Stimulated emission is the reason lasers are possible. Laser is an acronym for light amplification by stimulated emission of radiation. Even in the absence of an electromagnetic field, atoms and molecules can lose energy spontaneously and decay from an upper state to a lower energy state by emitting a photon. This process is called spontaneous emission. Stimulated emission therefore can be thought of as the inverse of absorption because both processes are driven by electromagnetic radiation, i.e. the presence of photons.

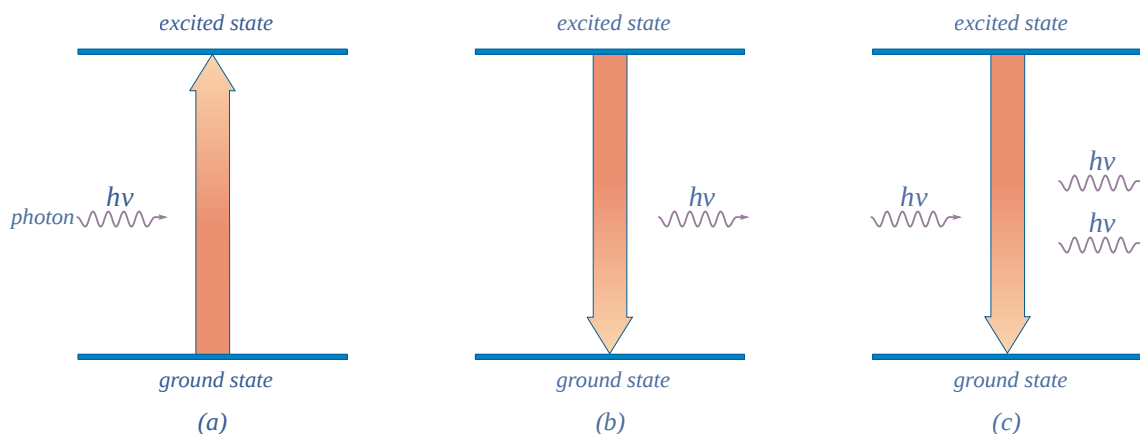


Figure 7.6.2: a) In absorption, an incident photon  $h\nu$  is absorbed by the system and drives the system from the ground state to an excited state. b) In spontaneous emission, a photon is produced when the system goes from an excited state to the ground state. c) In stimulated emission, an incident photon is not absorbed, but drives the system from an excited state to the ground state, accompanied by release of a second photon.

Whether absorption or stimulated emission is observed when electromagnetic radiation interacts with a sample depends upon the population difference,  $\Delta n$ , of the two states involved in the transition. For a rotational transition,

$$\Delta n = n_J - n_{J+1} \quad (7.6.16)$$

where  $n_J$  represents the number of molecules in the lower state and  $n_{J+1}$  represents the number in the upper state per unit volume. If this difference is 0, there will be no net absorption or stimulated emission because they exactly balance. If this difference is positive, absorption will be observed; if it is negative, stimulated emission will be observed.

We can develop an expression for  $\Delta n$  that uses only the population of the initial state,  $n_J$ , and the Boltzmann factor. The Boltzmann factor allows us to calculate the population of a higher state given the population of a lower state, the energy gap between the states and the temperature. Multiply the right-hand side of Equation 7.6.16 by  $n_J/n_J$  to obtain

$$\Delta n = \left(1 - \frac{n_{J+1}}{n_J}\right) n_J \quad (7.6.17)$$

Next recognize that the ratio of populations of the states is given by the Boltzmann factor which when substituted into yields

$$\Delta n = \left(1 - e^{\frac{-h\nu_J}{kT}}\right) n_J \quad (7.6.18)$$

where  $h\nu_J$  is the energy difference between the two states. For the rigid rotor model

$$\nu_J = 2B(J+1) \quad (7.6.19)$$

so Equation 7.6.18 can be rewritten as

$$\Delta n = \left(1 - e^{\frac{-2hB(J+1)}{kT}}\right) n_J \quad (7.6.20)$$

Equation expresses the population difference between the two states involved in a rotational transition in terms of the population of the initial state, the rotational constant for the molecule,  $B$ , the temperature of the sample, and the quantum number of the initial state.

To get the number density of molecules present in the initial state involved in the transition,  $n_J$ , we multiply the fraction of molecules in the initial state,  $F_J$ , by the total number density of molecules in the sample,  $n_{total}$ .

$$n_J = F_J \cdot n_{total} \quad (7.6.21)$$

The fraction  $F_J$  is obtained from the rotational partition function.

$$F_J = (2J+1) \left( \frac{hB}{kT} \right) \left( e^{\frac{-2hB(J+1)}{kT}} \right) \quad (7.6.22)$$

The exponential is the Boltzmann factor that accounts for the thermal population of the energy states. The factor  $2J+1$  in this equation results from the degeneracy of the energy level. The more states there are at a particular energy, the more molecules will be found with that energy. The  $(hB/kT)$  factor results from normalization to make the sum of  $F_J$  over all values of  $J$  equal to 1. At room temperature and below only the ground vibrational state is occupied; so all the molecules ( $n_{total}$ ) are in the ground vibrational state. Thus the fraction of molecules in each rotational state in the ground vibrational state must add up to 1.

#### Exercise 7.6.7

Show that the numerator,  $J(J+1)hB$  in the exponential of Equation 7.6.22 is the energy of level  $J$ .

#### Exercise 7.6.8: Hydrogen Chloride

Calculate the relative populations of the lowest ( $J=0$ ) and second ( $J=1$ ) rotational energy level in the HCl molecule at room temperature. Do the same for the lowest and second vibrational levels of HCl. Compare the results of these calculations. Are Boltzmann populations important to vibrational spectroscopy? Are Boltzmann populations important for rotational spectroscopy?

Now we put all these pieces together and develop a master equation for the maximum absorption coefficient for each line in the rotational spectrum, which is identified by the quantum number,  $J$ , of the initial state. Start with Equation 7.6.15 and replace  $\mu_T$  using Equation 7.6.2.

$$\gamma_{max} = C \left( \mu^2 \frac{J+1}{2J+1} \right) \cdot \Delta n \quad (7.6.23)$$

Then replace  $\Delta n$  using Equation 7.6.20

$$\gamma_{max} = C \left( \mu^2 \frac{J+1}{2J+1} \right) \left( e^{\frac{-2hB(J+1)}{kT}} \right) n_J \quad (7.6.24)$$

Finally replace  $n_J$  using Equations 7.6.21 and 7.6.22 to produce

$$\gamma_{max} = C \left[ \mu^2 \frac{J+1}{2J+1} \right] \left[ e^{\frac{-2hB(J+1)}{kT}} \right] \left[ (2J+1) \left( \frac{hB}{kT} \right) \left( e^{\frac{-2hB(J+1)}{kT}} \right) \right] n_{total} \quad (7.6.25)$$

Equation 7.6.25 enables us to calculate the relative maximum intensities of the peaks in the rotational spectrum shown in Figure 7.6.2, assuming all molecules are in the lowest energy vibrational state, and predict how this spectrum would change with temperature. The constant  $C$  includes the fundamental constants  $\epsilon_0$ ,  $c$  and  $h$ , that follow from a more complete derivation of the interaction of radiation with matter. The complete theory also can account for the line shape and width and includes an additional radiation frequency factor.

$$C = \frac{2\pi}{3\epsilon_0 ch} \quad (7.6.26)$$

In the spectrum shown in [Figure 7.6.1.1](#), the absorption coefficients for each peak first increase with increasing  $J$  because the difference in the populations of the states increases and the factor  $(J+1)$  increases. Notice that the denominator in the factor resulting from the transition moment cancels the degeneracy factor  $2J+1$ . After the maximum the second Boltzmann factor, which is a decreasing exponential as  $J$  increases, dominates, and the intensity of the peaks drops to zero. Exploration of how well Equation [7.6.25](#) corresponds to the data in Table 7.6.1 and discovering how a rotational spectrum changes with temperature are left to an end-of-the-chapter activity.

#### Exercise 7.6.9

Why does not the first Boltzmann factor in Equation [7.6.25](#) cause the intensity to drop to zero as  $J$  increases.

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