

9.3: Molecular Spectra

Learning Objectives

By the end of this section, you will be able to:

- Use the concepts of vibrational and rotational energy to describe energy transitions in a diatomic molecule
- Explain key features of a vibrational-rotational energy spectrum of a diatomic molecule
- Estimate allowed energies of a rotating molecule
- Determine the equilibrium separation distance between atoms in a diatomic molecule from the vibrational-rotational absorption spectrum

Molecular energy levels are more complicated than atomic energy levels because molecules can also vibrate and rotate. The energies associated with such motions lie in different ranges and can therefore be studied separately. Electronic transitions are of order 1 eV, vibrational transitions are of order 10^{-2} eV, and rotational transitions are of order 10^{-3} eV. For complex molecules, these energy changes are difficult to characterize, so we begin with the simple case of a diatomic molecule.

Quantum Rotation

According to classical mechanics, the energy of rotation of a diatomic molecule is given by

$$E_r = \frac{L^2}{2I},$$

where **I** is the moment of inertia and **L** is the angular momentum. According to quantum mechanics, the rotational angular momentum is quantized:

$$L = \sqrt{l(l+1)} \hbar (l = 0, 1, 2, 3, \dots),$$

where **l** is the orbital angular quantum number. The allowed **rotational energy level** of a diatomic molecule is therefore

$$E_r = l(l+1) \frac{\hbar^2}{2I} = l(l+1) E_{0r} \quad (l = 0, 1, 2, 3, \dots),$$

where the characteristic rotational energy of a molecule is defined as

$$E_{0r} = \frac{\hbar^2}{2I}.$$

For a diatomic molecule, the moment of inertia with reduced mass μ is

$$I = \mu r_0^2,$$

where r_0 is the total distance between the atoms. The energy difference between rotational levels is therefore

$$\Delta E_r = E_{l+1} - E_l = 2(l+1) E_{0r}.$$

A detailed study of transitions between rotational energy levels brought about by the absorption or emission of radiation (a so-called **electric dipole transition**) requires that

$$\Delta l = \pm 1. \quad (9.3.1)$$

This rule, known as a **selection rule**, limits the possible transitions from one quantum state to another. Equation 9.3.1 is the selection rule for rotational energy transitions. It applies only to diatomic molecules that have an electric dipole moment. For this reason, symmetric molecules such as H_2 and N_2 do not experience rotational energy transitions due to the absorption or emission of electromagnetic radiation.

✓ Example 9.3.1: The Rotational Energy of HCl

Determine the lowest three rotational energy levels of a hydrogen chloride ((HCl)) molecule.

Strategy

Hydrogen chloride (HCl) is a diatomic molecule with an equilibrium separation distance of 0.127 nm. Rotational energy levels depend only on the momentum of inertia I and the orbital angular momentum quantum number l (in this case, $l = 0, 1$, and 2). The momentum of inertia depends, in turn, on the equilibrium separation distance (which is given) and the reduced mass, which depends on the masses of the H and Cl atoms.

Solution

First, we compute the reduced mass. If Particle 1 is hydrogen and Particle 2 is chloride, we have

$$\begin{aligned}\mu &= \frac{m_1 m_2}{m_1 + m_2} = \frac{(1.0 \text{ u})(35.4 \text{ u})}{1.0 \text{ u} + 35.4 \text{ u}} \\ &= 0.97 \text{ u} = 0.97 \text{ u} \left(\frac{931.5 \frac{\text{MeV}}{c^2}}{1 \text{ u}} \right) \\ &= 906 \frac{\text{MeV}}{c^2}.\end{aligned}$$

The corresponding rest mass energy is therefore

$$\mu c^2 = 9.06 \times 10^8 \text{ eV}$$

This allows us to calculate the characteristic energy:

$$\begin{aligned}E_{0r} &= \frac{\hbar^2}{2(\mu r_0^2)} = \frac{(\hbar c)^2}{2(\mu c^2) r_0^2} \\ &= \frac{(197.3 \text{ eV} \cdot \text{nm})^2}{2(9.06 \times 10^8 \text{ eV})(0.127 \text{ nm})^2} \\ &= 1.33 \times 10^{-3} \text{ eV}.\end{aligned}$$

(Notice how this expression is written in terms of the rest mass energy. This technique is common in modern physics calculations.) The rotational energy levels are given by

$$E_r = l(l+1) \frac{\hbar^2}{2I} = l(l+1) E_{0r},$$

where l is the orbital quantum number. The three lowest rotational energy levels of an HCl molecule are therefore

$$\begin{aligned}l = 0: \quad E_r &= 0 \text{ eV (no rotation)} \\ l = 1: \quad E_r &= 2 E_{0r} = 2.66 \times 10^{-3} \text{ eV}, \\ l = 2: \quad E_r &= 6 E_{0r} = 7.99 \times 10^{-3} \text{ eV}.\end{aligned}$$

Significance

The rotational spectrum is associated with weak transitions (1/1000 to 1/100 of an eV). By comparison, the energy of an electron in the ground state of hydrogen is -13.6 eV .

? Exercise 9.3.1

What does the energy separation between absorption lines in a rotational spectrum of a diatomic molecule tell you?

Answer

the moment of inertia

Quantum Vibration

The **vibrational energy level**, which is the energy level associated with the vibrational energy of a molecule, is more difficult to estimate than the rotational energy level. However, we can estimate these levels by assuming that the two atoms in the diatomic molecule are connected by an ideal spring of spring constant k . The potential energy of this spring system is

$$U_{osc} = \frac{1}{2}k\Delta r^2,$$

Where Δr is a change in the “natural length” of the molecule along a line that connects the atoms. Solving Schrödinger’s equation for this potential gives

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega \quad (n = 0, 1, 2, \dots),$$

Where ω is the natural angular frequency of vibration and n is the vibrational quantum number. The prediction that vibrational energy levels are evenly spaced ($\Delta E = \hbar\omega$) turns out to be good at lower energies.

A detailed study of transitions between vibrational energy levels induced by the absorption or emission of radiation (and the specifically so-called electric dipole transition) requires that

$$\Delta n = \pm 1. \quad (9.3.2)$$

Equation 9.3.2 represents the selection rule for vibrational energy transitions. As mentioned before, this rule applies only to diatomic molecules that have an electric dipole moment. Symmetric molecules do not experience such transitions.

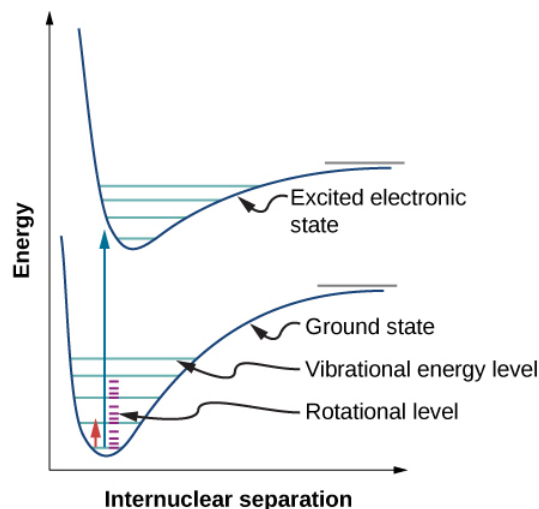


Figure 9.3.1: Three types of energy levels in a diatomic molecule: electronic, vibrational, and rotational. If the vibrational quantum number (n) changes by one unit, then the rotational quantum number (l) changes by one unit.

Due to the selection rules, the absorption or emission of radiation by a diatomic molecule involves a transition in vibrational and rotational states. Specifically, if the vibrational quantum number (n) changes by one unit, then the rotational quantum number (l) changes by one unit. An energy-level diagram of a possible transition is given in Figure 9.3.1. The absorption spectrum for such transitions in hydrogen chloride (HCl) is shown in Figure (PageIndex{2}). The absorption peaks are due to transitions from the $n = 0$ to $n = 1$ vibrational states. Energy differences for the band of peaks at the left and right are, respectively:

(right band)

$$\Delta E_{l \rightarrow l+1} = \hbar\omega + 2(l+1)E_{0r} = \hbar\omega + 2E_{0r}, \hbar\omega + 4E_{0r}, \hbar\omega + 6E_{0r}, \dots$$

(left band)

$$\Delta E_{l \rightarrow l-1} = \hbar\omega - 2lE_{0r} = \hbar\omega - 2E_{0r}, \hbar\omega - 4E_{0r}, \hbar\omega - 6E_{0r}, \dots$$

The moment of inertia can then be determined from the energy spacing between individual peaks ($2E_{0r}$) or from the gap between the left and right bands ($4E_{0r}$). The frequency at the center of this gap is the frequency of vibration.

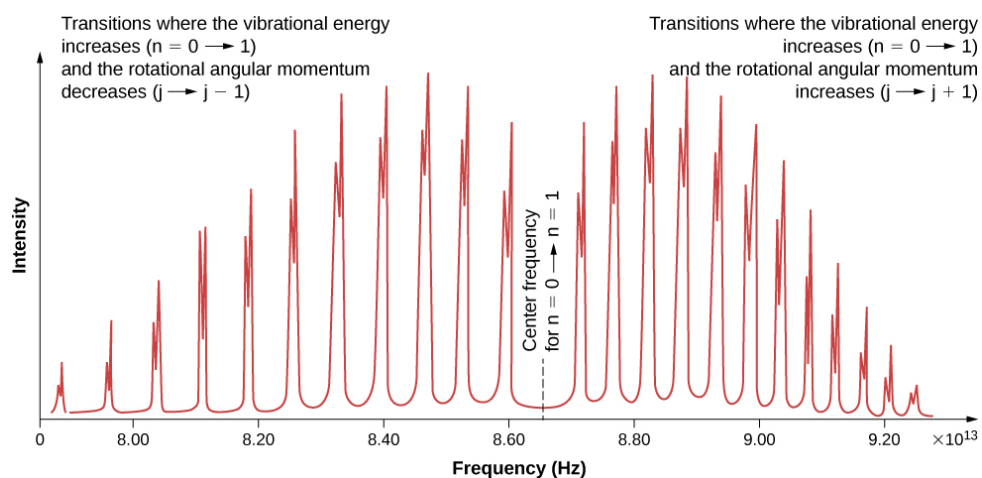


Figure 9.3.2: Absorption spectrum of hydrogen chloride (HCl) from the $n = 0$ to $n = 1$ vibrational levels. The discrete peaks indicate a quantization of the angular momentum of the molecule. The bands to the left indicate a decrease in angular momentum, whereas those to the right indicate an increase in angular momentum.

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