

Chapter 16

Vibrational Spectroscopy

Vibrational spectroscopy provides information on bond lengths, bond strengths, and molecular geometry. In addition, it has been a valuable tool for chemical analysis, identification of characteristic groups in molecules, and monitoring intermolecular interactions.

The first section of this chapter describes a simple but useful model of vibrational motion. This model—the harmonic oscillator—is then used to explain the observed vibrational spectra of diatomic molecules. The features of vibrational spectra that cannot be described by the harmonic oscillator model are examined in the following section. Since rotational changes accompany vibrational transitions, the rotational structure of vibrational bands is also described in this chapter. Bond lengths and molecular geometries may be determined from these rotational transitions by the methods described in the previous chapter.

Vibrational spectra of polyatomic molecules, with emphasis on triatomic molecules, are also described in this chapter.

16.1 THE HARMONIC OSCILLATOR MODEL

Very generally speaking, any device that interconverts potential energy and kinetic energy repeatedly is an **oscillator**. Some examples of oscillators are the simple pendulum, a mass on a spring, and vibrating molecules.

We will consider a single-particle oscillator in this section. If the dynamics of the oscillating particle are governed by the force

$$f = -kq \quad (16.1)$$

where q is the displacement, it is called a **harmonic oscillator**. The constant k is called the **force constant**. Equation (16.1) is very useful in describing small displacements from equilibrium.

The harmonic oscillator has been a persistent model throughout the history of physics. It was first proposed by Hooke in 1670 and has appeared in a variety of physical theories ever since.

Classical Picture

For a single-particle oscillator subject to the force given in Eq. (16.1), Newton's second law is

$$m \frac{d^2q}{dt^2} = -kq \quad (16.2)$$

A particular solution for this differential equation is

$$q = q_0 \sin \sqrt{\frac{k}{m}} t \quad (16.3)$$

Here q_0 is the maximum amplitude. (This particular solution corresponds to setting $q = 0$ when $t = 0$.) According to Eq. (16.3), the position of the particle varies sinusoidally and has a maximum displacement of q_0 (Fig. 16.1). The argument of the sine function changes from 0 to 2π during one period of oscillation. Hence the period of oscillation τ is given by

$$\sqrt{\frac{k}{m}} \tau = 2\pi \quad (16.4)$$

The frequency of oscillation ν_0 (s^{-1}) is therefore related to the force constant by the expression

$$\nu_0 = \frac{1}{\tau} = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (16.5)$$

We see from this equation that the frequency of the oscillator does not depend on the displacement. Hence ν_0 is called the **natural frequency** of the oscillator. The quantity ω_0 , where

$$\omega_0 = 2\pi\nu_0 \quad (16.6)$$

is called the **angular frequency** or simply the **frequency**.

The potential energy of the oscillator is given by

$$V = -\int f dq = \frac{1}{2}kq^2 \quad (16.7)$$

where we have set the integration constant equal to zero. This corresponds to assigning $V = 0$ at $q = 0$. Figure 16.1 also illustrates the potential energy function for a harmonic oscillator.

It is the potential energy (or force) that controls the dynamics of a system. The difference between a particle in a box and a harmonic oscillator, for example, is in their potential energy. When comparing different systems, it is sometimes

convenient to think of the potential energy function as a well (with an appropriate number of dimensions) and the particle (or particles) as rolling in it. A particle in a box, for example, is in a well with steep walls. A harmonic oscillator, in contrast, is confined to a parabolic well. Figure 16.1 shows how the shape of the well influences the dynamics of the particle.

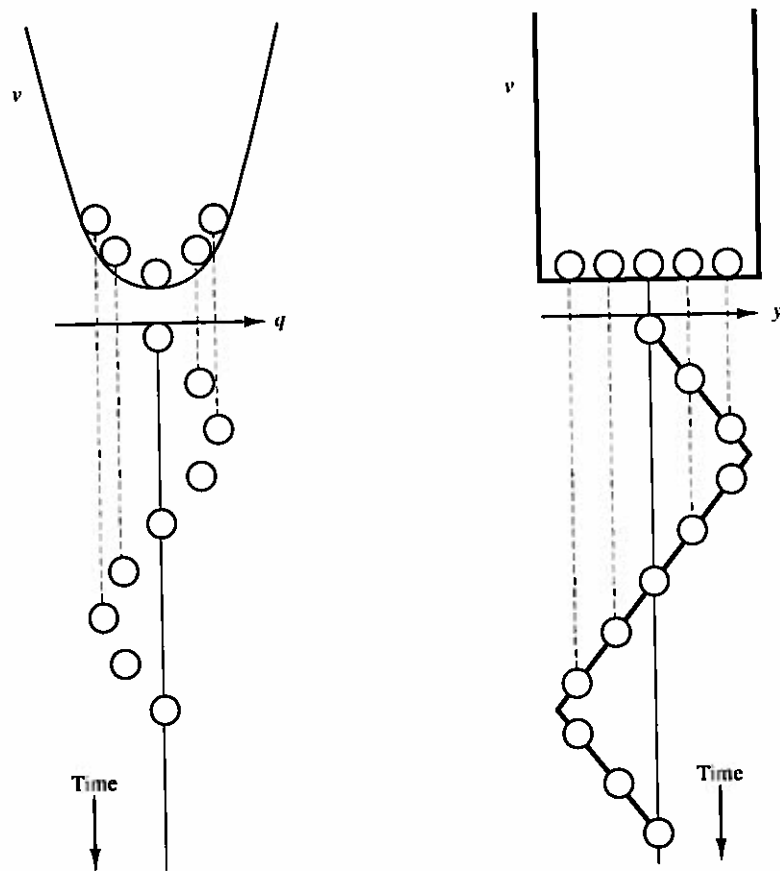


Figure 16.1. Pictorial representation of a harmonic oscillator (left) and a particle in a box (right). Here the particle is represented as moving within some bounds. Just as we interpret the particle-in-a-box motion as linear motion between two limits, we may visualize the harmonic oscillator as a particle rolling in a potential box. Both classical and quantum mechanics tell us that the frequency of oscillation of a harmonic oscillator is independent of the amplitude of displacement. We should keep in mind that these pictures are strictly classical.

Example 16.1

In Einstein's theory of specific heats, the atoms in a monatomic crystal are supposed to execute simple harmonic motion. The experimental data on graphite may be rationalized if we assume that carbon atoms oscillate at $1.0 \times 10^{11} \text{ s}^{-1}$. Calculate the force constant for carbon atoms in graphite.

From Eq. (16.5) we have

$$k = 4\pi^2\nu_0^2 m$$

Substitution of mass and frequency into this expression gives

$$\begin{aligned} k &= 4\pi^2(1.0 \times 10^{11} \text{ s}^{-1})^2 \frac{12.0 \times 10^{-3} \text{ kg mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} \\ &= 7.8 \times 10^{-3} \text{ kg s}^{-2} = 7.8 \times 10^{-3} \text{ J m}^{-2} \text{ or N m}^{-1} \end{aligned}$$

Quantized Energies

The Schrödinger equation for a harmonic oscillator is

$$\hat{H}\psi = \left(-\frac{\hbar^2}{2m} \frac{d^2}{dq^2} + \frac{1}{2}kq^2 \right) \psi = E\psi \quad (1)$$

where the first term in the Hamiltonian is the operator for kinetic energy, the second is the operator for potential energy. The following results can be appreciated without going through the mathematical details involved in solving the Schrödinger equation.

The quantized energies of a harmonic oscillator are given by

$$E_v = h\nu_0(v + \frac{1}{2}) \quad (16)$$

where $v = 0, 1, 2, \dots$. In this equation h is the familiar Planck's constant, ν_0 the natural frequency, and v is the vibrational quantum number. The quantization of harmonic oscillator energies is a consequence of the boundary conditions. The wave functions must vanish as $q \rightarrow \pm\infty$. Figure 16.2 shows a few of the allowed energies.

Spectroscopic data are often reported in wave number units (cm^{-1}). Hence Eq. (16.9) may be written in an alternative form:

$$G(v) = \frac{E_v}{hc} = \tilde{\nu} \left(v + \frac{1}{2} \right) \quad (16)$$

where $G(v)$ is called the spectroscopic term and $\tilde{\nu}$ is the wave number.

Besides quantization of energy there is another important difference between the classical and the quantum descriptions. The classical oscillator is allowed to have zero energy. The quantum oscillator, on the other hand, cannot have a minimum energy of $\frac{1}{2}h\nu_0$ corresponding to the $v = 0$ level. If it had zero energy, that is, if it was at the bottom of the well with zero momentum, the uncertainty principle would be violated.

The Wave Functions and Probability

The wave functions for the harmonic oscillator are given by

$$\psi_v(\xi) = \frac{(\beta/\pi)^{1/4}}{2^{v/2} v!} H_v(\xi) e^{-\xi^2/2} \quad (16)$$

where ξ is a weighted displacement,

$$\xi = \sqrt{\beta}q \quad (16)$$

and the constant β is related to the force constant by the expression

$$\beta = \frac{2\pi}{h} \sqrt{mk} \quad (16)$$

In Eq. (16.12) $H_v(\xi)$ represents the Hermite polynomials, the first six of which are

$$\begin{aligned} H_0(\xi) &= 1 & H_3(\xi) &= 8\xi^3 - 12\xi \\ H_1(\xi) &= 2\xi & H_4(\xi) &= 16\xi^4 - 48\xi^2 + 12 \\ H_2(\xi) &= 4\xi^2 - 2 & H_5(\xi) &= 32\xi^5 - 160\xi^3 + 120\xi \end{aligned} \quad (16.11)$$

A few of the wave functions in Eq. (16.12) are plotted in Fig. 16.2.

The classical oscillator has the largest kinetic energy, and therefore the maximum velocity, when $q = 0$. Hence it spends the least time in the neighborhood of $q = 0$; that is, the particle has the lowest probability density at $q = 0$. At the two extrema of displacement the oscillator has zero kinetic energy and

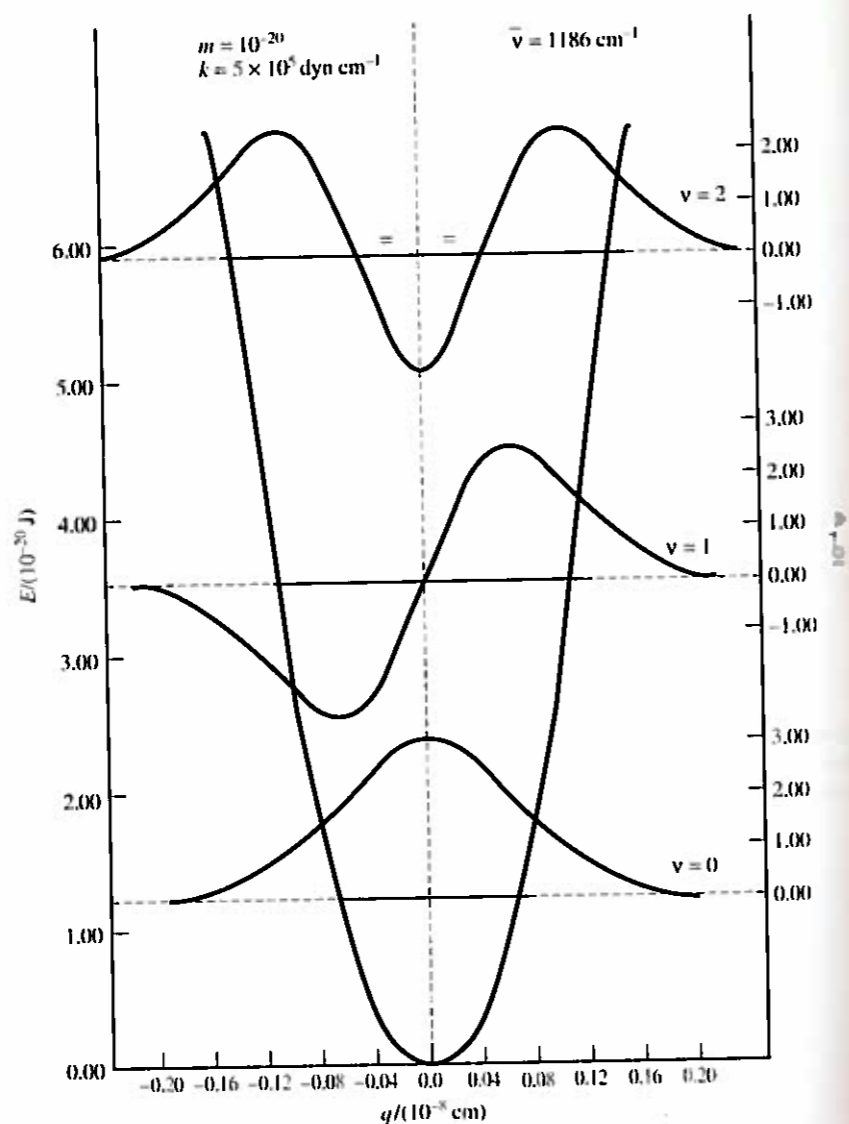


Figure 16.2. First three energies of a harmonic oscillator. (From H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry*, New York: John Wiley, 1944.)

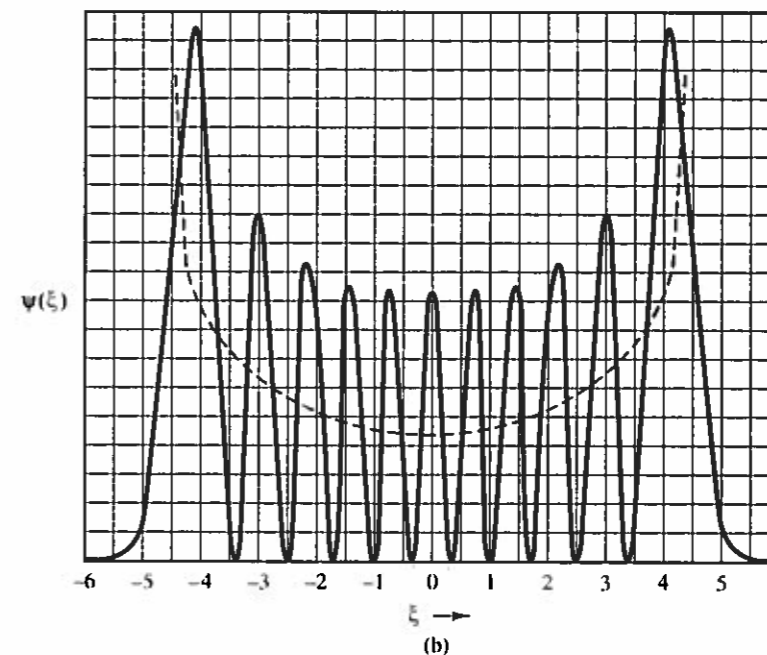
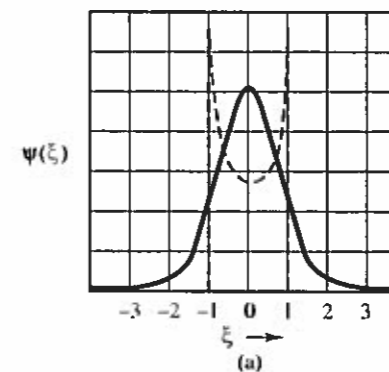


Figure 16.3. Classical (dashed lines) and quantum (solid lines) probabilities for a harmonic oscillator. (a) For $v = 0$ and (b) for $v = 10$. Note that the quantum and classical predictions differ markedly from each other for low v values. As v gets larger, however, quantum theory predictions approach those of classical mechanics. (From L. Pauling and J. Wilson, *Introduction to Quantum Mechanics*, New York: McGraw-Hill, 1937.)

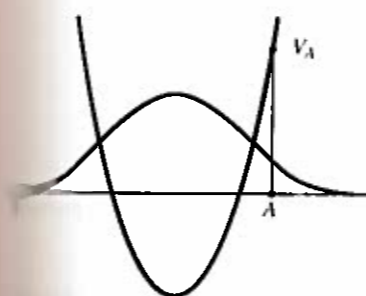


Figure 16.4. Tunneling phenomena. See text for discussion.

thus spends the greatest amount of time there. Consequently the probability density is highest at the turning points. The quantum oscillator, on the other hand, has the highest probability in the neighborhood of $q = 0$ for the $v = 0$ state. As v gets large, however, quantum probabilities approach the classical value. Figure 16.3 illustrates the classical and the quantum probabilities for a harmonic oscillator.

Tunneling

The quantum oscillator penetrates into regions not allowed for the classical oscillator. Consider point A in Fig. 16.4. Let the potential and kinetic energies at this point be V_A and T_A , respectively. From the conservation of energy we have

$$T_A + V_A = E_0$$

where E_0 is the total energy represented by the horizontal line in Fig. 16.4. Since $V_A > E_0$, this condition is satisfied only if the kinetic energy is negative! Such a possibility does not arise in the classical world of particles, for negative kinetic energy implies imaginary velocity. Hence the particle cannot cross the point of intersection in Fig. 16.4 according to the classical theory. In quantum theory the behavior of objects (which are both waves and particles) is governed by the wave function, which must be continuous if the potential energy varies continuously. The continuity condition leads to tunneling, that is, to nonzero probability for an object even in the classically forbidden regions.

Selection Rules

A harmonic oscillator subjected to electromagnetic radiation undergoes transitions between different energy levels. Only transitions between neighboring energy levels are allowed. The selection rules for the change in the vibrational quantum number v are

$$\Delta v = \pm 1 \quad (16.14)$$

where the positive sign corresponds to absorption, and the negative, to emission.

Example 16.2

Assume that all the atoms in Example 16.1 are in the $v = 0$ vibrational level. (This is the case at low temperatures.) What fraction of the atoms will you find within ± 0.01 nm of their equilibrium position?

We will first evaluate the probability density at $q = 0$. From the wave function in Eq. (16.12) we have

$$\rho_0(0) = \psi_0^2(0) = \left(\frac{\beta}{\pi}\right)^{1/2}$$

From Eq. (16.14) we have

$$\frac{\beta}{\pi} = \frac{2}{h} \sqrt{mk}$$

From the force constant calculated in Example 16.1, we have

$$\begin{aligned} \frac{\beta}{\pi} &= \frac{2}{6.62 \times 10^{-34} \text{ J s}} \left[\frac{12 \times 10^{-3} \text{ kg mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} (7.8 \times 10^{-3} \text{ J m}^{-1}) \right]^{1/2} \\ &= 3.8 \times 10^{19} \text{ m}^{-2} \end{aligned}$$

and

$$\rho_0(0) = \left(\frac{\beta}{\pi}\right)^{1/2} = 6.2 \times 10^9 \text{ m}^{-1}$$

The fraction of atoms between 0.01 and -0.01 nm is the same as the probability between these limits. Hence the fraction f is given by

$$\begin{aligned} f &= \rho_0(0)q = \rho_0(0)[0.01 - (-0.01)] \\ &= (6.2 \times 10^9 \text{ m}^{-1})(0.02 \times 10^{-9} \text{ m}) = 0.12 \end{aligned}$$

We have developed the theory of vibration for a model. Can we use this for real molecules?

Diatomic Molecule as a Harmonic Oscillator

We will now show that the kinetic energy of a diatomic molecule is identical, in mathematical form, to that of a harmonic oscillator. The kinetic energy of a diatomic molecule is given by

$$T = \frac{1}{2}(m_1 \dot{X}_1^2 + m_2 \dot{X}_2^2) \quad (16.17)$$

where \dot{X}_1 and \dot{X}_2 are the velocities of the atoms (see Fig. 16.5).

Displacements of the atoms are not independent of each other since vibrational motion leaves the center of mass and the orientation of molecules unaltered. Therefore,

$$m_1 \dot{X}_1 = -m_2 \dot{X}_2 \quad (16.18)$$

If we add $m_2 \dot{X}_1$ to both sides of the equation, we get

$$(m_2 + m_1) \dot{X}_1 = m_2 (\dot{X}_1 - \dot{X}_2) \quad (16.19)$$

It is convenient to define a "normal coordinate":

$$q = X_1 - X_2 \quad \dot{q} = \dot{X}_1 - \dot{X}_2 \quad (16.20)$$

We see from the above two equations that

$$\dot{X}_1 = \frac{m_2}{m_1 + m_2} \dot{q} \quad (16.21)$$

By proceeding similarly, we get

$$\dot{X}_2 = \frac{m_1}{m_1 + m_2} \dot{q} \quad (16.22)$$

Substitution for X_1 and X_2 in Eq. (16.17) gives

$$T = \frac{1}{2} m_r \dot{q}^2 \quad (16.23)$$

where m_r is the reduced mass of the molecules:

$$m_r = \frac{m_1 m_2}{m_1 + m_2} \quad (16.24)$$

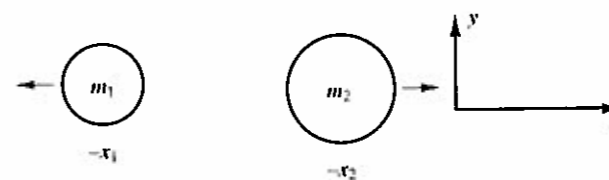


Figure 16.5. Vibrational motion of a diatomic molecule.

We see from Eq. (16.23) that the vibrational kinetic energy of a diatomic molecule may be expressed by a single term, just as in the case of a single-particle oscillator.

The potential energy between two atoms may be a fairly complicated function of internuclear distance. But for small displacements from the equilibrium position, the harmonic oscillator model is appropriate. Hence one assumes that the potential energy of a diatomic molecule is given by Eq. (16.7), with the understanding that q represents the displacement from the potential energy minimum and not the actual coordinates. Thus if R_e is the interatomic distance at the minimum potential energy,

$$q = R - R_e \quad (16.24)$$

The Ro-Vibrational Spectrum

Figure 16.6 shows a few vibrational and rotational levels of a diatomic molecule. In most molecules the vibrational levels are widely separated compared to the rotational levels. For example, the separation between neighboring vibrational levels in HCl is $3 \times 10^3 \text{ cm}^{-1}$, while the separation between $J = 0$ and $J = 1$ levels is 20 cm^{-1} . Hence when you measure the spectrum in the infrared, you will notice that rotational changes accompany vibrational transitions.

In the rigid rotor harmonic oscillator approximation, the ro-vibrational energies of a diatomic molecule are the sums of the rotational [Eq. (15.27)] and vibrational [Eq. (16.10)] energies:

$$E_{v,J} = hv_0(v + \frac{1}{2}) + BJ(J + 1) \quad (16.25)$$

Hence the spectroscopic terms are given by

$$G(v, J) = \tilde{\nu}_0(v + \frac{1}{2}) + \tilde{B}J(J + 1) \quad (16.26)$$

The selection rules for ro-vibrational spectra are

Dipole moment $\mu \neq 0$

$$\Delta v = \pm 1 \quad (16.27)$$

$$\Delta J = \pm 1$$

Let us consider the $v = 0$ to $v = 1$ transition. Since many rotational levels are occupied at ordinary temperatures, we must consider transitions from different J levels. In Fig. 16.6 rotational levels belonging to $v = 0$ are labeled by J'' , and those belonging to $v = 1$ by J' . Figure 16.6 also shows the allowed rotational lines for the $v = 0$ to $v = 1$ transition.

The group of lines with $\Delta J = 1$ is called the R branch. For the R branch $J' = J'' + 1$. Hence the frequency at which the R line appears is given by

$$\begin{aligned} \tilde{\nu}_R(J'') &= G(1, J'' + 1) - G(0, J'') \\ &= \tilde{\nu}_0 + 2\tilde{B}(J'' + 1) \end{aligned} \quad (16.28)$$

where $J'' = 0, 1, 2, \dots$. This equation shows that the successive R -branch lines are separated by $2B$ as illustrated in Fig. 16.6.

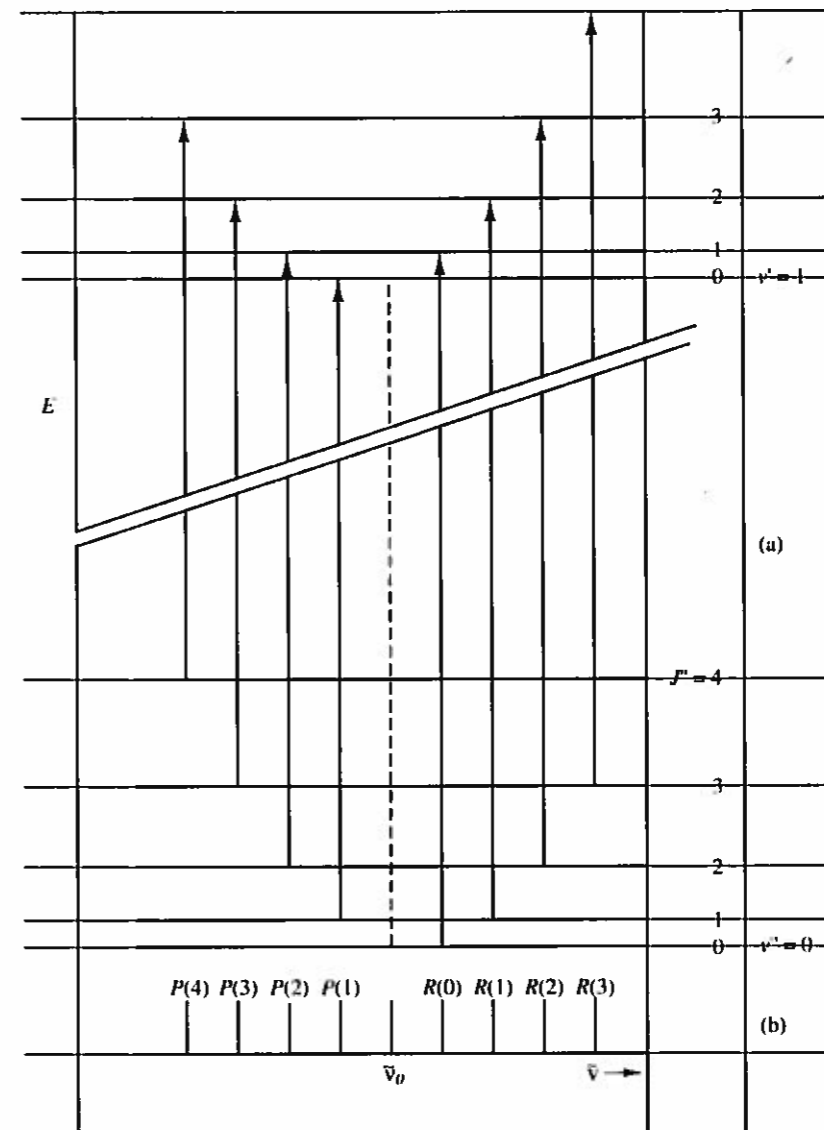


Figure 16.6. Energy levels and expected rotational-rotational spectrum of a diatomic molecule. Only frequencies of transitions are shown; intensities of rotation lines depend on temperature.

For the P branch of the spectrum, $J' = J'' - 1$. The frequencies of the P transitions are given by

$$\begin{aligned} \tilde{\nu}_P(J'') &= G(1, J'' - 1) - G(0, J'') \\ &= \tilde{\nu}_0 - 2\tilde{B}J'' \end{aligned} \quad (16.30)$$

where $J'' = 1, 2, \dots$.

Figure 16.7 shows the measured spectrum of HCl. Table 16.1 gives the wave numbers for several P and R lines. We see from the data that our model is quite successful in predicting the qualitative features of the spectrum. On the quantitative side it has to be refined for a better fit.

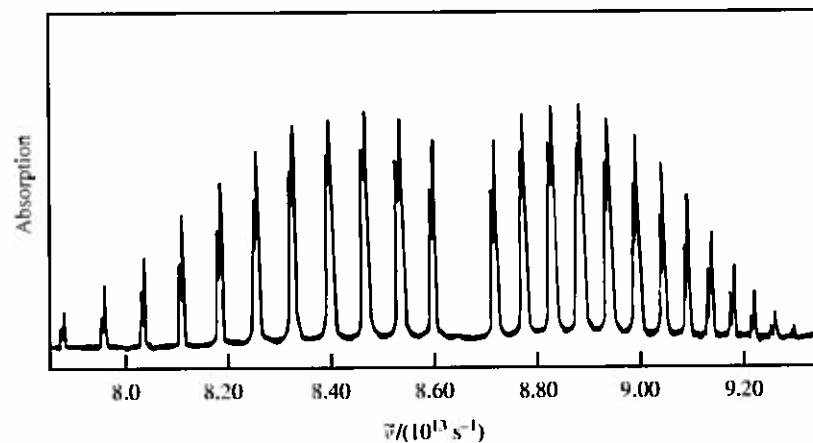


Figure 16.7. Infrared spectrum of HCl gas. The splitting of rotational lines is due to the two isotopes of chlorine, ^{35}Cl and ^{37}Cl .

TABLE 16.1 H^{35}Cl SPECTRUM*

Branch	Position (cm^{-1})	Δ	Branch	Position (cm^{-1})	Δ
R(11)	3085.62	12.86	P(1)	2865.09	21.33
R(10)	3072.76	13.69	P(2)	2843.56	22.00
R(9)	3059.07	14.19	P(3)	2821.49	22.11
R(8)	3044.88	14.92	P(4)	2798.78	22.06
R(7)	3029.96	15.67	P(5)	2775.79	23.74
R(6)	3014.29	16.51	P(6)	2752.03	24.28
R(5)	2997.78	16.88	P(7)	2727.75	24.00
R(4)	2980.90	17.66	P(8)	2703.06	25.33
R(3)	2963.24	18.43	P(9)	2677.73	25.71
R(2)	2944.89	19.03	P(10)	2651.97	26.23
R(1)	2925.78	19.53	P(11)	2625.74	26.71
R(0)	2906.25		P(12)	2599.00	

* If HCl were a rigid rotor, the Δ values would not change. Theory that includes the effects of nonrigidity and anharmonicity is presented in the next section.

Example 16.3

The two neighboring lines with maximum separation are at 4096.6 and 4180.4 cm^{-1} in the ro-vibrational spectrum of $^1\text{H}^{19}\text{F}$. Calculate the bond length of the molecule.

The maximum separation occurs between the P(1) and R(0) lines. Hence

$$\bar{\nu}_P(1) = 4096.6 \text{ cm}^{-1} \quad \text{and} \quad \bar{\nu}_R(0) = 4180.4 \text{ cm}^{-1}$$

Since the separation between these two lines is $4B$, we have

$$\bar{B} (\text{cm}^{-1}) = (4180.4 - 4096.6)/4 = 20.95 \text{ cm}^{-1}$$

The rotational constant in energy units is given by

$$\begin{aligned} B (\text{J}) &= \bar{B}hc \\ &= (20.95 \text{ cm}^{-1})(3.00 \times 10^{10} \text{ cm s}^{-1})(6.626 \times 10^{-34} \text{ J s}) \\ &= 4.164 \times 10^{-22} \text{ J} \end{aligned}$$

The reduced mass of the molecule is given by

$$m_r = \left(\frac{1.008 \times 19}{20.008} \times 10^{-3} \text{ kg mol}^{-1} \right) \left(\frac{1 \text{ mol}}{6.022 \times 10^{23}} \right) = 1.590 \times 10^{-27} \text{ kg}$$

From Eq. (15.27), which relates the bond length and the rotational constant, we find

$$\begin{aligned} R &= \frac{h}{(8\pi^2 B m_r)^{1/2}} = \frac{6.626 \times 10^{-34} \text{ J s}}{[8\pi^2(4.164 \times 10^{-22} \text{ J})(1.577 \times 10^{-27} \text{ kg})]^{1/2}} \\ &= 9.164 \times 10^{-11} \text{ m} = 91.64 \text{ pm} \end{aligned}$$

Intensities

The intensity of a ro-vibrational transition is governed by the population of the level from which it arises. The population in turn is governed by the Boltzmann distribution law. Therefore, the intensities of transitions arising from two different ro-vibrational levels are governed by the equation

$$\frac{N_{v',J'}}{N_{v'',J''}} = \frac{2J' + 1}{2J'' + 1} e^{-(E_{v',J'} - E_{v'',J''})/kT} \quad (1)$$

Only the degeneracies of the rotational levels appear in the equation since vibrational levels are nondegenerate.

Example 16.4

Calculate the relative intensities of the P(1) and R(0) branches of $^1\text{H}^{19}\text{F}$ at 20.0°C .

Since R(0) originates from the $J'' = 0$ level and P(1) from the $J'' = 1$ level, the intensities of these two lines are in the ratio of molecules in the respective J'' levels. I

$$\begin{aligned} \frac{I_P(1)}{I_R(0)} &= \frac{N_{01}}{N_{00}} = \frac{3}{1} e^{-2B/kT} \\ &= 3 \exp \frac{-2(4.164 \times 10^{-22} \text{ J})}{(1.381 \times 10^{-23} \text{ J K}^{-1})(273 \text{ K})} \\ &= 2.41 \end{aligned}$$

Except for the degeneracy of the $J' = 1$ level, the P(1) line would have a greater intensity than R(0).

RAMAN SCATTERING

Rotational and vibrational energies may be deduced from scattering experiments, as will be shown in this section. This technique complements the absorption studies and offers unique advantages in some cases.