molecules become dissociated by thermal agitation. A corresponding dissociation temperature for LiF is

$$T_{LiF} = \frac{6 \text{ eV}}{8.62 \times 10^{-5} \text{ eV/K}} \approx 7 \times 10^4 \text{ K}.$$

Obviously the van der Waals interaction is quite weak by comparison. For a pair of helium atoms the well depth is only 8.8×10^{-4} eV. The equivalent thermal energy is only 10.2 K. However, below this temperature we do not find bound He_2 molecules. Quantum mechanical zero-point motion is large enough to prevent these light atoms from forming any bound state at all. (See Problem 19 at the end of the chapter.)

10-5   Polyatomic Molecules: H₂O and CH₄

The electronic configuration of oxygen is $1s^2 2s^2 2p^4$. As discussed in connection with Figures 10-8 and 6-8 the p functions have threefold degeneracy; one (call it $2p_x$) has lobes along the x axis, another ($2p_y$) along y, and the third ($2p_z$) along z. If the four $2p$ electrons occupy only two of these three states, with two electrons each, then each of those two states is full. Then, according to the discussion at the end of Section 10-2, none of the electrons is available to form a covalent bond. However, if the four occupied states are, say, $2p_z^2 2p_x 2p_y$, then two of the states each have only one electron, which is said to be *unpaired*. Such a situation allows the possibility of the formation of *two* covalent bonds, one with each of the unpaired electrons. In water this results in the bonding with two hydrogen atoms. A first-approximation model of this molecule involves simply the one hydrogen s function overlapping with an oxygen $2p_x$ and the other with $2p_y$ as shown in Figure 10-12. This model has the bonds at a 90° angle.

Figure 10-12
Simple model of the water molecule H_2O. The electron of one hydrogen has its $1s$ function involved in a covalent bond with an oxygen $2p_x$ function. Another is bonded with the oxygen $2p_y$ function. The angle between the bonds is 90° in this model instead of the experimental value of 104.5°.
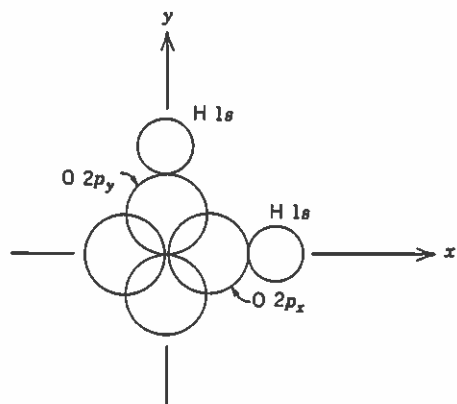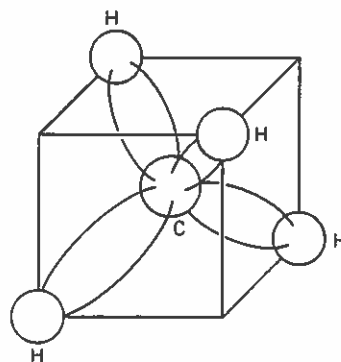

Figure 10-13
Methane molecule CH_4.

The repulsion between the two hydrogen ions causes the angle in the actual molecule to increase to 104.5°. We have seen this example briefly at the end of Section 9-3.

The bonds in H_2O have a fixed angle. Further examples of such *directed bonds* occur in the many compounds of carbon. One such molecule is methane, CH_4. Carbon's electronic state is $1s^2 2s^2 2p^2$. For a $2p^2$ configuration of $2p_x 2p_y$, it seems that carbon should form just two directed bonds like oxygen. However, carbon can bond to four hydrogens by a kind of trick. One of the $2s$ electrons goes into an excited p state so that the configuration becomes $1s^2 2s 2p_x 2p_y 2p_z$. There are then four unpaired electrons that can form bonds.

These bonds are not formed by use of the bare states ϕ_{2s}, ϕ_{2p_x}, ϕ_{2p_y}, ϕ_{2p_z}. Four linear combinations of these four functions can be formed as follows:

$$\psi_1 = \tfrac{1}{2}\big(\phi_{2s} + \phi_{2p_x} + \phi_{2p_y} + \phi_{2p_z}\big), \tag{10-37a}$$

$$\psi_2 = \tfrac{1}{2}\big(\phi_{2s} - \phi_{2p_x} + \phi_{2p_y} - \phi_{2p_z}\big), \tag{10-37b}$$

$$\psi_3 = \tfrac{1}{2}\big(\phi_{2s} + \phi_{2p_x} - \phi_{2p_y} - \phi_{2p_z}\big), \tag{10-37c}$$

$$\psi_4 = \tfrac{1}{2}\big(\phi_{2s} - \phi_{2p_x} - \phi_{2p_y} + \phi_{2p_z}\big). \tag{10-37d}$$

It can be shown that these states are directed toward the vertices of a tetrahedron with the carbon at the center as shown in Figure 10-13. These four states are completely equivalent to one another in contrast to the original four functions. The ψ_i of Equations (10-37) are known as *hybrid orbitals*. The energy cost of having a $2s$ electron move to an excited $2p$ state is more than offset by the binding energy of the four hydrogens whose $1s$ functions each pair up with one of the states of Equations (10-37). It costs 8.3 eV to excite the $2s$ electron but the binding of the four hydrogens yields an energy of 25.3 eV.

10-6 Rotation

In the previous sections of this chapter we have assumed the nuclei are fixed while solving for the electronic states. Starting with this section we consider how the nuclei move if we allow the electronic energy found in the previous sections to act as an interaction potential energy function between the nuclei. In a stable state the electronic energy has a minimum at some internuclear separation R_0. This distance is usually an approximate equilibrium position for the molecule. As a first approximation we can consider the nuclei to be rigidly fixed at that equilibrium separation but allow the molecule to rotate freely in space. In Section 10-7 the other possible nuclear motion, vibration of the molecule about R_0 along the internuclear line, is considered.

A rotational problem analogous to the one taken up here is treated in the example at the end of Section 6-5 and the system in question is shown in Figure 6-6. The rotational energy levels we seek are those given in that example. However, because it is important to see precisely what approximations are involved we start here from scratch.

The time-independent Schrödinger equation for the two nuclei of a homonuclear diatomic molecule is

$$-\frac{\hbar^2}{2m}\big(\nabla_1^2 + \nabla_2^2\big)\psi(\mathbf{R}_1, \mathbf{R}_2) + V(R_{12})\psi(\mathbf{R}_1, \mathbf{R}_2) = E\psi(\mathbf{R}_1, \mathbf{R}_2), \tag{10-38}$$

where $\mathbf{R}_1, \mathbf{R}_2$ are the positions of the two nuclei and $R_{12} = |\mathbf{R}_1 - \mathbf{R}_2|$. If we separate

variables into center-of-mass and relative coordinates, we find, as with the hydrogen atom, that the center-of-mass motion corresponds to that of a free particle, while the Schrödinger equation for the relative motion is (compare with Equation (6-16))

$$\left[-\frac{\hbar^2}{2\mu} \left\{ \frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{\Lambda^2}{R^2} \right\} + V(R) \right] \psi_{\text{rel}}(R, \Theta, \Phi) = E_{\text{rel}} \psi_{\text{rel}}(R, \Theta, \Phi),$$

(10-39)

where R, Θ, Φ are the spherical coordinates of the vector $\mathbf{R}_{12}$, μ is the reduced mass $m_1 m_2/(m_1 + m_2)$ equal in this case to $m/2$, and Λ^2 is the angular operator (Equation (6-12))

$$\Lambda^2 = \frac{1}{\sin \Theta} \frac{\partial}{\partial \Theta} \sin \Theta \frac{\partial}{\partial \Theta} + \frac{1}{\sin^2 \Theta} \frac{\partial^2}{\partial \Phi^2}.$$

(10-40)

From Chapter 6 it is known that ψ can be written in the separable form

$$\psi_{\text{rel}}(R, \Theta, \Phi) = F(R) Y_{\ell m}(\Theta, \Phi),$$

(10-41)

where $Y_{\ell m}(\Theta, \Phi)$ is a spherical harmonic. The operator Λ^2 acting on $Y_{\ell m}$ yields $-\ell(\ell + 1)$, where $\ell = 0, 1, 2, \ldots$ with ℓ the *nuclear* orbital angular momentum quantum number. That is, ℓ is a measure of the angular momentum of the pair of nuclei rotating about an axis perpendicular to the line between the nuclei.

In general, the total angular momentum of the molecule is the sum of the nuclear plus electronic angular momenta. In the case where the electrons are in a state of zero angular momentum, the nuclear quantum number ℓ may be replaced by the total quantum number j. In many situations in which there is nonzero electronic angular momentum we can replace $L^2 \rightarrow -\hbar^2 \Lambda^2$ by the operator $J^2 =$ (total angular momentum)^2 with the difference being absorbed into the electronic energy $V(R)$. In either case we end up with the relative motion equation

$$\left\{ -\frac{\hbar^2}{2\mu} \left[\frac{1}{R^2} \frac{d}{dR} R^2 \frac{d}{dR} - \frac{j(j + 1)}{R^2} \right] + V(R) \right\} F(R) = E_{\text{rel}} F(R).$$

(10-42)

Given a functional form for $V(R)$ we could now solve this equation for $F(R)$ and then find the average value of the rotational energy $(\hbar^2/2\mu) j(j + 1)\langle 1/R^2 \rangle$. However, a simpler approach is possible. $V(R)$ has a minimum at R_0 so that the equilibrium separation of the nuclei, that is, the mean value of R, is approximately R_0. The kinetic and rotational energies are usually small enough that they do not significantly alter this estimate of the mean value. So the molecular rotation energy is very nearly

$$E_{\text{rot}} = \frac{\hbar^2}{2\mu} \frac{j(j + 1)}{R_0^2}, \qquad j = 0, 1, 2, \ldots .$$

(10-43)

The quantity μR_0^2 in Equation (10-43) is the moment of inertia of the molecule. E_{rot} is the energy associated with the rotation of a rigid dumbbell as obtained in Section 6-5. The energy levels represented by Equation (10-43) lead to spectral lines whose separation is so small that they are often unresolved and appear as *bands*, as discussed in Section 10-8.

Occasionally, it is necessary to go beyond the approximation made in replacing $\langle R^{-2}\rangle$ by R_0^{-2} to arrive at Equation (10-43). Some spectra involving high rotational quantum numbers show the effect of "stretching" of the dumbbell, and the resulting increase of the moment of inertia becomes evident.

<div align="center">Example</div>

A numerical estimate of the rotational energy is easily obtained. Consider the hydrogen molecule H_2 for which 2μ is the proton mass and $R_0 \approx 0.07$ nm. We have from Equation (10-43)

$$E_{rot} \sim \frac{\left(1 \times 10^{-34} \text{ J} \cdot \text{s}\right)^2}{\left(1.7 \times 10^{-27} \text{ kg}\right)\left(0.7 \times 10^{-10} \text{ m}\right)^2} = 1.2 \times 10^{-21} \text{ J}$$

or

$$E_{rot} \sim \frac{1.2 \times 10^{-21} \text{ J}}{1.6 \times 10^{-19} \text{ J/eV}} = 7 \times 10^{-3} \text{ eV}.$$

This energy is to be compared to a typical size of a molecular electronic energy, which can be shown (see Problem 16 at the end of the chapter) to be of order

$$E_{el} \sim \frac{\hbar^2}{m_e R_0^2} = \frac{M_p}{m_e} \frac{\hbar^2}{M_p R_0^2} = \left(1.8 \times 10^3\right)\left(7 \times 10^{-3} \text{ eV}\right) = 13 \text{ eV},$$

where m_e and M_p are the electron and proton masses, respectively.

10-7 Vibration

The problem of the relative motion of two nuclei in a diatomic molecule (as described by Equation (10-42)) is that of a particle in a potential well, $V(R)$, having a minimum. If the well is deep and narrow, it is reasonable to assume that the nuclear rotation is the most easily excited type of motion. However, we know that a particle in any well—for example, in a parabolic well—vibrates about the position of the minimum, even in the ground state. The harmonic oscillator treated in Section 5-5 is our prime model in this regard. We now consider molecular vibrations and show this problem can usually be reduced to the case of a one-dimensional harmonic oscillator.

Returning to Equation (10-42), we write

$$E_{rel} = E_{vib} + E_{rot},$$

where E_{vib} is the vibrational energy that we want to determine and E_{rot} is the rotational energy of Equation (10-43). We then have

$$-\frac{\hbar^2}{2\mu} \frac{1}{R^2} \frac{d}{dR}\left(R^2 \frac{dF}{dR}\right) + V(R)F(R) = E_{vib}F(R).$$

In analogy with the hydrogen-atom problem we let $U(R) = RF(R)$. This results in

Figure 10-14
Morse potential energy $V(R)$ with depth $-A$
at R_0. The dashed line is a parabolic potential
$\tilde{V}$ that fits the Morse potential at the
minimum.
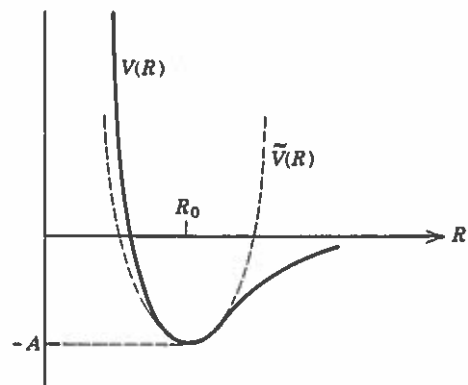
the equation

$$-\frac{\hbar^2}{2\mu}\frac{d^2U(R)}{dR^2} + V(R)U(R) = E_{\text{vib}}U(R), \qquad (10\text{-}44)$$

so the problem has been reduced to that of a one-dimensional Schrödinger equation.

For many covalently bonded molecules a suitable form for $V(R)$ is the *Morse potential energy*. This expression, deduced by P. M. Morse, is given by

$$V(R) = A\big(e^{-2a(R-R_0)} - 2e^{-a(R-R_0)}\big), \qquad (10\text{-}45)$$

where A, a, and R_0 are parameters varying from molecule to molecule. The form of this function is basically just an intelligent guess, as in the cases of Equations (10-24) and (10-36), but it does do an adequate job of correlating many molecular properties. For only a very few molecules, notably H_2, can accurate theoretical potential energy functions be derived from first principles. Most molecules are much too complicated for one to do much better than to fit Equation (10-45) or an equivalent form to several pieces of molecular data. Figure 10-14 indicates that the depth of the Morse minimum is $-A$, which occurs at $R = R_0$. The parameter a determines how fast the potential energy falls off with distance and curvature of the well.

For small oscillations about equilibrium such that the nuclear separation does not deviate very far from R_0, it is reasonable to approximate $V(R)$ by a parabola centered on R_0. Such a parabolic potential energy is shown as the dashed curve in Figure 10-14 and is denoted as $\tilde{V}(R)$. We can write

$$\tilde{V}(R) = V(R_0) + \tfrac{1}{2}K(R - R_0)^2, \qquad (10\text{-}46)$$

where the constant K is to be determined so that $V(R)$ and $\tilde{V}(R)$ have the same curvature at R_0. This means the second derivatives of $V(R)$ and $\tilde{V}(R)$ have to be the

same:

$$\tilde{V}''(R_0) = K = V''(R_0) = 2a^2A. \tag{10-47}$$

Equation (10-46), with K given as $2a^2A$, is the result obtained with a Taylor expansion of $V(R)$ about $R = R_0$ if only up to quadratic terms in $R - R_0$ are kept.

With the substitution of $\tilde{V}$ for V, the Schrödinger equation becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2U(R)}{dR^2} + \frac{1}{2}K(R - R_0)^2U(R) = \left[E_{\text{vib}} - V(R_0)\right]U(R).$$

If we let $y = R - R_0$, $\varepsilon = E_{\text{vib}} - V(R_0)$, and $u(y) = U(y + R_0)$, this becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2u(y)}{dy^2} + \frac{1}{2}Ky^2u(y) = \varepsilon u(y). \tag{10-48}$$

This equation is almost the Schrödinger equation for simple harmonic motion, as treated in Section 5-5. The one small difference is that the radial coordinate R is restricted to $R > 0$ so that $y > -R_0$. However, this is really an unimportant restriction because if the particle motion had such an amplitude that it got to $y = -R_0$ it would certainly be in a region where the parabolic approximation is invalid anyway. The gaussian wave functions for the low states of the harmonic oscillator restrict y to avoid this forbidden region and we can simply forget the restriction. On the other hand, the highly excited states in the oscillator well have much wider amplitudes than the ground state and they should not be expected to be reliable approximations to the true states of $V(R)$.

The radial Schrödinger equation with the exact Morse function in Equation (10-45) can actually be solved analytically. However, the mathematics involved is sufficiently complicated that we lose sight of the simple physics of the vibratory motion if we attempt to review the exact solution here.

The energy eigenvalues derived from Equation (10-48) are just those of the harmonic oscillator (see Equation (5-46)) with quantum number v:

$$\varepsilon_v = \hbar\omega_0\left(v + \tfrac{1}{2}\right), \qquad v = 0, 1, 2, \ldots$$

where

$$\omega_0 = \sqrt{\frac{K}{\mu}}. \tag{10-49}$$

We therefore obtain

$$E_{\text{vib}} = -A + \hbar\omega_0\left(v + \tfrac{1}{2}\right), \qquad v = 0, 1, 2, \ldots. \tag{10-50}$$

These are the energy levels corresponding to oscillations in the length of the diatomic molecule, in the approximation in which we think of the two nuclei as being connected by a stiff spring. For highly excited states this approximation fails and the Morse or other appropriate potential energy must be used to find E_{vib}.

Polyatomic molecules can often be thought of as several atoms connected by a number of springs. Such a system has a number of oscillatory patterns known as *normal modes*. The techniques of classical mechanics may be used to find the frequencies of these modes from which the vibration spectrum may then be found.

Example

The values of the Morse potential energy parameters for the O_2 molecule are

$$A = 5.2 \text{ eV}, \qquad R_0 = 0.12 \text{ nm}, \qquad a = 27 \text{ nm}^{-1}.$$

From these values we find

$$K = 2a^2A = 2(27 \text{ nm}^{-1})^2(5.2 \text{ eV}) = 7600 \text{ eV/nm}^2 = 1.2 \times 10^3 \text{ J/m}^2$$

so that a characteristic vibrational energy is

$$\hbar\omega_0 = \hbar\sqrt{\frac{K}{\mu}} = \frac{1.05 \times 10^{-34} \text{ J} \cdot \text{s}}{1.6 \times 10^{-19} \text{ J/eV}}\sqrt{\frac{1.2 \times 10^3 \text{ J/m}^2}{8(1.7 \times 10^{-27} \text{ kg})}} = 0.2 \text{ eV}.$$

Note that the reduced mass used is one-half the oxygen atomic mass. This vibrational energy should be compared with typical electronic and rotational energies of about 10 eV and 10^{-3} eV, respectively, as computed in Section 10-6.

Example

The dissociation energy D, the energy to pull the molecule apart, is approximately A, the depth of the potential energy well. This is not exactly right because the molecule has zero-point vibrational energy $\frac{1}{2}\hbar\omega_0$. Thus, we have

$$D = A - \tfrac{1}{2}\hbar\omega_0.$$

For O_2 we obtain

$$D = 5.2 - 0.1 = 5.1 \text{ eV},$$

in agreement with the experimental value.

10-8 Spectra

Much of what is known about molecules comes from examining spectra. Because a molecule is inherently more complex than an atom, molecular spectra are often more complicated than atomic spectra. From the spectral lines the various effects caused by electronic, vibrational, and rotational transitions must be disentangled. The energy scales of these three types of transition are quite different, as we have seen above, with typical values being of order 10, 10^{-1}, and 10^{-3} eV, respectively. Because the rotational energy is so small, the spectra often appear as *bands* of very closely spaced lines, the most noticeable characteristic of molecular spectra.

We examine three main spectral types: pure rotational, rotation–vibrational, and electronic. To keep the discussion simple only those transitions between molecular states having the angular momentum quantum number $\lambda = 0$ are considered. Our analysis is therefore not quite as general as possible but does illustrate most of the essential elements.

Figure 10-15

Molecular absorption transitions. Transition I is pure rotational with $\Delta j = 1$ and no change in vibrational or electronic state. Transition II involves a vibrational change $\Delta v = 1$; the rotational change is $\Delta j = \pm 1$. Transition III involves an electronic change of state with possible vibrational and rotational changes as well.
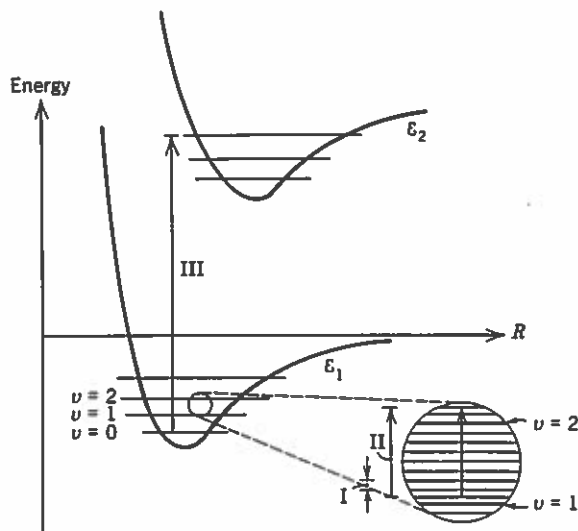
A molecular energy level within the approximations discussed in previous sections is, by Equations (10-43) and (10-50),

$$\varepsilon = \varepsilon_{el} + \hbar\omega_0\left(v + \tfrac{1}{2}\right) + Bj(j + 1), \tag{10-51}$$

where

$$B = \frac{\hbar^2}{2\mu R_0^2}. \tag{10-52}$$

Figure 10-15 presents a schematic illustration of transitions involving all three terms in Equation (10-51).

The first transition to be considered is a pure rotational change of state. Such a change is shown in Figure 10-15 as I. Because of symmetry considerations, a pure rotational transition, that is, one in which j changes but the electronic and vibrational quantum numbers remain the same, cannot occur for a homonuclear diatomic molecule, such as H_2. It can occur, however, in a heteronuclear molecule having a permanent electric dipole moment, such as LiF.

There is a selection rule for a pure rotational transition tl at forbids transitions other than
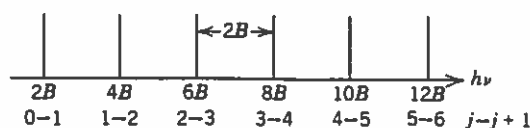
$$\Delta j = \pm 1.$$

For absorption spectra $j \rightarrow j + 1$ and from Equation (10-51) the frequencies are given by

$$h\nu = B\left[(j + 1)(j + 2) - j(j + 1)\right] = 2B(j + 1). \tag{10-53a}$$

Figure 10-16
Spectral form for a pure rotational transition as I in Figure 10-15. The lines are equally spaced with energy interval $2B$.

For emission spectra $j \rightarrow j - 1$ so

$$hv = B[j(j+1) - (j-1)j] = 2Bj. \tag{10-53b}$$

In both cases the frequencies vary linearly with j, which means the lines are evenly spaced with frequency separation

$$\Delta v = \frac{2B}{h} \tag{10-54}$$

as shown in Figure 10-16. These transitions are in the far-infrared or microwave range.

From pure rotational spectra, and in particular from Equation (10-54), we can find B. The equilibrium interatomic spacing R_0 is then found from Equation (10-52).

Vibrational transitions cannot take place in a homonuclear molecule without an accompanying electronic change but can in a molecule with a permanent dipole moment. In such a case the selection rules are

$$\Delta v = \pm 1 \quad \text{and} \quad \Delta j = \pm 1.$$

A typical vibrational transition is shown as II in Figure 10-15. Absorption always implies $\Delta v = +1$ since the vibrational energy is so much larger than the rotational. In the usual situation the initial vibrational state is $v = 0$ since the higher vibrational states are not thermally excited at room temperature. Then the energy change is either that with $j \rightarrow j + 1$ given by

$$hv_R = \hbar\omega_0\left(1 + \tfrac{1}{2}\right) + B(j+1)(j+2) - \tfrac{1}{2}\hbar\omega_0 - Bj(j+1)$$
$$= \hbar\omega_0 + 2B(j+1), \quad j = 0, 1, 2, \ldots, \tag{10-55}$$

or that with $j \rightarrow j - 1$ given by

$$hv_P = \hbar\omega_0\left(1 + \tfrac{1}{2}\right) + B(j-1)j - \tfrac{1}{2}\hbar\omega_0 - Bj(j+1)$$
$$= \hbar\omega_0 - 2Bj, \quad j = 1, 2, \ldots. \tag{10-56}$$

As indicated by the subscripts on the v's, these spectral lines are known as the R and P branches. Each of these branches gives a group of lines much like that due to the pure rotational transitions except that the frequencies are in the range about $\hbar\omega_0$ so that they fall in the infrared.

Figure 10-17

Spectral form for a vibrational–rotational transition. There are two branches with a missing line at $\hbar\omega_0$. The corresponding transition in Figure 10-15 is II.
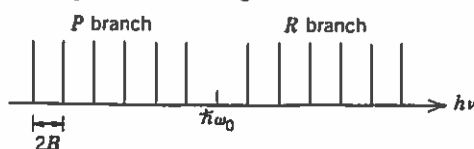

Figure 10-17 shows how the vibrational–rotational spectrum splits into the two branches in accord with Equations (10-55) and (10-56). Note that there is a gap between the two bands at the vibrational frequency $\omega_0/2\pi$. This exists because $\Delta j = 0$ is not allowed and because in Equation (10-56) $j = 0$ does not occur. (That would correspond to the transition $j = 0$ to $j = -1$.)

Transitions in which there is an electronic change of energy are represented by III in Figure 10-15. The transition frequencies can again be deduced from Equation (10-51). However, now note that ω_0 and B are not generally the same for the initial and final electronic states. B depends on the molecular moment of inertia and hence on the interatomic separation R_0, which varies with the electronic state. In Figure 10-15, for example, the minima in ε_1 and ε_2 occur at different values of R. The vibrational frequency ω_0 depends on the curvature of the electronic energy in the neighborhood of its minimum. (See Equations (10-47) and (10-49).) The curvature is also expected to be different for different states. For absorption the change in electronic and vibrational energy is

$$h\nu_{ev} = \varepsilon_{s's} + \hbar\omega_0'\left(v' + \tfrac{1}{2}\right) - \hbar\omega_0\left(v + \tfrac{1}{2}\right), \tag{10-57}$$

where ω_0 and ω_0' are the vibrational frequencies for initial and final states, s and v are the initial state electronic and vibrational quantum numbers, and s' and v' are those of the final state. In absorption the initial electronic and vibrational states are usually ground states so $s = 0$ and $v = 0$.

Equation (10-57) sets the scale of the transitions, which run from the near infrared to the ultraviolet. The fine structure of the spectrum is determined by examining the rotational transitions that occur simultaneously with the above change $h\nu_{ev}$. What the rotational structure does is to spread the electronic–vibrational line into a *band* of many very closely spaced lines. The selection rule is again $\Delta j = \pm 1$ so that there is an R branch corresponding to $j \rightarrow j + 1$ with energy changes

$$h\nu_R = h\nu_{ev} + B'(j + 1)(j + 2) - Bj(j + 1), \qquad j = 0, 1, 2, \ldots, \tag{10-58a}$$

and a P branch for $j \rightarrow j - 1$ given by

$$h\nu_P = h\nu_{ev} + B'j(j - 1) - Bj(j + 1), \qquad j = 1, 2, \ldots . \tag{10-58b}$$

Because $B \neq B'$ the quadratic terms in j no longer cancel out and the spectra are not made up of evenly spaced lines as in the previous situations. We can write

$$h\nu_R = h\nu_{ev} + (B' - B)j^2 + (3B' - B)j + 2B' \tag{10-59a}$$

Figure 10-18

Spectral form for an electronic transition. The electronic–vibrational transition energy is $h\nu_{ev}$. The band due to rotational transitions has a band head at the left (red) and degrades to the right (blue).

Figure 10-19

Pure rotational absorption spectrum of HCl gas. Note the even line spacing as indicated schematically in Figure 10-16. The frequency axis is $\tilde{\nu} = \nu/c$ in units of cm^{-1}.
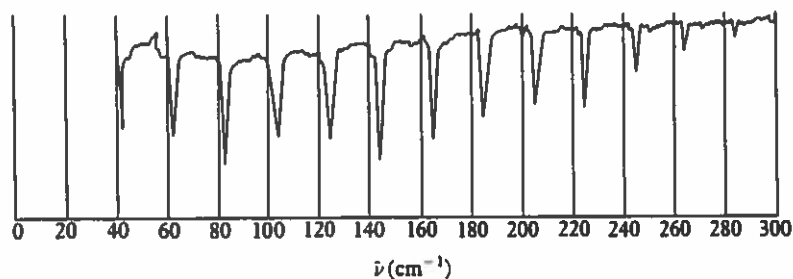

Figure 10-20

Vibrational–rotational absorption spectrum of a diatomic molecule like that shown schematically in Figure 10-17. The absent line is denoted by $\tilde{\nu}_v$.
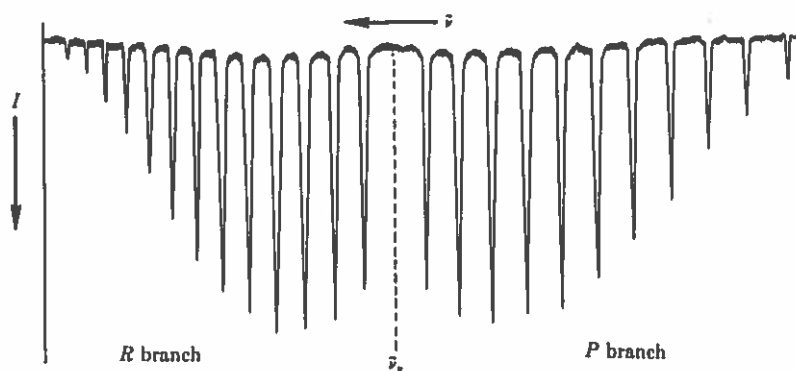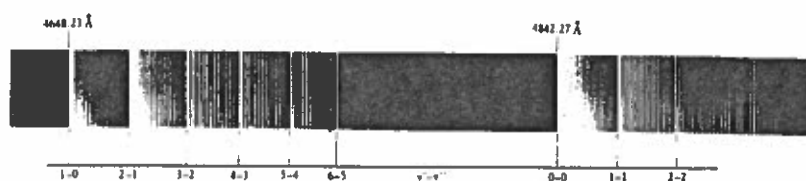
Figure 10-21
Electronic spectrum of the molecule AlO. See Figure 10-18 for a similar schematic version. Note the bands caused by the small spacing of the rotational states.

and

$$hv_P = hv_{cv} + (B' - B)j^2 - (B' + B)j. \tag{10-59b}$$

If $B' > B$ these v_R and v_P results increase quadratically toward higher frequency. The function $v_P(j)$ has a minimum at a frequency somewhat lower than v_{cv}. In this region the lines are also more closely spaced than at high j values; at high j the spacing becomes greater because of the increasing influence of the j^2 term. A schematic drawing of this spectrum is shown in Figure 10-18. The band is said to be *degraded* to the blue (i.e., the high-frequency end) and to have a *band head* (the minimum) at the red (low-frequency) end. If $B' < B$, the band head is at the blue end and the degradation is toward the red. The details of just how the spectrum comes to look like that of Figure 10-18 are given in the example below. Such a band appears for each possible $v \to v'$ transition. The spectra appear as a series of adjacent bands.

Examples of real spectra of the types discussed in this section are shown in Figures 10-19, 10-20, and 10-21.

Example

To see how the frequencies in Equations (10-59) produce a spectrum like that shown in Figure 10-18, rewrite the equations in the form

$$y_R(j) = 10^2 \left(\frac{v_R}{v_{cv}} - 1 \right) = (b' - b)j^2 + (3b' - b)j + 2b' \tag{10-60a}$$

and

$$y_P(j) = 10^2 \left(\frac{v_P}{v_{cv}} - 1 \right) = (b' - b)j^2 - (b' + b)j, \tag{10-60b}$$

where

$$b = \frac{10^2 B}{hv_{cv}} \quad \text{and} \quad b' = \frac{10^2 B'}{hv_{cv}}.$$

Then let b and b' take on the typical values $b = 3$, $b' = 4$, so that

$$y_R(j) = j^2 + 9j + 8 \quad \text{and} \quad y_P(j) = j^2 - 7j.$$

Figure 10-22

Frequency functions $y_R(j)$ and $y_P(j)$ of Equations (10-60) for $b = 3$ and $b' = 4$. The y values corresponding to integers are the allowed frequencies and are indicated by arrows on the y axis. The band head is at the left end corresponding to the minimum in y_P.
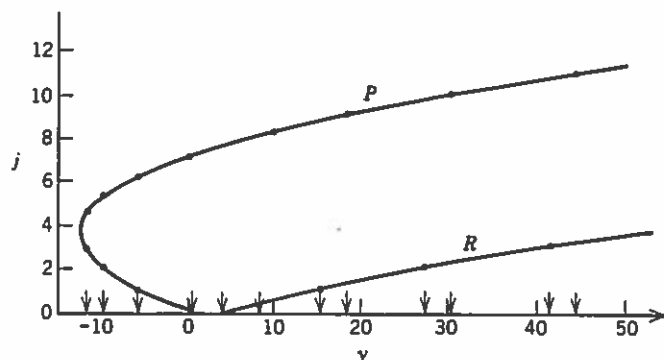
If we consider y_R or y_P to be a function of j as a continuous variable, we can plot each as shown in Figure 10-22. The plot is laid on its side so that the frequency variable y runs horizontally. Integral values of j are shown as dots along the curves; their projections on the y axis give the frequencies of the allowed transitions. It is easy to see that y_P has a minimum:

$$\frac{dy_P}{dj} = 2j - 7 = 0 \quad \text{at } j = \tfrac{7}{2} = 3.5.$$

The value of y_P at the minimum is $(\tfrac{7}{2})^2 - 7(\tfrac{7}{2}) = -12.25$. The minimum frequency occurs at the band head. The y_P parabola opens to the right so that the allowed y values become more separated in moving to larger y values. This is band degradation to the blue. The R branch does not have a minimum for positive j but also degrades to the blue.

Problems

1. A particle of mass m moves in a "double-oscillator" potential energy given by $V(x) = \tfrac{1}{2}k(|x| - a)^2$, as plotted in the figure. When the separation $2a$ between wells is sufficiently large, good approximations to the eigenfunctions for the two lowest states are

    $$\psi_\pm = \frac{1}{\sqrt{2}}(\phi_a \pm \phi_{-a}),$$

    where

    $$\phi_{\pm a}(x) = \left(\frac{2\alpha}{\pi}\right)^{1/4} e^{-\alpha(x \mp a)^2}$$

    is the single oscillator ground-state eigenfunction centered on $x = \pm a$, with $\alpha = \tfrac{1}{2}m\omega_0/\hbar$ and $\omega_0 = \sqrt{k/m}$.