LiF are also used for special purposes, but rock salt is the transparent material used in most infrared spectroscopy studies. (If one has the opportunity to work in the infrared spectral region, one must remember that the cells are, in fact, made of salt and, unless a very expensive salt solution is desired, water must not be used as a sample or as a solvent!)

The dispersing element most frequently found in an infrared spectrometer is a prism made of rock salt. It should be mentioned, however, that an alternative dispersing element is available and is increasingly found in commercial instruments. Instead of a prism, an appropriately ruled grating can be used. There are some special advantages to the use of gratings; in particular, their use does away with the need for preparing large prisms of materials such as NaCl. Also, since gratings are used as reflection devices, the problems that arise—particularly, far out in the infrared region—with lack of transparency of materials are avoided.

Although a heated tungsten filament, as used in an ordinary light bulb, does give off infrared radiation, it is more satisfactory to use a heated ceramic element as a source of radiation. Such an element is generally heated by means of an electric current until it appears red or even white.

The nature of the detector that is used is governed by the fact that the energy of the quanta in the infrared region is so low that the radiation is not able to eject electrons effectively enough to make a phototube or a photomultiplier operative. One can, however, detect infrared radiation through the heating that occurs when the radiation is absorbed. A very sensitive thermocouple, for example, can be used as a detector.

Finally, the instruments that will be encountered will operate with the double-beam principal, will make use of chopped radiation, and will be so arranged that the absorption spectrum is automatically recorded on chart paper. One of the commercial instruments that operates in the infrared region is illustrated in Fig. 3–1.

3–2 VIBRATION OF
BALL-AND-SPRING SYSTEMS

As in the previous study of the rotation of molecules, it is first desirable to treat systems which behave according to the classical,
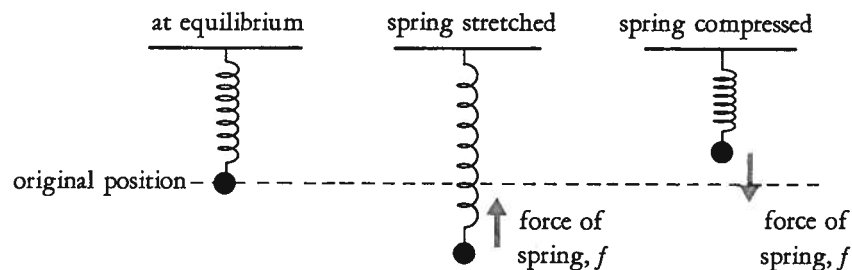
Figure 3–2 The simple vibrating system of a ball and spring showing the displacement from the equilibrium position, and the force f, the restoring force of the spring acting on the ball.

i.e., Newtonian, equations of motion. The way in which molecules vibrate can be approached by considering first the vibrational motion of a single ball attached to a spring, as in Fig. 3–2, and then treating the system consisting of two balls connected by a spring, the counterpart of a diatomic molecule.

Let us first consider the nature of the spring of Fig. 3–2. We shall assume that it behaves, as do many ordinary springs, according to Hooke's law. This law states that the ball, when it is displaced from its equilibrium position by a given amount, experiences a restoring force acting to bring it back to its equilibrium position that is proportional to the amount of the displacement. (Later we shall see that chemical bonds also behave pretty much in accordance with Hooke's law.) If f represents the force of the spring on the particle and x measures the displacement from the equilibrium position, one can write the proportionality equation

$$f \propto x \qquad (1)$$

or the equality

$$f = (-k)x. \qquad (2)$$

The equality is written with a minus sign shown explicitly so that, although f acts in the direction opposite to that in which x increases, the proportionality constant k will have a positive value. The

constant k is known as the *force constant* of the spring. It measures, as is seen by noticing that k is the value of the restoring force for a unit displacement, the stiffness of the spring. A strong, inflexible spring will have a large value of k; a weak, easily extended or compressed spring will have a small value of k.

Now let us consider the motion of the ball attached to the spring. The vibratory motion that we expect implies that the coordinate x that describes the displacement of the ball from its equilibrium position is some repeating function of the time t. If one makes measurements of x at various times t or if one solves the equation that describes the behavior of such systems, one sees that x varies as the sine or the cosine of t according to an equation of the type

$$x = A \sin(\text{const})\, t \quad \text{or} \quad x = A \cos(\text{const})\, t. \quad (3)$$

The term A gives the amplitude of the vibration; and, although in some connections it is important, we shall not be concerned with this term here. Either the sine or the cosine function can be used to describe the oscillating motion of the ball. Here we shall proceed with the cosine function.

In discussing the way in which x varies with t it is helpful to look further into the significance of the term written merely as (const) in Eqs. (3). The periodic nature of the motion makes it convenient to write this constant coefficient of t as $2\pi\nu$. When this is done, ν can be identified as a frequency of oscillation, i.e., as the number of vibrations or cycles that the ball makes in 1 sec. One sees this by recognizing that the cosine function completes a cycle every time the argument $2\pi\nu t$ increases by 2π. This occurs every time t increases by $1/\nu$, and it follows that the time interval $1/\nu$ is the number of seconds required for the ball to move through one vibration or cycle. Thus if $1/\nu$ is the number of seconds per cycle, it follows that ν is the number of cycles per second, i.e., the frequency of the vibration.

It now remains to relate the properties of the spring system, i.e., the mass m of the ball and the force constant k of the spring, to the quantity ν, the vibrational frequency in the expression $x = A \cos 2\pi\nu t$ which describes the motion.

The equation to which the motion of the ball must conform is

Newton's $f = ma$ relation. We have already seen that the force on the ball is equal to $-kx$. Furthermore, it will be recalled that the acceleration a is the rate of change of the velocity with respect to time and that the velocity itself is the rate of change of x with respect to time. It follows that the acceleration is the second derivative with respect to time of x and, writing d^2x/dt^2 for a and $-kx$ for f, Newton's equation has the form

$$-kx = m\frac{d^2x}{dt^2}$$

or

$$-\left(\frac{k}{m}\right)x = \frac{d^2x}{dt^2}. \quad (4)$$

One can now readily verify that description of the motion given by $x = A \cos 2\pi\nu t$ satisfies this equation. Substitution for x and for its second derivative gives

$$-\left(\frac{k}{m}\right)A \cos(2\pi\nu t) = -4\pi^2\nu^2 A \cos 2\pi\nu t.$$

The $A \cos 2\pi\nu t$ terms can be canceled and the equality is seen to hold if

$$\frac{k}{m} = 4\pi^2\nu^2$$

or

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}. \quad (5)$$

In this way we see that $x = A \cos 2\pi\nu t$ does satisfy Newton's equation and that the vibrational frequency ν is related to the properties, k and m, of the system by Eq. (5). This important classical result implies that for a given spring and mass there is one characteristic, or natural, frequency of vibration and that this frequency can be calculated from Eq. (5). In the following section, where quantum effects are considered, we shall make use of this result; and to emphasize that it is obtained for ordinary-sized systems, we shall then write $\nu_\text{classical}$ instead of ν. (The energy of the vibrating system would be found to depend on the amplitude A of the oscillating mass. We are, however, not concerned with this aspect.)
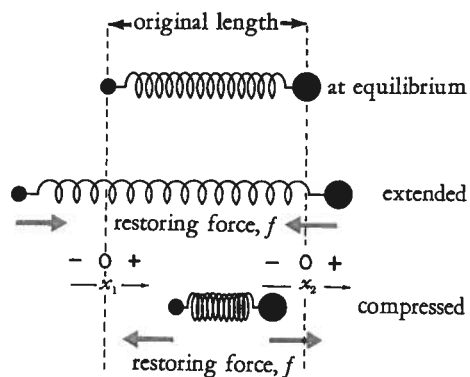
Figure 3–3   The vibrating system of two balls and a spring showing the displacement coordinates x_1 and x_2 and the restoring force f.

The other classical ball-and-spring problem that must be solved in preparation for a study of the vibrations of molecular systems is the spring-and-two-ball arrangement of Fig. 3–3. One can imagine the balls as lying on a frictionless table or suspended from long cords. The vibrational motion of this dumbbell arrangement can be deduced in a manner analogous to that used for the single-particle system. One need only notice that the magnitude of the restoring force on each ball depends on the extent of stretching or compression of the spring. The extension of the spring is given by $x_2 - x_1$, and by comparison with the one-particle system already treated we can write the restoring force as $f = -k(x_2 - x_1)$. This force acts, as indicated in Fig. 3–3, to move particle 2 to the left when it moves particle 1 to the right. When care is taken with these different directions, one can substitute the force expression in Newton's $f = ma$ equation for each particle to give the equations

$$+k(x_2 - x_1) = m_1 \frac{d^2 x_1}{dt^2} \tag{6}$$

and

$$-k(x_2 - x_1) = m_2 \frac{d^2 x_2}{dt^2}. \tag{7}$$

We can again look for solution functions of the type found for a single particle; and in so doing we try

$$x_1 = A_1 \cos 2\pi \nu t \tag{8}$$

and

$$x_2 = A_2 \cos 2\pi \nu t, \tag{9}$$

where the amplitude terms for particles 1 and 2 may be different but the frequency ν must be the same for both particles.

As before, we can relate ν to the properties of the system by substituting these functions back into the equations of motion. We obtain, first,

$$kA_2 \cos 2\pi \nu t - kA_1 \cos 2\pi \nu t = -4\pi^2 \nu^2 m_1 A_1 \cos 2\pi \nu t \tag{10}$$

and

$$-kA_2 \cos 2\pi \nu t + kA_1 \cos 2\pi \nu t = -4\pi^2 \nu^2 m_2 A_2 \cos 2\pi \nu t. \tag{11}$$

The $\cos 2\pi \nu t$ terms can be canceled, and these two equations can be simplified and rearranged to give

$$(-4\pi^2 \nu^2 m_1 + k)A_1 = kA_2 \tag{12}$$

and

$$(-k)A_1 = (4\pi^2 \nu^2 m_2 - k)A_2. \tag{13}$$

Finally, the amplitudes can be eliminated by, for instance, dividing one equation by the other to give, after rearrangement,

$$\frac{4\pi^2 \nu^2}{k} = \frac{m_1 + m_2}{m_1 m_2} \tag{14}$$

or

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}, \tag{15}$$

where the reduced mass μ, equal to $m_1 m_2/(m_1 + m_2)$ as introduced in Sec. 2–1, has again been used. With this symbol the expression for the vibration of a two-particle system has the same form as that of Eq. (5) deduced for a one-particle system.

Again we reach the conclusion that the system has a natural

frequency of vibration and that this frequency is related to the force constant and the masses of the system. The amount of energy stored in the vibrations of such a ball-and-spring system would again be found to depend on the amplitude of the vibrational motion.

With this introduction to the vibrational motion of systems that behave classically, we can proceed to see what differences arise when systems of molecular dimensions are encountered and quantum restrictions become important.

3-3 VIBRATIONAL ENERGIES OF DIATOMIC MOLECULES

In more advanced studies of molecular behavior one might proceed directly to solve for the allowed vibrational energies of the molecule by application of Schrödinger's, rather than Newton's, equation. As for the treatment of rotation, one can avoid this procedure and can impose restrictions on the classical results of the preceding section to obtain the allowed vibrational energies.

The way in which the quantum restrictions are introduced into a vibrating system is suggested, in part, by Planck's equation $\Delta\epsilon = h\nu$, which relates the quantum energy to the frequency of the waves of electromagnetic radiation. The allowed vibrational energies of atomic- or molecular-sized systems are given by expressions with a similar form. (The relation $\Delta\epsilon = h\nu$ came, in fact, from Planck's considerations of the vibrational energy of the atoms of a hot object emitting radiation.) Thus the vibrational states that the system is allowed to be in are separated from one another by an energy $\Delta\epsilon_{\text{vib}}$, which is given by the expression

$$\Delta\epsilon_{\text{vib}} = h\nu_{\text{classical}}, \tag{16}$$

where $\nu_{\text{classical}}$ is the frequency of the natural vibrations that would occur if the system behaved as do ordinary-sized systems. The general expression for the allowed vibrational energies themselves—in contrast to the *spacing* of these levels given by Eq. (16) in molecular-sized systems—is found to be

$$\epsilon_{\text{vib}} = h\nu_{\text{classical}}(v + \tfrac{1}{2}) \qquad v = 0, 1, 2 \ldots \tag{17}$$

As for the expression for the allowed rotational energies, an integer appears, here denoted by v. It is called the vibrational

quantum number. According to this equation, if the system is in a state described by $v = 0$, it will have a vibrational energy of $\tfrac{1}{2}h\nu_{\text{classical}}$; if it is in the $v = 1$ state, it will have an energy $\tfrac{3}{2}h\nu_{\text{classical}}$; if in the $v = 2$ state, it will have an energy $\tfrac{5}{2}h\nu_{\text{classical}}$; and so forth. One sees that, in spite of the presence of the $\tfrac{1}{2}$ term in Eq. (17), the allowed vibrational energies are spaced by an amount $h\nu_{\text{classical}}$.

In addition to a restriction on the allowed energies, which we should by now recognize as normal for molecular-dimensioned systems, a second peculiarity now enters. One sees that the lowest vibrational energy that a particle governed by Eq. (17) can have is $\tfrac{1}{2}h\nu_{\text{classical}}$. This is, of course, in contrast to ordinary-sized systems which are "allowed" to have zero vibrational energy. There are, it should be mentioned, some very interesting consequences of this *zero-point energy* that is retained by all vibrating molecular systems. (At low temperatures, for instance, all the molecules will go into the allowed energy level with the lowest energy. Since there is no allowed energy level at the zero of energy, the molecules cannot get into a zero-energy state.) Thus even at the temperature of absolute zero, vibrating systems will retain some vibrational energy.

For the particular case of a single atomic particle attached by a spring-like chemical bond to a fixed reference point, the expression for the allowed energies is given by Eq. (17) and the expression $\nu_{\text{classical}} = (1/2\pi)\sqrt{k/m}$, which relates $\nu_{\text{classical}}$ to the properties of the particle and the spring. We can write

$$\epsilon_{\text{vib}} = \frac{h}{2\pi}\sqrt{\frac{k}{m}}\,(v + \tfrac{1}{2}) \qquad v = 0, 1, 2, \ldots \tag{18}$$

In a similar manner the allowed vibrational energies of the chemically more interesting system of a diatomic molecule are given by Eq. (17) and the relation $\nu_{\text{classical}} = (1/2\pi)\sqrt{k/\mu}$ deduced for the classical counterpart of the diatomic molecule. Thus for a diatomic molecule we write

$$\epsilon_{\text{vib}} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\,(v + \tfrac{1}{2}) \qquad v = 0, 1, 2, \ldots \tag{19}$$

This important result allows us to show diagrammatically the allowed vibrational energies of a diatomic molecule, and this is done schematically in Fig. 3-4. Furthermore, the spectral results to be
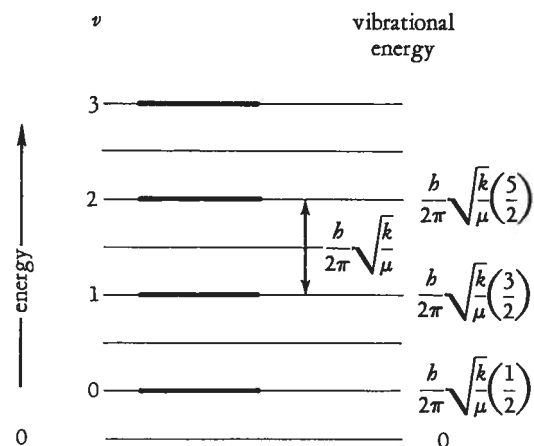
Figure 3–4   The vibrational energies of a diatomic molecule according to the expression $\epsilon_{\text{vib}} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}\,(v + \tfrac{1}{2})$ with $v = 0, 1, 2, \ldots$.

given shortly can here be anticipated to allow the scale diagrams of Fig. 3–5 to be drawn for CO and Cl_2.

These diagrams allow us to compare typical vibrational energy level spacings with our reference energy, the room temperature value of kT. One now finds, in contrast to the situation for rotational energies, that the spacing is large compared to kT. It follows, either from the qualitative discussion of Sec. 1–5 that claimed that few molecules would have an energy much greater than the average classical amount or from application of Boltzmann's expression, that at ordinary temperatures most molecules will have the vibrational energy corresponding to $v = 0$ or, as we say, will be in the $v = 0$ state or energy level.

We now have an expression and diagrams for the allowed vibrational energies, and we know that most molecules of our sample will be in the lowest of these levels. We are in a position, therefore, to understand what happens when infrared radiation, whose quanta
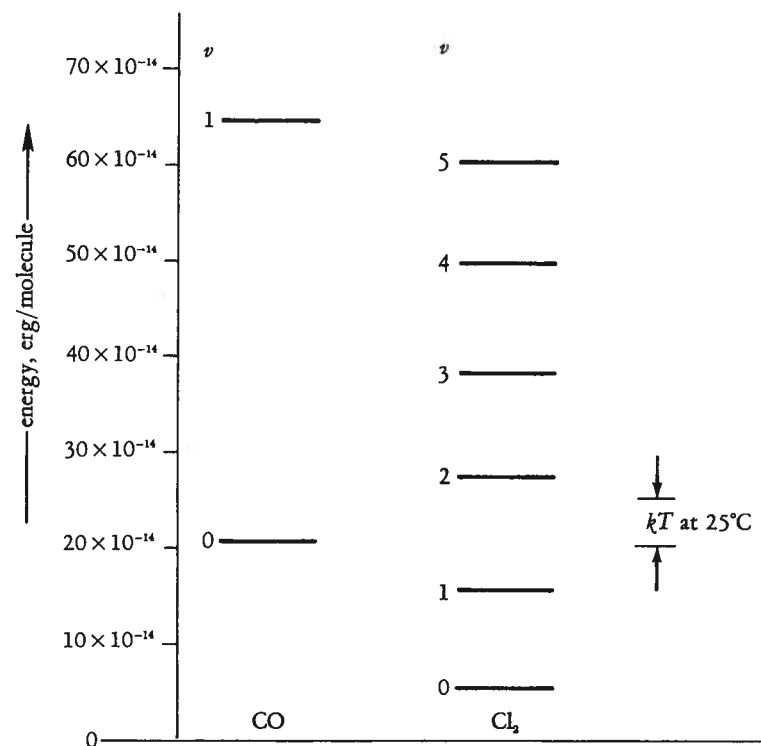
Figure 3–5   The vibrational energies of CO, which are spaced by the relatively large amount of 42×10^{-14} erg, and those energies of Cl_2, which are spaced by the relatively small amount of 11×10^{-14} erg, compared with the value of kT at 25°C.

have energies comparable to the energy spacing of vibrational levels, falls on a sample of diatomic molecules.

3–4   VIBRATIONAL SPECTRA AND FORCE CONSTANTS OF DIATOMIC MOLECULES

Most compounds are found to absorb radiation in the infrared spectral region, and these absorptions can be attributed to changes in
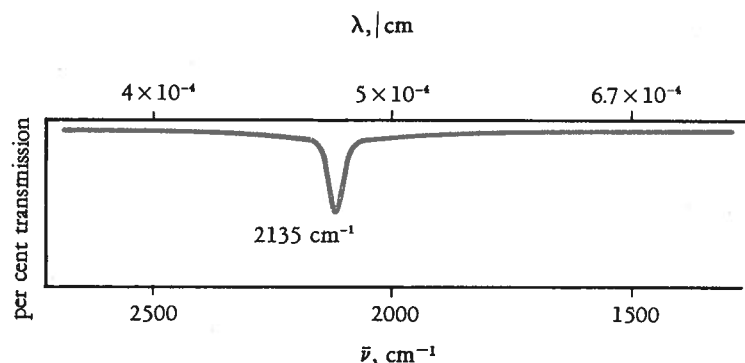
Figure 3-6 The absorption of infrared radiation by CO molecules showing the absorption band at 2135 cm⁻¹.

the vibrational energy of the absorbing molecule. More specifically, if carbon monoxide is dissolved in the inert solvent carbon tetrachloride, it is found that, as Fig. 3-6 shows, radiation at $\lambda = 0.000468$ cm—or in terms of the frequency units of centimeters⁻¹ usually used in the infrared region, $\bar{\nu} = 2140$ cm⁻¹—is absorbed. At this wavelength the solvent is transparent and the absorption of this radiation must be attributed to the CO molecules in the sample. In similar experiments with other diatomic molecules other absorption bands in this infrared spectral region are observed. We must now ask how the infrared absorption band of a diatomic molecule is related to the energy of the molecules of the sample.

The vibrational energy level diagram of Figs. 3-4 and 3-5 suggests that each molecule might absorb a quantum of radiation and move from the $\nu = 0$ to $\nu = 1$ vibrational energy level. The process is indicated by the arrow of Fig. 3-7. If the observed infrared absorption band is attributed to such a transition, the energy spacing of the two vibrational levels can be deduced from the energy of the quanta of the radiation absorbed. For the CO case, for example, the quantum energy of radiation with $\bar{\nu} = 2140$ cm—¹, or $\nu = 6.40 \times 10^{13}$ cycles/sec, is

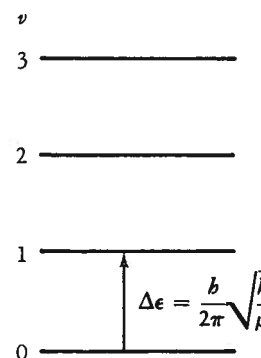$$\Delta\epsilon = h\nu = 4.24 \times 10^{-13} \text{ erg.} \tag{20}$$

Figure 3-7 The transition from the $\nu = 0$ to the $\nu = 1$ vibrational energy level that leads to the absorption of infrared radiation as shown for CO in Fig. 3-6.

Furthermore, the theory of the preceding section tells us that this energy must be equal to the quantity $(h/2\pi)\sqrt{k/\mu}$, where k and μ are, respectively, the force constant and the reduced mass of the molecule absorbing the radiation. For the CO example, for which we deduced in Sec. 2-3 the value of μ to be 1.14×10^{-23} g, we can write

$$4.24 \times 10^{-13} = \frac{h}{2\pi}\sqrt{\frac{k}{\mu}}$$

or

$$k = \frac{4\pi^2(1.14 \times 10^{-23})(4.24 \times 10^{-13})^2}{(6.62 \times 10^{-27})^2}$$

$$= 18.4 \times 10^5 \text{ dyne/cm.}$$

Thus, when the infrared absorption band corresponding to the vibrational transition from $\nu = 0$ to $\nu = 1$ can be identified, its frequency, called the *fundamental frequency*, can be used to deduce a value for the force constant of the bond of the molecule. In a similar way the infrared absorption bands of other diatomic molecules can be used to obtain bond force constants. Some results are listed in Table 3-1.

Table 3–1

The Positions of the Fundamental Vibrational Absorptions of Some Diatomic Molecules and the Bond Force Constants Deduced from These Values

Molecule	$\bar{\nu}$, cm^{-1}, for the $v = 0$ to $v = 1$ absorption band	Force constant, dynes/cm
HF	2907	9.7×10^5
HCl	2886	4.8×10^5
HBr	2559	4.1×10^5
HI	2230	3.2×10^5
CO	2143	18.4×10^5
NO	1876	15.3×10^5

It should be recognized that the deduction of the stiffness of a chemical bond, which is the quantity measured by the force constant, is a rather impressive feat. An appreciation of the results is, perhaps, most easily reached by comparing the variation in the stiffness of different molecules. One notices, for example, the great rigidity of the HF molecule as compared to the HI molecule. Similarly, the multiple-bonded CO molecule shows a greater rigidity than the single-bond molecules.

3–5   AMPLITUDE OF MOLECULAR VIBRATIONS

One can also attempt to appreciate the degree of stiffness, or flexibility, of molecules by investigating the amplitude of their vibrations when, for example, they have the energy corresponding to the $v = 0$ level. This can be done in a simple, but not entirely correct, manner by resorting to some extent to the classical picture of a vibrating system. With this view one can recognize that at the limits of a vibration, as the particles are turning around to reverse their direction, there is no kinetic energy and all the energy of the system must be potential energy. For the molecular case and the $v = 0$ level we can ask how much the bond will stretch if the energy of this level is used up in increasing the potential energy. The

potential-energy increase that accompanies bond stretching can be calculated as stored work. If the bond is to be stretched to an extension x, a force must be exerted in opposition to that of the spring. We can perform the necessary integration to give the potential energy of the system as a function of the displacement from the equilibrium position as

$$\text{increase in PE} = \int_0^x kx\, dx = \frac{kx^2}{2}\Big]_0^x,$$

whence

$$\text{increase in PE} = \tfrac{1}{2}kx^2. \tag{21}$$

This general result can be applied to find the maximum displacement, i.e., the amplitude for the $v = 0$ state. The potential energy at $x = x_{max}$ is equal to the total energy of the $v = 0$ state, and one writes

$$\frac{1}{2}\left(\frac{h}{2\pi}\right)\sqrt{\frac{k}{\mu}} = \frac{1}{2}kx_{max}^2 \tag{22}$$

For HCl, for example, one has from Table 3–1, $k = 4.8 \times 10^5$ dynes/cm and with $\mu = 1.61 \times 10^{-24}$ g one can calculate

$$\text{amplitude of vibration} = 0.11 \times 10^{-8} \text{ cm} = 0.11 \text{ A}. \tag{23}$$

When this result is compared with the equilibrium bond length of 1.27×10^{-8} cm, or 1.27 A, obtained by the methods of the preceding chapter, one sees that the vibrational amplitude is about 10 per cent of the bond length. This calculation shows that molecules are not to be thought of as rigid structures even in the lowest allowed vibrational state. They, in fact, compare with rather flexible spring systems.

3–6   MECHANISM OF INFRARED-RADIATION ABSORPTION

Now that we see that molecular properties can be deduced from an identification of the infrared absorption band of a diatomic molecule with the $v = 0$ to $v = 1$ vibrational transition, we can go back and comment on the way in which the transfer of energy between the

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Gordon Pinkerton

Gordon M. Barrow

THE
STRUCTURE
OF
MOLECULES
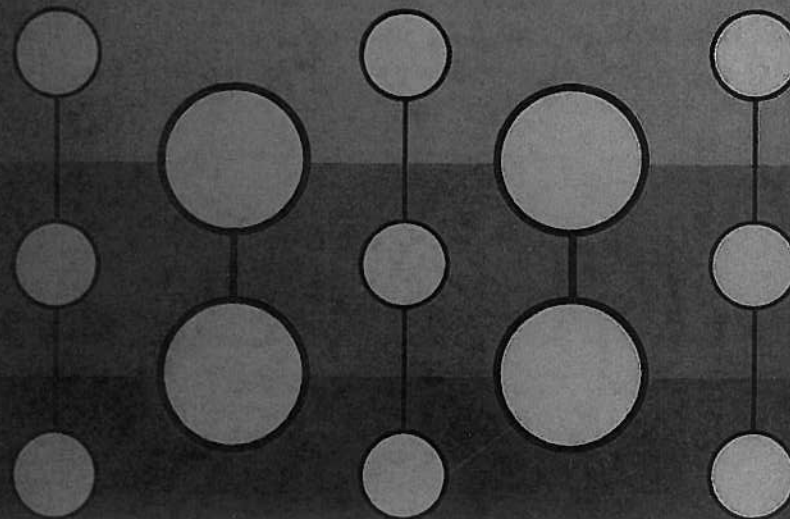
THE STRUCTURE OF MOLECULES
An Introduction to Molecular Spectroscopy

Editor's Foreword

The teaching of general chemistry to beginning students becomes each day a more challenging and rewarding task as subject matter becomes more diverse and more complex and as the high school preparation of the student improves. These challenges have evoked a number of responses; this series of monographs for general chemistry is one such response. It is an experiment in the teaching of chemistry which recognizes a number of the problems that plague those who select textbooks and teach chemistry. First, it recognizes that no single book can physically encompass all the various aspects of chemistry that all instructors collectively deem important. Second, it recognizes that no single author is capable of writing authoritatively on *all* the topics that are included in everybody's list of what constitutes general chemistry. Finally, it recognizes the instructor's right to choose those topics that he considers to be important without having to apologize for having omitted large parts of an extensive textbook.

This volume, then, is one of approximately fifteen in the General Chemistry Monograph Series, each written by one or more highly qualified persons very familiar with the current status of the subject by virtue of research in it and also conversant with the problems associated with teaching the subject matter to beginning students. Each volume deals broadly with one of the subdivisions of general chemistry and constitutes a complete entity, far more comprehensive in its coverage than is permitted by the limitation of the standard one-volume text. Taken together, these volumes provide a range of topics from which the individual instructor can easily select those that will provide for his class an appropriate coverage of the material he considers most important.