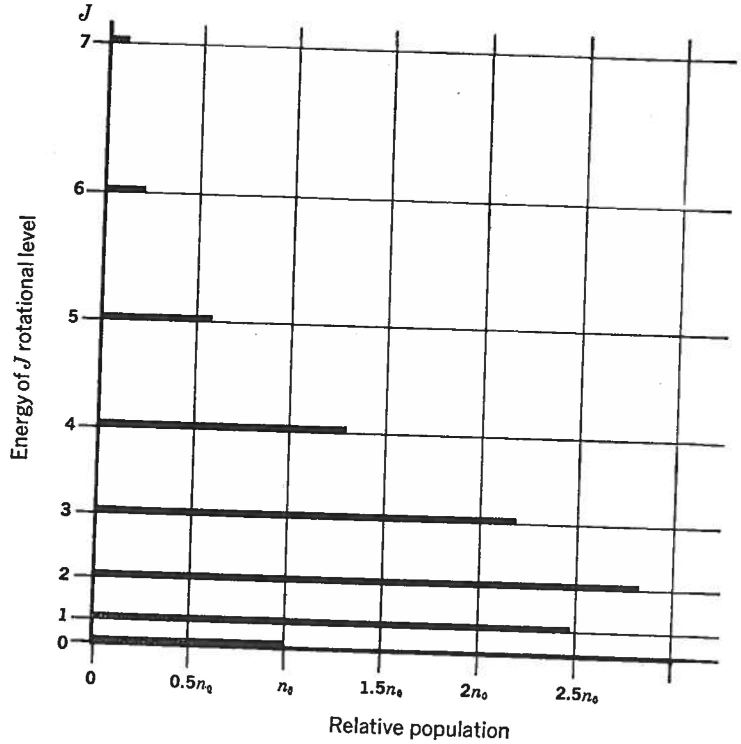

Fig. 10-5. The relative populations of the lower rotational-energy levels of HCl at 25°C.

Some results obtained from studies of rotational spectra are shown in Table 10-2. As these data indicate, the method, when applicable, leads to extremely precise internuclear distances. One should be impressed by the fact that rotational spectra allow the measurement of distances within molecules relatively more accurately than one can measure the length of a desk top with a meterstick.

There are, of course, limitations to this method of structure determination. Only molecules with dipole moments can be studied. Large molecules have so many internuclear distances that these quantities cannot be sorted out from the three determined moments of inertia. Finally, all measurements must be made on gases where the rotation is free and behaves according to Eq. (11). Molecules of liquids or solids are interfered with by their neighbors to such an extent that no well-defined, discrete rotational-energy levels exist and no rotational spectra are therefore observed.

10-2. Vibrational Spectra. The molecular motion that has the next larger energy-level spacing after the rotation of molecules is the vibration of the atoms of the molecule with respect to one another. It will be shown that the study of the absorptions of radiation that result from transitions among the vibrational-energy levels leads to further detailed insight into the nature of molecules.

Table 10-2. Some Molecular Dimensions from Analyses of Rotational Spectra*

	Molecule	Bond	Bond distance (A)
Diatomic....................	HF	H—F	0.917
	HCl	H—Cl	1.275
	HBr	H—Br	1.414
	HI	H—I	1.604
	CO	C═O	1.128
	FCl	F—Cl	1.628
	NaCl	Na—Cl	2.361
	CsCl	Cs—Cl	2.904
Polyatomic linear............	HCN	C—H	1.064
		C≡N	1.156
	OCS	C≡O	1.164
		C═S	1.558
	OCSe	C═O	1.159
		C═Se	1.709
	HCCCl	C—H	1.052
		C≡C	1.211
		C—Cl	1.632
Polyatomic nonlinear.........	CH_3Cl	$\text{H—}\overset{\curvearrowright}{\text{C}}\text{—H}$	110°20′ ± 1°
		C—H	1.103 ± 0.010
		C—Cl	1.782 ± 0.003
	CH_2Cl_2	$\text{H—}\overset{\curvearrowright}{\text{C}}\text{—H}$	112°0′ ± 20′
		$\text{Cl—}\overset{\curvearrowright}{\text{C}}\text{—Cl}$	111°47′ ± 1′
		C—H	1.068 ± 0.005
		C—Cl	1.7724 ± 0.0005

* From Gordy, Smith, and Trambarulo, "Microwave Spectroscopy," John Wiley & Sons, Inc., New York, 1953.

Although the vibrations of diatomic molecules will primarily be considered, it is convenient at first to consider the vibrations of a single mass attached by a flexible bond, i.e., by a spring, to a fixed point, as in Fig. 10-6. The vibrational characteristics of such a particle are determined by the mass of the particle and by the nature of the spring. For both ordinary-sized objects held by actual springs and for atoms held by chemical bonds it turns out to be quite a good approximation to make the simplest assumption about the spring or bond. This assumption, known as *Hooke's law*, is that the particle experiences a restoring force pulling or pushing it back to its equilibrium position and that this force is proportional to the distance to which the particle has been displaced from its equilibrium position. Since displacing the particle in one direction brings about a force in the opposite direction, Hooke's law is written

$$f = -kx \tag{19}$$

where f is the restoring force and x is the displacement from the equilibrium position. The proportionality constant k is known as the *force constant* and is a measure of the stiffness of the spring. The force constant is equal to the restoring force operating for a unit displacement from the equilibrium position. For molecular systems the force constant is usually given in the units of dynes per centimeter.

It is frequently more convenient to state Hooke's law in terms of the potential energy of the vibrating particle. The potential energy U at the equilibrium position can be arbitrarily taken as zero. Displacement of the particle from a position x to a position $x\ dx$ requires a force to be exerted to overcome that of the spring. The work done, all of which is stored in the system and is therefore potential energy, is equal to this applied force times the distance dx through which it acts. Thus

$$\begin{aligned} dU &= (\text{applied force})\ dx \\ &= (-f)\ dx \end{aligned} \tag{20}$$

which with Eq. (19) gives

$$dU = kx\ dx$$

Integration gives the potential as a function of distance, according to Hooke's law, as

$$U = \tfrac{1}{2}kx^2 \tag{21}$$

The potential energy therefore rises parabolically on either side of the equilibrium position, as illustrated in Fig. 10-6.

Once a potential function for the motion to be studied has been arrived at, it is possible to substitute this function in the Schrödinger equation and to solve

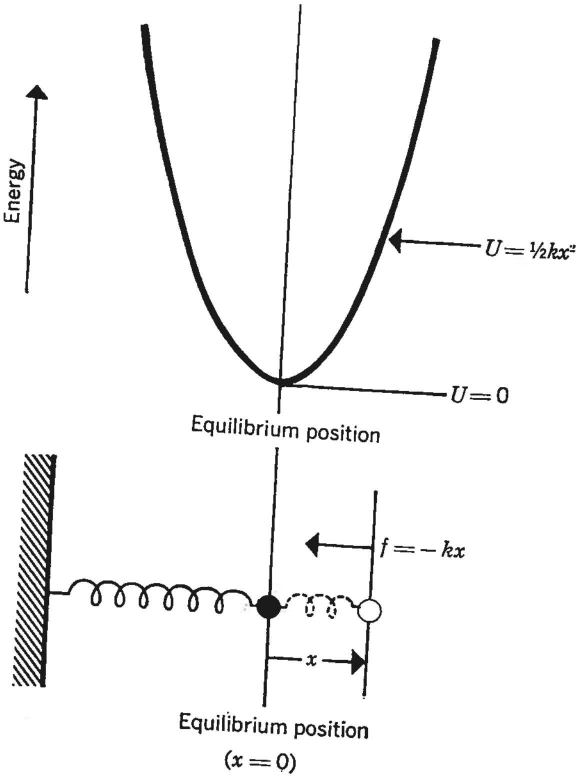

Fig. 10-6. Hooke's law of force for a single particle.

for the allowed energy-level pattern. Again this procedure is avoided, and some classical relations which are more easily visualized are obtained.

The classical motion of a particle, such as that of Fig. 10-6, can be deduced from Newton's law $f = ma$. If $f = -kx$ and $a = d^2x/dt^2$ are substituted, one obtains

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

or

$$\frac{m}{k}\frac{d^2x}{dt^2} = -x \tag{22}$$

A solution to this equation can be seen by inspection and verified by substitution to be

$$x = A \sin \sqrt{\frac{k}{m}}\, t \tag{23}$$

A is a constant that is equal to the maximum value of x; that is, it is the vibrational amplitude. The position of the particle, therefore, varies sinusoidally with time. The time corresponding to one oscillation, or vibration, is $2\pi\sqrt{m/k}$ since every time t increases by $2\pi\sqrt{m/k}$ the quantity $\sqrt{k/m}\,t$ increases by 2π and the particle traces out one complete cycle. More directly useful is the reciprocal of this quantity, which is the frequency of vibration, i.e., the number of cycles performed per second. If this quantity is denoted by $\nu_{\text{classical}}$, we have

$$\nu_{\text{classical}} = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \tag{24}$$

For a system of ordinary dimension there is, therefore, a natural frequency of oscillation that depends on the values of k and m. Any amount of energy can be imparted to the vibrating system, and this energy changes only the amplitude of the vibration.

The quantum-mechanical solution to this problem provided by the Schrödinger equation differs, of course, in that only certain vibrational levels are allowed. These can be calculated by the substitution of the potential-energy expression of Eq. (21) in the one-dimensional Schrödinger equation. Solutions to the differential equation will not be obtained here but can be shown to exist only for vibrational energies

$$\epsilon_{\text{vib}} = \left(v + \frac{1}{2}\right)\frac{h}{2\pi}\sqrt{\frac{k}{m}} \qquad \text{where } v = 0, 1, 2, \ldots \tag{25}$$

The quantum-mechanical result, therefore, indicates a pattern of energy levels with a constant spacing $(h/2\pi)\sqrt{k/m}$. It is this result that was assumed in Sec. 4-14 for the calculation of the average vibrational energy per degree of freedom.

It is interesting that the quantum-mechanical solution introduces the collection of terms $(1/2\pi)\sqrt{k/m}$ that correspond to the natural vibrational frequency of a classical oscillator. Equation (25) can, therefore, be written

$$\epsilon_{\text{vib}} = (v + \tfrac{1}{2})h\nu_{\text{classical}} \tag{26}$$

if the term $\nu_{\text{classical}}$ is interpreted according to Eq. (24).

It is now necessary to consider the vibration of the atoms of a molecule. Here the atoms vibrate against one another instead of against a fixed wall as in the one-particle problem of Fig. 10-6. It is adequate for our purposes to consider the simple example of a diatomic molecule. The coordinates that locate the positions of the atoms relative to the center of gravity of the molecule are those shown in Fig. 10-1. As the previous single-particle vibrational problem showed, it is necessary first to determine the form of the forces that restore the particles to their equilibrium position, or, what is equivalent, to specify the potential energy of the system as a function of the internuclear distance.

The difficulties encountered in the determination of the energy of molecular systems were seen in Chap. 8 to prevent potential-energy diagrams from being deduced for any but the simplest molecule. Figure 8-9 indicates the type of results that are obtained in such cases, and these can be taken as representative of the form of the potential-energy vs. internuclear-distance curves for molecular bonds. Vibrational energies, as we shall see, generally are sufficiently small so that the problem concerns itself with the portion of the potential-energy curve near the minimum. This portion, it turns out, can be satisfactorily approximated (Fig. 10-7) by a parabola, and the expression

$$U = \tfrac{1}{2}k(r - r_e)^2 \qquad (27)$$

can be written. Here k is the force constant and measures the stiffness of the chemical bond, r is the variable internuclear distance, and r_e is the equilibrium internuclear distance.

The classical solution can again be obtained from Newton's $f = ma$ relation. If the bond is distorted from its equilibrium length r_e to a new length r, as indicated in Fig. 10-8, the restoring forces on each atom are $-k(r - r_e)$. These forces can be equated to the ma terms for each atom as

$$m_1 \frac{d^2 r_1}{dt^2} = -k(r - r_e)$$

and

$$m_2 \frac{d^2 r_2}{dt^2} = -k(r - r_e) \qquad (28)$$

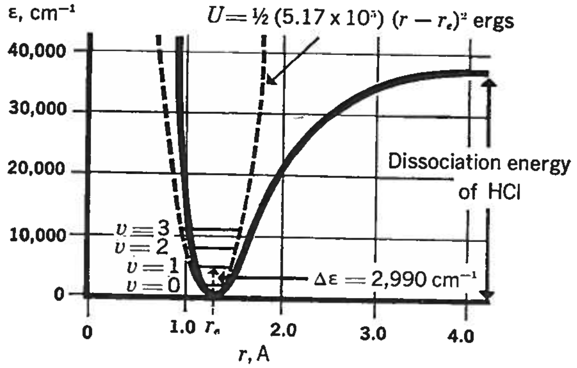

Fig. 10-7. Solid curve is the potential-energy curve for HCl deduced from a number of spectroscopic results (not all discussed here). The dashed curve is the Hooke's-law approximation which is satisfactory near the minimum where the first few vibrational-energy levels occur.

where r_1 and r_2 are the positions of atoms 1 and 2 relative to the center of gravity of the molecule. The relations between r_1, r_2, and r that keep the center of gravity fixed have been given by Eq. (5) as

$$r_1 = \frac{m_2}{m_1 + m_2} r$$

$$r_2 = \frac{m_1}{m_1 + m_2} r$$

Substitution in the $f = ma$ equation for particle 1, for example, gives

$$\frac{m_1 m_2}{m_1 + m_2} \frac{d^2 r}{dt^2} = -k(r - r_e) \tag{29}$$

which, since r_e is a constant, can also be written as

$$\frac{m_1 m_2}{m_1 + m_2} \frac{d^2(r - r_e)}{dt^2} = -k(r - r_e) \tag{30}$$

The term $r - r_e$ is the displacement of the bond length from its equilibrium position, and if the symbol x is introduced as $x = r - r_e$ and the reduced mass μ of Eq. (8) is inserted for the mass term, Eq. (30) becomes

$$\mu \frac{d^2 x}{dt^2} = -kx \tag{31}$$

This expression is identical to the corresponding equation for a single particle except for the replacement of the mass m by the reduced mass μ. It follows that the classical vibrational frequency for a two-particle system such as that of Fig. 10-8 is given by

$$\nu_{\text{classical}} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \tag{32}$$

and that the quantum-mechanical vibrational-energy-level result is

$$\epsilon = \left(v + \frac{1}{2}\right) \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} \qquad v = 0, 1, 2, \ldots \tag{33}$$

or

$$\epsilon = \left(v + \frac{1}{2}\right) h\nu_{\text{classical}} \tag{34}$$

The vibrational energies of a diatomic molecule consist of a set of levels as shown with the potential-energy functions in Fig. 10-7. If these allowed energies are expressed in the spectroscopically convenient units of reciprocal centimeters, they are found to be spaced by the amount

$$\Delta\epsilon = \frac{1}{hc} \frac{h}{2\pi} \sqrt{\frac{k}{\mu}} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \qquad \text{cm}^{-1} \tag{35}$$

At room temperature the value of kT is sufficiently small compared with typical values of $\Delta\epsilon$ so that most of the molecules are in the lowest allowed vibrational state. In a spectroscopic study, therefore, one investigates the absorption of radiation by these $v = 0$ state molecules.

Electromagnetic radiation can induce transitions among the vibrational-energy levels. For energy to be transferred between the radiation and the vibrating molecule, an electrical coupling must be present. This coupling can occur if the vibrating molecule produces an oscillating dipole moment that can interact with the electric field of the radiation. It follows that homonuclear diatomic molecules like H_2, N_2, and O_2, which necessarily have a zero dipole moment for any bond length, will fail to interact. The dipole moment of molecules such as HCl, on the other hand, can be expected to be some function, usually unknown, of the internuclear distance. The vibration of such molecules leads to an oscillating dipole moment, and a vibrational spectrum can be expected.

Even when interaction between the vibrating molecule and the radiation occurs, a further selection rule applies. This rule restricts transitions resulting from the absorption or emission of a quantum of radiation by the relation

$$\Delta v = \pm 1 \tag{36}$$

Vibrational spectra are usually determined by absorption spectroscopy, and then the rule $\Delta v = +1$ is the only part of this selection rule which is pertinent.

The experimental approach to the study of the $v = 0$ to $v = 1$ vibrational transitions is generally carried out with a spectrometer which has the same units as that indicated in Fig. 3-3.

The values of $\Delta\epsilon$ for vibrational-energy levels, however, are such that infrared radiation has quanta of this magnitude. For studies in the infrared region the source often consists of some ceramic element heated to a dull red, and the detector is a heat-sensitive element which frequently is a thermocouple. Since neither glass nor quartz is transparent to infrared radiation, other materials must be resorted to. The most frequently used material is rock salt. Large single crystals of NaCl are cleaved and polished to form prisms and windows for cells.

One use of vibrational spectra can now be illustrated by again using the example of HCl. One observes in the infrared region an absorption band centered at about 2,890 cm^{-1}. This absorption of radiation can be correlated with the vibrational transition $v = 0$ to $v = 1$, as shown in Fig. 10-7. It follows according to Eq. (35) that 2,890 cm^{-1} is the value of $\Delta\epsilon = (1/2\pi c)\sqrt{k/\mu}$ and, therefore, that

$$\begin{aligned} k &= 4\pi^2 c^2 \mu (2{,}890)^2 \\ &= 4\pi^2 (3 \times 10^{10})^2 (1.627 \times 10^{-24})(2{,}890)^2 \\ &= 4.84 \times 10^5 \text{ dynes/cm} \end{aligned} \tag{37}$$

The theory of vibrational spectra, together with the observed absorption, has now led to a value for the force constant of a chemical bond. The force constant, it will be recalled, measures the force required to deform a bond by a given amount. The qualitative feature to be appreciated from results such as that worked out for HCl is that molecules are flexible. While it is at first difficult to appreciate the significance of the numerical values obtained for bond force constants, one can make interesting comparisons of the stiffness of different bonds. Some results for diatomic molecules and for bonds of polyatomic molecules are shown in Table 10-3. The increased stiffness of multiple bonds compared with single bonds is apparent and is in line with the greater strength of multiple bonds. It should be observed from the data of the table that the vibrational frequency, being determined by both the reduced mass and

Table 10-3. The Force Constants of Some Chemical Bonds*

Bond	Molecule	Force constant (dynes/cm)
H—F	HF	9.7×10^5
H—Cl	HCl	4.8
H—Br	HBr	4.1
H—I	HI	3.2
H—O	H_2O	7.8
H—S	H_2S	4.3
H—C	CH_3X	4.7–5.0
H—C	C_2H_4	5.1
H—C	C_2H_2	5.9
Cl—C	CH_3Cl	3.4
C—C	.....	4.5–5.6
C═C	.....	9.5–9.9
C≡C	.....	15.6–17.0
N—N	.....	3.5–5.5
N═N	....	13.0–13.5
N≡N	.....	22.9
C—O	.....	5.0–5.8
C═O	.....	11.8–13.4

* From E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Company, Inc., New York, 1955.

the force constant, according to Eq. (33), is not itself a simple measure of the bond stiffness.

In contrast to pure rotational spectra, only one vibrational-absorption band has been treated for a given diatomic molecule. This has followed from the assumption, which can now be checked, that almost all the molecules occupy the $v = 0$ level at ordinary temperatures and the fact that the vibrational-energy levels show an equally spaced set of levels. For HCl, for example, the absorption frequency, attributed to the $v = 0$ to $v = 1$ transition, is 2,890 cm^{-1}. The energy of a quantum of radiation of this frequency is

$$\begin{aligned}\Delta\epsilon &= 2{,}890\ \text{cm}^{-1}\\ &= 5.75 \times 10^{-13}\ \text{erg}\end{aligned} \tag{38}$$

This quantity is equal to the energy of a molecule in the $v = 1$ state compared with one in the $v = 0$ state. The Boltzmann distribution at 25°C gives the ratio of the populations of these two states as

$$\begin{aligned}\frac{N_1}{N_0} &= e^{-\Delta\epsilon/kT}\\ &= 8 \times 10^{-7}\end{aligned} \tag{39}$$

This result confirms the statement that only a very small fraction of the molecules populate the higher vibrational levels at ordinary temperatures.

A closer look at the vibrational-absorption band of a molecule like HCl shows that it does not consist of an absorption region with a single maximum but

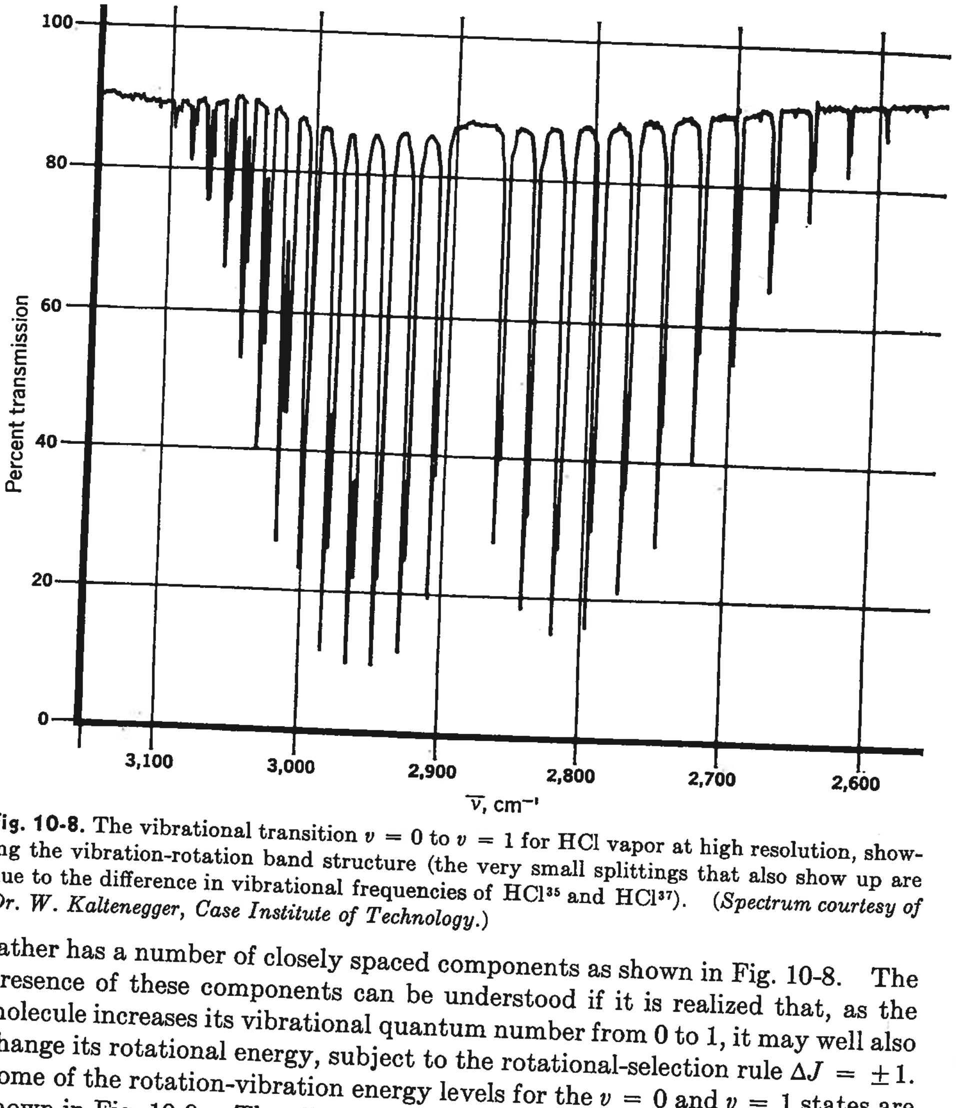

Fig. 10-8. The vibrational transition $v = 0$ to $v = 1$ for HCl vapor at high resolution, showing the vibration-rotation band structure (the very small splittings that also show up are due to the difference in vibrational frequencies of HCl^{35} and HCl^{37}). (*Spectrum courtesy of Dr. W. Kaltenegger, Case Institute of Technology.*)

rather has a number of closely spaced components as shown in Fig. 10-8. The presence of these components can be understood if it is realized that, as the molecule increases its vibrational quantum number from 0 to 1, it may well also change its rotational energy, subject to the rotational-selection rule $\Delta J = \pm 1$. Some of the rotation-vibration energy levels for the $v = 0$ and $v = 1$ states are shown in Fig. 10-9. The allowed transitions for absorption of energy are indicated by the arrows. The energies of these transitions show that the spectrum of this band should consist of a series of absorptions spaced by an amount $2(h^2/8\pi^2 I)$ ergs on either side of the band center. The center corresponds to the absent $v = 0, J = 0$ to $v = 1, J = 0$ transition. When such rotational spacing is resolved in a vibrational band, the moment of inertia and therefore the internuclear distance can be deduced, the spacing in the "fine structure" of the vibration-rotation spectra.

Polyatomic molecules exhibit vibrational spectra which can be interpreted as arising from transitions within each of a number of energy-level patterns like that of Fig. 10-7. Each energy-level pattern corresponds to one of the characteristic, or *normal*, vibrations of the molecule. Since a molecule of

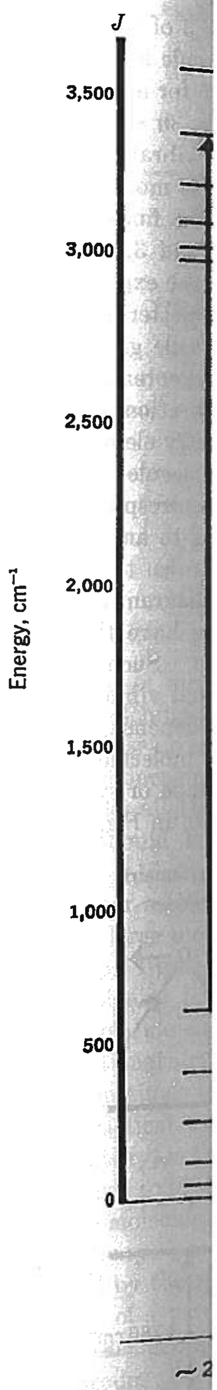

Fig. 10-9. The rotational
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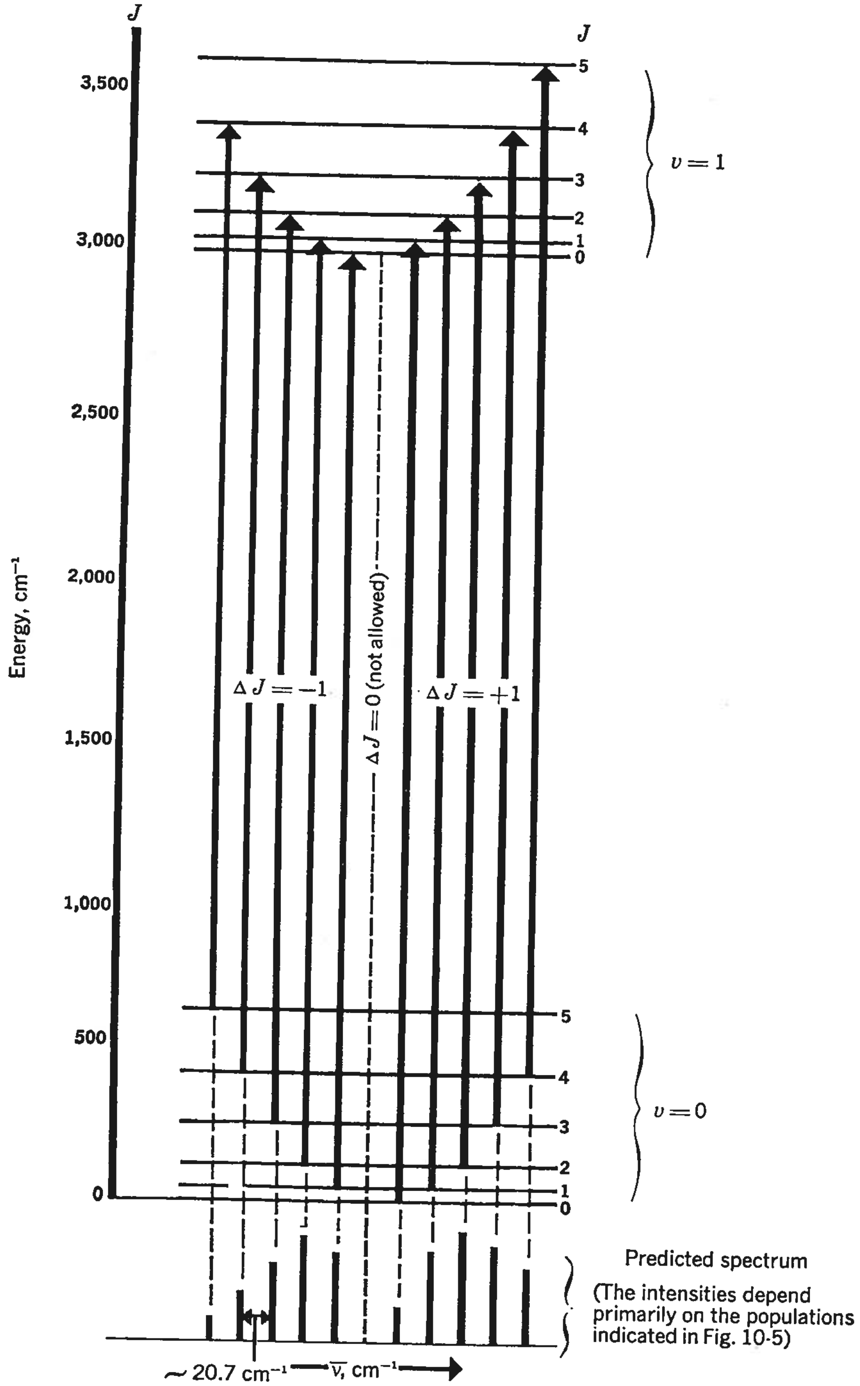

Fig. 10-9. The rotational levels of the $v = 0$ and $v = 1$ vibrational levels of HCl. The allowed transitions ($\Delta v = 1$, $\Delta J = \pm 1$) lead to the prediction of a vibration-rotation spectrum with spacing of about 20.7 cm^{-1}.

n atoms has a total of $3n$ degrees of freedom and since 3 of these are over-all translational degrees of freedom and 3 (or 2 if the molecule is linear) are rotational degrees of freedom, there will be $3n - 6$ ($3n - 5$ for a linear molecule) vibrational degrees of freedom. There are therefore $3n - 6$ (or $3n - 5$) energy-level patterns each with its own spacing. If the vibrations corresponding to all these patterns have associated oscillating dipole moments, there will be $3n - 6$ (or $3n - 5$) observed absorption bands. One finds, for example, for H_2O vapor, absorptions centered at 1,595, 3,652, and 3,756 cm^{-1}. For molecules with many atoms $3n - 6$ becomes large, and one expects very many vibrational transitions and a very complicated spectral pattern.

The presence of any amount of symmetry in a molecule greatly simplifies the study of its modes of vibration. There is a general theorem, which cannot be dealt with here, that each of the $3n - 6$ (or $3n - 5$) vibrations must be either symmetric or antisymmetric with respect to any symmetry element (such as a plane of symmetry or a center of symmetry) of the molecule. For H_2O, for example, it can be shown that the two lower frequencies correspond to symmetric vibrations, while the highest frequency corresponds to an antisymmetric mode. The diagrams of Fig. 10-10 can therefore be drawn to show how the atoms might move in each of these vibrations. The diagram is intended to approximate pure vibrational motions, and the arrows have therefore been drawn so that there is no over-all translation or rotation. Such diagrams can easily be drawn to represent the symmetry of the actual vibrational modes. The exact motion of the atoms in a vibrational mode depends, however, on the masses of the atoms and the force constants of the molecule.

The use of vibrational spectroscopy to deduce the shape or symmetry of a molecule can be illustrated by the example of NO_2 shown in Fig. 10-11. The

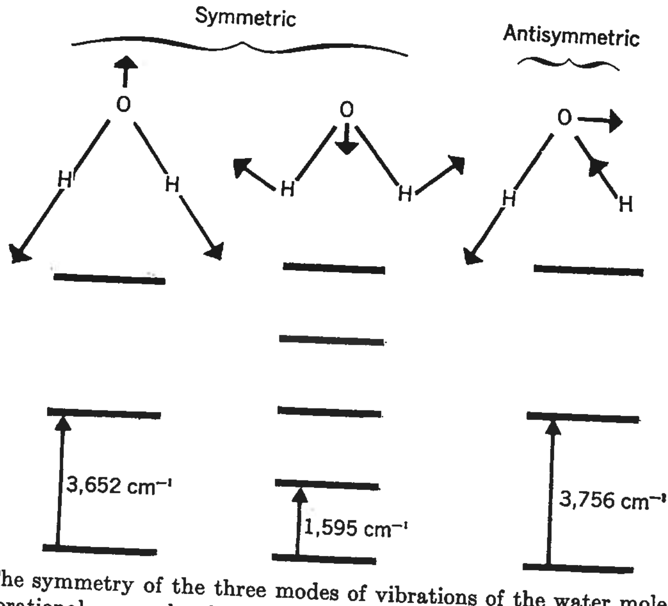

Fig. 10-10. The symmetry of the three modes of vibrations of the water molecule and the associated vibrational-energy-level patterns.

Fig. 10

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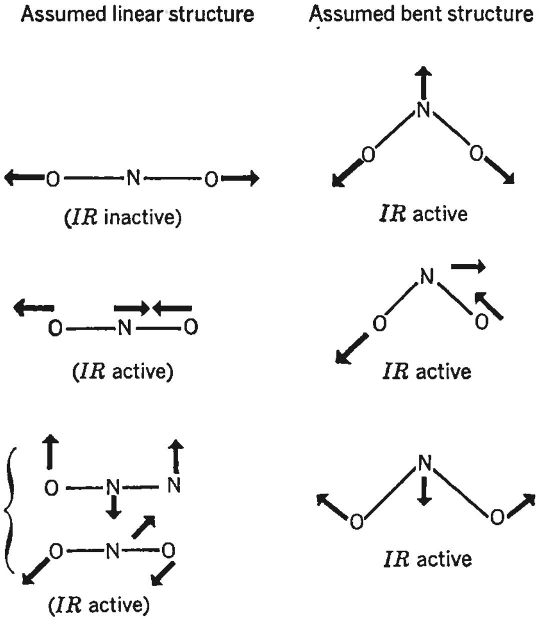


Fig. 10-11. The vibrations of NO_2 on the basis of linear and bent structures.

expected forms of vibration for a bent and a linear model are shown. The symmetric stretching vibration of the linear model cannot lead to absorption of energy because no oscillating dipole moment is associated with such a vibration. For the linear model only two absorption bands are expected, while for the bent model all three vibrations should absorb radiation in the infrared region, i.e., should be *infrared active*. Absorptions are observed, as mentioned in Sec. 4-15, at 750, 1,323, and 1,616 cm^{-1}, showing that NO_2 is a bent and not a linear molecule. Arguments such as this can be extended and can be applied to large molecules with various amounts of symmetry.

The principal direct applications of vibrational spectroscopy to molecular-structure problems have now been mentioned. The force constant of the bonds of a molecule can be evaluated, the moments of inertia can be deduced from the rotational structure of the vibrational band, and, finally, the molecular shape can sometimes be deduced from the number of observed absorptions.

A more practical use, and one of great value, particularly in the field of organic chemistry, is that in which the infrared absorption spectrum of a large molecule is used to identify the compound or to indicate the presence of certain groups in the molecule. Bonds or groups within a molecule sometimes vibrate with a frequency, i.e., have an energy-level pattern with a spacing, that is little affected by the rest of the molecule. Absorption at a frequency that is characteristic of a particular group can then be taken as an indication of the presence of that group in the compound being studied. Table 10-4 shows a few of the groups that have useful *characteristic frequencies*.

An even simpler use of vibrational spectra consists in verifying the identity of a compound by matching its infrared spectrum to that of a known sample.

Table 10-4. Some Characteristic Bond-stretching Frequencies

Group	$\bar{\nu}$ *(cm^{-1})*
—O—H	3,500–3,700
—N—H	3,300–3,500
≡C—H	3,340
=C—H	3,000–3,120
—C—H	2,880–3,030
—C≡C—	2,200–2,260
—C≡N	2,250
>C=O	1,660–1,870
>C=C<	1,600–1,680

Large molecules have such complicated spectra, as shown in Fig. 10-12, for example, that identical spectra can be taken as a sure indication of identical compounds. Thus, although for large molecules the complete vibrational spectrum can seldom be understood in terms of the nature of the $3n - 6$ vibrations, there are many uses to which such spectra can be put.

Brief mention can be made of the fact that vibrational transitions can be studied in a way other than that of infrared absorption spectroscopy. An arrangement such as that shown schematically in Fig. 10-13 is used. The sample is illuminated, at right angles to the spectrometer, by an intense source of monochromatic radiation, usually the 4,358 A visible line of a mercury-vapor lamp. One observes on the photographic plate of the spectrograph, as shown in Fig. 10-14, not only this 4,358 A line, which has been scattered into the spectrometer, but also a number of weaker lines, predominantly on the long-wavelength low-energy side of the 4,358 A line. These additional lines were first observed by C. V. Raman, and such spectra are now called *Raman spectra.*

The earlier prediction of the effect by Smekal explained these additional lines as resulting from the gain or, less likely, the loss of vibrational energy in a process depicted in Fig. 10-15. The quantum of visible light that is sent into the system is very large compared with the vibrational-energy spacings. The process can be understood by recognizing that the large energy quantum of radiation can interact with the sample molecules and can give up some of its energy to the vibrating molecules or can withdraw some of the vibrational energy. The difference between the frequency of a Raman line and that of the exciting line is therefore a measure of the vibrational-energy-level spacing. Both Raman and infrared spectroscopy therefore study the same molecular energy levels. Both methods have their special advantages, but one finds that the infrared absorption method is at present generally easier to use and is the more popular technique.

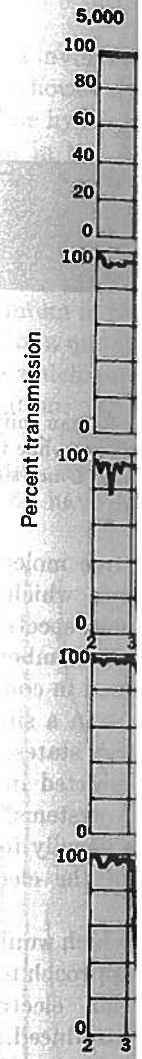
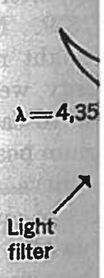


Fig. 1



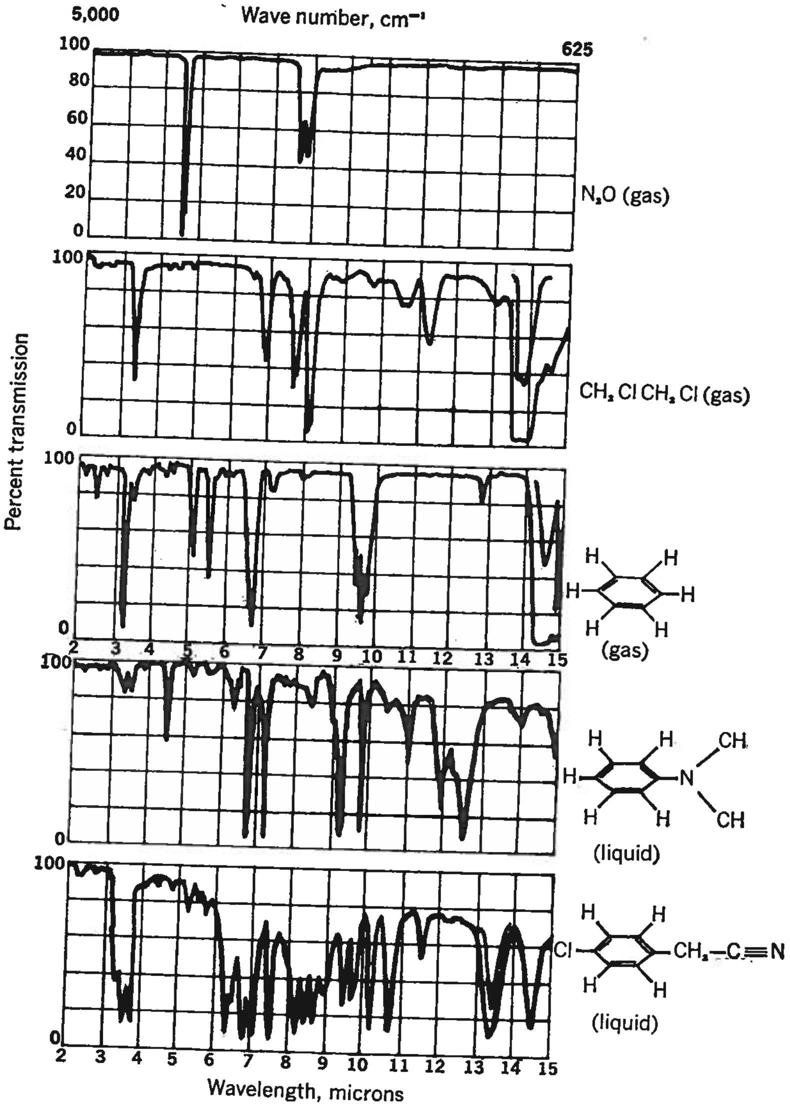


Fig. 10-12. The infrared absorption spectra of several compounds.

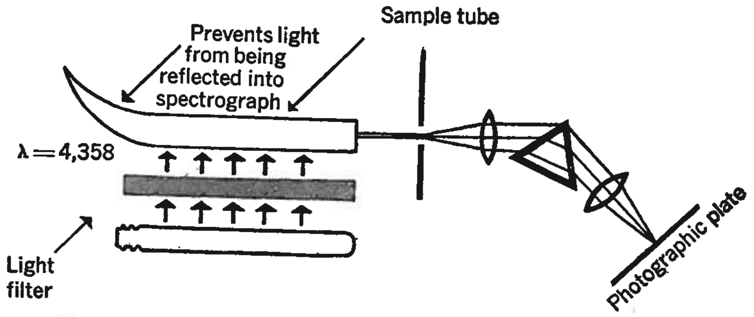


Fig. 10-13. Arrangement for Raman spectroscopy.

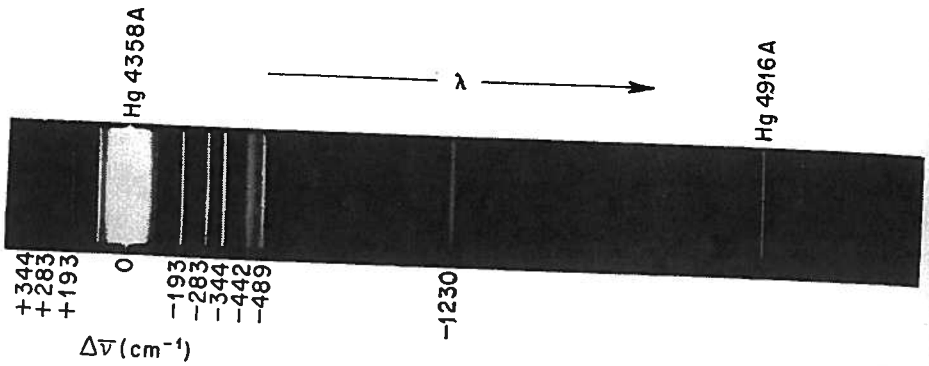


Fig. 10-14. The Raman spectrum of thionyl chloride ($SOCl_2$) showing the Raman shifts of the six vibrations. All six appear at longer wavelengths than the exciting line, while three can be seen at shifts to shorter wavelengths. (*Courtesy of Dr. D. A. Long, University of Wales, Swansea.*)

10-3. Electronic Spectra. The final type of energy levels of free molecules that lead to spectroscopically observable transitions are those in which the electron arrangement of the molecule is altered. The electronic spectra of atoms in which the electronic state, as described by the quantum numbers of the electrons of the atom, is changed have already been mentioned in connection with the spectra and Bohr theory of the hydrogen atom. In a similar manner, the electrons of a molecule can be excited to higher energy states, and the radiation that is absorbed in this process or the energy emitted in the return to the ground state can be studied. As with atomic systems, the energies involved are generally large, and electronic spectra are usually found in the ultraviolet region of the electromagnetic radiation.

Some of the information which would be necessary for a theoretical approach to the understanding of molecular electronic spectra has already been introduced. In the theory of the H_2 molecule two different electronic configurations, as described by two different wave functions, were considered, and the energy of the two states as a function of the internuclear distance was shown in Fig. 8-9. Molecular electronic transitions might result if radiation of sufficient energy were sent into a system like H_2 so as to cause the transition from the equilibrium position in the lower, ground-state curve to the upper state. For molecules of any complexity it is not possible to deduce theoretically such energy curves for the

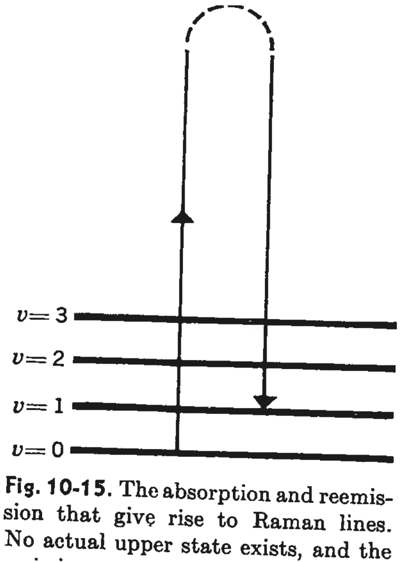


Fig. 10-15. The absorption and reemission that give rise to Raman lines. No actual upper state exists, and the emission occurs immediately following absorption.

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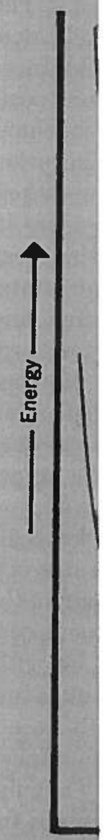

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states involved in the transition. The electronic spectra of a number of molecules, however, can be interpreted as arising from transitions like that described for the hydrogen molecule. The higher electronic energy state, lacking a minimum in the potential-energy curve, may lead to the formation of atoms, or fragments of the original molecule, and these fragments may be formed in some excited electronic state rather than in the ground atomic state indicated for H_2 in Fig. 8-9. The more general situation is shown in Fig. 10-16*a*.

Other transitions occur to higher-energy electronic states which have a minimum in the potential-energy versus internuclear-distance curve. Absorption of a quantum of radiation then leads to the formation of an excited molecule which need not instantaneously break up. Figure 10-16*b* represents this situation. In general, the bond strength in the excited state will be less than that in the ground state, and the equilibrium internuclear distance in the excited state will be longer than in the ground state. The curves of Fig. 10-16*b* have been drawn to indicate this. The electronic spectra of many

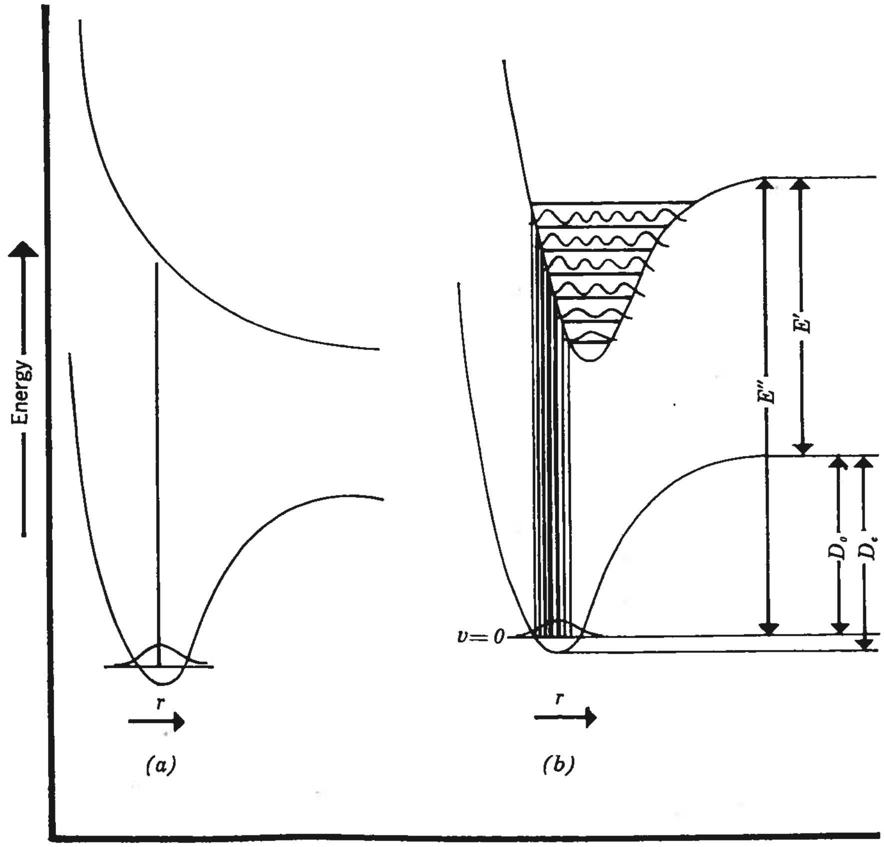

Fig. 10-16. Electronic energies as a function of internuclear distance for two typical situations. (The vibrational-energy levels and the probability functions are indicated for the vibrational levels involved in the transitions.)

simple molecules can be explained in terms of a number of excited electronic states with potential-energy curves of one or the other of the types shown in Fig. 10-16.

The observed spectral transitions are related to such electronic-energy diagrams on the basis of the *Franck-Condon principle.* This principle stems from the idea that electrons move and rearrange themselves much faster than can the nuclei of molecules. For example, the time for an electron to circle a hydrogen nucleus can be calculated from Bohr's model to be about 10^{-16} sec, while a typical period of vibration of a molecule is a thousand times longer, or about 10^{-13} sec. Comparison of these times suggests that an electronic configuration will change in a time so short that the nuclei will not change their positions. The spectral transitions must be drawn vertically in Fig. 10-16 and not, as one might otherwise be tempted to do, from the potential minimum of the lower curve to that of the upper curve.

One further feature of the transitions between electronic-energy curves must be mentioned. Since a molecule vibrates, even when it is in the lowest vibrational-energy level, a range of internuclear distances must be considered. The quantum-mechanical solution for a vibrating molecule, as Fig. 10-16 indicates, shows that in the lowest energy state, contrary to classical ideas, the most probable internuclear distance is that corresponding to the equilibrium position. For the higher energy states, on the other hand, the quantum-mechanical result is more like the classical result that the most probable configuration is at the ends of the vibration, where the atoms must stop and reverse their direction. The transitions of Fig. 10-16 have been drawn with these ideas in mind. Transitions are expected to have greater probability of starting near the midpoint of the lowest vibrational level of the ground electronic state. The excited species, however, must have the same internuclear separation, and for the transitions to lead to probable arrangements it is necessary for them to be drawn to the energy levels for which the square of the wave function has a large value at the internuclear distance of the transition. It follows that an electronic transition, in absorption, may show a series of closely spaced lines corresponding to different vibrational and rotational energies of the upper state.

Although no detailed discussion can be given here of the types of electronic arrangements that can occur and that correspond to higher energy states of a molecule, it is worth pointing out the situation with regard to the pairing of the spins of the electrons. Most molecules have a ground-state electronic configuration in which the spin of each electron is opposed to, or paired up with, the spin of another electron which otherwise has the same spatial quantum numbers. Such ground states are known as *singlet states* since, with no net spin angular momentum, the imposition of a reference direction by an applied electric or magnetic field can produce only the single component of zero angular momentum in the field direction. The ground state of the H_2 molecule is the simplest example of such a singlet state. Molecules will have, in addition to a ground state that is usually a singlet state, a number of excited states that also have all the electrons paired and that are, therefore, also singlet states.

Whether or not the ground state is a singlet state, there will always be excited states in which two electrons have their spins in the same direction, giving the molecule a net spin angular momentum of $1(h/2\pi)$. Angular components along a specified direction can now have the values $1(h/2\pi)$, 0, and $-1(h/2\pi)$, and such an electronic configuration is known as a *triplet state.*

Electronic spectra of compounds containing no heavy atoms, i.e., most organic compounds, indicate that the absorption of electromagnetic radiation does not unpair the electrons of the molecule. The important selection rule that *transitions occur between states of like multiplicity* is obtained. This rule is a powerful guide to the deduction of the nature of excited electronic states.

For molecules exposed to strong magnetic fields or containing a high-atomic-number atom whose nucleus exerts such a field, this selection rule is broken down, and the spin coupling is readily broken down in an electromagnetic transition.

The assignment of the multiplicity to the state reached by an absorption of radiation and to the states that the molecule goes into as it loses its high energy is a matter of great importance in the study of fluorescence, phosphorescence, and photochemistry. These subjects will, however, be postponed until the following chapter.

The study of electronic spectra leads to a wealth of information about the electronic states and energies of molecules and to the bond distances and force constants of the molecule in excited electronic states. For small diatomic molecules it is frequently possible to assign quantum numbers to the various excited states in which the molecule can occur. For larger molecules, however, a more limited goal must be set. It is frequently sufficient to attempt to decide which of the electrons of the molecule are primarily responsible, i.e., which electron has its quantum number altered, for the observed transition.

The electrons in covalent single bonds, such as C—C and C—H, can be recognized as being very resistant to excitation. Saturated hydrocarbons absorb only very high-energy radiation, usually beyond 1,600 A, far in the ultraviolet. A simple olefin, however, has an absorption band at around 1,700 A, and this can be attributed to the excitation of the π electrons from the electron-paired bonding configuration to a high-energy, or antibonding, state. Such a transition is referred to as a $\pi \rightarrow \pi^*$ transition, the * implying an excited state.

Some molecules have electronic configurations which can be altered in different ways to lead to an excited, or high-energy, electronic state. This situation arises, for example, with compounds containing a carbonyl group $C{=}\ddot{O}{:}$. For such a group the possibility of exciting the π electrons to the excited π^* state exists, as with an olefin, to give a $\pi \rightarrow \pi^*$ transition. Alternatively, the nonbonding electrons of the oxygen might be excited to the higher-energy π^*-electron state, and the absorption would then be characterized as an $n \rightarrow \pi^*$

transition, where the n signifies a nonbonding electron. The two types of transitions are represented in Fig. 10-17.

The recognition of the type of transition occurring on irradiation of a molecule is important for the understanding of the absorption process itself and is basic for the treatment of the behavior of the excited molecule. In spite of the difficulties in completely understanding the electron configurations involved in electronic transitions, it is frequently possible to deduce two important quantities from such studies. These quantities are the *dissociation energy* of a bond or molecule and the *ionization potential* of a molecule. The first quantity is shown as D_e and D_0 in Fig. 10-16. It is clear that, if the quantity E' of that figure can be deduced from the observed transitions and if the excess energy E'' of the dissociation fragments can be determined, one can evaluate the dissociation energy D_0 measured from the lowest vibrational state. Addition of $\frac{1}{2}h\nu_{\text{classical}}$ yields the total depth of the potential-energy curve. This dissociation energy, measured from the equilibrium position, is referred to as D_e. Some of the dissociation energies listed in Table 5-5 have been deduced from spectroscopic measurements of transition such as those of Fig. 10-16.

The ionization potential is the least energy, usually expressed in electron volts, which must be put into a molecule to remove an electron. This energy will generally be greater than the amounts that have been discussed and that lead merely to excited states. Any energy above the ionization potential can be absorbed by the molecule. The excess over that required to free the electron goes into the kinetic energy of the electron. By this process a continuous absorption, i.e., one which shows no discrete lines, should appear in the spectrum, and the onset of such a continuum can be taken as a measure of the

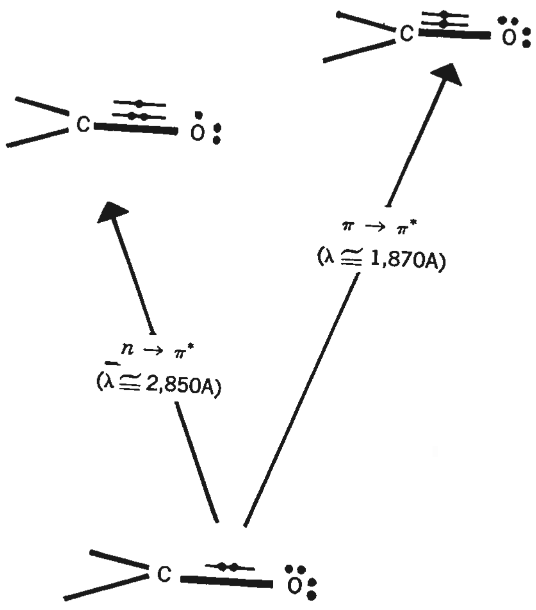

Fig. 10-17. Schematic representation of the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions such as those exhibited by a carbonyl group.

ionization potential of the molecule. Ionization potentials of atoms have been mentioned previously and have been used in the deduction of electronegativities. Ionization potentials of molecules are much more difficult to understand but are representative of the interesting data on the behavior of electrons in molecules that can be deduced from the study of electronic spectra. A few values obtained spectroscopically and from the more direct measurements of the minimum energy required in an impinging electron beam to knock an electron out of a molecule are shown in Table 10-6.

Finally, it should be pointed out that not all electronic transitions occur in the ultraviolet region. The occurrence of colored compounds indicates absorption of radiation in the visible spectrum. Such absorption requires the electronic energy levels to be more closely spaced than in most molecules. The most frequently encountered type of organic molecule that absorbs in the visible region, i.e., is colored, consists of a conjugated system frequently involving aromatic rings. The qualitative explanation for the closer spacing that results from the delocalization of the conjugated electrons is most easily given by regarding such electrons as being free particles within the potential box of the molecule as discussed in Secs. 3-9 and 9-6. For sufficiently long "boxes" the spacing is small enough to bring the absorption of radiation into the visible part of the spectrum.

ELECTRON DIFFRACTION

Much of the present information on the geometry and the bond lengths of molecules, other than the simpler ones which can be well-treated spectroscopically, comes from diffraction experiments. The two principal diffraction techniques make use of the diffraction of X rays and the diffraction of electrons. To these might be added the less general applied technique of neutron diffraction. X-ray diffraction is most applicable to the study of crystal structures and to the structures of the molecules in crystal lattices. It is convenient to leave this part of the subject until the general study of solids is undertaken. For the present, the nature of diffraction experiments will be studied in terms of electron diffraction. Such experiments are frequently performed on gases, and the net diffraction effect is the sum of the effects from the individual molecules. The analysis of electron-diffraction results is, therefore, easier to present than is that for X-ray diffraction, where the effect is due to the collective action of all the atoms in the crystal.

10-4. The Interference Phenomenon. The general principle of diffraction methods depends on the phenomenon of *interference*, which occurs when any wave motion is scattered from a number of centers. This phenomenon, for example, is exhibited by visible radiation when a beam of light passes through a series of closely spaced slits, as illustrated in Fig. 10-18. If the light is monochromatic, i.e., consists of radiation of only a single wavelength, the wave motions of the light emerging from the slits will add together in only certain directions. In these directions *constructive interference* is said to occur, and at

PHYSICAL CHEMISTRY

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McGRAW-HILL BOOK COMPANY, INC. 1961
New York Toronto London

PHYSICAL CHEMISTRY

Library of Congress Catalog Card Number 60-53030

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