

CHAPTER 8

Molecules



This infrared spectrometer measures the absorption of infrared radiation by a sample as a function of wavelength, which provides information about the structure of the molecules in the sample.

8.1 THE MOLECULAR BOND

Electric forces hold atoms together to form molecules

8.2 ELECTRON SHARING

The mechanism of the covalent bond

8.3 THE H_2^+ MOLECULAR ION

Bonding requires a symmetric wave function

8.4 THE HYDROGEN MOLECULE

The spins of the electrons must be antiparallel

8.5 COMPLEX MOLECULES

Their geometry depends on the wave functions of the outer electrons of their atoms

8.6 ROTATIONAL ENERGY LEVELS

Molecular rotational spectra are in the microwave region

8.7 VIBRATIONAL ENERGY LEVELS

A molecule may have many different modes of vibration

8.8 ELECTRONIC SPECTRA OF MOLECULES

How fluorescence and phosphorescence occur

Individual atoms are rare on the earth and in the lower part of its atmosphere. Only inert gas atoms occur by themselves. All other atoms are found joined together in small groups called molecules and in large groups as liquids and solids. Some molecules, liquids, and solids are composed entirely of atoms of the same element; others are composed of atoms of different elements.

What holds atoms together? This question, of fundamental importance to the chemist, is no less important to the physicist, whose quantum theory of the atom cannot be correct unless it provides a satisfactory answer. The ability of the quantum theory to explain chemical bonding with no special assumptions is further testimony to the power of this approach.

8.1 THE MOLECULAR BOND

Electric forces hold atoms together to form molecules

A molecule is an electrically neutral group of atoms held together strongly enough to behave as a single particle.

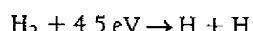
A molecule of a given kind always has a certain definite composition and structure. Hydrogen molecules, for instance, always consist of two hydrogen atoms each, and water molecules always consist of one oxygen atom and two hydrogen atoms each. If one of the atoms of a molecule is somehow removed or another atom becomes attached, the result is a molecule of a different kind with different properties.

A molecule exists because its energy is less than that of the system of separate noninteracting atoms. If the interactions among a certain group of atoms reduce their total energy, a molecule can be formed. If the interactions increase their total energy, the atoms repel one another.

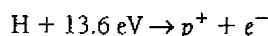
Let us see what happens when two atoms are brought closer and closer together. Three extreme situations can occur:

1 *A covalent bond is formed.* One or more pairs of electrons are shared by the two atoms. As these electrons circulate between the atoms, they spend more time between the atoms than elsewhere, which produces an attractive force. An example is H₂, the hydrogen molecule, whose electrons belong to both protons (Fig. 8.1). The attractive force the electrons exert on the protons is more than enough to counterbalance the direct repulsion between them. If the protons are too close together, however, their repulsion becomes dominant and the molecule is not stable.

The balance between attractive and repulsive forces occurs at a separation of 7.42×10^{-11} m, where the total energy of the H₂ molecule is -4.5 eV. Hence 4.5 eV of work must be done to break a H₂ molecule into two H atoms:



By comparison, the binding energy of the hydrogen atom is 13.6 eV:



This is an example of the general rule that it is easier to break up a molecule than to break up an atom.

2 *An ionic bond is formed.* One or more electrons from one atom may transfer to the other and the resulting positive and negative ions attract each other. An example is

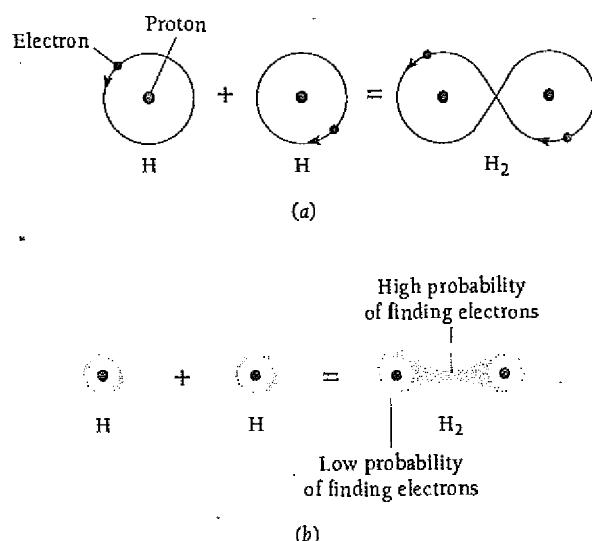


Figure 8.1 (a) Orbit model of the hydrogen molecule. (b) Quantum-mechanical model of the hydrogen molecule. In both models the shared electrons spend more time on the average between the nuclei, which leads to an attractive force. Such a bond is said to be covalent.

rock salt, NaCl , where the bond exists between Na^+ and Cl^- ions and not between Na and Cl atoms (Fig. 8.2). Ionic bonds usually do not result in the formation of molecules. The crystals of rock salt are aggregates of sodium and chlorine ions which, although always arranged in a certain definite structure (Fig. 8.3), do not pair off into molecules consisting of one Na^+ ion and one Cl^- ion. Rock salt crystals may have any size and shape. There are always equal numbers of Na^+ and Cl^- ions in rock salt, so that the formula NaCl correctly represents its composition. Molten NaCl also consists of Na^+ and Cl^- ions: these ions form molecules rather than crystals only in the gaseous state. Ionic bonding is further discussed in Chap. 10.

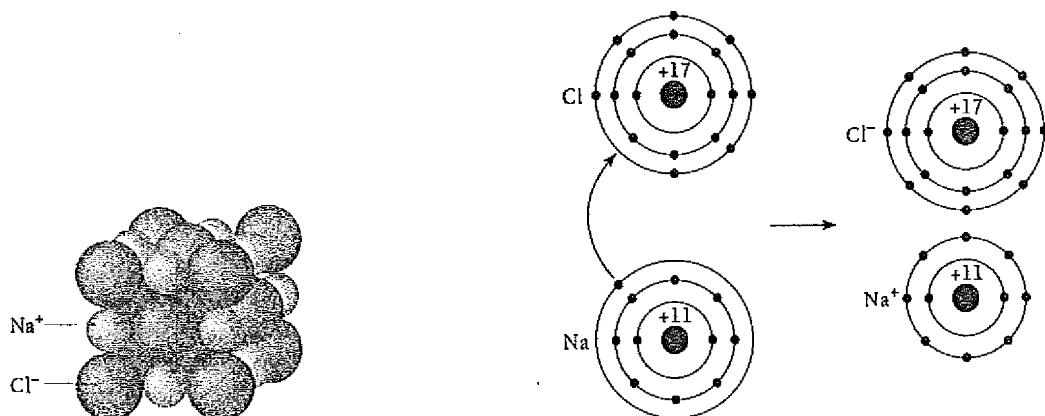


Figure 8.3 Scale model of an NaCl crystal.

Figure 8.2 An example of ionic bonding. Sodium and chlorine combine chemically by the transfer of electrons from sodium atoms to chlorine atoms; the resulting ions attract each other electrically.

In H_2 the bond is purely covalent and in $NaCl$ it is purely ionic. In many molecules an intermediate type of bond occurs in which the atoms share electrons to an unequal extent. An example is the HCl molecule, where the Cl atom attracts the shared electrons more strongly than the H atom. We can think of the ionic bond as an extreme case of the covalent bond.

3 *No bond is formed.* When the electron structures of two atoms overlap, they constitute a single system. According to the exclusion principle, no two electrons in such a system can exist in the same quantum state. If some of the interacting electrons are forced into higher energy states than they occupied in the separate atoms, the system may have more energy than before and be unstable. Even when the exclusion principle can be obeyed with no increase in energy, there will be an electric repulsive force between the various electrons. This is a much less significant factor than the exclusion principle in influencing bond formation, however.

8.2 ELECTRON SHARING

The mechanism of the covalent bond

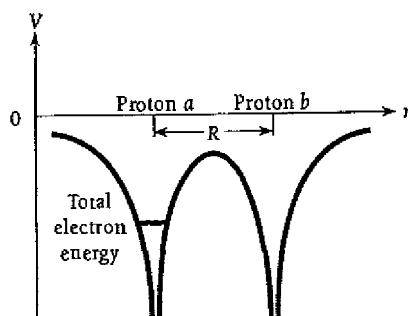
The simplest possible molecular system is H_2^+ , the hydrogen molecular ion, in which a single electron bonds two protons. Before we consider the bond in H_2^+ in detail, let us look in a general way into how it is possible for two protons to share an electron and why such sharing should lead to a lower total energy and hence to a stable system.

In Chap. 5 the phenomenon of quantum-mechanical barrier penetration was examined. There we saw that a particle can "leak" out of a box even without enough energy to break through the wall because the particle's wave function extends beyond it. Only if the wall is infinitely strong is the wave function wholly inside the box.

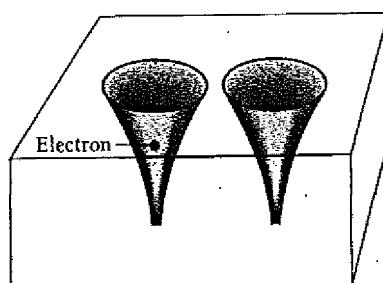
The electric field around a proton is in effect a box for an electron, and two nearby protons correspond to a pair of boxes with a wall between them (Fig. 8.4). No mechanism in classical physics permits the electron in a hydrogen atom to jump spontaneously to a neighboring proton more distant than its parent proton. In quantum physics, however, such a mechanism does exist. There is a certain probability that an electron trapped in one box will tunnel through the wall and get into the other box, and once there it has the same probability for tunneling back. This situation can be described by saying the electron is shared by the protons.

To be sure, the likelihood that an electron will pass through the region of high potential energy—the "wall"—between two protons depends strongly on how far apart the protons are. If the proton-proton distance is 0.1 nm, the electron may be regarded as going from one proton to the other about every 10^{-15} s. We can legitimately consider such an electron as being shared by both. If the proton-proton distance is 1 nm, however, the electron shifts across an average of only about once per second, which is practically an infinite time on an atomic scale. Since the effective radius of the 1s wave function in hydrogen is 0.053 nm, we conclude that electron sharing can take place only between atoms whose wave functions overlap appreciably.

Granting that two protons can share an electron, a simple argument shows why the energy of such a system could be less than that of a separate hydrogen atom and proton. According to the uncertainty principle, the smaller the region to which we restrict a particle, the greater must be its momentum and hence kinetic energy. An electron



(a)



(b)

Figure 8.4 (a) Potential energy of an electron in the electric field of two nearby protons. The total energy of a ground-state electron in the hydrogen atom is indicated. (b) Two nearby protons correspond quantum-mechanically to a pair of boxes separated by a barrier.

shared by two protons is less confined than one belonging to a single proton, which means that it has less kinetic energy. The total energy of the electron in H_2^+ is therefore less than that of the electron in $\text{H} + \text{H}^+$. Provided the magnitude of the proton-proton repulsion in H_2^+ is not too great, then, H_2^+ ought to be stable.

8.3 THE H_2^+ MOLECULAR ION

Bonding requires a symmetric wave function

What we would like to know is the wave function ψ of the electron in H_2^+ , since from ψ we can calculate the energy of the system as a function of the separation R of the protons. If $E(R)$ has a minimum, we will know that a bond can exist, and we can also determine the bond energy and the equilibrium spacing of the protons.

Solving Schrödinger's equation for ψ is a long and complicated procedure. An intuitive approach that brings out the physics of the situation is more appropriate here. Let us begin by trying to predict what ψ is when R , the distance between the protons, is large compared with a_0 , the radius of the smallest Bohr orbit in the hydrogen atom. In this event ψ near each proton must closely resemble the $1s$ wave function of the hydrogen atom, as pictured in Fig. 8.5. The $1s$ wave function around proton a is called ψ_a and that around proton b is called ψ_b .

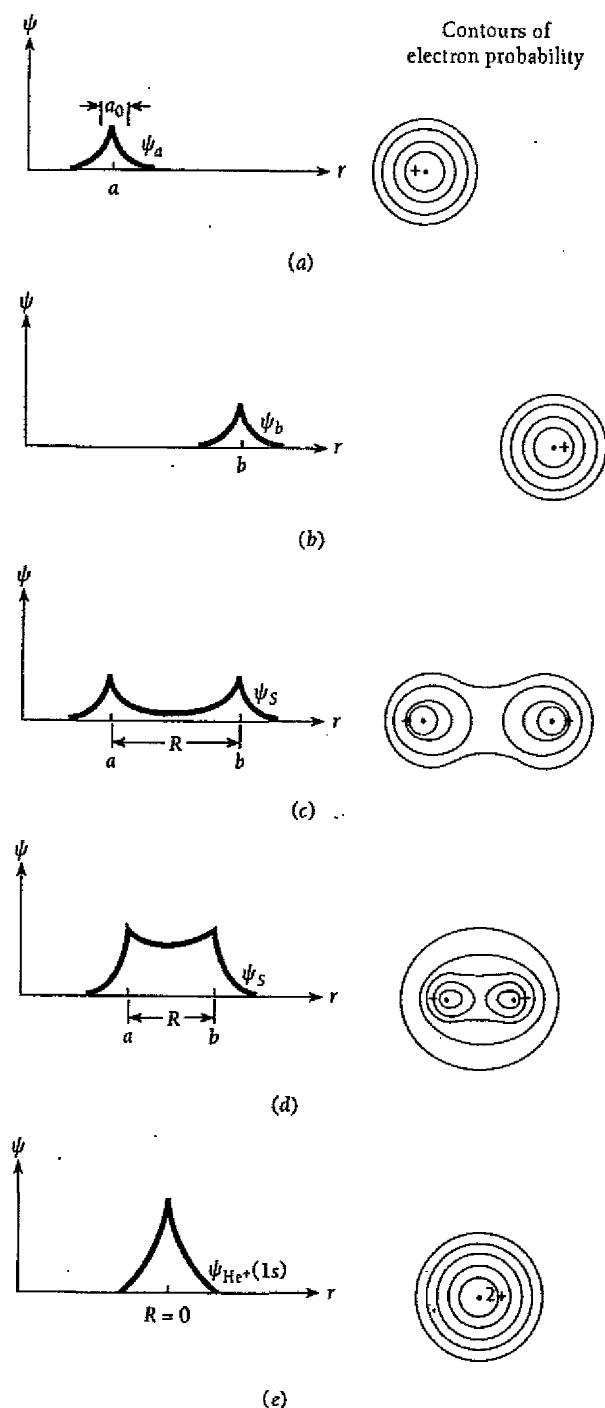


Figure 8.5 (a)–(d) The combination of two hydrogen-atom 1s wave functions to form the symmetric H_2^+ wave function ψ_s . The result is a stable H_2^+ molecular ion because the electron has a greater probability of being between the protons than outside them. (e) If the protons could join together, the resulting wave function would be the same as the 1s wave function of a He^+ ion.

We also know what ψ looks like when R is 0, that is, when the protons are imagined to be fused together. Here the situation is that of the He^+ ion, since the electron is now near a single nucleus whose charge is $+2e$. The 1s wave function of He^+ has the same form as that of H but with a greater amplitude at the origin, as in Fig. 8.5e. Evidently ψ is going to be something like the wave function sketched in Fig. 8.5d when R is comparable with a_0 . There is an enhanced likelihood of finding the electron in the region between the protons, which corresponds to the sharing of the electron by the protons. Thus there is on the average an excess of negative charge between the protons, and this attracts the protons together. We have still to establish whether this attraction is strong enough to overcome the mutual repulsion of the protons.

The combination of ψ_a and ψ_b in Fig. 8.5 is symmetric, since exchanging a and b does not affect ψ (see Sec. 7.3). However, it is also conceivable that we could have an antisymmetric combination of ψ_a and ψ_b , as in Fig. 8.6. Here there is a node between a and b where $\psi = 0$, which implies a reduced likelihood of finding the electron between the protons. Now there is on the average a deficiency of negative charge between the protons and in consequence a repulsive force. With only repulsive forces acting, bonding cannot occur.

An interesting question concerns the behavior of the antisymmetric H_2^+ wave function ψ_A as $R \rightarrow 0$. Obviously ψ_A does not become the 1s wave function of He^+ when $R = 0$. However, ψ_A does approach the 2p wave function of He^+ (Fig. 8.6e), which has a node at the origin. But the 2p state of He^+ is an excited state whereas the 1s state is the ground state. Hence H_2^+ in the antisymmetric state ought to have more energy than when it is in the symmetric state, which agrees with our inference from the shapes of the wave functions ψ_A and ψ_S that in the former case there is a repulsive force and in the latter, an attractive one.

System Energy

A line of reasoning similar to the preceding one lets us estimate how the total energy of the H_2^+ system varies with R . We first consider the symmetric state. When R is large, the electron energy E_S must be the -13.6-eV energy of the hydrogen atom, while the electric potential energy U_p of the protons,

$$U_p = \frac{e^2}{4\pi\epsilon_0 R} \quad (8.1)$$

falls to 0 as $R \rightarrow \infty$. (U_p is a positive quantity, corresponding to a repulsive force.) When $R \rightarrow 0$, $U_p \rightarrow \infty$ as $1/R$. At $R = 0$, the electron energy must equal that of the He^+ ion, which is Z^2 , or 4 times, that of the H atom. (See Exercise 35 of Chap. 4; the same result is obtained from the quantum theory of one-electron atoms.) Hence $E_S = -54.4\text{ eV}$ when $R = 0$.

Both E_S and U_p are sketched in Fig. 8.7 as functions of R . The shape of the curve for E_S can only be approximated without a detailed calculation, but we do have its value for both $R = 0$ and $R = \infty$ and, of course, U_p obeys Eq. (8.1).

The total energy E_S^{total} of the system is the sum of the electron energy E_S and the potential energy U_p of the protons. Evidently E_S^{total} has a minimum, which corresponds to a stable molecular state. This result is confirmed by the experimental data on H_2^+ which indicate a bond energy of 2.65 eV and an equilibrium separation R of 0.106 nm . By "bond energy" is meant the energy needed to break H_2^+ into $\text{H} + \text{H}^+$. The total

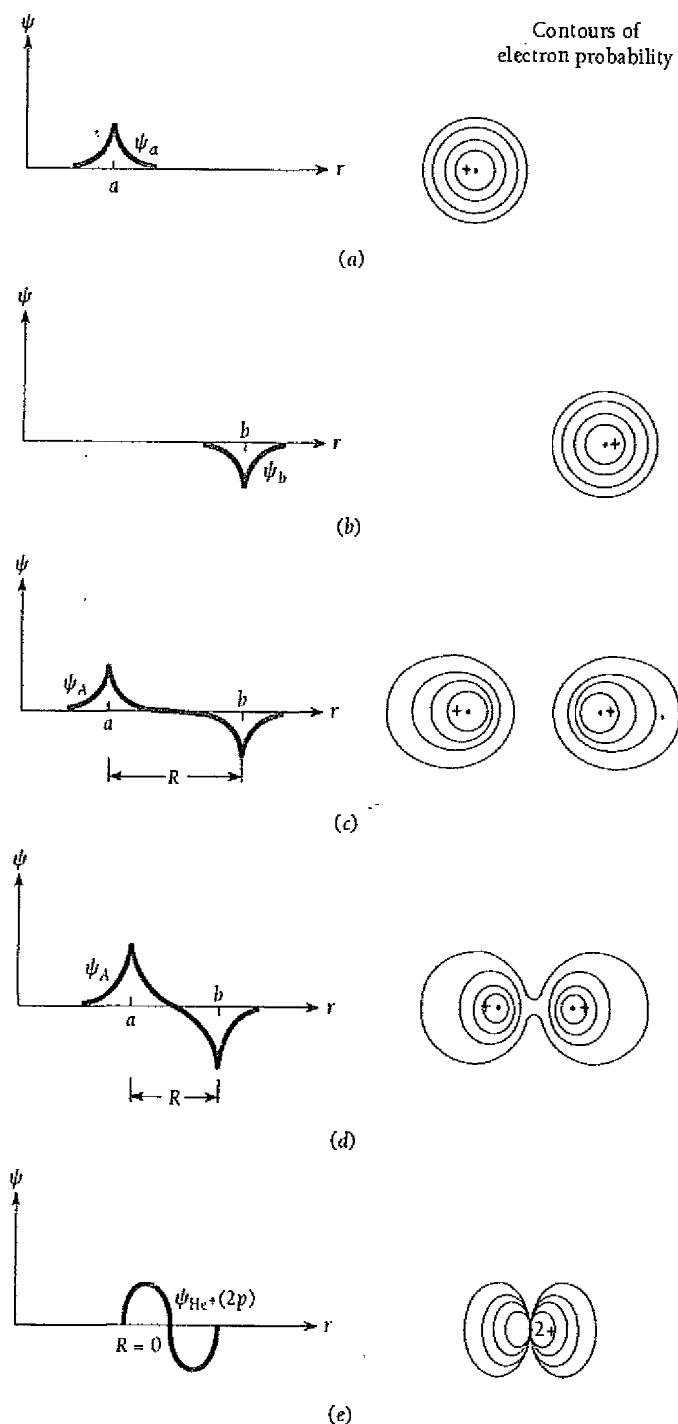


Figure 8.6 (a)-(d) The combination of two hydrogen-atom 1s wave functions to form the antisymmetric H_2^+ wave function ψ_A . A stable H_2^+ molecular ion is not formed because now the electron has a smaller probability of being between the protons than outside them. (e) If the protons could join together, the resulting wave function would be the same as the 2p wave function of a He^+ ion. In the 2p state a He^+ ion has more energy than in the 2s state.

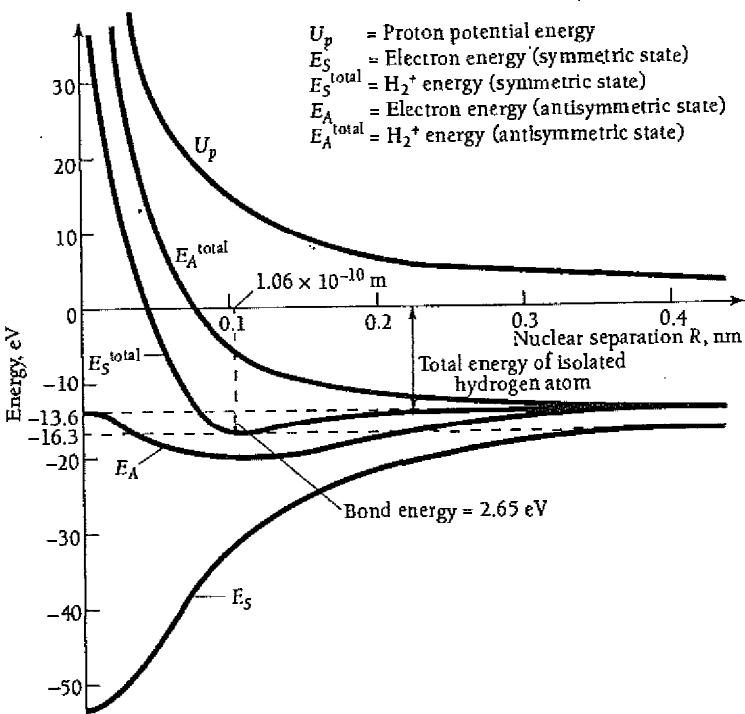


Figure 8.7 Electron, proton repulsion, and total energies in H_2^+ as a function of nuclear separation R for the symmetric and antisymmetric states. The antisymmetric state has no minimum in its total energy.

energy of H_2^+ is the -13.6 eV of the hydrogen atom plus the -2.65-eV bond energy, or -16.3 eV in all.

In the case of the antisymmetric state, the analysis proceeds in the same way except that the electron energy E_A when $R = 0$ is that of the $2p$ state of He^+ . This energy is proportional to Z^2/n^2 . With $Z = 2$ and $n = 2$, E_A is just equal to the -13.6 eV of the ground-state hydrogen atom. Since $E_A \rightarrow 13.6\text{ eV}$ also as $R \rightarrow \infty$, we might think that the electron energy is constant, but actually there is a small dip at intermediate distances. However, the dip is not nearly enough to yield a minimum in the total energy curve for the antisymmetric state, as shown in Fig. 8.7, and so in this state no bond is formed.

8.4 THE HYDROGEN MOLECULE

The spins of the electrons must be antiparallel

The H_2 molecule has two electrons instead of the single electron of H_2^+ . According to the exclusion principle, both electrons can share the same orbital (that is, be described by the same wave function ψ_{nlm}) provided their spins are antiparallel.

With two electrons to contribute to the bond, H_2 ought to be more stable than H_2^+ —at first glance, twice as stable, with a bond energy of 5.3 eV compared with

2.65 eV for H_2^+ . However, the H_2 orbitals are not quite the same as those of H_2^+ because of the electric repulsion between the two electrons in H_2 , a factor absent in the case of H_2^+ . This repulsion weakens the bond in H_2 , so that the actual energy is 4.5 eV instead of 5.3 eV. For the same reason, the bond length in H_2 is 0.074 nm, which is somewhat larger than the use of unmodified H_2^+ wave functions would indicate. The general conclusion in the case of H_2^+ that the symmetric wave function ψ_S leads to a bound state and the antisymmetric wave function ψ_A to an unbound one remains valid for H_2 .

In Sec. 7.3 the exclusion principle was formulated in terms of the symmetry and antisymmetry of wave functions, and it was concluded that systems of electrons are always described by antisymmetric wave functions (that is, by wave functions that reverse sign upon the exchange of any pair of electrons). However, the bound state in H_2 corresponds to both electrons being described by a symmetrical wave function ψ_S , which seems to contradict the above conclusion.

A closer look shows that there is really no contradiction. The complete wave function $\Psi(1, 2)$ of a system of two electrons is the product of a spatial wave function $\psi(1, 2)$ which describes the coordinates of the electrons and a spin function $s(1, 2)$ which describes the orientations of their spins. The exclusion principle requires that the complete wave function

$$\Psi(1, 2) = \psi(1, 2)s(1, 2)$$

be antisymmetric to an exchange of both coordinates and spins, not $\psi(1, 2)$ by itself. An antisymmetric complete wave function Ψ_A can result from the combination of a symmetric coordinate wave function ψ_S and an antisymmetric spin function s_A or from the combination of an antisymmetric coordinate wave function ψ_A and a symmetric spin function s_S . That is, only

$$\Psi(1, 2) = \psi_S s_A \quad \text{and} \quad \Psi(1, 2) = \psi_A s_S$$

are acceptable.

If the spins of the two electrons are parallel, their spin function is symmetric since it does not change sign when the electrons are exchanged. Hence the coordinate wave function ψ for two electrons whose spins are parallel must be antisymmetric:

$$\begin{array}{ll} \text{Spins parallel} & \Psi(1, 2) = \psi_A s_S \end{array}$$

On the other hand, if the spins of the two electrons are antiparallel, their spin function is antisymmetric since it reverses sign when the electrons are exchanged. Hence the coordinate wave function ψ for two electrons whose spins are antiparallel must be symmetric:

$$\begin{array}{ll} \text{Spins antiparallel} & \Psi(1, 2) = \psi_S s_A \end{array}$$

Schrödinger's equation for the H_2 molecule has no exact solution. In fact, only for H_2^+ is an exact solution possible, and all other molecular systems must be treated approximately. The results of a detailed analysis of the H_2 molecule are shown in Fig. 8.8 for the case when the electrons have their spins parallel and the case when their spins are antiparallel. The difference between the two curves is due to the exclusion principle, which leads to a dominating repulsion when the spins are parallel.

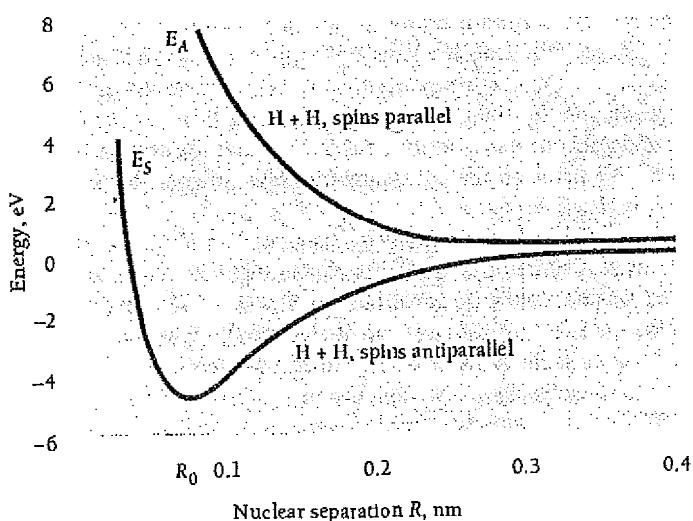


Figure 8.8 The variation of the energy of the system $\text{H} + \text{H}$ with their distances apart when the electron spins are parallel and antiparallel.

8.5 COMPLEX MOLECULES

Their geometry depends on the wave functions of the outer electrons of their atoms

Covalent bonding in molecules other than H_2 , diatomic as well as polyatomic, is usually a more complicated story. It would be yet more complicated but for the fact that any alteration in the electronic structure of an atom due to the proximity of another atom is confined to its outermost, or valence, electron shell. There are two reasons for this:

- 1 The inner electrons are much more tightly bound and hence less responsive to external influences, partly because they are closer to their parent nucleus and partly because they are shielded from the nuclear charge by fewer intervening electrons.
- 2 The repulsive interatomic forces in a molecule become predominant while the inner shells of its atoms are still relatively far apart.

The idea that only the valence electrons are involved in chemical bonding is supported by x-ray spectra that arise from transitions to inner-shell electron states. These spectra are virtually independent of how the atoms are combined in molecules or solids.

We have seen that two H atoms can combine to form an H_2 molecule; and, indeed, hydrogen molecules in nature always consist of two H atoms. The exclusion principle is what prevents molecules such as He_2 and H_3 from existing, while permitting such other molecules as H_2O to be stable.

Every He atom in its ground state has a $1s$ electron of each spin. If it is to join with another He atom by exchanging electrons, each atom will have two electrons with the same spin for part of the time. That is, one atom will have both electron spins up ($\uparrow\uparrow$) and the other will have both spins down ($\downarrow\downarrow$). The exclusion principle, of course,

prohibits two 1s electrons in an atom from having the same spins, which is manifested in a repulsion between He atoms. Hence the He_2 molecule cannot exist.

A similar argument holds in the case of H_3 . An H_2 molecule contains two 1s electrons whose spins are antiparallel ($\uparrow\downarrow$). Should another H atom approach whose electron spin is, say, up, the resulting molecule would have two spins parallel ($\uparrow\uparrow\downarrow$), and this is impossible if all three electrons are to be in 1s states. Hence the existing H_2 molecule repels the additional H atom. The exclusion-principle argument does not apply if one of the three electrons in H_3 is in an excited state. All such states are of higher energy than the 1s state, however, and the resulting configuration therefore has more energy than $\text{H}_2 + \text{H}$ and so will decay rapidly to $\text{H}_2 + \text{H}$.

Molecular Bonds

The interaction between two atoms that gives rise to a covalent bond between them may involve probability-density distributions for the participating electrons that are different from those of Fig. 6.12 for atoms alone in space. Figure 8.9 shows the

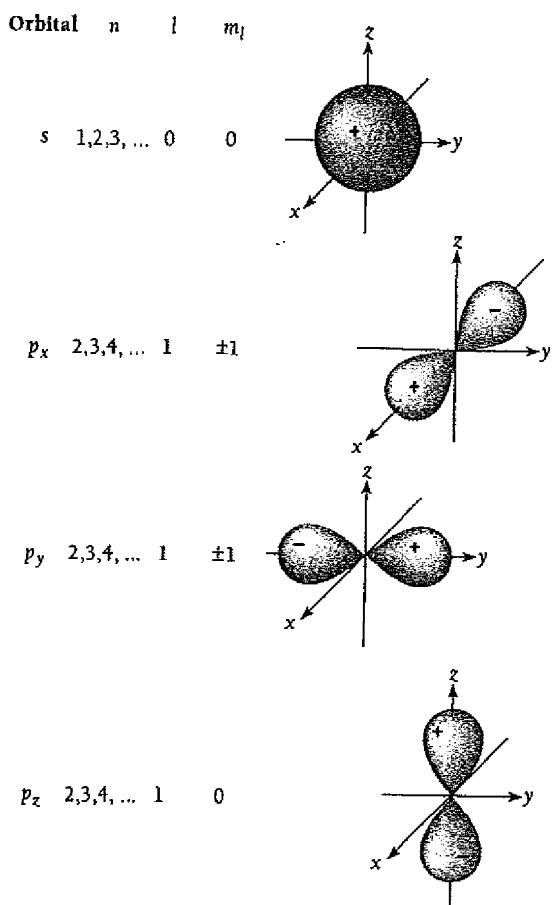


Figure 8.9 Boundary surface diagrams for s and p atomic orbitals. Each orbital can "contain" two electrons. There is a high probability of finding an electron described by one of these orbitals in the shaded regions. The sign of the wave function in each lobe is indicated.

configurations of the s and p atomic orbitals important in bond formation. What are drawn are boundary surfaces of constant $|\psi|^2 = |R\Theta\Phi|^2$ that outline the regions within which the probability of finding the electron has some definite value, say 90 or 95 percent. The diagrams thus show $|\Theta\Phi|^2$ in each case; Fig. 6.11 gives the corresponding radial probabilities. The sign of the wave function ψ is indicated in each lobe of the orbitals.

In Fig. 8.9 the s and p_z orbitals are the same as the hydrogen-atom wave functions for s and p ($m_l = 0$) states. The p_x and p_y orbitals are linear combinations of the p ($m_l = +1$) and p ($m_l = -1$) orbitals, where

$$\psi_{p_x} = \frac{1}{\sqrt{2}}(\psi_{+1} + \psi_{-1}) \quad \psi_{p_y} = \frac{1}{\sqrt{2}}(\psi_{+1} - \psi_{-1}) \quad (8.2)$$

The $1/\sqrt{2}$ factors are needed to normalize the wave functions. Because the energies of the $m_l = +1$ and $m_l = -1$ orbitals are the same, the superpositions of the wave functions in Eq. (8.2) are also solutions of Schrödinger's equation (see Sec. 5.4).

When two atoms come together, their orbitals overlap. If the result is an increased $|\psi|^2$ between them, the combined orbitals constitute a bonding molecular orbital. In Sec. 8.4 we saw how the 1s orbitals of two hydrogen atoms could join to form the bonding orbital ψ_s . Molecular bonds are classified by Greek letters according to their angular momenta L about the bond axis, which is taken to be the z axis: σ (the Greek equivalent of s) corresponds to $L = 0$, π (the Greek equivalent of p) corresponds to $L = \hbar$, and so on in alphabetic order.

Figure 8.10 shows the formation of σ and π bonding molecular orbitals from s and p atomic orbitals. Evidently ψ_s for H_2 is an $ss\sigma$ bond. Since the lobes of p_z orbitals are on the bond axis, they form σ molecular orbitals; the p_x and p_y orbitals usually form π molecular orbitals.

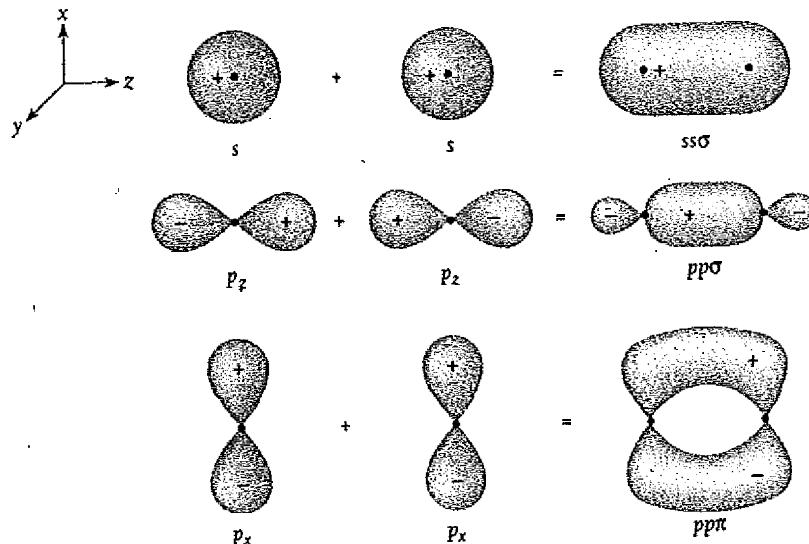


Figure 8.10 The formation of $ss\sigma$, $pp\sigma$, and $pp\pi$ bonding molecular orbitals. Two p_z atomic orbitals can combine to form a $pp\sigma$ molecular orbital in the same way as shown for two p_x atomic orbitals but with a different orientation.

The atomic orbitals that combine to form a molecular orbital may be different in the two atoms. An example is the water molecule H₂O. Although one 2p orbital in O is fully occupied by two electrons, the other two 2p orbitals are only singly occupied and so can join with the 1s orbitals of two H atoms to form $sp\sigma$ bonding orbitals (Fig. 8.11). The mutual repulsion between the H nuclei (which are protons) widens the angles between the bond axes from 90° to the observed 104.5°.

Hybrid Orbitals

The straightforward way in which the shape of the H₂O molecule is explained fails in the case of methane, CH₄. A carbon atom has two electrons in its 2s orbital and one electron in each of two 2p orbitals. Thus we would expect the hydride of carbon to be CH₂, with two $sp\sigma$ bonding orbitals and a bond angle of a little over 90°. The 2s electrons should not participate in the bonding at all. Yet CH₄ exists and is perfectly symmetrical in structure with tetrahedral molecules whose C—H bonds are exactly equivalent to one another.

The problem of CH₄ (and those of many other molecules) was solved by Linus Pauling in 1928. He proposed that linear combinations of both the 2s and 2p atomic orbitals of C contribute to each molecular orbital in CH₄. The 2s and 2p wave functions are both solutions of the same Schrödinger's equation if the corresponding energies are the same, which is not true in the isolated C atom. However, in an actual CH₄ molecule the electric field experienced by the outer C electrons is affected by the nearby H nuclei, and the energy difference between 2s and 2p states then can disappear. Hybrid orbitals that consist of mixtures of s and p orbitals occur when the bonding energies they produce are greater than those which pure orbitals would produce. In CH₄ the four hybrid orbitals are mixtures of one 2s and three 2p orbitals, and accordingly are called sp^3 hybrids (Fig. 8.12). The wave functions of these hybrid orbitals are

$$\psi_1 = \frac{1}{2}(\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z}) \quad \psi_3 = \frac{1}{2}(\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z})$$

$$\psi_2 = \frac{1}{2}(\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z}) \quad \psi_4 = \frac{1}{2}(\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z})$$

Figure 8.13 shows the resulting structure of the CH₄ molecule.

Two other types of hybrid orbital in addition to sp^3 can occur in carbon atoms. In sp^2 hybridization, one outer electron is in a pure p orbital and the other three are

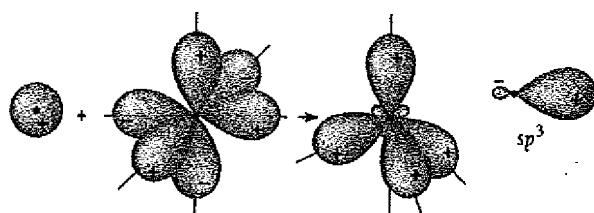


Figure 8.12 In sp^3 hybridization, an s orbital and three p orbitals in the same atom combine to form four sp^3 hybrid orbitals.

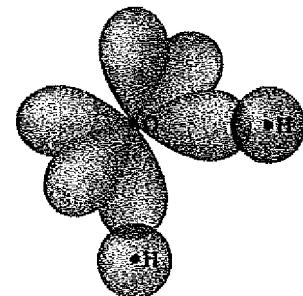


Figure 8.11 Formation of an H₂O molecule. Overlaps represent $sp\sigma$ covalent bonds. The angle between the bonds is 104.5°.

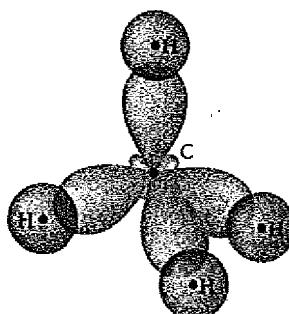


Figure 8.13 The bonds in the CH₄ (methane) molecule involve sp^3 hybrid orbitals.



Linus Pauling (1901–1994), a native of Oregon, received his Ph.D. from the California Institute of Technology and remained there for his entire scientific career except for a period in the middle 1920s when he was in Germany to study the new quantum mechanics. A pioneer in the application of quantum theory to chemistry, he provided many of the key insights that permitted the details of chemical bonding to be understood. His *The Nature of the Chemical Bond* has been one of the most influential books in the history of science. Pauling also did important work in molecular biology, in particular protein structure: with the help of x-ray diffraction, he discovered the helical and pleated sheet forms that protein molecules can have. It was Pauling who realized that sickle cell anemia is a "molecular disease" due to

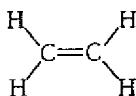
hemoglobin with one wrong amino acid resulting from a genetic fault. He received the Nobel Prize in chemistry in 1954.

In 1923 Pauling met Ava Helen Miller in a chemistry class, and she married him despite his admission that "If I had to choose between you and science, I'm not sure that I would choose you." She introduced him to the world outside the laboratory, and he became more and more politically active in his later years. Pauling fought to stop the atmospheric testing of nuclear weapons with its attendant radioactive fallout, a crusade that did not endear him to Caltech or to the FBI, whose file on him grew to 2500 pages. Elsewhere his ideas were better received in the forms of a nuclear test ban treaty and the Nobel Peace Prize. Pauling championed large daily doses of vitamin C as an aid to good health, an idea rejected at first by the medical establishment but eventually shown to have much in its favor. He died at ninety-three of cancer, certain that vitamin C had prolonged his life.

in hybrid orbitals that are $\frac{1}{3}s$ and $\frac{2}{3}p$ in character. In sp hybridization, two outer electrons are in pure p orbitals and the other two are in hybrid orbitals that are $\frac{1}{2}s$ and $\frac{1}{2}p$ in character.

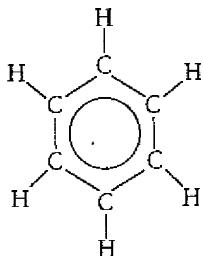
Ethylene, C_2H_4 , is an example of sp^2 hybridization in which the two C atoms are joined by two bonds, one a σ bond and one a π bond (Fig. 8.14). The conventional structural formula of ethylene shows these two bonds:

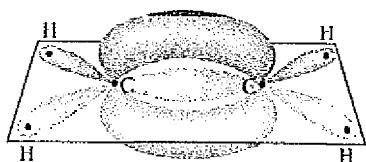
Ethylene



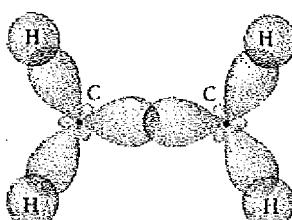
The electrons in the π bond are "exposed" outside the molecule, so ethylene and similar compounds are much more reactive chemically than compounds whose molecules have only σ bonds between their C atoms.

In benzene, C_6H_6 , the six C atoms are arranged in a flat hexagonal ring, as in Fig. 8.15, with three sp^2 orbitals per C atom forming σ bonds with each other and with the H atoms. This leaves each C atom with one $2p$ orbital. The total of six $2p$ orbitals in the molecule combine into bonding π orbitals that are continuous above and below the plane of the ring. The six electrons involved belong to the molecule as a whole and not to any particular pair of atoms; these electrons are delocalized. An appropriate structural formula for benzene is therefore

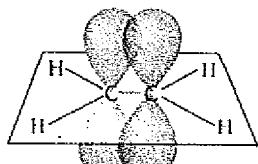




(a)

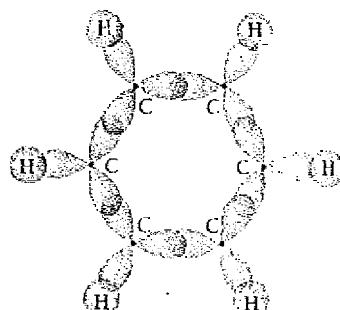


(b)

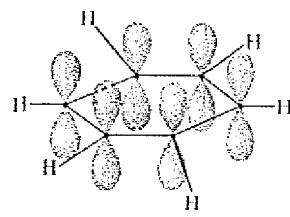


(c)

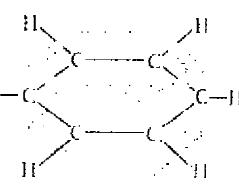
Figure 8.14 (a) The ethylene (C_2H_4) molecule. All the atoms lie in a plane perpendicular to the plane of the paper. (b) Top view, showing the sp^2 hybrid orbitals that form σ bonds between the C atoms and between each C atoms. (c) Side view, showing the pure p_x orbitals that form a π bond between the C atoms.



(a)



(b)



(c)

Figure 8.15 The benzene molecule. (a) The overlaps between the sp^2 hybrid orbitals in the C atoms with each other and with the s orbitals of the H atoms lead to σ bonds. (b) Each C atom has a pure p_x orbital occupied by one electron. (c) The bonding π molecular orbitals formed by the six p_x atomic orbitals constitute a continuous electron probability distribution around the molecule that contains six delocalized electrons.



Dorothy Crowfoot Hodgkin (1910–1994) was fascinated at the age of ten by the growth of crystals in alum and copper sulfate solutions as their solvent water evaporated. This fascination with crystals never left her. She studied chemistry at Oxford University despite the difficulties women students of science had to face in those days, and as an undergraduate had mastered x-ray crystallography well enough to have a research paper published. In this technique a narrow beam of x-rays is directed at a crystal

from various angles and the resulting interference patterns are analyzed to yield the arrangement of the atoms in the crystal. Dorothy Crowfoot (as she then was) went on to Cambridge University to work with J. D. Bernal, who had just begun to use x-rays to investigate biological molecules. Under the right conditions many such molecules form crystals from whose struc-

tures the structures of the molecules themselves can be inferred. In particular, the structures of protein molecules are important because they are closely related to their biological functions. She and Bernal were the first to map the arrangement of the atoms in a protein, the digestive enzyme pepsin.

After two intense years at Cambridge, Dorothy Crowfoot returned to Oxford where she married Thomas Hodgkin and had three children while continuing active research. Her most notable work was on penicillin (then the most complex molecule to be successfully analyzed), vitamin B_{12} , and insulin (it took thirty-five years of on-and-off effort to finish the job). She was a pioneer in using computers to interpret x-ray data, an arduous task for all but the simplest molecules. For all her achievements and their recognition in the scientific world, Hodgkin was for many years shabbily treated at Oxford: poor laboratory facilities, the lowest possible official status, half the pay of her male colleagues with continual worries about making ends meet until outside support (much of it from the Rockefeller Foundation of the United States) became available. She received the Nobel Prize in chemistry in 1964, the third woman to do so.

8.6 ROTATIONAL ENERGY LEVELS

Molecular rotational spectra are in the microwave region

Molecular energy states arise from the rotation of a molecule as a whole, from the vibrations of its atoms relative to one another, and from changes in its electronic configuration:

1 *Rotational states* are separated by quite small energy intervals (10^{-3} eV is typical). The spectra that arise from transitions between these states are in the microwave region with wavelengths of 0.1 mm to 1 cm. The absorption by water molecules of rotational energy from microwaves underlies the operation of microwave ovens.

2 *Vibrational states* are separated by somewhat larger energy intervals (0.1 eV is typical). Vibrational spectra are in the infrared region with wavelengths of 1 μm to 0.1 mm.

3 *Molecular electronic states* have the highest energies, with typical separations between the energy levels of outer electrons of several eV. The corresponding spectra are in the visible and ultraviolet regions.

A detailed picture of a particular molecule can often be obtained from its spectrum, including bond lengths, force constants, and bond angles. For simplicity the treatment here will cover only diatomic molecules, but the main ideas apply to more complicated ones as well.

The lowest energy levels of a diatomic molecule arise from rotation about its center of mass. We may picture such a molecule as consisting of atoms of masses m_1 and m_2 a distance R apart, as in Fig. 8.16. The moment of inertia of this molecule about an axis passing through its center of mass and perpendicular to a line joining the atoms is

$$I = m_1 r_1^2 + m_2 r_2^2 \quad (8.3)$$

where r_1 and r_2 are the distances of atoms 1 and 2, respectively, from the center of mass. From the definition of center of mass,

$$m_1 r_1 = m_2 r_2 \quad (8.4)$$

Hence the moment of inertia may be written

$$\text{Moment of inertia} \quad I = \frac{m_1 m_2}{m_1 + m_2} (r_1 + r_2)^2 = m' R^2 \quad (8.5)$$

Here

$$\text{Reduced mass} \quad m' = \frac{m_1 m_2}{m_1 + m_2} \quad (8.6)$$

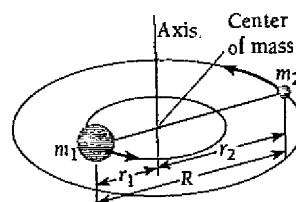


Figure 8.16 A diatomic molecule can rotate about its center of mass.

is the reduced mass of the molecule. Equation (8.5) states that the rotation of a diatomic molecule is equivalent to the rotation of a single particle of mass m' about an axis located a distance R away.

The angular momentum L of the molecule has the magnitude

$$L = I\omega \quad (8.7)$$

where ω is its angular velocity. Angular momentum is always quantized in nature, as we know. If we denote the rotational quantum number by J , we have here

Angular momentum	$L = \sqrt{J(J+1)}\hbar \quad J = 0, 1, 2, 3, \dots$	(8.8)
------------------	--	-------

The energy of a rotating molecule is $\frac{1}{2}I\omega^2$, and so its energy levels are specified by

Rotational energy levels	$E_J = \frac{1}{2}I\omega^2 = \frac{L^2}{2I}$	(8.9)
	$= \frac{J(J+1)\hbar^2}{2I}$	

Rotations about the Bond Axis

We have been considering only rotation about an axis perpendicular to the bond axis of a diatomic molecules, as in Fig 8.16—end-over-end rotations. What about rotations about the axis of symmetry itself?

Such rotations can be neglected because the mass of an atom is located almost entirely in its nucleus, whose radius is only $\sim 10^{-4}$ of the radius of the atom itself. The main contribution to the moment of inertia of a diatomic molecule about its bond axis therefore comes from its electrons, which are concentrated in a region whose radius about the axis is roughly half the bond length R but whose total mass is only about $\frac{1}{400}$ of the total molecular mass. Since the allowed rotational energy levels are proportional to $1/I$, rotation about the symmetry axis must involve energies $\sim 10^4$ times the E_J values for end-over-end rotations. Hence energies of at least several eV would be involved in any rotation about the symmetry axis of a diatomic molecule. Bond energies are also of this order of magnitude, so the molecule would be likely to dissociate in any environment in which such a rotation could be excited.

Example 8.1

The carbon monoxide (CO) molecule has a bond length R of 0.113 nm and the masses of the ^{12}C and ^{16}O atoms are respectively 1.99×10^{-26} kg and 2.66×10^{-26} kg. Find (a) the energy and (b) the angular velocity of the CO molecule when it is in its lowest rotational state.

Solution

(a) The reduced mass m' of the CO molecule is

$$\begin{aligned} m' &= \frac{m_1 m_2}{m_1 + m_2} = \left[\frac{(1.99)(2.66)}{1.99 + 2.66} \right] \times 10^{-26} \text{ kg} \\ &= 1.14 \times 10^{-26} \text{ kg} \end{aligned}$$

and its moment of inertia I is

$$\begin{aligned} I &= m'R^2 = (1.14 \times 10^{-26} \text{ kg})(1.13 \times 10^{-10} \text{ m})^2 \\ &= 1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2 \end{aligned}$$

The lowest rotational energy level corresponds to $J = 1$, and for this level in CO

$$\begin{aligned} E_{J=1} &= \frac{J(J+1)\hbar^2}{2I} = \frac{\hbar^2}{I} = \frac{(1.054 \times 10^{-34} \text{ J} \cdot \text{s})^2}{1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2} \\ &= 7.61 \times 10^{-23} \text{ J} = 4.76 \times 10^{-4} \text{ eV} \end{aligned}$$

This is not a lot of energy, and at room temperature, when $kT \approx 2.6 \times 10^{-2} \text{ eV}$, nearly all the molecules in a sample of CO are in excited rotational states.

(b) The angular velocity of the CO molecule when $J = 1$ is

$$\begin{aligned} \omega &= \sqrt{\frac{2E}{I}} = \sqrt{\frac{(2)(7.61 \times 10^{-23} \text{ J})}{1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2}} \\ &= 3.23 \times 10^{11} \text{ rad/s} \end{aligned}$$

Rotational Spectra

Rotational spectra arise from transitions between rotational energy states. Only molecules that have electric dipole moments can absorb or emit electromagnetic photons in such transitions. For this reason nonpolar diatomic molecules such as H₂ and symmetric polyatomic molecules such as CO₂ (O=C=O) and CH₄ (Fig. 8.13) do not exhibit rotational spectra. Transitions between rotational states in molecules like H₂, CO₂, and CH₄ can take place during collisions, however.

Even in molecules with permanent dipole moments, not all transitions between rotational states involve radiation. As in the case of atomic spectra, certain selection rules summarize the conditions for a radiative transition between rotational states to be possible. For a rigid diatomic molecule the selection rule for rotational transitions is

$$\text{Selection rule} \quad \Delta J = \pm 1 \quad (8.10)$$

In practice, rotational spectra are always obtained in absorption, so that each transition that is found involves a change from some initial state of quantum number J to the next higher state of quantum number $J + 1$. In the case of a rigid molecule, the frequency of the absorbed photon is

$$\begin{aligned} \nu_{J \rightarrow J+1} &= \frac{\Delta E}{h} = \frac{E_{J+1} - E_J}{h} \\ \text{Rotational spectra} &= \frac{\hbar}{2\pi I}(J + 1) \quad (8.11) \end{aligned}$$

where I is the moment of inertia for end-over-end rotations. The spectrum of a rigid molecule therefore consists of equally spaced lines, as in Fig. 8.17. The frequency of each line can be measured, and the transition it corresponds to can often be found from the sequence of lines. From these data the moment of inertia of the molecule can be calculated. Alternatively, the frequencies of any two successive lines may be used to determine I if the lowest-frequency lines in a particular spectral sequence are not recorded.

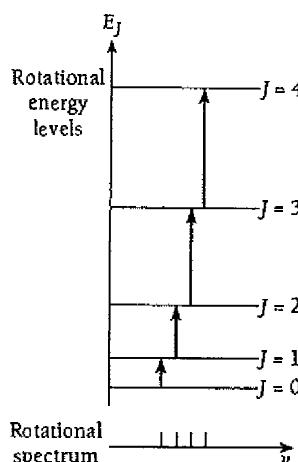


Figure 8.17 Energy levels and spectrum of molecular rotation.

Example 8.2

In CO the $J = 0 \rightarrow J = 1$ absorption line occurs at a frequency of 1.15×10^{11} Hz. What is the bond length of the CO molecule?

Solution

First we find the moment of inertia of this molecule from Eq. (8.11):

$$I_{\text{CO}} = \frac{\hbar}{2\pi\nu} (J + 1) = \frac{1.054 \times 10^{-34} \text{ J} \cdot \text{s}}{(2\pi)(1.15 \times 10^{11} \text{ s}^{-1})} = 1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2$$

In Example 8.1 we saw that the reduced mass of the CO molecule is $m' = 1.14 \times 10^{-26}$ kg. From Eq. (8.5), $I = m'R^2$, we obtain

$$R_{\text{CO}} = \sqrt{\frac{I}{m'}} = \sqrt{\frac{1.46 \times 10^{-46} \text{ kg} \cdot \text{m}^2}{1.14 \times 10^{-26} \text{ kg}}} = 1.13 \times 10^{-10} \text{ m} = 0.113 \text{ nm}$$

This is the way in which the bond length for CO quoted earlier was determined.

8.7 VIBRATIONAL ENERGY LEVELS

A molecule may have many different modes of vibration

When sufficiently excited, a molecule can vibrate as well as rotate. Figure 8.18 shows how the potential energy of a diatomic molecule varies with the internuclear distance R . Near the minimum of this curve, which corresponds to the normal configuration of the molecule, the shape of the curve is very nearly a parabola. In this region, then,

$$\text{Parabolic approximation} \quad U = U_0 + \frac{1}{2}k(R - R_0)^2 \quad (8.12)$$

where R_0 is the equilibrium separation of the atoms.

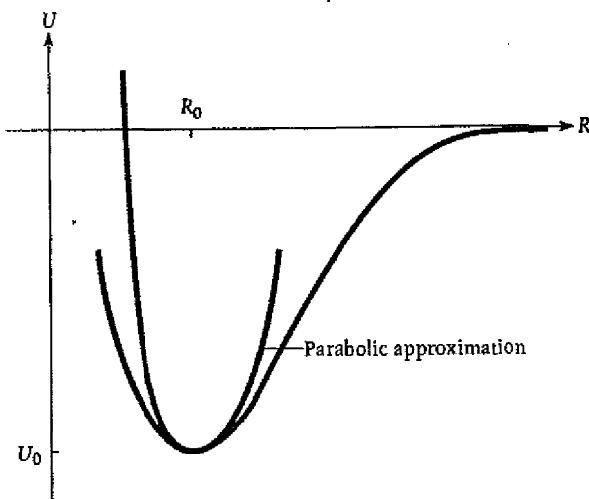


Figure 8.18 The potential energy of a diatomic molecule as a function of internuclear distance.

The interatomic force that gives rise to this potential energy is given by differentiating U :

$$F = -\frac{dU}{dR} = -k(R - R_0) \quad (8.13)$$

The force is just the restoring force that a stretched or compressed spring exerts—a Hooke's law force—and, as with a spring, a molecule suitably excited can undergo simple harmonic oscillations.

Classically, the frequency of a vibrating body of mass m connected to a spring of force constant k is

$$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad (8.14)$$

What we have in the case of a diatomic molecule is the somewhat different situation of two bodies of masses m_1 and m_2 joined by a spring, as in Fig. 8.19. In the absence

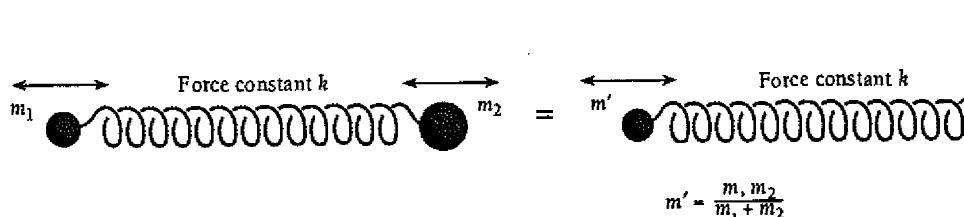


Figure 8.19 A two-body oscillator behaves like an ordinary harmonic oscillator with the same spring constant but with the reduced mass m' .

of external forces the linear momentum of the system remains constant, and the oscillations of the bodies therefore cannot effect the motion of their center of mass. For this reason m_1 and m_2 vibrate back and forth relative to their center of mass in opposite directions, and both reach the extremes of their respective motions at the same times. The frequency of oscillation of such a two-body oscillator is given by Eq. (8.14) with the reduced mass m' of Eq. (8.6) substituted for m :

$$\text{Two-body oscillator} \quad \nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m'}} \quad (8.15)$$

When the harmonic-oscillator problem is solved quantum mechanically (see Sec. 5.11), the energy of the oscillator turns out to be restricted to the values

$$\text{Harmonic oscillator} \quad E_v = (v + \frac{1}{2})\hbar\nu_0 \quad (8.16)$$

where v , the vibrational quantum number, may have the values

$$\text{Vibrational quantum number} \quad v = 0, 1, 2, 3, \dots$$

The lowest vibrational state ($v = 0$) has the zero-point energy $\frac{1}{2}\hbar\nu_0$, not the classical value of 0. This result is in accord with the uncertainty principle, because if the oscillating particle were stationary, the uncertainty in its position would be $\Delta x = 0$ and its momentum uncertainty would then have to be infinite—and a particle with $E = 0$ cannot have an infinitely uncertain momentum. In view of Eq. (8.15) the vibrational energy levels of a diatomic molecule are specified by

$$\text{Vibrational energy levels} \quad E_v = (v + \frac{1}{2})\hbar \sqrt{\frac{k}{m'}} \quad (8.17)$$

The higher vibrational states of a molecule do not obey Eq. (8.16) because the parabolic approximation to its potential-energy curve becomes less and less valid with increasing energy. As a result, the spacing between adjacent energy levels of high v is less than the spacing between adjacent levels of low v , which is shown in Fig. 8.20.



Gerhard Herzberg (1904–1999) was born in Hamburg, Germany, and received his doctorate from the Technical University of Darmstadt in 1928. The rise to power of the Nazis led Herzberg to leave Germany in 1935 for Canada, where he joined the University of Saskatchewan. From 1945 to 1948

he was at Yerkes Observatory in Wisconsin, and after that he directed the Division of Pure Physics of Canada's National Research Council in Ottawa until he retired in 1969. Herzberg was a pioneer in using spectra to determine molecular structures, and also did important work in analyzing the spectra of stars, interstellar gas, comets, and planetary atmospheres. His books under the general title *Molecular Spectra and Molecular Structure* are classics in the field. He received the Nobel Prize in chemistry in 1971.

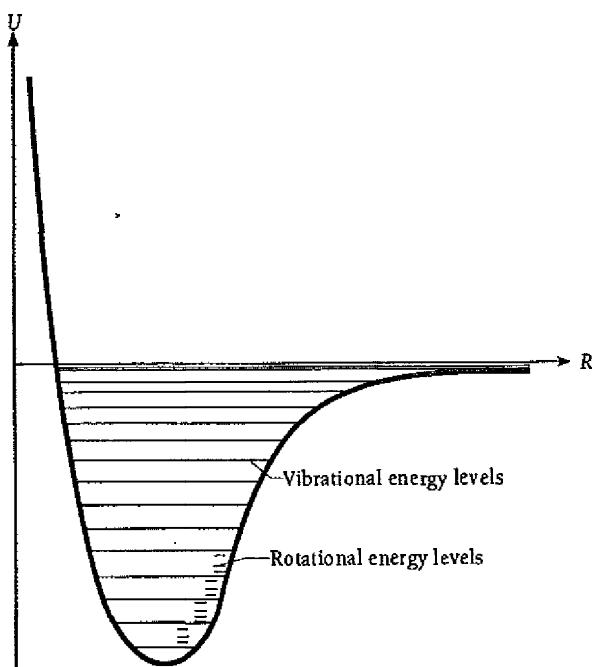


Figure 8.20 The potential energy of a diatomic molecule as a function of interatomic distance, showing vibrational and rotational energy levels.

This diagram also shows the fine structure in the vibrational levels caused by the simultaneous excitation of rotational levels.

Vibrational Spectra

The selection rule for transitions between vibrational states is

$$\text{Selection rule} \quad \Delta\nu = \pm 1 \quad (8.18)$$

in the harmonic-oscillator approximation. This rule is easy to understand. An oscillating dipole whose frequency is ν_0 can absorb or emit only electromagnetic radiation of the same frequency and all quanta of frequency ν_0 have the energy $\hbar\nu_0$. The oscillating dipole accordingly can only absorb $\Delta E = \hbar\nu_0$ at a time, in which case its energy increases from $(\nu + \frac{1}{2})\hbar\nu_0$ to $(\nu + \frac{1}{2} + 1)\hbar\nu_0$. It can also emit only $\Delta E = \hbar\nu_0$ at a time, in which case its energy decreases from $(\nu + \frac{1}{2})\hbar\nu_0$ to $(\nu + \frac{1}{2} - 1)\hbar\nu_0$. Hence the selection rule $\Delta\nu = \pm 1$.

Example 8.3

When CO is dissolved in liquid carbon tetrachloride, infrared radiation of frequency 6.42×10^{13} Hz is absorbed. Carbon tetrachloride by itself is transparent at this frequency, so the absorption must be due to the CO. (a) What is the force constant of the bond in the CO molecule? (b) What is the spacing between its vibrational energy levels?

Solution

(a) As we know, the reduced mass of the CO molecule is $m' = 1.14 \times 10^{-26}$ kg. From Eq. (8.15), $\nu_0 = (1/2\pi) \sqrt{k/m'}$, the force constant is

$$\begin{aligned} k &= 4\pi^2 \nu_0^2 m' = (4\pi^2)(6.42 \times 10^{13} \text{ Hz})^2(1.14 \times 10^{-26} \text{ kg}) \\ &= 1.86 \times 10^3 \text{ N/m} \end{aligned}$$

This is about 10 lb/in.

(b) The separation ΔE between the vibrational levels in CO is

$$\begin{aligned} \Delta E &= E_{v+1} - E_v = \hbar\nu_0 = (6.63 \times 10^{-34} \text{ J} \cdot \text{s})(6.42 \times 10^{13} \text{ Hz}) \\ &= 4.26 \times 10^{-20} \text{ J} = 0.266 \text{ eV} \end{aligned}$$

This is considerably more than the spacing between its rotational energy levels. Because $\Delta E > kT$ for vibrational states in a sample at room temperature, most of the molecules in such a sample exist in the $v = 0$ state with only their zero-point energies. This situation is very different from that characteristic of rotational states, where the much smaller energies mean that the majority of the molecules in a room-temperature sample are excited to higher states.

A complex molecule may have many different modes of vibration. Some of these modes involve the entire molecule (Figs. 8.21 and 8.22), but others ("local modes") involve only groups of atoms whose vibrations occur more or less independently of the rest of the molecule. Thus the $-\text{OH}$ group has a characteristic vibrational frequency of 1.1×10^{14} Hz and the $-\text{NH}_2$ group has a frequency of 1.0×10^{14} Hz.

The characteristic vibrational frequency of a carbon-carbon group depends upon the number of bonds between the C atoms: the ---C---C--- group vibrates at about 3.3×10^{13} Hz, the ---C=C--- group vibrates at about 5.0×10^{13} Hz, and the ---C\equiv C--- group vibrates at about 6.7×10^{13} Hz. (As we would expect, the more carbon-carbon bonds, the larger the force constant k and the higher the frequency.) In each case the frequency does not depend strongly on the particular molecule or the location in the molecule of the group, which makes vibrational spectra a valuable tool in determining molecular structures.

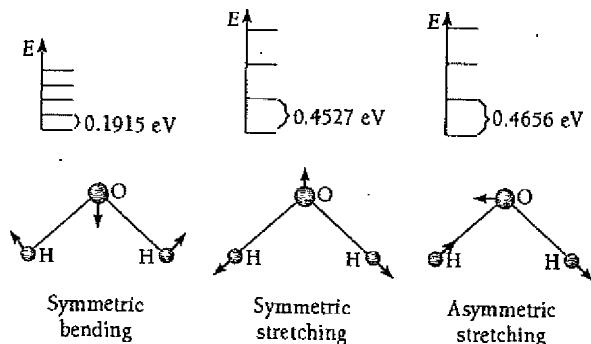


Figure 8.21 The normal modes of vibration of the H_2O molecule and the energy levels of each mode. More energy is needed to stretch the molecule than to bend it, which is generally true.

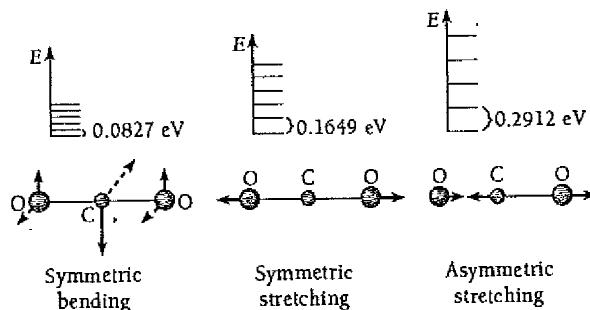
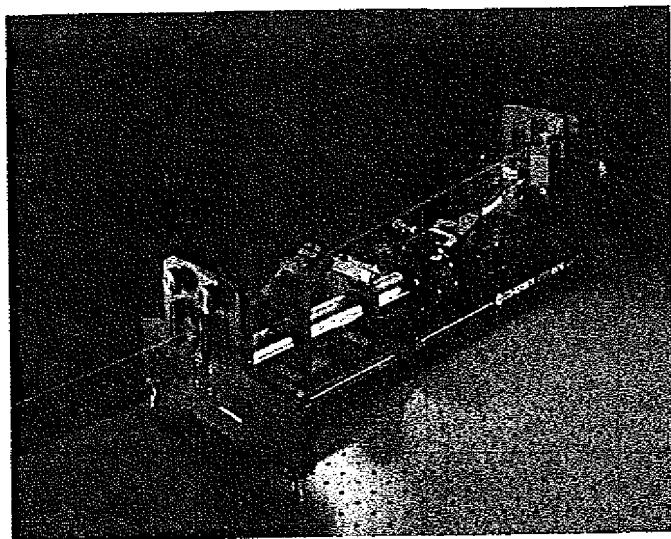


Figure 8.22 The normal modes of vibration of the CO_2 molecule and the energy levels of each mode. The symmetric bending mode can occur in two perpendicular planes. In this molecule the O atoms are negatively charged and the C atom is positively charged. The symmetric stretching mode cannot be initiated by the absorption of a photon because the overall charge distribution in the molecule does not change in this mode. In the other modes of vibration, however, the charge distribution does change and the molecule can absorb photons of appropriate wavelength (4.26 μm and 15.00 μm for the asymmetric stretching and symmetric bending modes, respectively). The absorption of infrared radiation from the earth by atmospheric CO_2 molecules is partly responsible for the greenhouse effect (see Fig. 9.8), and the increase in the CO_2 content of the atmosphere due to the burning of fossil fuels seems to be the chief cause of the global warming trend now under way. Other molecules in the atmosphere, such as H_2O and CH_4 (methane), also contribute to the greenhouse effect, but N_2 and O_2 do not because, since their overall charge distributions do not change when they vibrate, they do not absorb infrared radiation.

An example is thioacetic acid, whose structure might conceivably be either $\text{CH}_3\text{CO}-\text{SH}$ or $\text{CH}_3\text{CS}-\text{OH}$. The infrared absorption spectrum of thioacetic acid contains lines at frequencies equal to the vibrational frequencies of the $\text{C}=\text{O}$ and —SH groups, but no lines corresponding to the $\text{C}=\text{S}$ or —OH groups. The first alternative is evidently the correct one.



This tunable dye laser emits light with wavelengths from 370 to 900 nm, which includes the entire visible spectrum. The bandwidth can be as narrow as 500 kHz.

Vibration-Rotation Spectra

Pure vibrational spectra are observed only in liquids where interactions between adjacent molecules inhibit rotation. Because the excitation energies involved in molecular rotation are much smaller than those involved in vibration, the freely moving molecules in a gas or vapor nearly always are rotating, regardless of their vibrational state. The spectra of such molecules do not show isolated lines corresponding to each vibrational transition, but instead a large number of closely spaced lines due to transitions between the various rotational states of one vibrational level and the rotational states of the other. In spectra obtained using a spectrometer with inadequate resolution, the lines appear as a broad streak called a vibration-rotation band.

Tunable Dye Lasers

The existence of bands of extremely closely spaced lines in molecular spectra underlies the operation of the tunable dye laser. Such a laser uses an organic dye whose molecules are "pumped" to excited states by light from another laser. The dye then fluoresces in a broad emission band. From this band, light of the desired wavelength λ can be selected for laser amplification with the help of a pair of facing mirrors, one of them partly transparent. The separation of the mirrors is set to an integral multiple of $\lambda/2$. As in the case of the lasers discussed in Sec. 4.9, the trapped laser light forms an optical standing wave that emerges through the partly transparent mirror. A dye laser of this kind can be tuned to a precision of better than one part in a million by adjusting the spacing of the mirrors.

8.8 ELECTRONIC SPECTRA OF MOLECULES

How fluorescence and phosphorescence occur

The energies of rotation and vibration in a molecule are due to the motion of its atomic nuclei, which contain virtually all the molecule's mass. The molecule's electrons also can be excited to higher energy levels than those corresponding to its ground state. However, the spacing of these levels is much greater than the spacing of rotational or vibrational levels.

Electronic transitions involve radiation in the visible or ultraviolet parts of the spectrum. Each transition appears as a series of closely spaced lines, called a band, due to the presence of different rotational and vibrational states in each electronic state (Fig. 8.23). All molecules exhibit electronic spectra, since a dipole moment change always accompanies a change in the electronic configuration of a molecule. Therefore homonuclear molecules, such as H_2 and N_2 , which have neither rotational nor

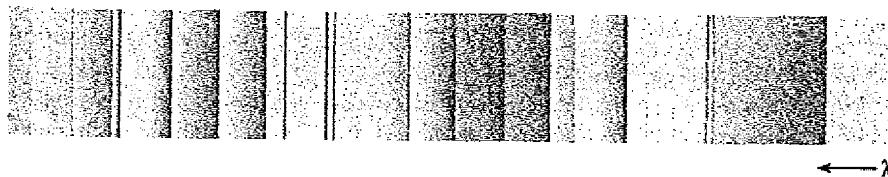


Figure 8.23 A portion of the band spectrum of PN.

vibrational spectra because they lack permanent dipole moments, nevertheless have electronic spectra whose rotational and vibrational fine structures enable moments of inertia and bond force constants to be found.

Electronic excitation in a polyatomic molecule often leads to a change in the molecule's shape, which can be determined from the rotational fine structure in its band spectrum. The origin of such changes lies in the different characters of the wave functions of electrons in different states, which lead to correspondingly different bond geometries. For example, the molecule beryllium hydride, BeH₂, is linear (H—Be—H) in one state and bent (H—Be) in another.



Fluorescence

A molecule in an excited electronic state can lose energy and return to its ground state in various ways. The molecule may, of course, simply emit a photon of the same frequency as that of the photon it absorbed, thereby returning to the ground state in a single step. Another possibility is fluorescence. Here the molecule gives up some of its vibrational energy in collisions with other molecules, so that the downward radiative transition originates from a lower vibrational level in the upper electronic state (Fig. 8.24). Fluorescent radiation is therefore of lower frequency than that of the absorbed radiation.

Fluorescence excited by ultraviolet light has many applications, for instance to help identify minerals and biochemical compounds. Fabric "brighteners" that are sometimes

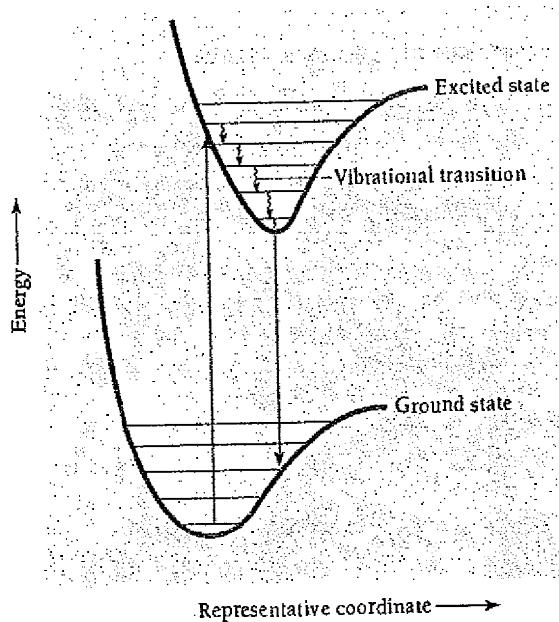


Figure 8.24 The origin of fluorescence. The emitted radiation is lower in frequency than the absorbed radiation.

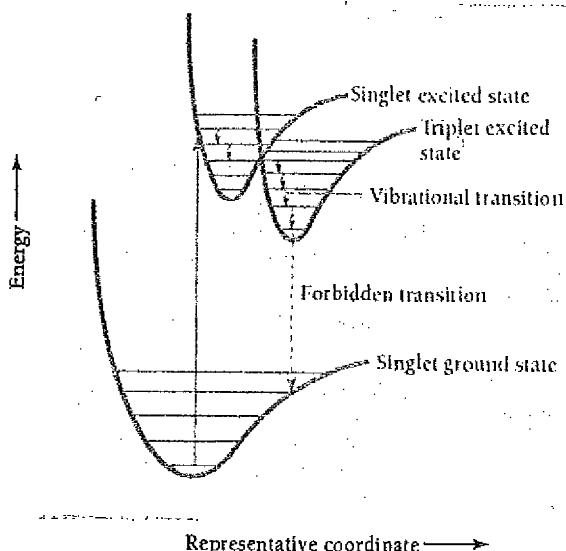


Figure 8.25 The origin of phosphorescence. The final transition is delayed because it violates the selection rules for electronic transitions.

added to detergents absorb ultraviolet radiation in daylight and then fluoresce blue light. In a fluorescent lamp, a mixture of mercury vapor and an inert gas such as argon inside a glass tube gives off ultraviolet radiation when an electric current is passed through it. The inside of the tube is coated with a fluorescent material called a phosphor that emits visible light when excited by the ultraviolet radiation. The process is much more efficient than using a current to heat a filament to incandescence, as in ordinary light bulbs.

Phosphorescence

In molecular spectra, radiative transitions between electronic states of different total spin are prohibited. Figure 8.25 shows a situation in which the molecule in its singlet (total spin quantum number $S = 0$) ground state absorbs a photon and is raised to a singlet excited state. In collisions the molecule can undergo radiationless transitions to a lower vibrational level that may happen to have about the same energy as one of the levels in the triplet ($S = 1$) excited state. There is then a certain probability for a shift to the triplet state to occur. Further collisions in the triplet state bring the molecule's energy below that of the crossover point, so that it is now trapped in the triplet state and ultimately reaches the $v = 0$ level.

A radiative transition from a triplet to a singlet state is "forbidden" by the selection rules, which really means not that it is impossible but that it has only a small likelihood of occurring. Such transitions accordingly have long half-lives, and the resulting phosphorescent radiation may be emitted minutes or even hours after the initial absorption.

EXERCISES*

We are wiser than we know. —Ralph Waldo Emerson

8.3 The H_2^+ Molecular Ion

8.4 The Hydrogen Molecule

- The energy needed to detach the electron from a hydrogen atom is 13.6 eV, but the energy needed to detach an electron from a hydrogen molecule is 15.7 eV. Why do you think the latter energy is greater?
- The protons in the H_2^+ molecular ion are 0.106 nm apart, and the binding energy of H_2^+ is 2.65 eV. What negative charge must be placed halfway between two protons this distance apart to give the same binding energy?
- At what temperature would the average kinetic energy of the molecules in a hydrogen sample be equal to their binding energy?

8.6 Rotational Energy Levels

- Microwave communication systems operate over long distances in the atmosphere. The same is true for radar, which locates objects such as ships and aircraft by means of microwave pulses they reflect. Molecular rotational spectra are in the microwave region. Can you think of the reason why atmospheric gases do not absorb microwaves to any great extent?
- When a molecule rotates, inertia causes its bonds to stretch. (This is why the earth bulges at the equator.) What effects does this stretching have on the rotational spectrum of the molecule?
- Find the frequencies of the $J = 1 \rightarrow J = 2$ and $J = 2 \rightarrow J = 3$ rotational absorption lines in NO, whose molecules have the moment of inertia $1.65 \times 10^{-46} \text{ kg} \cdot \text{m}^2$.
- The $J = 0 \rightarrow J = 1$ rotational absorption line occurs at $1.153 \times 10^{11} \text{ Hz}$ in $^{12}\text{C}^{16}\text{O}$ and at $1.102 \times 10^{11} \text{ Hz}$ in $^{13}\text{C}^{16}\text{O}$. Find the mass number of the unknown carbon isotope.
- Calculate the energies of the four lowest non-zero rotational energy states of the H_2 and D_2 molecules, where D represents the deuterium atom ^2H .
- The rotational spectrum of HCl contains the following wavelengths:

$$\begin{aligned} & 12.03 \times 10^{-5} \text{ m} \\ & 9.60 \times 10^{-5} \text{ m} \\ & 8.04 \times 10^{-5} \text{ m} \\ & 6.89 \times 10^{-5} \text{ m} \\ & 6.04 \times 10^{-5} \text{ m} \end{aligned}$$

If the isotopes involved are ^1H and ^{35}Cl , find the distance between the hydrogen and chlorine nuclei in an HCl molecule.

- The lines of the rotational spectrum of HBr are $5.10 \times 10^{11} \text{ Hz}$ apart in frequency. Find the internuclear distance in HBr. (Note: Since the Br atom is about 80 times more massive than the

proton, the reduced mass of an HBr molecule can be taken as just the ^1H mass.)

- A $^{200}\text{Hg}^{35}\text{Cl}$ molecule emits a 4.4-cm photon when it undergoes a rotational transition from $J = 1$ to $J = 0$. Find the internuclear distance in this molecule.
- The lowest frequency in the rotational absorption spectrum of $^1\text{H}^{19}\text{F}$ is $1.25 \times 10^{12} \text{ Hz}$. Find the bond length in this molecule.
- In Sec. 4.6 it was shown that, for large quantum numbers, the frequency of the radiation from a hydrogen atom that drops from an initial state of quantum number n to a final state of quantum number $n - 1$ is equal to the classical frequency of revolution of an electron in the n th Bohr orbit. This is an example of Bohr's correspondence principle. Show that a similar correspondence holds for a diatomic molecule rotating about its center of mass.
- Calculate the classical frequency of rotation of a rigid body whose energy is given by Eq. (8.9) for states of $J = J$ and $J = J + 1$, and show that the frequency of the spectral line associated with a transition between these states is intermediate between the rotational frequencies of the states.

8.7 Vibrational Energy Levels

- The hydrogen isotope deuterium has an atomic mass approximately twice that of ordinary hydrogen. Does H_2 or HD have the greater zero-point energy? How does this affect the binding energies of the two molecules?
- Can a molecule have zero vibrational energy? Zero rotational energy?
- The force constant of the $^1\text{H}^{19}\text{F}$ molecule is approximately 966 N/m. (a) Find the frequency of vibration of the molecule. (b) The bond length in $^1\text{H}^{19}\text{F}$ is approximately 0.92 nm. Plot the potential energy of this molecule versus internuclear distance in the vicinity of 0.92 nm and show the vibrational energy levels as in Fig. 8.20.
- Assume that the H_2 molecule behaves exactly like a harmonic oscillator with a force constant of 573 N/m. (a) Find the energy (in eV) of its ground and first excited vibrational states. (b) Find the vibrational quantum number that approximately corresponds to its 4.5-eV dissociation energy.
- The lowest vibrational states of the $^{23}\text{Na}^{35}\text{Cl}$ molecule are 0.063 eV apart. Find the approximate force constant of this molecule.
- Find the amplitude of the ground-state vibrations of the CO molecule. What percentage of the bond length is this? Assume the molecule vibrates like a harmonic oscillator.
- The bond between the hydrogen and chlorine atoms in a $^1\text{H}^{35}\text{Cl}$ molecule has a force constant of 516 N/m. Is it likely that an HCl molecule will be vibrating in its first excited vibrational state at room temperature?

*Atomic masses are given in the Appendix.

22. The observed molar specific heat of hydrogen gas at constant volume is plotted in Fig. 8.26 versus absolute temperature. (The temperature scale is logarithmic.) Since each degree of freedom (that is, each mode of energy possession) in a gas molecule contributes ~ 1 kcal/kmol · K to the specific heat of the gas, this curve is interpreted as indicating that only translational motion, with three degrees of freedom, is possible for hydrogen molecules at very low temperatures. At higher temperatures the specific heat rises to ~ 5 kcal/kmol · K, indicating that two more degrees of freedom are available, and at still higher temperatures the specific heat is ~ 7 kcal/kmol · K, indicating two further degrees of freedom. The additional pairs of degrees of freedom represent respectively rotation, which can take place about two independent axes perpendicular to the axis of symmetry of the H₂ molecule, and vibration, in which the two degrees of freedom correspond to the kinetic and potential modes of energy possession by the molecule. (a) Verify this interpretation of Fig. 8.26 by calculating the temperatures at which kT is equal to the minimum rotational energy and to the minimum vibrational energy an H₂ molecule can have. Assume that the force constant of the bond in H₂ is 573 N/m and that the H atoms are 7.42×10^{-11} m apart. (At these temperatures, approximately half the molecules are rotating or vibrating, respec-

tively, though in each case some are in higher states than $J = 1$ or $v = 1$.) (b) To justify considering only two degrees of rotational freedom in the H₂ molecule, calculate the temperature at which kT is equal to the minimum nonzero rotational energy an H₂ molecule can have for rotation about its axis of symmetry. (c) How many vibrations does an H₂ molecule with $J = 1$ and $v = 1$ make per rotation?

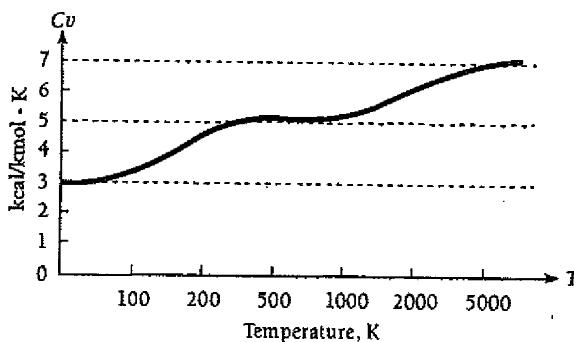


Figure 8.26 Molar specific heat of hydrogen at constant volume.