

Chapter Eight: Molecular Physics

8.1 Types of bonding

8.1.1 Hydrogen bond

A *hydrogen bond* is the attractive interaction of a hydrogen atom with an electronegative atom, like nitrogen, oxygen or fluorine (thus the name "hydrogen bond", which must not be confused with (a covalent bond to hydrogen). The hydrogen must be covalently bonded to another electronegative atom to create the bond. These bonds can occur between molecules (intermolecularly), or within different parts of a single molecule (intramolecularly). The hydrogen bond is stronger than a van der Waals interaction, but weaker than covalent or ionic bonds. This type of bond occurs in both inorganic molecules such as water and organic molecules such as DNA.

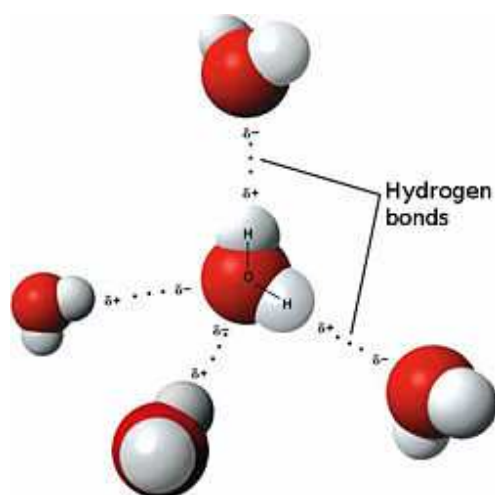


Fig. 8.1 Model of hydrogen bonds between molecules of water

8.1.2 Covalent bond

A covalent bond is a form of chemical bonding that is characterized by the sharing of pairs of electrons between atoms, and other covalent bonds. In short, the attraction-to-repulsion stability that forms between atoms when they share electrons is known as covalent bonding.

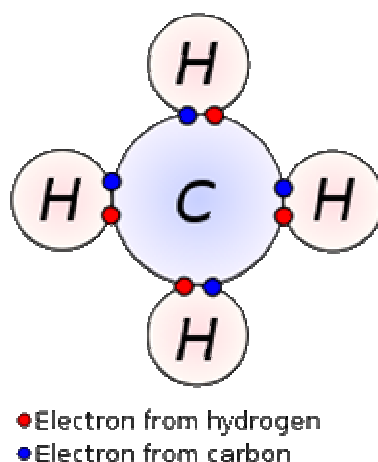


Fig. 8.2: Early concepts in covalent bonding arose from this kind of image of the molecule of methane. Covalent bonding is implied in the Lewis structure that indicates sharing of electrons between atoms.

8.1.3 Ionic bond

An ionic bond is a type of chemical bond that involves a metal and a nonmetal ion (or polyatomic ions such as ammonium) through electrostatic attraction. In short, it is a bond formed by the attraction between two oppositely charged ions.

The metal donates one or more electrons, forming a positively charged ion or cation with a stable electron configuration. These electrons then enter the non metal, causing it to form a negatively charged ion or anion which also has a stable electron configuration. The electrostatic attraction between the oppositely charged ions causes them to come together and form a bond.

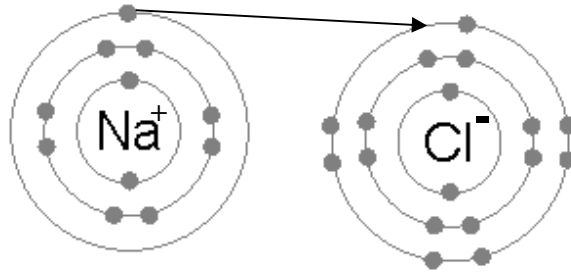


Fig. 8.3: Sodium and chlorine bonding ionically to form sodium chloride. Sodium loses its outer electron to give it a noble gas electron configuration, and this electron enters the chlorine atom exothermically. The oppositely charged ions are then attracted to each other, and their bonding releases energy. The net transfer of energy is that energy leaves the atoms, so the reaction is able to take place.

8.2 Molecular Spectra

8.2.1 Molecular Energies

We can picture a molecule as an assembly of small almost point masses-the nuclei of its component atoms, linked together by almost massless springs-the bonding electrons (Fig 8.5). In this model, the total energy of a molecule, $E_{molecule}$, can be viewed as the sum of its electronic energy, $E_{electronic}$, its vibrational energy, $E_{vibration}$ and its rotational energy, $E_{rotation}$:

$$E_{molecule} = E_{electronic} + E_{vibration} + E_{rotation}$$

The vibrational and rotational energies are both related to the motion of the nuclei of the molecule's constituent atoms.



Fig. 8.5: A diatomic molecule pictured as two spherical masses linked by a massless spring.

Like its electronic energy, a molecule's vibrational and rotational energies are also quantized, i.e., they can only take certain discrete values. Thus, every molecule has a characteristic set of vibrational energy levels and rotational energy levels. Typical values for the differences, ΔE_{elec} , ΔE_{vib} and ΔE_{rot} , between adjacent electronic, vibrational and rotational energy levels are, respectively:

$$\Delta E_{elec} = 1 - 10 \text{ eV}$$

$$\Delta E_{vib} \approx 10^{-1} \text{ eV}$$

$$\Delta E_{rot} \approx 10^{-4} \text{ eV}$$

8.2.2 Rotational Spectra

Fig. 8.6, shows a typical rotational absorption spectrum, that of gaseous hydrogen chloride, $\text{HCl}_{(g)}$. The spectrum exhibits two principle characteristics:

1. It comprises many lines, all of comparable intensity.
2. The absorption lines are equally spaced along the frequency axis.

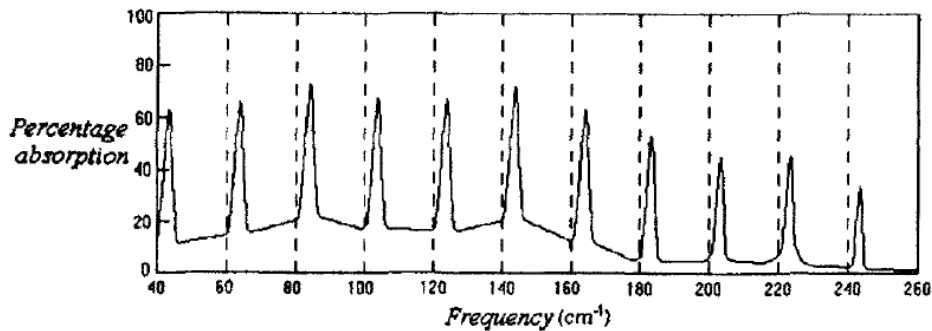


Fig. 8.6 : Rotational absorption spectrum of $\text{HCl}_{(g)}$, The horizontal frequency axis is scaled in units of the wave number, $1/\lambda$, where λ is the radiation's wavelength in centimeters ($1\text{cm}^{-1} = 3.10^{10} \text{ Hz}$).

By analogy with the expression $K = \frac{P^2}{2m}$, that relates an object's kinetic energy, K , to its linear momentum, p , and the rotational energy, E_{rot} , of a diatomic molecule, such as that pictured schematically in Fig. 8.7, revolving around an axis through its centre of mass is given by:

$$E_{rot} = \frac{L^2}{2I} \quad (8.1)$$

where L is the molecule's angular momentum and I is its moment of inertia about this axis,

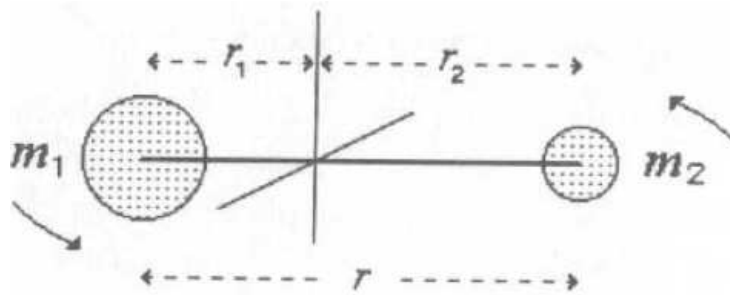


Fig. 8.7: Schematic representation of a diatomic molecule such as HCl rotating around an axis through its centre of mass.

The rotational energy eigenvalues of the molecule emerge from the quantization of its angular momentum. The square, L^2 , of the magnitude of the molecule's angular momentum obeys the quantization condition:

$$L^2 = J(J+1)\hbar^2 \quad (8.2)$$

where the rotational quantum number J can take the values $J = 0, 1, 2, 3, \dots$. Substituting the allowed values of L^2 in equation (8.1) gives for the rotational energy eigenvalues (the rotational energy levels):

$$E_{rot} = \frac{J(J+1)\hbar^2}{2I} = J(J+1)Bh \quad (8.3)$$

where the constant B is defined by

$$B = \frac{h}{8\pi^2 I} \quad (8.4)$$

The difference, ΔE_{rot} , between two adjacent rotational energy levels, the J level and the $J+1$ level, is:

$$\begin{aligned} \Delta E_{rot} &= [(J+1)(J+2) - J(J+1)]Bh \\ &= 2Bh(J+1) \end{aligned} \quad (8.5)$$

It follows, that the difference, ΔE_{rot} , increases by an amount $2Bh$ with each unit increase in the quantum number J , i.e., the differences between adjacent rotational energy levels increase linearly with the quantum number J .

The selection rule for radiative rotational transitions is $\Delta J = \pm 1$. Hence, the frequencies, ν of the photons associated with such transitions will be:

$$\nu = \frac{\Delta E_{rot}}{h} = 2B(J+1) \quad (8.6)$$

and the difference, $\Delta\nu$, between the frequencies of successive spectral lines a constant:

$$\Delta\nu = 2B \quad (8.7)$$

Example 8.1: The Interatomic Distance in the HCl Molecule

The spacing, $\Delta(1/\lambda)$, between the lines in the rotational spectrum of $\text{HCl}_{(g)}$ is 20cm^{-1} . Calculate the distance between the nuclei (the length of the bond) in the HCl molecule.

Calculation: The moment of inertia, I , relative to its centre of mass, of a diatomic molecule can be calculated (i) from its rotational absorption spectrum and (ii) from mechanics.

The interatomic distance can be computed by equating the mathematical expressions for the two methods.

(i) Combining equations (8.4) and (8.7) gives the following expression for the molecule's moment of inertia, I , relative to its centre of mass:

$$I = \frac{h}{4\pi^2 \Delta\nu} \quad (8.8)$$

In terms of the frequency, the spacing, $\Delta\nu$, between the spectral lines is

$$\begin{aligned} \Delta\nu &= \Delta(1/\lambda) \cdot c \\ &= 20 \times 10^2 \cdot 3 \times 10^8 \\ &= 6 \times 10^{11} \text{ Hz} \end{aligned}$$

Substituting this value in equation (8.8) gives:

$$I = \frac{6.62 \times 10^{-34}}{4\pi^2 \cdot 6 \times 10^{11}} = 2.8 \times 10^{-47} \text{ kg.m}^2$$

(ii) The moment of inertia, I , relative to its centre of mass, of a dumbbell, comprising two masses, m_1 and m_2 , at a distance r from one another is:

$$I = m' r^2 \quad (8.9)$$

where m' , the molecule's reduced mass, is given by

$$m' = \frac{m_1 m_2}{m_1 + m_2}$$

In the case of the HCl molecule:

$$\begin{aligned} m_1 &= m_{\text{H}} = 1.66 \times 10^{-27} \text{ kg} \\ m_2 &= m_{\text{Cl}} = 35 \cdot 1.66 \times 10^{-27} \text{ kg} \end{aligned}$$

Hence,

$$m' = \frac{1 \cdot 35}{1 + 35} \cdot 1.66 \times 10^{-27} \text{ kg}$$

$$= 1.61 \times 10^{-27} \text{ kg}$$

Substituting the value of the reduced mass, m' , and that of the moment of inertia, I , obtained from the rotational spectrum in equation (4.31) gives for the bond length, r ,

$$r = \sqrt{\frac{I}{m'}} = \sqrt{\frac{2.8 \times 10^{-47}}{1.61 \times 10^{-27}}} = 1.3 \times 10^{-10} \text{ m} = 1.3 \text{ \AA}$$

8.2.3 Vibrational Spectra

The diatomic molecules can vibrate in just one mode, to and fro along the axis joining their atomic centers, polyatomic molecules comprising (n) atoms have ($3n - 6$) vibrational modes. If the molecule is also linear it has one more mode, i.e., ($3n - 5$) modes altogether (Fig. 8.8).

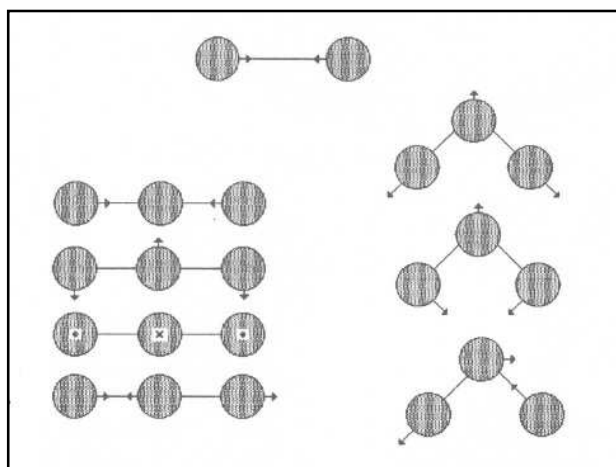


Fig. 8.8: The vibrational modes of a diatomic and triatomic molecule.

At low energies, the vibrations of a diatomic molecule can be described in terms of a harmonic oscillator. According to Planck's quantum hypothesis, the energy, E , of a harmonic oscillator of natural frequency ν_0 can only take the values $E = nh\nu_0$ where $n = 0, 1, 2, 3 \dots$. This implies that in its ground state,

$n = 0$, the energy of the oscillator should equal zero and that the oscillator should be completely at rest. However, this would contravene the Heisenberg Uncertainty Principle; complete rest implies no uncertainty whatsoever as to the system's position and linear momentum.

The correct expression for the energy, E_{vib} , of the oscillator is obtained from quantum mechanics. The potential energy, U , of a simple harmonic oscillator is given by:

$$U = k \frac{x^2}{2} \quad (8.10)$$

where k is the oscillator (spring) constant. Substituting this expression for the potential energy in the one-dimensional time independent Schrödinger equation gives:

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2m'}{\eta^2} \left(E_{vib} - \frac{kx^2}{2} \right) \psi = 0 \quad (8.11)$$

The energy eigenvalues given by the solution to this equation are

$$E_{vib} = \left(n + \frac{1}{2} \right) h \nu_o \quad (8.12)$$

where the oscillator's natural frequency, ν_o , is given by

$$\nu_o = \frac{1}{2\pi} \sqrt{\frac{k}{m'}} \quad (8.13)$$

The integer n is called the vibrational quantum number and can take the values $n = 0, 1, 2, 3 \dots$. Thus, in its ground state, $n = 0$, the oscillator has a 'zero-point' energy of $h \nu_o / 2$ and so is never completely at rest.

At low energies, where the diatomic molecule can be regarded as a harmonic oscillator, the vibrational energy levels are equally spaced. However, at higher

energies, i.e., higher vibrational quantum numbers, the oscillator becomes anharmonic as is shown in Fig. 8.9 and the energy levels close up. As the energy increases, so does the amplitude of the vibrations. At the energy corresponding to the quantum number, n_c , the bond linking the atoms breaks. In practice, the vibrational spectra of diatomic molecules are very simple, usually comprising just a single strong line called the fundamental line. There are two reasons for this:

1. The selection rule for radiative vibrational transitions is $\Delta n = \pm 1$. It follows, from equation (8.12) that only photons of frequency ν_0 will be absorbed or emitted in transitions between low energy vibrational states.
2. A typical value for the difference between two adjacent vibrational energy levels is $\Delta E_{vib} = 0.5\text{eV}$.

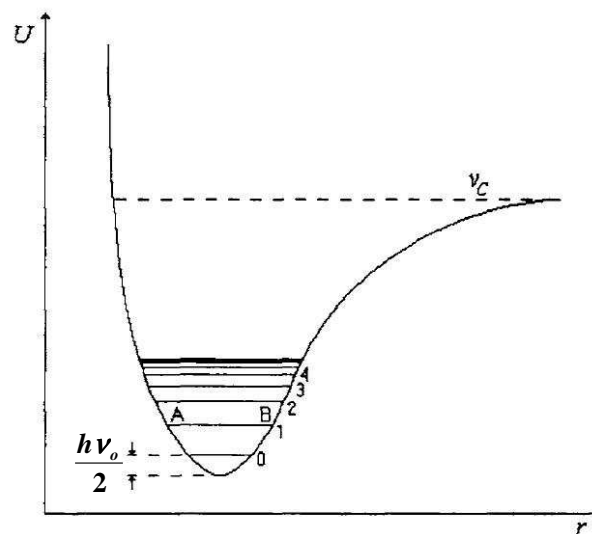


Fig. 8.9: The potential energy, U , of a diatomic molecule as a function of the interatomic distance r . The horizontal line represents the vibrational energy levels, E_{vib} , of the molecule. At low energies the curve is parabolic, consistent with the harmonic oscillator.

At low resolution, the fundamental line appears as a broad band. This is because the transitions between the vibrational states are accompanied by

transitions between rotational states (Fig 8.10). In these transitions, photons with energies in the range $E_{\text{photon}} = \Delta E_{\text{vib}} + \Delta E_{\text{rot}}$ where ΔE_{rot} is the energy involved in these rotational transitions, are absorbed or emitted by the molecule. This range of photon energies shows up as a broadening of the fundamental line.

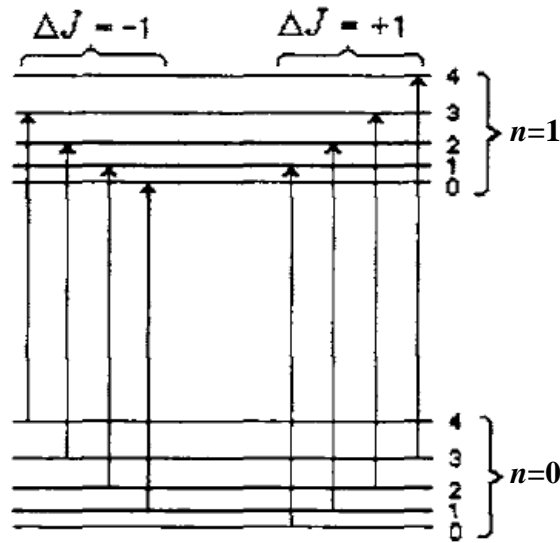


Fig. 8.10: Vibrational-rotational radiative transitions in a diatomic molecule. The transitions obey the selection rules $\Delta n = \pm 1$ and $\Delta J = \pm 1$.

Example 8.2: Vibrational Spectrum of CO

An intense line of wave number 2144cm^{-1} appears in the infra-red spectrum of carbon monoxide gas, $\text{CO}_{(g)}$. Calculate:

- the period of the molecule's vibrations,
- the force constant of the molecule's bond;
- the zero-point energy per mole of carbon monoxide.

Calculation:

a) The period, T , of the molecule's vibrations is inversely proportional to the frequency, ν_0 , of its vibrations, i.e.,

$$T = \frac{1}{\nu_0} = \frac{1}{2144 \times 10^2 \cdot 3 \times 10^8} = 1.55 \times 10^{-14} \text{ s}$$

b) From equation (8.13), the force constant, k , of the bond in a diatomic molecule is given by:

$$k = 4\pi^2 m' \nu_o^2$$

$$\ominus m' = \frac{m_1 * m_2}{m_1 + m_2} = \frac{12 \cdot 16}{12 + 16} \times 1.66 \times 10^{-27} = 1.14 \times 10^{-26} \text{ kg}$$

$$\therefore k = 4\pi^2 \cdot 1.14 \times 10^{-26} \cdot \left(\frac{1}{1.55 \times 10^{-14}} \right)^2 = 1862 \text{ N.m}^{-1}$$

c) In its ground state, $n = 0$, an oscillator has a zero-point energy of $E_o = \frac{h \nu_o}{2}$.

The zero-point energy of a mole of carbon monoxide molecules is therefore

$$E_o = \frac{6.63 \times 10^{-34} \cdot \left(\frac{10^{14}}{1.55} \right)}{2} \cdot 6.02 \times 10^{23} = 1.28 \times 10^4 \text{ J/mol}$$

8.2.4 Electronic Spectra

Transitions between molecular electronic levels ($\Delta E_{elec} = 1-10 \text{ eV}$) are usually accompanied by transitions between the molecule's vibrational and rotational levels. Accordingly, the frequencies of the photons emitted and absorbed in such transitions are given by:

$$\nu = \frac{\Delta E_{elec} + \Delta E_{vib} + \Delta E_{rot}}{h}$$

These frequencies are in the visible and the near ultra-violet. Transitions between electronic states appear as a spectral band. At higher resolutions these bands are seen to comprise closely packed lines corresponding to the various upper and lower vibrational and rotational levels.

8.2.5 Raman Spectra

In 1928, *Raman* discovered that the light scattered by molecules contains frequencies other than those of the incident radiation; the phenomenon is

called *Raman scattering*. The source of the additional frequencies is in the internal structure of the scattering particles. Molecules both vibrate and rotate, and these motions can add to the vibrations induced by the electric field in the incident radiation. The phenomenon is best understood in terms of photons.

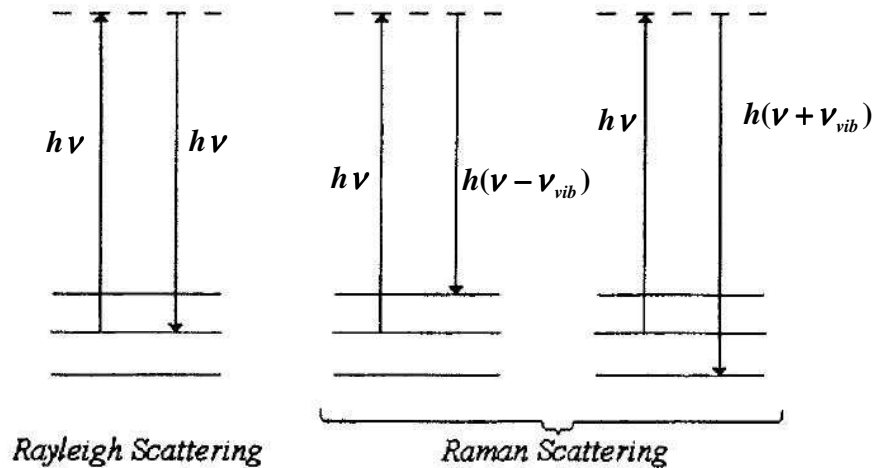


Fig. 8.11: Raman and Rayleigh scattering interpreted in terms of the absorption and emission of photons. In Rayleigh scattering the photon emitted is identical to that absorbed. In Raman scattering the emitted photon can have a slightly higher or lower energy than that of the incident photon.

As a first possibility, a photon of energy $h\nu$ striking a molecule will be scattered without any change in its energy (frequency). The molecule rises to a higher energy state from which it returns at once to its ground state by emitting an identical photon.

This is the mechanism of the normal *Rayleigh scattering*. A second possibility is that the excited molecule emits a photon of lower energy (frequency) than that which struck it, using the surplus to enhance the energy of its vibrations and rotations. In this case, the energy of the emitted photon is $h(\nu - \nu_{vib})$ and the increase in the molecule's vibrational and/or rotational energy is $h\nu_{vib}$ (see Fig. 8.11).

In rare instances, the incident photon will strike a molecule whose vibrational and/or rotational energy has already been enhanced. In this case, the molecule can emit a photon of energy $h(\nu + \nu_{vib})$. Thus, the scattered radiation can contain frequencies that are both slightly higher, $\nu + \nu_{vib}$, and slightly lower, $\nu - \nu_{vib}$, than that of the incident radiation.

Raman scattering is employed in the elucidation of molecular structures. For example, the molecule N_2O has two possible configurations: NON and NNO. The first configuration is symmetrical; the second is asymmetrical. This difference in their structures expresses itself as a difference in their vibrational modes. The Raman scattering of N_2O corresponds to vibrations of the asymmetrical configuration and thus the molecule's structure was determined.