

Infrared Spectroscopy

Infrared Spectroscopy is one of the most powerful analytical techniques which offers the possibility of chemical identification. This technique when coupled with intensity measurements may be used for quantitative analysis.

This technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region. After absorption of IR radiations, the molecules of a chemical substance vibrate at many rates of vibration giving rise to close-packed absorption bands called an IR absorption spectrum which may extend over a wide wavelength range.

Various bands will present in IR absorption spectrum which will correspond to the characteristic functional groups and bonds present in a chemical substance. Thus an IR spectrum of a chemical substance is a fingerprint for its identification.

~~Atomic vibrating rotator~~

Vibrational study of diatomic molecule Harmonic oscillator

Let us consider a diatomic molecule associated with a dipole moment.

The vibratory motion of the nuclei of diatomic molecule may be similar to the vibration of linear harmonic oscillator. In linear harmonic oscillator, the force tending to restore an atom to its original state is proportional to the displacement of the vibratory atom from the original position (Hooke's law). Suppose the bond between the two nuclei of a diatomic molecule is distorted from its equilibrium length r_e to a new length r . Then the restoring forces on each atom of the diatomic molecule, given by

$$m_1 \frac{d^2 r_1}{dt^2} = -k(r - r_e) \quad \text{--- (1)}$$

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

where k is the proportionality constant known as force constant; it is regarded as a measure of the stiffness of the bond.

r_1, r_2 are the positions of the atoms 1 and 2 relative to the centre of gravity of the molecule.

$$r_1 = \frac{m_2}{m_1 + m_2} r \quad \text{--- (3)}$$

$$r_2 = \frac{m_1}{m_1 + m_2} r \quad \text{--- (4)}$$

m_1, m_2 are the mass of the two atoms

substituting the value of r_1 eq 3 in eq 1

$$\frac{m_1 m_2}{(m_1 + m_2)} \frac{d^2 r}{dt^2} = -k(r - r_e) \quad \text{--- (5)}$$

As r_e is a const

$$\frac{d^2 r}{dt^2} = \frac{d^2 (r - r_e)}{dt^2} \quad \text{--- (6)}$$

substituting eqn (6) in (5)

$$\left(\frac{m_1 m_2}{m_1 + m_2} \right) \frac{d^2 (r - r_e)}{dt^2} = -k(r - r_e) \quad \text{--- (7)}$$

put $r - r_e = x$ and $\frac{m_1 m_2}{m_1 + m_2} = \mu$ --- (8)

substituting eqn (8) in eqn (7)

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

$$\frac{d^2 x}{dt^2} + \frac{k}{\mu} x = 0 \quad \text{--- (9)}$$

$$\frac{d^2x}{dt^2} + \omega^2 x = 0 \text{ when}$$

$$\omega^2 = \frac{k}{\mu} \text{ or } \omega = \sqrt{\frac{k}{\mu}}$$

Equation (10) is the expression of a simple harmonic motion with frequency of vibration (v) as follows

$$\nu = \frac{\omega}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$$\therefore c = \nu \lambda$$

$$\frac{1}{\lambda} = \frac{\nu}{c}$$

$$\bar{\nu} = \frac{1}{\lambda c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1}$$

ω energy in cm^{-1}
 ω energy in cm^{-1}

Energy levels

Vibrational energies, E_v , like all other energies for any vibrational system may be evaluated from Schrodinger's equation. The eigen values for the energy of a linear harmonic oscillator are of the type

$$E_v = (v + \frac{1}{2}) h c \bar{\omega}$$

$$E = h \nu$$

$$E = h c \bar{\nu}$$

$$\frac{E}{h c} = \bar{\nu}$$

$$= \bar{\nu}$$

v is the vibrational quantum no. It can have values 0, 1, 2, ...

$\bar{\omega}$ is the frequency of the oscillator expressed in wave numbers.

Spectrum (derivation)

Suppose a transition occurs from an upper vibrational level v' to lower

vibrational level v'' the change in vibrational energy

$$\Delta E_v = (v' - v'') h c \bar{\omega}$$

The frequency of transition in wave numbers, accompanying the vibrational transition

$$\nu_v = \frac{(v' - v'') h c \bar{\omega}}{h c}$$

$$\lambda_v = (v' - v'') \bar{\omega} \quad \text{--- (11)}$$

Suppose a transition occurs between $v' = 1$ and $v'' = 0$

$$\text{Then } (\Delta E)_{1,0} = E_1' - E_0''$$

$$= (1 + 1/2) h c \bar{\omega} - (0 + 1/2) h c \bar{\omega}$$

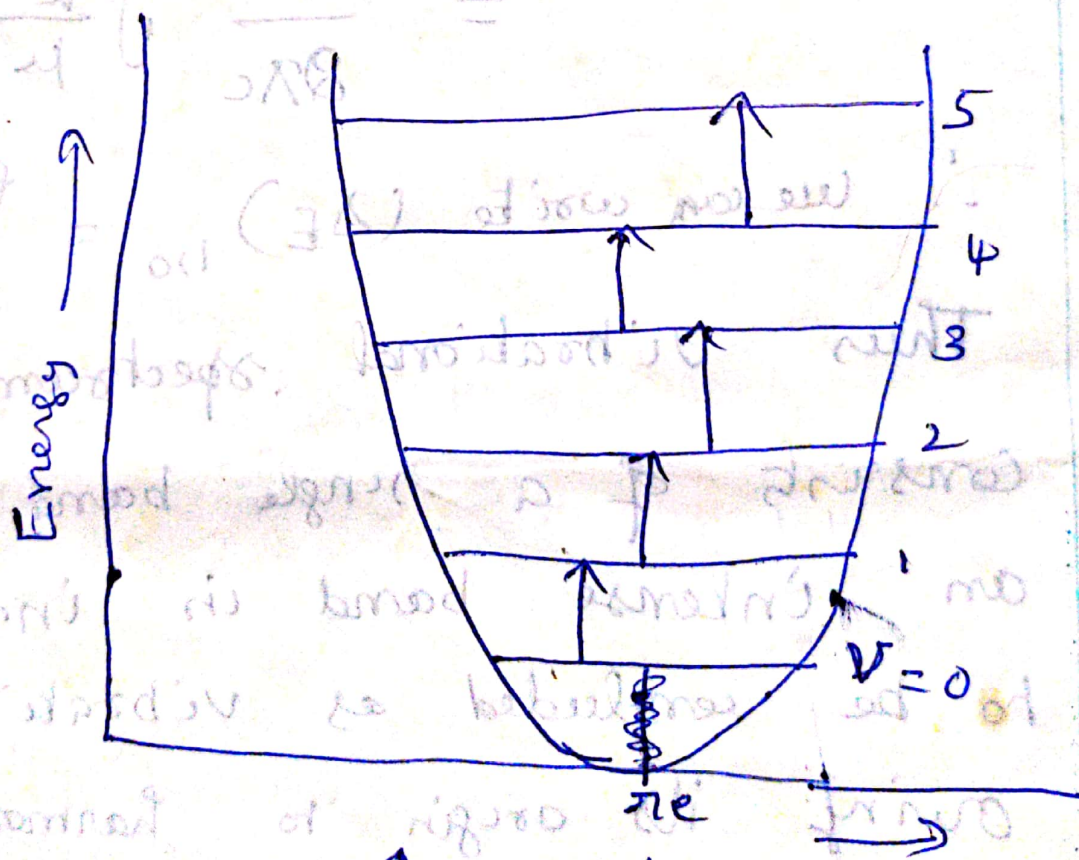
$$= h c \bar{\omega}$$

Then frequency of the radiated light is equal to the frequency of the oscillator.

$\Delta v = +1$ — applied to the absorption spectra

$\Delta v = -1$ applies to emission spectra

fig The allowed vibrational energy levels and transitions between them for a diatomic molecule undergoing simple harmonic motion



Inter-nuclear distance

$v=0 \rightarrow E = \frac{1}{2} \omega$, $v=1 \rightarrow E = \frac{3}{2} \omega$

The Anharmonic Oscillator

Real molecules do not obey the laws of simple harmonic motion. If the bond between the atom is stretched, ~~at~~ at a particular point the bond will break and the molecule dissociate into atoms. Now the shape of the energy curve changes. It is not a parabolic as in the case of simple harmonic one. In diatomic molecule the actual potential energy curve is not a parabola and is shown in fig.

A purely empirical expression which fits this curve to a good approximation was derived by P. M. Morse and is called the Morse function.

$$\rightarrow U(r) = D_e \left[1 - \exp\{a(r_{eq} - r)\} \right]^2 \quad (1)$$

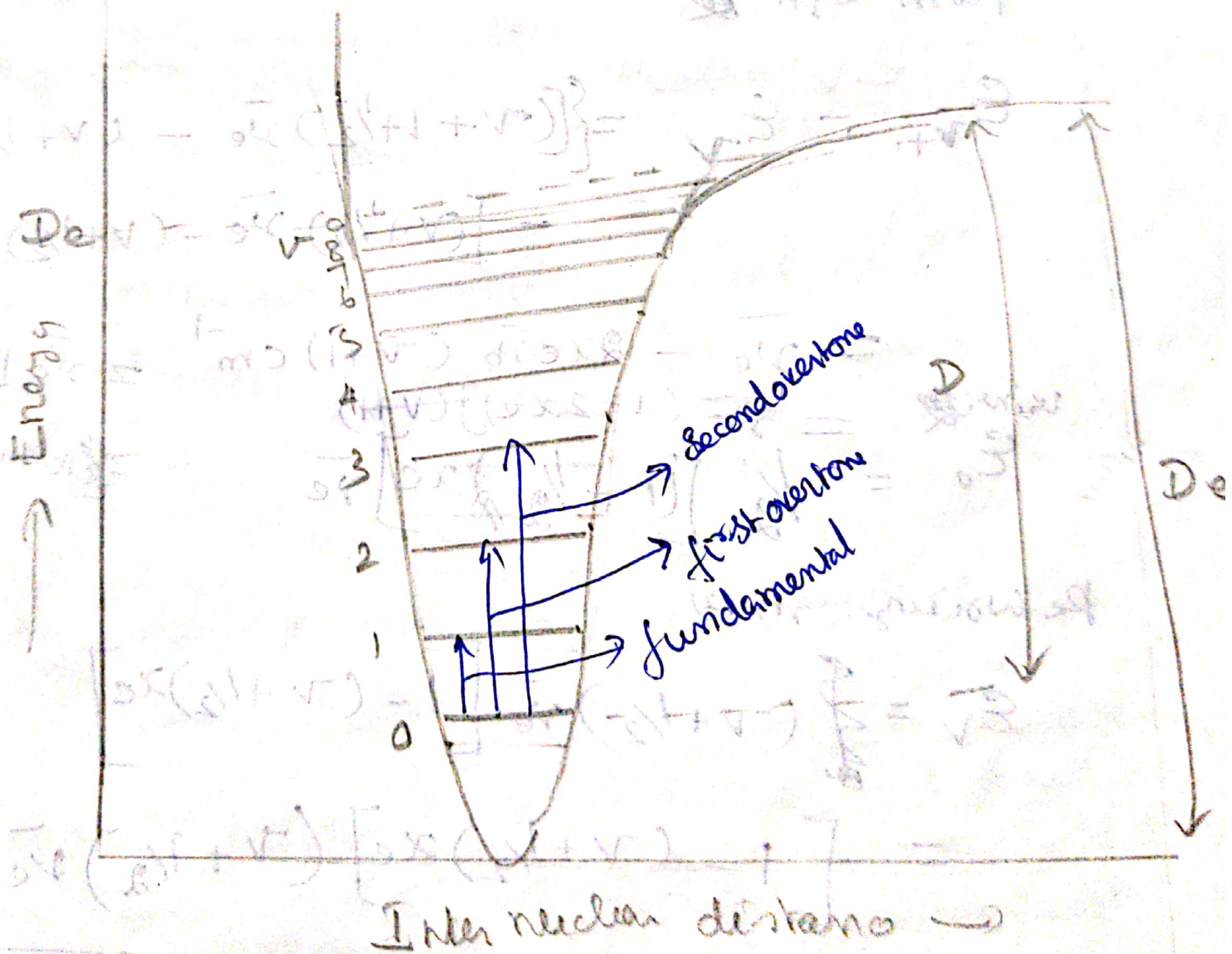
r - internuclear distance
 a - constant for a particular molecule

D_e - dissociation energy for a particular molecule

r_{eq} - the value of internuclear distance which corresponds to a minimum of Morse curve
 The potential energy function - $U(r)$.

Fig (2) shows the shape of the function wherein one atom is fixed at $r=0$ while other oscillates between the two branches of Morse curve.

Fig: The Morse curve and the energy levels of a diatomic molecule.



Using Schrodinger eqn the allowed vibrational energy for an anharmonic oscillator is given by

$$E_v = (v + 1/2) \bar{\nu}_e - (v + 1/2)^2 x_e \bar{\nu}_e + (v + 1/2)^3 y_e \bar{\nu}_e + \dots$$

$$v = 0, 1, 2, 3$$

$\bar{\nu}_e = \bar{\nu}_{eq}$ is equilibrium frequency of the anharmonic system x_e and y_e

are anharmonicity constants.

x_e is small

Retaining the first anharmonic term

$$E_v = (v + 1/2) \bar{\nu}_e - (v + 1/2)^2 x_e \bar{\nu}_e \text{ cm}^{-1}$$

$$v = 0, 1, 2, \dots \quad (2)$$

x_e is small and positive, the effect of anharmonicity is to crowd more closely the vibration levels. As v increases, the energy levels are more ~~close~~ nearer.

$$\left[-\frac{v^2}{4} + \frac{bv}{2} + v + \frac{1}{4} + \frac{bv}{2} \right] x_e \bar{\nu}_e$$

The selection rule for anharmonic oscillators:

$$\Delta v = \pm 1, \pm 2, \pm 3$$

The frequencies of first few transitions are

$$\bar{\nu}_{0 \rightarrow 1} = \left\{ (1 + \frac{1}{2}) \bar{\nu}_e - (1 + \frac{1}{2})^2 x_e \bar{\nu}_e \right\} - \left\{ \frac{1}{2} \bar{\nu}_e - \frac{1}{4} x_e \bar{\nu}_e \right\}$$

$$= \bar{\nu}_e (1 - 2x_e) \text{ cm}^{-1} \quad \text{--- (5)}$$

This is called the fundamental band i.e. transition from $v=1$ to $v=0$

$$\bar{\nu}_{0 \rightarrow 2} = \left\{ (2 + \frac{1}{2}) \bar{\nu}_e - (2 + \frac{1}{2})^2 x_e \bar{\nu}_e \right\} - \left\{ \frac{1}{2} \bar{\nu}_e - \frac{1}{4} x_e \bar{\nu}_e \right\}$$

$$= 2 \bar{\nu}_e (1 - 3x_e) \text{ cm}^{-1} \quad \text{--- (6)}$$

The first overtone band $v=2$ to $v=0$

The second overtone band $v=3$ to $v=0$

$$\bar{\nu}_{0 \rightarrow 3} = \left\{ (3 + \frac{1}{2}) \bar{\nu}_e - (3 + \frac{1}{2})^2 x_e \bar{\nu}_e \right\} - \left\{ \frac{1}{2} \bar{\nu}_e - \frac{1}{4} x_e \bar{\nu}_e \right\}$$

$$= 3 \bar{\nu}_e (1 - 4x_e) \text{ cm}^{-1} \quad \text{--- (7)}$$

$\bar{\nu}_e$ is called the fundamental absorption

$2\bar{\nu}_e$ and $3\bar{\nu}_e$ are first and second overtones respectively. As the frequencies of the first and second overtone bands are 2 to 3 times the frequency of the fundamental they appear in the region of shorter wavelengths as compared to the fundamental band.

Diatomic Vibrating rotor - Diatomic molecule as a rigid rotor and harmonic oscillator

In the energies of vibrational and rotational motions differ considerably, a diatomic molecule can execute both vibrations and rotations independently. The total energy

$$E_{\text{Total}} = E_{\text{rot}} + E_{\text{vib}} \quad \text{--- (1)}$$

E_{rot} - rotational energy

E_{vib} - vibrational energy

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) \text{ Joules} \quad \text{--- (2)}$$

$J = 0, 1, 2, \dots$, J - rotational q. no

$$E_v = (v + \frac{1}{2}) h\nu \text{ where } v = 0, 1, 2 \quad \text{--- (3)}$$

ν - frequency of vibrating rotor
 v - vibrational quantum number

$$E_{J,v} = \frac{h^2}{8\pi^2 I} J(J+1) + (v + \frac{1}{2}) h\nu \quad \text{--- (4)}$$

$$E_{J,v} = B J(J+1) + (v + \frac{1}{2}) h\nu$$

Selection rule $\Delta J = \pm 1$

$$\Delta v = +1, \quad \Delta J = \pm 1$$

$$\nu = \frac{E_{J',v'} - E_{J'',v''}}{h} \quad (J' + J'')(J' - J'' + 1)$$

$$= \frac{E_{J',v'} - E_{J'',v''}}{h}$$

$$= (v' - v'') \omega + B [J'(J'+1) - J''(J''+1)]$$

$$= (v' - v'') \omega + B (J'^2 + J' - J''^2 - J'')$$

$$= (v' - v'') \omega + B (J' - J'')(J' + J'' + 1) \quad \text{--- (5)}$$

Consider the $0 \rightarrow 1$ trans. $v''=0, v'=1$

$$\nu = \omega + (J' - J'')(J' + J'' + 1) \quad \text{--- (5)}$$

The frequency of the emitted spectral lines depends on the value of J' and J'' .

R-branch

$$\Delta J = +1$$

$$J' - J'' = 1$$

$$J' = J'' + 1$$

Sub in eqn (5)

$$\begin{aligned}
 \nu &= \omega + B(1)(J''+1 + J''+1) \\
 &= \omega + B(2J''+2) \\
 &= \omega + 2B(J''+1) \text{ cm}^{-1} \quad \text{--- (6)}
 \end{aligned}$$

when $J'' = 0, 1, 2, \dots$

P-branch

$$\Delta J = -1, \quad J' - J'' = -1, \quad J'' = J' + 1$$

1st in eqn (5)

$$\begin{aligned}
 \nu &= \omega + B(-1)(J'+1 + J'+1) \\
 &= \omega - 2B(J'+1) \text{ cm}^{-1} \quad \text{--- (7)}
 \end{aligned}$$

when $J' = 0, 1, 2, \dots$

$$\nu = \omega \pm 2Bm \quad \text{--- (8)} \quad \text{when } m = \pm 1, \pm 2, \pm 3, \dots$$

when $m = J'' + 1$ in eq (6)

$m = J' + 1$ in eq (7)

Since $m \neq 0$

It consists of equally spaced lines (spacing $2B$) on each side of the band w

$$\text{If } \nu' - \nu'' = 1, \quad J' - J'' = 0$$

$$\nu = \omega \quad \text{--- (9)}$$

According to eqn (9)

Frequency of the vibrating rotator is equal to the frequency of the spectral lines

According to eqn (8) the theory is in agreement with experimental results. So we cannot consider a diatomic molecule as a rigid vibrating rotator. We should consider a non-rigid rotator and anharmonic oscillator.

response in intensity. When operating in the restricted range, usually limited to the visible region, it can be broadened by drastic cooling.

3.9. Single Beam and Double Beam Spectrophotometers

A diagram of the optical system of a single-beam infrared spectrophotometer is shown in Fig. 3.12.

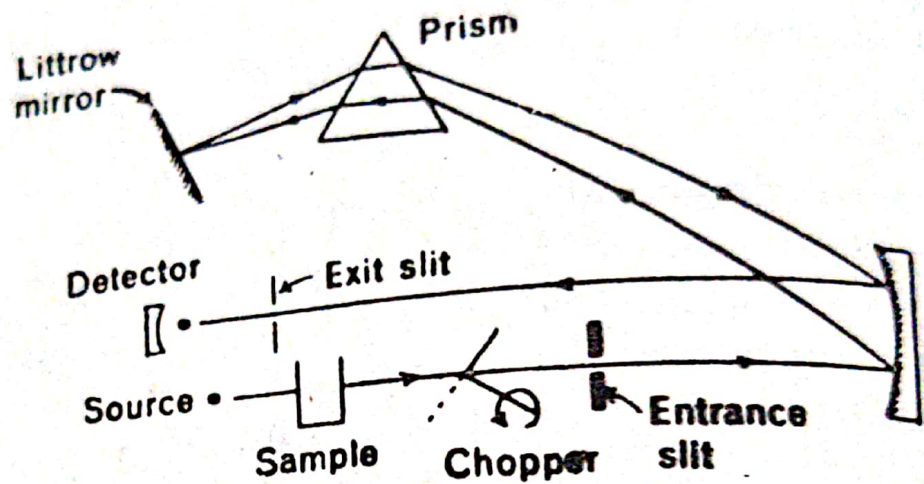


Fig. 3.12 Schematic diagram showing the optical path in a single beam infrared spectrophotometer.

In the single-beam system, the radiation is emitted by the source, passes through the sample and then through a fixed prism and a Littrow mirror. Both prism and Littrow mirror select the desired wavelength and then allow it to pass on to the detector. The detector measures the intensity of radiation after it passes through the sample. Knowing the original intensity of radiation, one can measure how much radiation has been absorbed. By measuring the degree of absorption at wavelengths, the absorption spectrum of the sample can be obtained.

Disadvantages : The various disadvantages of a single beam spectrophotometer are as follows :

- (i) This type of instrument has the basic disadvantage that the intensity of the emission of the radiation source varies

point to point in IR absorption spectrum; therefore, the resulting spectrum is considerably deformed. The necessary correction by the continuous variation of slit is cumbersome.

(ii) When the sample is analyzed in solution, the bands of solvent appear in the spectrum. In this case, the spectrum of the sample is obtained by subtracting the spectrum of the solvent from the resultant spectrum, the former must be recorded under identical conditions (thickness of layer, etc.)

In order to overcome the above mentioned difficulties, a double-beam spectrophotometer is used. This is shown in Fig. 3.13.

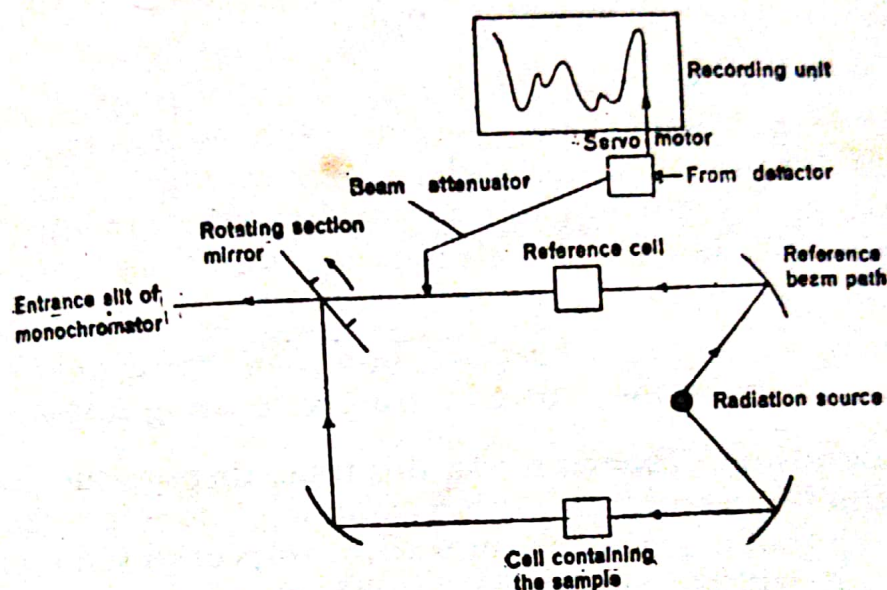


Fig. 3.13. Schematic Diagram of a Double-Beam Infrared Spectrophotometer.

The energy emitted by the radiation source is split by the instrument into two beams, which are energetically and optically identical. One of the beams passes through the sample and the other through the reference sample. The sample is placed in the sample beam and a reference material, such as the solvent used in the sample, is placed in the reference beam. The two half-beams are recombined and pass along the optical path to the detector.

When there is no sample in the reference beam, it arrives at the detector unabsorbed. When there is no sample in the sample cell, the half-beam travelling along the sample beam is not absorbed and is equal to the reference beam. When these two equal half-beams recombine, a steady signal reaches the detector.

When the sample cell contains the sample, the half-beam travelling through it undergoes a decrease in intensity. After the two half-beams are recombined, they produce an oscillating signal which is measured by the detector. The signal from the detector is passed on to the recording unit through a servomotor.

3.10. Modes of Vibrations of Atoms in Polyatomic Molecules

In a polyatomic molecule, each atom is having three degrees of freedom in three directions which are perpendicular to one another. Consequently a polyatomic molecule is requiring three times as many degrees of freedom as the number of its atoms. Thus a molecule of n atoms has $3n$ degrees of freedom. For a non-linear molecule, three of the degrees of freedom describe rotation and three describe translation; the remaining $3n-6$ degrees are vibrational degrees of freedom or fundamental vibrations. In a linear molecule only two degrees of freedom are required to describe rotation. Thus a linear molecule has $3n-5$ vibrational degrees of freedom.

According to the character of vibration, normal vibrations can be divided into two principal groups.

1. Stretching Vibration : In this type of vibrations, the atoms move essentially along the bond axis, so that the bond length increases or decreases periodically, i.e., at regular intervals. As this type of vibrations corresponds to one-dimensional motion, it means that there will be $(n-1)$ stretching vibrations for non-cyclic systems.

During stretching vibrations, bond angles change only if it is required to do so by the centre of gravity resisting displacement.

2. Bending Vibration : In this type, there occurs a change in bond angles between bonds with a common atom or there occurs the movement of a group of atoms with respect to the remainder of the molecule without movement of the atoms in the group with respect to one another. For example, twisting, rocking and torsional belong to this type. In these, there occurs a change in bond angles with reference to a set of coordinates arbitrarily set up within the molecule.

In bending vibrations, *bond lengths* will change only if required to do so by the centre of gravity resisting displacement.

The bending vibrations are also called *deformation vibrations*. As these vibrations are describing two dimensional motions, there will be $2n-5$ bending vibrations for non-cyclic and linear molecules. These appear at lower frequencies, whereas stretching vibrations appear at higher frequencies. The force constants of deformation vibrations are generally less than those of the stretching vibrations. Due to the smaller force constants, the deformation vibrations are more sensitive to environmental influence.

Types of stretching and deformation vibrations : In a polyatomic molecule, the same bond can perform stretching and deformation vibrations simultaneously.

Stretching vibrations are of two types : symmetric and asymmetric. These are denoted by ' ν '. In Fig. 3.14, (a) illustrates the symmetric vibration and (b) the asymmetric stretching vibration.

tion of the AB_2 molecule. In Fig. 3.14, (c) and (d) illustrate the symmetric and antisymmetric vibrations of the AB_3 molecule respectively.

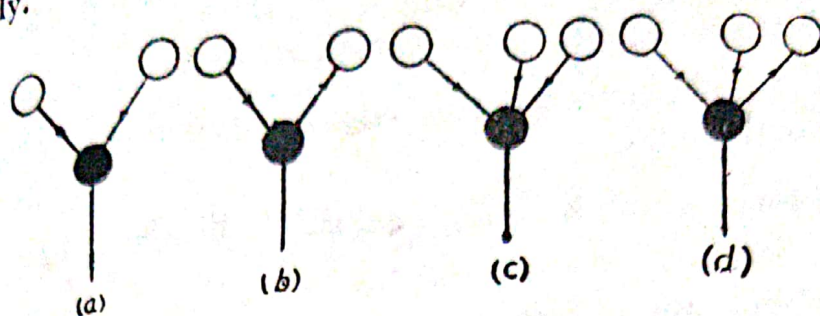


Fig. 3.14. Stretching vibrations.

- a=Symmetric stretching vibration of molecule AB_2
 b=Asymmetric stretching vibration of the AB_2 molecule
 c=Symmetric stretching vibration of molecule AB_3
 d=Asymmetric stretching vibration of the AB_3 molecule

Deformation vibrations are more as compared to stretching vibrations. The most important deformation vibrations are illustrated in Fig. 3.15.

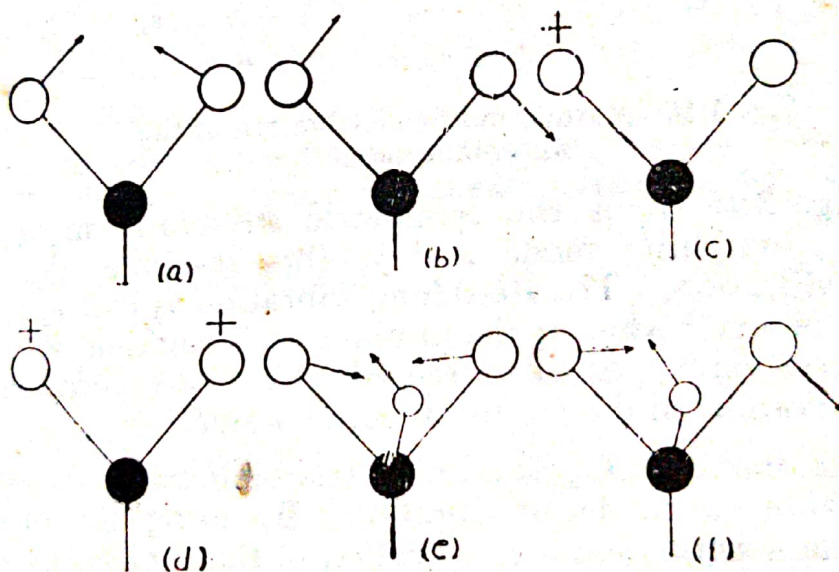


Fig. 3.15. Deformation vibrations of the AB_2 and AB_3 molecules. In plane deformation vibrations of AB_2 molecule : (a) scissoring, (b) rocking vibrations of the AB_2 molecule : (c) twisting, (d) wagging vibrations. Deformation vibrations of AB_3 molecule : (e) symmetric (f) asymmetric.

Deformation vibrations are of two types :

1. In-plane deformation vibrations.
2. Out-of-plane deformation vibrations.

In-plane deformation vibrations include scissoring [(Fig. 3.15 (a))] and rocking vibrations [(Fig. 3.15 (b))]. Out-of-plane deformation vibrations include twisting [(Fig. 3.15 (c))] and wagging vibra-