CHAPTER

3

Infra-red Spectroscopy

3.1 Introduction

Infra-red spectrum is an important record which gives sufficient information about the structure of a compound. Unlike ultraviolet spectrum which comprises of relatively few peaks, this technique provides a spectrum containing a large number of absorption bands from which a wealth of information can be derived about the structure of an organic compound. The absorption of Infra-red radiations (quantised) causes the various bands in a molecule to stretch and bend with respect to one another. The most important region for an organic chemist is 2.5 μ to 15 μ* in which molecular vibrations can be detected and measured in an infra-red spectrum and in a Raman spectrum. The ordinary infra-red region extends from 2.5 μ to 15 μ. The region from 0.8 μ to 2.5 μ is called **Near infra-red** and that from 15 μ to 200 μ is called **Far IR Region.**
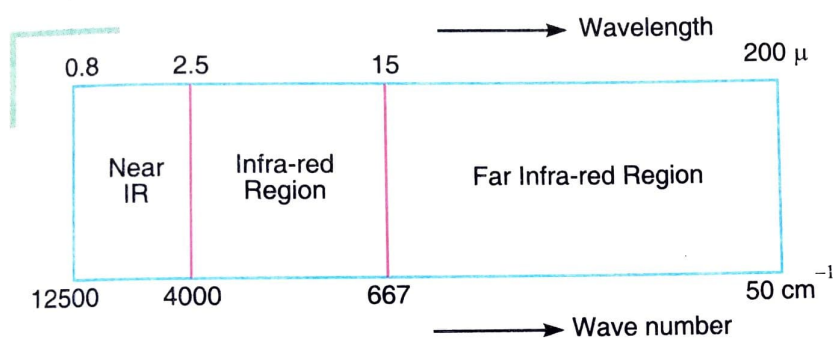

Radiation.

Fig. 3.1. Infra-red region.

The absorption of Infra-red radiations can be expressed either in terms of wavelength (λ) or in wave number ($\bar{v}$). Mostly infra-red spectra of organic compounds are plotted as percentage transmittance against wave number. The relationship between wavelength and wave number is as follows:

$$\text{Wave number} = \frac{1}{\text{wavelength in centimetres}}$$

If wavelength (λ) is 2.5 μ $= 2.5 \times 10^{-4}$ cm, then

$$\text{Wave number } (\bar{v}) = \frac{1}{2.5 \times 10^{-4}\text{ cm}}$$

$$= 4000 \text{ cm}^{-1} \qquad \left[\bar{v} = \frac{1}{\lambda \text{ in cm}}\right]$$

The wavelength 15 μ corresponds to wave number equal to 667 cm^{-1}. Thus, in terms of wave number, the ordinary infra-red region covers 4000 cm^{-1} to 667 cm^{-1}.

Band intensity is either expressed in terms of absorbance (A) or Transmittance (T).

$$A = \log_{10}(1/T)$$

This technique can be employed to establish the identity of two compounds or to determine the structure of a new compound. In revealing the structure of a new compound, it is quite useful

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*   μ represents microns. $1\ \mu$ $= 10^{-4}$ cm $= 10^{-6}$ m

$$\text{Wave number in cm}^{-1} = \frac{10000}{\text{wavelength in microns}}.$$

to predict the presence of certain functional groups which absorb at definite frequencies. For example, the hydroxyl group in a compound absorbs at 3600-3200 cm^{-1}; carbonyl group of ketones gives a strong band at 1710 cm^{-1}. The shift in the absorption position helps in predicting the factors which cause this shift. Some of the factors which shift the absorption band for a particular group from its characteristic frequency (or wave number) are inductive effect, conjugation, angle of strain, hydrogen bonding etc. It is, thus, a very reliable technique for disclosing the identity of a compound.

3.2 Principle of Infra-red Spectroscopy

The absorption of Infra-red radiations causes an excitation of molecule from a lower to the higher vibrational level. We know that each vibrational level is associated with a number of closely spaced rotational levels. Clearly, the Infra-red spectra is considered as **vibrational-rotational spectra.** All the bonds in a molecule are not capable of absorbing infra-red energy but only those bonds which are accompanied by **a change** in **dipole moment** will absorb in the infra-red region. Such vibrational transitions which are accompanied by a change in the dipole-moment of the molecule are called infra-red active transitions. Thus, these are responsible for absorption of energy in the Infra-red region. On the other hand, the vibrational transitions which are not accompanied by a change in dipole-moment of the molecule are not directly observed and these are Infra-red inactive. For example, vibrational transitions of C = O, N—H, O—H etc. bands are accompanied by a change in dipole-moment and thus, absorb strongly in the Infra-red region. But transitions in Carbon-Carbon bonds in symmetrical alkenes and alkynes are not accompanied by the change in dipole-moment and hence do not absorb in the infra-red region. It is important to note that since the absorption in infra-red region is quantised, a molecule of the organic compound will show a number of peaks in the infra-red region.

3.3 Theory—Molecular Vibrations

Absorption in the infra-red region is due to the changes in the vibrational and rotational levels (see Fig. 3.2). When radiations with frequency range less than 100 cm^{-1} are absorbed, molecular rotation takes place in the substance. As this absorption is quantised, discrete lines are formed in the spectrum due to molecular rotation. Molecular vibrations are set in, when more energetic radiation in the region 10^4 to 10^2 cm^{-1} are passed through the sample of the substance. The absorption causing molecular vibration is also quantised. Clearly, a single vibrational energy change is accompanied by a large number of rotational energy changes. Thus, the vibrational spectra appear as vibrational-rotational bands. In the Infra-red spectroscopy (Region 2.5 μ – 15 μ), the absorbed energy brings about predominant changes in the vibrational energy which depends upon:

(i) Masses of the atoms present in a molecule,

(ii) Strength of the bonds, and

(iii) The arrangement of atoms within the molecule.

It has been found that no two compounds except the enantiomers can have similar Infra-red spectra.

It may be noted that the atoms in a molecule are not held rigidly. The molecule may be visualised as consisting of balls of different sizes tied with springs of varying strengths. Here balls and springs correspond to atoms and chemical bonds respectively. When Infra-red light is passed through the sample, the vibrational and the rotational energies of the molecules are increased. Two kinds of fundamental vibrations are:

(a) **Stretching.** In this type of vibrations, the distance between the two atoms increases or decreases but the atoms remain in the same bond axis.
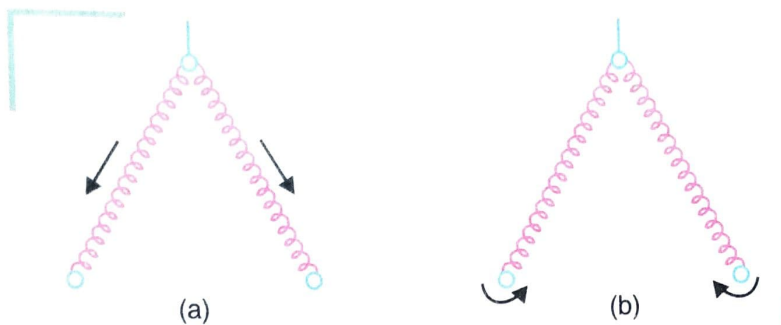
Fig. 3.2. Types of vibrations : (a) Stretching, (b) Bending.

(b) **Bending.** In this type of vibrations, the positions of the atoms change with respect to the original bond axis. We know that more energy is required to stretch a spring than that required to bend it. Thus, we can safely say that stretching absorptions of a bond appear at high frequencies (higher energy) as compared to the bending absorptions of the same bond.

The various stretching and bending vibrations of a bond occur at certain quantised frequencies. When Infra-red radiation is passed through the substance, energy is absorbed and the amplitude of that vibration is increased. From the excited state, the molecule returns to the ground state by the release of extra energy by rotational, collision or translational processes. As a result, the temperature of the sample under investigation increases.

Types of stretching vibrations. There are two types of stretching vibrations:

(i) **Symmetric stretching.** In this type, the movement of the atoms with respect to a particular atom in a molecule is in the same direction.

(ii) **Asymmetric stretching.** In these vibrations, one atom approaches the central atom while the other departs from it.
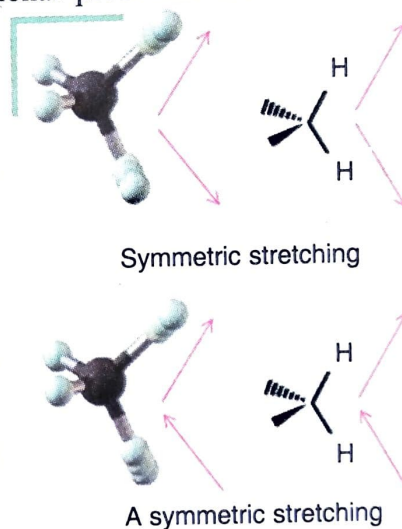
Types of bending vibrations. (*Deformations*). Bending vibrations are of four types:

(i) **Scissoring.** In this type, two-atoms approach each other.

(ii) **Rocking.** In this type, the movement of the atoms takes place in the same direction.

(iii) **Wagging.** Two atoms move 'up and down' the plane with respect to the central atom.

(iv) **Twisting.** In this type, one of the atoms moves up the plane while the other moves down the plane with respect to the central atoms.

Symmetric stretching

A symmetric stretching

Fig. 3.3. Types of stretching vibrations.

Scissoring   Rocking   Wagging   Twisting

Fig. 3.4. Types of bending vibrations. (a) Scissoring, (b) Rocking, (c) Wagging, (d) Twisting

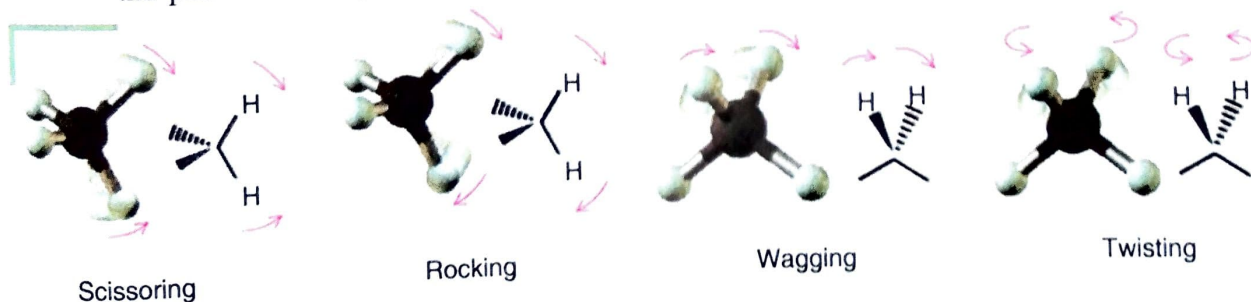**Note.** Bending vibrations require lesser energy and hence occur at higher wavelength lower numbers than stretching vibrations.

3.4 Vibrational Frequency

The value of the stretching vibrational frequency of a bond can be calculated fairly accurate by the application of **Hooke's law** which may be represented as:

$$\frac{v}{c} = \bar{v} = \frac{1}{2\pi c}\left[\frac{k}{\frac{m_1 m_2}{m_1 + m_2}}\right]^{1/2}$$

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

where μ is the reduced mass.

m_1 and m_2 are the masses of the atoms concerned in grams in a particular bond.

k = Force constant of the bond and relates to the strength of the bond. For a single bond, is approximately 5×10^5 gm sec^{-2}. It becomes double and triple for the double and triple bond respectively.

c = Velocity of the radiation = 2.998×10^{10} cm sec^{-1}

Thus, the value of vibrational frequency or wave number depends upon:

(*i*) Bond strength, and   (*ii*) Reduced mass.

Clearly, if the bond strength increases or the reduced mass decreases, the value of the vibrational frequency increases.

Let us calculate the approximate frequency of C—H stretching vibration from the following data:

$$k = 5 \times 10^5 \text{ gm sec}^{-2}$$
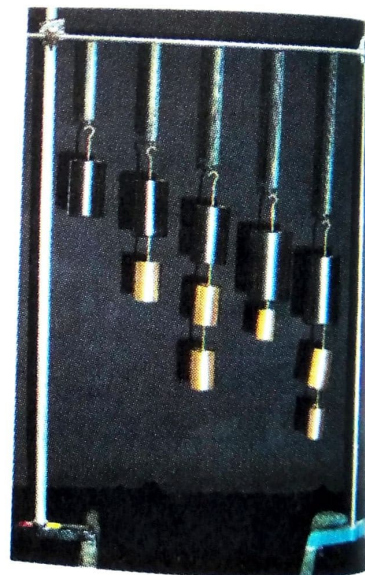$$\text{Mass of carbon atom } (m_1) = 20 \times 10^{-24} \text{ gm}$$
$$\text{Mass of hydrogen atom } (m_2) = 1.6 \times 10^{-24} \text{ gm}$$

$$v = \frac{1}{2\pi}\sqrt{\frac{k}{\frac{m_1 m_2}{m_1 + m_2}}}$$

$$= \frac{7}{2 \times 22}\left(\frac{5 \times 10^5 \text{ gm sec}^{-2}}{\frac{20 \times 10^{-24} \text{ gm} \times 1.6 \times 10^{-24} \text{ gm}}{(20 + 1.6)10^{-24} \text{ gm}}}\right)^{1/2}$$

$$= 9.3 \times 10^{13} \text{ sec}^{-1}$$

Hooke's Law

This value of frequency can be converted into wave number as follows:

$$\bar{v} = \frac{v}{c} = \frac{9.3 \times 10^{13} \text{ sec}^{-1}}{3.0 \times 10^8 \text{ m sec}^{-1}} = 3.1 \times 10^5 \text{ m}^{-1} = \mathbf{3100 \text{ cm}^{-1}}$$

C = C stretching is expected to absorb at higher frequency than C—C stretching. It is due to the higher bond strength (value of k) of the double bond compared to the single bond. Similarly, O—H stretching absorbs at higher frequency compared to C—C bond. It can be explained on the basis of the smaller value of reduced mass for O—H compared with C—C bond. We can expect O—H to absorb at higher frequency as compared to F—H. But this is not true. Actually, F—H absorbs at the higher frequency. This can be explained due to the higher electronegativity of fluorine compared to that of oxygen.

EXAMPLE 1. Calculate the wave number of stretching vibration of a carbon-carbon double bond. Give force constant ($k = 10 \times 10^5$ dynes cm^{-1})

SOLUTION. Atomic mass of carbon = 12 amu

Reduced mass (μ) $= \dfrac{m_1 m_2}{m_1 + m_2} = \dfrac{12 \times 12}{12 + 12} = 6 \ amu = \dfrac{6}{6.02 \times 10^{23}} \ gm = 9.97 \times 10^{-24} gm$

Wave number $\bar{v} = \dfrac{1}{2\pi c} \sqrt{\dfrac{k}{\mu}}$

$$\bar{v} = \dfrac{1}{2 \times 3.142 \times 3 \times 10^{10} \ cm \ s^{-1}} \sqrt{\dfrac{10 \times 10^5 \ gm \ sec^{-2}}{\dfrac{6 \ gm}{6.02 \times 10^{23}}}}$$

$$= \dfrac{1}{18.852 \times 10^{10} \ cm \ s^{-1}} \times \sqrt{10.03 \times 10^{28}} = 0.1680 \times 10^4 \ cm^{-1}$$

$$= \textbf{1680 } \textbf{cm}^{-1}.$$

EXAMPLE 2. The reduced mass of a diatomic molecule is 2.5×10^{-26} kg and its vibrational frequency is 2900 cm^{-1}. Calculate the force constant.

SOLUTION. Given reduced mass, $\mu = 2.5 \times 10^{-26}$ kg

vibrational frequency, $\bar{v} = 2900 \ cm^{-1}$.

Applying the relation $\bar{v} = \dfrac{1}{2\pi c} \sqrt{\dfrac{k}{\mu}}$ or force constant, $k = 4\pi^2 c^2 \cdot \mu \cdot \bar{v}^2$

or $k = 4 \times (3.142)^2 \ (3 \times 10^8 \ ms^{-1})^2 \ (2900 \times 10^2 \ m^{-1})^2 \ (2.5 \times 10^{-26} \ kg)$

$= \textbf{7476.4 } \textbf{Nm}^{-1}$ $\qquad$ [$1N = 1 \ kg \ ms^{-2}$]

EXAMPLE 3. The force constant for carbon monoxide molecule is 1840 Nm^{-1}. Calculate the vibrational frequency (in cm^{-1}). Given atomic masses are: $^{12}C = 19.9 \times 10^{-27}$ kg; $^{16}O = 26.6 \times 10^{-27}$ kg.

SOLUTION. We know that fundamental vibrational frequency (v) is expressed as:

$$\bar{v} = \dfrac{1}{2\pi c} \sqrt{\dfrac{k}{\mu}} \quad \text{Given } k = 1840 \ Nm^{-1}$$

Reduced mass $= \mu_{CO} = \dfrac{m_C \times m_O}{(m_C + m_O)} = \dfrac{19.9 \times 10^{-27} \ kg \times 26.6 \times 10^{-27} \ kg}{(19.9 \times 10^{-27} + 26.6 \times 10^{-27}) \ kg}$

$$= 1.138 \times 10^{-26} \ kg.$$

The relation is : $\bar{v} = \dfrac{1}{2\pi c} \sqrt{\dfrac{k}{\mu}}$

Substituting the values: $\bar{v} = \dfrac{1}{2 \times 3.142 \times 3 \times 10^8 \ ms^{-1}} \sqrt{\dfrac{1840 \ kg \ s^{-2}}{1.138 \times 10^{-26} \ kg}} = 2.132 \times 10^5 m^{-1}$

$$\bar{v} = 2.132 \times 10^5 \times 10^{-2} \ cm^{-1} = \textbf{2132 } \textbf{cm}^{-1}.$$

or

EXAMPLE 4. *The force constant of HF is listed at 880 Nm^{-1}. At what wave number is fundamental $v = 0 \rightarrow v = 1$ vibrational absorption expected?*

SOLUTION. We know the relation: $\bar{v} = \dfrac{1}{2\pi c} \cdot \sqrt{\dfrac{k}{\mu}}$

Assuming vibrations to be simple harmonic,

$$\bar{v} = \frac{1}{2 \times 3.142 \times 3 \times 10^8 \, ms^{-1}} \times \sqrt{\frac{800 Nm^{-1}(or \ kg \ s^{-2})(1+19) \times 6.02 \times 10^{23}}{1 \times 19 \times 10^{-3} \, kg}}$$

$$= 396071.8 \ m^{-1} = \mathbf{3960.7 \ cm^{-1}}$$

3.5 Number of Fundamental Vibrations

The Infra-red light is absorbed when the oscillating dipole-moment interacts with the oscillating electric vector of an Infra-red beam. For this interaction or absorption to occur, it is important th the dipole-moment at one extreme of the vibration must be different from the dipole-moment the other extreme of the vibration in a molecule. For Infra-red absorption, the vibrations shou not be centro-symmetric. Only those vibrations are Infra-red active which are not centro-symmetri As most of the functional groups in organic chemistry are not centro-symmetric, this technique most informative to organic chemists. The symmetry properties of a molecule in a solid can b different from those of an isolated molecule.

The Infra-red spectrum of a molecule results due to the transitions between two differer vibrational energy levels. The vibrational motion resembles the motion observed for a ball attache to a spring, i.e., harmonic oscillator. A chemical bond can be visualised as two balls attached a spring. But it differs from this system since in Infra-red certain vibrational energy levels only ar allowed in molecules. The vibrational energy of a chemical bond is quantised and can have th value.

$$E_{vib} = \left(V + \frac{1}{2}\right)hv$$

where V is the number of the vibrational level and can have the values 0, 1, 2, 3........

h = Planck's constant

and v = vibrational frequency of the bond.

It is already known that

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{\dfrac{m_1 m_2}{m_1 + m_2}}}$$

The energy difference between the two vibrational energy levels can be written as

$$\Delta E_{vib} = hv$$

At ordinary temperature, where molecules are in their lowest vibrational energy levels, the potential energy diagram approximates that of a harmonic oscillator. But at higher temperatures, the deviations do occur (see Fig. 3.5).
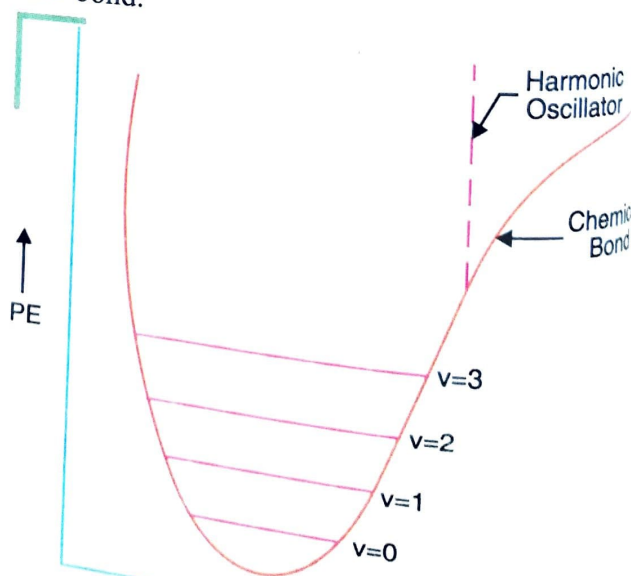

Fig. 3.5. Potential Energy diagram.

INFRA-RED SPECTROSCOPY

Absorption of radiation with energy equal to the difference between two vibrational energy levels (ΔE_{vib}) will cause a vibrational transition to occur. Radiation with energy sufficient to cause vibrational transition is found in the Infra-red region of the electromagnetic spectrum.

Transitions from the ground state ($V = 0$) to the first excited state ($V = 1$) absorb light strongly and give rise to intense bands called the Fundamental bands. The energy difference (ΔE_{vib}) between the lowest possible energy level of a bond and the next higher energy level is given as:

$$\Delta E_{vib} = E_{vib(V = 1)} - E_{vib(V = 0)}$$

$$= \left(1 + \frac{1}{2}\right)h\nu - \left(0 + \frac{1}{2}\right)h\nu$$

$$= \frac{3}{2}h\nu - \frac{1}{2}h\nu = h\nu$$

This gives the frequency of a fundamental band. Transitions from the ground state ($V = 0$) to the second excited state ($V = 2$) with the absorption of Infra-red radiation give rise to weak bands, called overtones.

Assuming that all the vibrational bands are equally spaced (in fact, these are not), the energy of the first overtone is given by

$$\Delta E_{vib} = E_{vib(V = 2)} - E_{vib(V = 0)}$$

$$= \left(2 + \frac{1}{2}\right)h\nu - \left(0 + \frac{1}{2}\right)h\nu$$

$$= 2\,h\nu$$

Polyatomic molecules may exhibit more than one fundamental vibrational absorption bands. The number of these fundamental bands is related to the **degrees of freedom** in a molecule. The number of degrees of freedom is equal to the sum of the co-ordinates necessary to locate all the atoms of a molecule in space. Each atom has three degrees of freedom corresponding to the three cartesian co-ordinates (X, Y, Z) necessary to describe its position relative to other atoms in a molecule. An isolated atom which is considered as a point mass has only translational degrees of freedom. It cannot have vibrational and rotational degrees of freedom. When atoms combine to form a molecule, no degrees of freedom are lost, i.e., the total number of degrees of freedom of a molecule will be equal to $3n$ where n is the number of atoms in a molecule. A molecule which is of finite dimensions will, thus, be made up of rotational, vibrational and translational degrees of freedom. So,

3n degrees of freedom = Translational + Rotational + Vibrational.

Rotational degrees of freedom result from the rotation of a molecule about an axis through the centre of gravity. Since we are concerned only with the number of fundamental vibrational modes of a molecule, so we calculate only the number of vibrational degrees of freedom of a molecule. Since only three co-ordinates are necessary to locate a molecule in space, we say that a **molecule has always three translational degrees of freedom.**

In case of linear molecule, there are only two degrees of rotation. It is due to the fact that the rotation of such a molecule about its axis of linearity does not bring about any change in the position of the atoms while rotation about the other two axes changes the position of the atoms. Thus, for a linear molecule of n atoms.

Total degrees of freedom = 3n

Translational degrees of freedom = 3

Rotational degrees of freedom = 2

∴ Vibrational degrees of freedom = 3n – 3 – 2 = 3n – 5

Each vibrational degree of freedom corresponds to the fundamental mode of vibration and

each fundamental mode corresponds to a band. Hence, theoretically there will be $3n - 5$ poss fundamental bands for the linear molecules.

In a linear molecule of carbon dioxide (CO_2), the number of vibrational degrees of freed can be calculated as follows:

Number of atoms (n)	= 3
Total degrees of freedom	= $3n = 3 \times 3 = 9$
Translational	= 3
Rotational	= 2
$\therefore$ Vibrational degrees of freedom	= $9 - 3 - 2 = 4$

Hence, for carbon dioxide molecule, the theoretical number of fundamental bands should equal to four.

In the case of non-linear molecule, there are three degrees of rotation as the rotation about the three axes (X, Y, Z) will result in a change in the position of the atoms. So, for a non-line molecule of n atoms, the vibrational degrees of freedom can be calculated as follows:

Total degrees of freedom	= $3n$
Translational degrees of freedom	= 3
Rotational degrees of freedom	= 3
$\therefore$ Vibrational degrees of freedom	= $3n - 3 - 3 = 3n - 6$

Thus, in a non-linear molecule, C_6H_6, the number of vibrational degrees of freedom can calculated as follows:

Number of atoms (n)	= 12
Total degrees of freedom	= $3 \times 12 = 36$
Translational	= 3
Rotational	= 3
$\therefore$ Vibrational degrees of freedom	= $36 - 3 - 3 = 30$

So, theoretically there should be 30 fundamental bands in the Infra-red spectrum of benzene

It has been observed that the theoretical number of fundamental vibrations are seldom obtained It is because of the following reasons:

(i) Fundamental vibrations that fall outside the region under investigation, i.e., 2.5 to 15 μ

(ii) Fundamental vibrations that are too weak to be observed as bands.

(iii) Fundamental vibrations that are so close that they overlap, i.e., degenerate vibrations.

(iv) Certain vibrational bands do not appear for want of the required change in the dipole moment in a molecule.

(v) There may appear some additional bands called combination bands, difference bands and overtones. Thus, due to these, a large number of bands will be observed as compared to the theoretical number. If there are two fundamental bands at x and y, then the additional bands can be expected at:

(i) 2x, 2y (Overtones)

(ii) x + y, x + 2y, 2x + y etc.   (Combination bands)

(iii) (x − y), (x − 2y), (2y − x) etc.   (Difference bands)

It may be noted that these additional bands are usually 10-100 times less intense as compared to the fundamental bands.

(i) H_2S

(ii) C_2H_2

SOLUTION. (i) H_2S molecule. This a non-linear molecule. Thus, the number of normal modes of vibration $= (3n - 6)$.

Where $n =$ Total number of atoms in the molecule. Here $n = 3$.

Number of normal modes of vibrations in $H_2S = 3 \times 3 - 6 = $ **3**

(ii) $HC \equiv CH$. Acetylene is a linear molecule

Here $n = 4$

$\therefore$ Number of normal modes of vibrations $= (3n - 5) = 3 \times 4 - 5 = 7$

Note. Absorptions due to bending vibrations occur at frequencies below 1500 cm^{-1}. These are not very useful for structural information as confusion of one with the other may occur. Moreover, bands are obscured due to overtones and combination bands. The region below 1500 cm^{-1} is called **Finger print region.** This region is important for comparing the identity of the two compounds and also for the detection of certain functional groups like esters, ethers, type of disubstitution on the benzene ring etc.
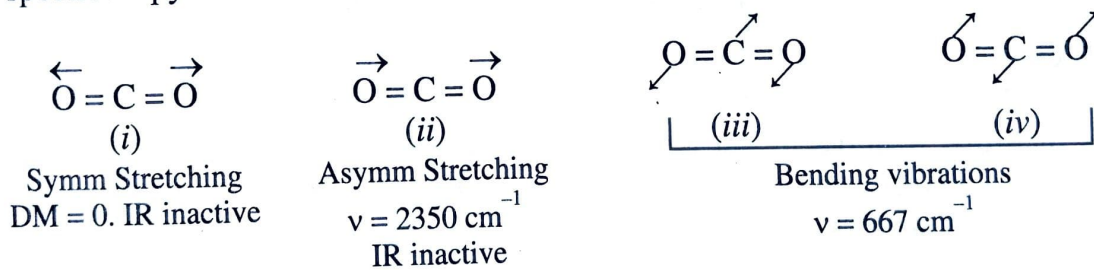
3.6 Selection Rules (Active and Forbidden Vibrations)

Infra-red light is absorbed only when a change in dipole character of the molecule takes place. Complete symmetry about a bond eliminates some absorption bands. Clearly, some of the fundamental vibrations are Infra-red active and some are not. It is governed by the selection rules which are explained below:

(i) If a molecule has a centre of symmetry, then the vibrations are centrosymmetric and are **inactive** in the Infra-red but are active in the Raman.

(ii) The vibrations which are not centrosymmetric are active in Infra-red but inactive in Raman.

Since in most of the organic compoun, the functional groups are not centrosymmetric. Infra-red spectroscopy is most informative. Consider various vibrations in case of carbon dioxide.

$$\overleftarrow{O}=C=\overrightarrow{O} \qquad \overrightarrow{O}=C=\overrightarrow{O} \qquad O=C=O \qquad O=C=O$$

(i)	(ii)	(iii)	(iv)
Symm Stretching	Asymm Stretching	Bending vibrations	
DM = 0. IR inactive	$v = 2350$ cm^{-1}	$v = 667$ cm^{-1}	
	IR inactive		

The above vibrations are all fundamental vibrations of carbon dioxide. Since (i) does not give rise to any change in dipole-moment, it is infra-red inactive. Asymmetric stretching causes, a net change in dipole-moment and thus is infra-red active and absorbs at 2350 cm^{-1} vibrations (iii) and (iv) are said to be degenerate. The bending of bonds in the molecule are identical but occur in perpendicular planes and thus appear in the same position ($v = 667$ cm^{-1}) in the spectrum. Thus the spectrum of carbon dioxide consists of two bands (i) 2350 cm^{-1} due to asymmetric stretching and (ii) 667 cm^{-1} due to bending vibrations.

Intensity and position of Infra-red absorption bands. The intensity of a fundamental absorption depends upon the difference between the dipole moments of the molecule in the ground state and the vibrational excited state. Greater the difference, more is the intensity of absorption. In case, there is no change in the dipole moment, then the vibrational mode is said to be Infra-red inactive. Since the intensity of absorption band in infra-red spectroscopy cannot be measured with greater accuracy, it is sufficient to know whether the absorption is strong, medium or weak. If the most intense peak is assigned an intensity of 100%, then the relative intensities of other

peaks can be estimated. Frequency of absorption is generally expressed in terms of wave num... (cm^{-1}) as wave number is directly proportional to frequency as well as energy.

3.7 Factors Influencing Vibrational Frequencies

We know that the probable frequency or wave-number of absorption can be calculated by application of Hooke's law. It has been found that the calculated value of frequency of absorpti... for a particular bond is never exactly equal to its experimental value. The difference arises fro... the fact that vibration of each group is influenced by the structure of the molecule in the immedia... neighbourhood of the bond. If a particular vibration is absolutely free from any influence, then t... Infra-red spectrum would tell us whether a certain group is/or is not present in the molecu... Moreover, the value of absorption frequency is also shifted since the force constant of a bo... changes with its electronic structure. There are many factors which are responsible for vibration... shifts and one factor cannot be isolated from another. Frequency shifts also take place on workin... with the same substance in different states (solids, liquids or vapours). In the vapour state, ... substance, usually absorbs at higher frequency as compared to that when it is in the liquid and soli... states. Following are some of the factors responsible for shifting the vibrational frequencies fro... their normal values:

1. **Coupled Vibrations and Fermi Resonance.** We expect one stretching absorption frequenc... for an isolated C—H bond but in the case of methylene (—CH_2—) group, two absorptions occu... which correspond to symmetric and asymmetric vibrations as follows:
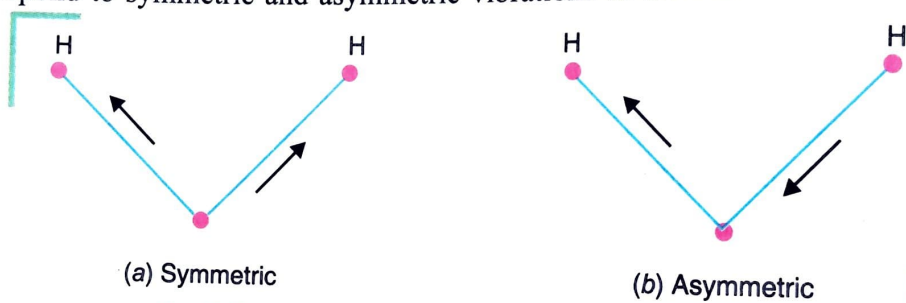

(a) Symmetric   (b) Asymmetric

Fig. 3.6. Stretching vibrations in methylene group.

In such cases, asymmetric vibrations always occur at higher wave number compared with the symmetric vibrations. These are called coupled vibrations since these vibrations occur at different frequencies than that required for an isolated C—H stretching. Similarly, coupled vibrations of —CH_3 group take place at different frequencies compared to —CH_2— group. For methyl group, symmetric vibrations are as follows:
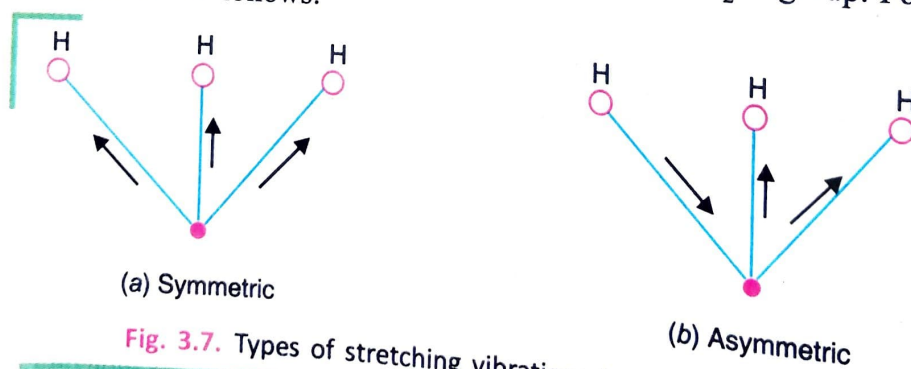

(a) Symmetric   (b) Asymmetric

Fig. 3.7. Types of stretching vibrations in methyl group.

Sometimes, it happens that two different vibrational levels have nearly the same energy. If such vibrations belong to the same species (as in the case of —CH_2— group or —CH_3 group), then a mutual perturbation of energy may occur, resulting in the shift of one towards lower frequency and the other towards higher frequency. It is also accompanied by a substantial increase in the intensity of the respective bands.

Acid anhydrides show two C=O stretching absorptions between 1850-1800 and 1790-1745 cm^{-1} with a difference of about 65 cm^{-1}. This can be explained due to the symmetric and asymmetric stretching. In Infra-red spectrum, absorption bands are spread over a wide range of frequencies. It may happen that the energy of an overtone level chances to coincide with the fundamental mode of different vibration. A type of resonance occurs as in the case of coupled pendulums. This type of resonance is called **Fermi Resonance**. This can be explained by saying that a molecule transfers its energy from fundamental to overtone and back again. Quantum mechanically, resonance pushes the two levels apart and mixes their character so that each level becomes partly fundamental and partly overtone in character. Thus, this type of resonance gives rise to a pair of transitions of equal intensity.

This phenomenon was first observed by Enrico Fermi in the case of carbon dioxide. Carbon dioxide molecule (Triatomic) is linear and four fundamental vibrations are expected for it. Out of these, symmetric stretching vibration is Infra-red inactive since it produces no change in the dipole-moment (**D.M.**) of the molecule.

DM = 0

(a)   (b)

**Fig. 3.8.** (a) Symmetric stretching, (b) Asymmetric stretching.

For symmetric stretching, Raman spectrum shows a strong band at 1337 cm^{-1}. The two bending vibrations are equivalent and absorb at the same frequency of 667.3 cm^{-1}. The overtone of this is 1334.6 cm^{-1} (2 × 667.3) which is very close to 1337 cm^{-1}. Thus, Fermi Resonance takes place resulting in the shift of first level towards higher frequency. The mutual perturbation of 1337 cm^{-1} (Fundamental) and 1334.6 cm^{-1} (Overtone) gives rise to two bands at 1285.5 cm^{-1} and 1388.3 cm^{-1} having intensity ratio of 1 : 0.9.

Another example of Fermi Resonance is given by aldehydes in which C—H stretching absorption usually appears as a doublet (~2820 cm^{-1} and ~2720 cm^{-1}) due to the interaction between C—H stretching (fundamental) and the overtone of C—H deformation (bending). Fermi Resonance is also shown by the spectrum of n-butyl vinyl ether. In this case, the overtone of the fundamental vibration at 810 cm^{-1} chances to coincide with the band at 1640 cm^{-1}. The mixing of the two bands (Fundamental and Overtone) in accordance with Fermi Resonance gives two bands of almost equal intensity at 1640 cm^{-1} and 1630 cm^{-1}.

Similarly, Fermi Resonance is required to explain the doublet in case of certain lactones and cycloketones. In cyclopentanone, the absorption due to carbonyl group occurs at 1746 cm^{-1} and 1750 cm^{-1}. This splitting can be explained by Fermi Resonance. In large molecules, Fermi Resonance is observed only when the normal vibrations and the overtones are in the same area of the molecule and also if certain symmetrical conditions are fulfilled (Two bands should be of the same symmetry).

2. Electronic Effects. Changes in the absorption frequencies for a particular group take place when the substituents in the neighbourhood of that particular group are changed. The frequency shifts are due to the electronic effects which include *Inductive effect, Mesomeric effects, Field effects* etc. These effects cannot be isolated from one another and the contribution of one of them can only be estimated approximately. Under the influence of these effects, the force constant or the bond strength changes and its absorption frequency shifts from the normal value. The introduction of alkyl group causes + I effect which results in the lengthening or the weakening of the bond and hence the force constant is lowered and wave number of absorption decreases. Let us compare the wave numbers of v (C=O) absorptions for the following compounds:
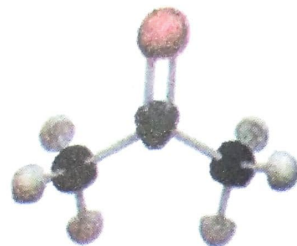
(i) Formaldehyde (HCHO) 1750 cm^{-1}

(ii) Acetaldehyde (CH_3CHO) 1745 cm^{-1}

(iii) Acetone (CH_3COCH_3) 1715 cm^{-1}
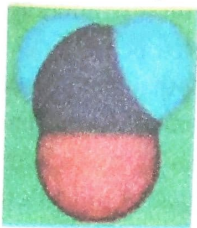
Formaladehyde   Acetaldehyde   Acetone

Note. Aldehydes absorb at higher wave number than ketones.

The introduction of an electronegative atom or group causes–I effect which results in the bo order to increase. Thus, the force constant increases and hence the wave number of absorptio rises. Now, let us consider the wave numbers of absorptions in the following compounds:

(i) Acetone (CH_3COCH_3) 1715 cm^{-1}

(ii) Chloroacetone (CH_3COCH_2Cl) 1725 cm^{-1}

(iii) Dichloroacetone ($CH_3COCHCl_2$) 1740 cm^{-1}

(iv) Tetrachloroacetone ($Cl_2CH-CO-CHCl_2$)   1750, 1778 cm^{-1}

In most of the cases, mesomeric effect works alongwith inductive effect and cannot be ignored Conjugation lowers the absorption frequency of C=O stretching whether the conjugation is due t α, β-unsaturation or due to an aromatic ring. In some cases, inductive effect dominates over mesomeric effect while reverse holds for other cases. *Mesomeric effect* causes lengthening or the weakening of a bond leading in the lowering of absorption frequency. Consider the following compounds:

In these two cases, –I effect is dominated by mesomeric effect and thus, the absorption frequency falls.
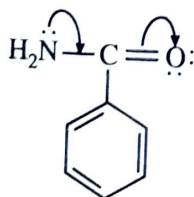

$$CH_3-C \overset{\overset{\displaystyle ..O:}{||}}{} CH=CH_2$$
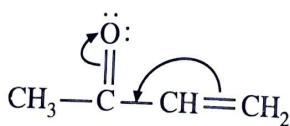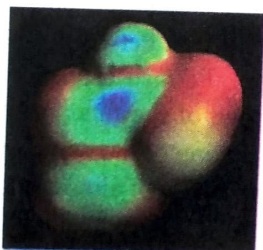
Methyl Vinyl Ketone
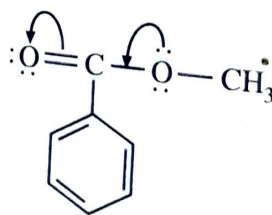$v C=O$ 1706 cm^{-1}

$$H_3C-C \overset{..}{=} O$$
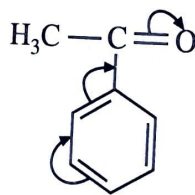
Acetophenone
$v C=O$ 1693 cm^{-1}

In some cases, where the lone pair of electrons present on an atom is in conjugation with the double bond of a group, say carbonyl group, the mobility of the lone pair of electrons matters. Let us compare the absorption frequencies of v(C=O) stretching in amides and esters.
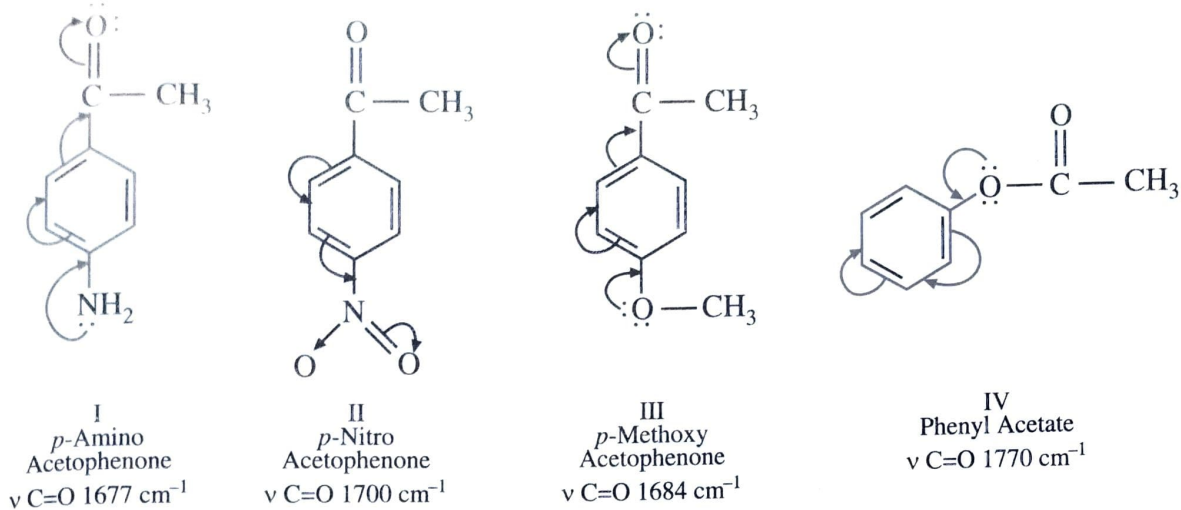
$$H_2\overset{..}{N}-C \overset{..}{=} \overset{..}{O}:$$

Benzamide
$v C=O$ 1693 cm^{-1}

$$:\overset{..}{O}=C-\overset{..}{\underset{..}{O}}-CH_3$$

Methyl benzoate
$v C=O$ 1730 cm^{-1}

As nitrogen atom is less electronegative than oxygen atom, the electron pair on nitrogen atom in amide is more labile and participates more in conjugation. Due to this greater degree of conjugation, the C=O absorption frequency is much less in amides as compared to that in esters.

Let us compare the absorption frequencies of the following compounds:

I	II	III	IV
p-Amino Acetophenone	p-Nitro Acetophenone	p-Methoxy Acetophenone	Phenyl Acetate
v C=O 1677 cm^{-1}	v C=O 1700 cm^{-1}	v C=O 1684 cm^{-1}	v C=O 1770 cm^{-1}

Due to the low electronegativity of nitrogen atom, the lone pair of electrons participates more in conjugation in compound I as compared to that in compound III. Thus, in compound I, v (C=O) absorption occurs at lower wave number compared to that in compound III. In compounds II and IV, inductive effect dominates over mesomeric effect and hence absorption takes place at comparatively higher frequencies.

It is important to note that only inductive effect is considered when the compound is meta substituted.

In para substitution, both inductive and mesomeric effects become important and the domination of one over the other will decide the wave number of absorption. In ortho substitution, inductive effect, mesomeric effect alongwith steric effect are considered. In ortho substituted compounds, the lone pairs of electrons on two atoms influence each other through space interactions and change the vibrational frequencies of both the groups. This effect is called **Field effect**. Consider ortho haloacetophenone.
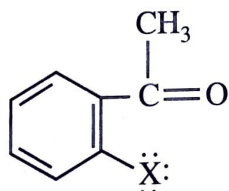
The non-bonding electrons present on oxygen atom and halogen atom cause electrostatic repulsions. This causes a change in the state of hybridisation of C=O group and also makes it to go out of the plane of the double bond. Thus, the conjugation is diminished and absorption occurs at a higher wave number. Thus, for such ortho substituted compounds, cis absorbs (field effect) at a higher frequency as compared to the trans isomer.

3. **Hydrogen bonding.** Hydrogen bonding brings about remarkable downward frequency shifts. Stronger the hydrogen bonding, greater is the absorption shift towards lower wave number than the normal value. Two types of hydrogen bonds can be readily distinguished in Infra-red technique. Generally, intermolecular hydrogen bonds give rise to broad bands whereas bands arising from intramolecular hydrogen bonds are sharp and well defined. Intermolecular hydrogen
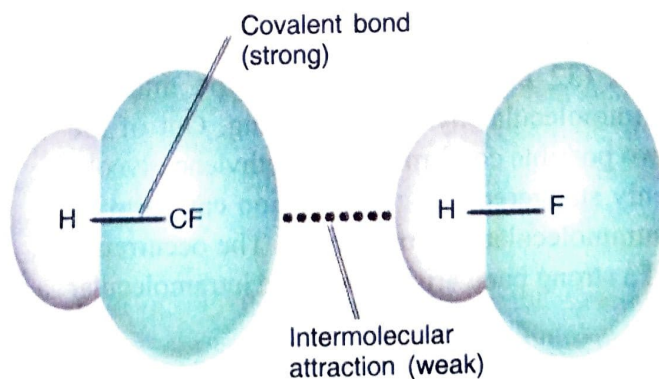
Inter-molecular Hydrogen bonding

bonds are **concentration dependent**. On dilution, the intensities of such bands are independent of concentration. The absorption frequency difference between free and associated molecule is small in case of intramolecular hydrogen bonding than that in intermolecular association.

Hydrogen bonding in O—H and N—H compounds deserve special attention. Mostly n associating solvents like carbon disulphide, chloroform, carbon tetrachloride are used beca a some solvents like benzene, acetone etc., influence O—H and N—H compounds to a consider t extent. As nitrogen atom is less electronegative than an oxygen atom, hydrogen bonding in ami is weaker than that in alcohols and thus, the frequency shifts in amines are less dramatic. i example, amines show N—H stretching at 3500 cm^{-1} in dilute solutions while in condensed ph spectra, absorption occurs at 3300 cm^{-1}.

In aliphatic alcohols, a sharp band* appears at 3650 cm^{-1} in dilute solutions due to f O—H group while a broad band is noticed at 3350 cm^{-1} due to hydrogen bonded O—H gro Alcohols are strongly hydrogen bonded in condensed phases. These are usually associated dimers and polymers which result in the broadening of bands at lower absorption frequencies. vapour state or in inert solvents, molecules exist in free state and absorbs strongly at 3650 cm Alcohols can be written in the following resonating structures.

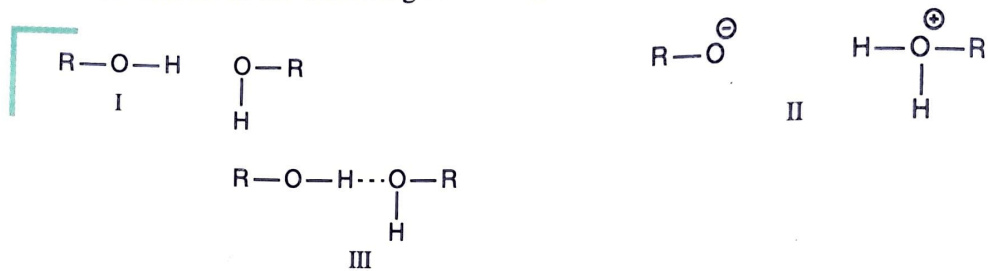
Fig. 3.9. Resonating structures of alcohols.

Structure III is the hybrid of structures I and II. This results in the lengthening of the origin O—H group. The electrostatic force of attraction with which hydrogen atom of one molecule attracted by the oxygen atom of another molecule makes it easier to pull hydrogen away from t oxygen atom. Thus, small energy will be required to stretch such a bond (O—H) and henc absorption occurs at a lower wave number.

Intramolecular hydrogen bonding can be observed in dilute solutions of di- and polyhydroy compounds in carbon tetrachloride where no intermolecular hydrogen bonds are formed. Und these conditions, it was observed that a number of cyclic and acyclic diols have two bands an others have a single band in the O—H stretching mode region.

The spectrum of glycol in dilute carbon tetrachloride shows two vO—H bands at 3644 cm^{-1} and 3612 cm^{-1}. The band at 3644 cm^{-1} is due to free O—H and that at 3612 cm^{-1} is due to O—H···O bonding. As the absorption shift (32 cm^{-1}) is small, the type must be intramolecular hydrogen bonding. Out of the two possible conformations of ethylene glycols, only staggered syn conformation can form an intramolecular hydrogen bond. The occurrence of a strong band arising from the intramolecular
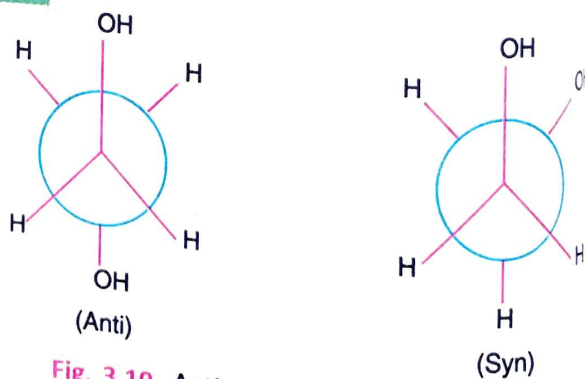

Fig. 3.10. Anti and Syn conformations of Ethylene glycol.

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* The band due to free O—H group is usually less intense while that due to bonded O—H group is broad and sharp.

hydrogen bond shows that the molecule exists in staggered-syn conformation.

The energy of the hydrogen bond compensates for excess energy (5 kcal mole^{-1}) due to steric and dipolar repulsions of the two O—H groups. The small frequency shift ($\Delta v = 32$ cm^{-1}) shows that hydrogen bonding is weak.

At higher concentrations, the I.R spectra of diols show a third band arising from the intermolecular hydrogen bonding of the hydroxy group. This new band shows all the characteristics observed in monohydric alcohols, *i.e.*, the bands formed are strong and broad. The intermolecular association of diols results in a larger shift of vO—H than intramolecular hydrogen bonding does. If the free vO—H in diols is 3626 cm^{-1}, then intermolecularly bonded O—H abosrbs at 3477 cm^{-1}.

Note. In aromatic amines, differences between intramolecularly associated and free N—H bond absorption frequencies are small and difficult to observe.

In enols and chelates, hydrogen bonding is exceptionally strong and absorptions due to O—H stretching occurs at very low values. As these bonds are not broken easily on dilution by an inert solvent, free O—H stretching may not be seen at low concentrations. It is due to the fact that the bonded structure is stabilised by resonance. Consider acetyl acetone:
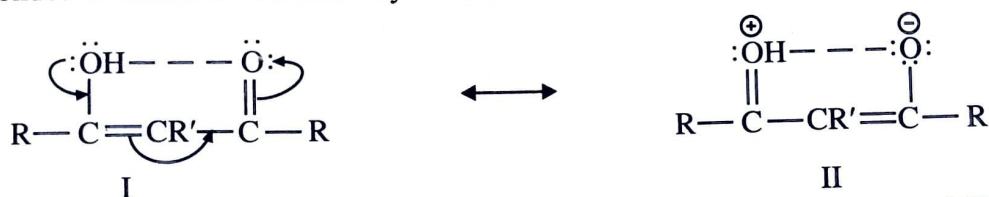
The O—H group involved in chelation gives rise to broad absorptions between 3000 and 2500 cm^{-1}. The vCO absorption in the enolic form occurs at 1630 cm^{-1} and that in the keto form at 1725 cm^{-1}. From the intensities of the two peaks, it is possible to determine the quantities of the enolic and the ketonic forms.

Mostly the acids exist as dimers and bridges formed are stabilised by resonance.
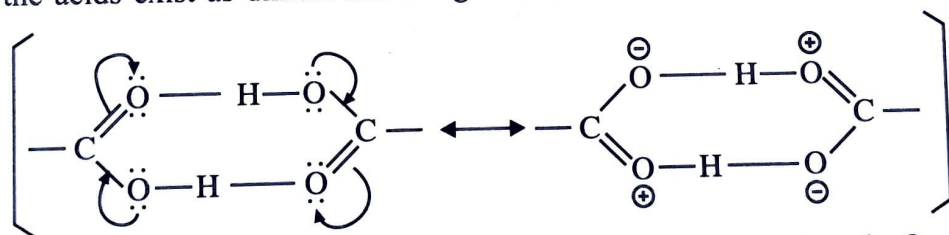
The formation of bridges lowers the force constants and thus vC=O and vO—H decreases. The larger decrease in the frequency in these dimers indicates the exceptional strengths of hydrogen bonds.

The carboxylic acid dimers display very broad band at 3000-2500 cm^{-1} due to O—H stretching. In vapour phase, vC=O absorption occurs at 1770 cm^{-1} in acetic acid and in the liquid state, absorption band appears at 1739 cm^{-1}. Infra-red spectrum of benzoic acid shows a broad band at 3000-2500 cm^{-1} due to O—H stretching. Pi (π) cloud interactions are also noted when acidic hydrogen interacts with lewis bases (Nucleophiles) such as alkenes and benzene. For example, the frequency of O—H stretching in phenols is lowered by 40-100 cm^{-1} when spectrum is taken in benzene solution as compared to that in carbon tetrachloride solution. Due to this interaction, lengthening and hence weakening of O—H bond occurs.

4. Bond angles. It has been found that the highest vC=O frequencies arise in the strained cyclobutanones. This can be explained in terms of bond angles strain. The C—CO—C bond angle is reduced below the normal angle of 120° and this leads to increased *s*-character in the C=O bond. Greater *s*-character causes shortening of C=O bond and thus C=O str occurs at higher frequency.

In case the bond angle is pushed outwards above 120°, the opposite effect operates. Due ... reason, di-tert-butyl ketone absorbs at 1697 cm^{-1} (low) as a result of C=O str.

It is also assumed that there is no change in the C=O force constant and it is an inc... rigidity in the C—CO—C bond system as the ring size decreases. In such cases, C=O str ... more effectively with C—C str leading to higher C=O str frequencies.

3.8 Scanning of Infra-red Spectrum (Instrumentation)

The most important source of Infra-red light for scanning the spectrum of an organic com... is **Nernst glower** which consists of a rod of the sintered mixture of the oxides of Zirc... Ytterium and Erbium. The rod is electrically heated to 1500°C to produce Infra-red radiat...

A rod of silicon carbide (Globar) can also be electrically heated to produce Infra-red radia... To obtain monochromatic light, optical prisms or gratings can be used. For prism material, or quartz cannot be used since they absorb strongly through most of the Infra-red region. S... chloride or certain alkali metal halides are commonly used as cell containers or for prism mat... as these are transparent to most of the Infra-red region under consideration. Sodium chlor... hygroscopic and is, therefore, protected from the condensation of moisture by working at su... temperature. Gratings give better resolution than do prisms at high temperatures.

Light from the source is split into two beams. One of the beams is passed through the sa... under examination and is called the sample beam. The other beam is called the reference t... When the beam passes through the sample, it becomes less intense due to the absorption of ce... frequencies. Now, there will be a difference in the intensities of the two beams. Let I_0 b... intensity of the reference beam and I be the intensity of the beam after interaction with the sa... respectively.
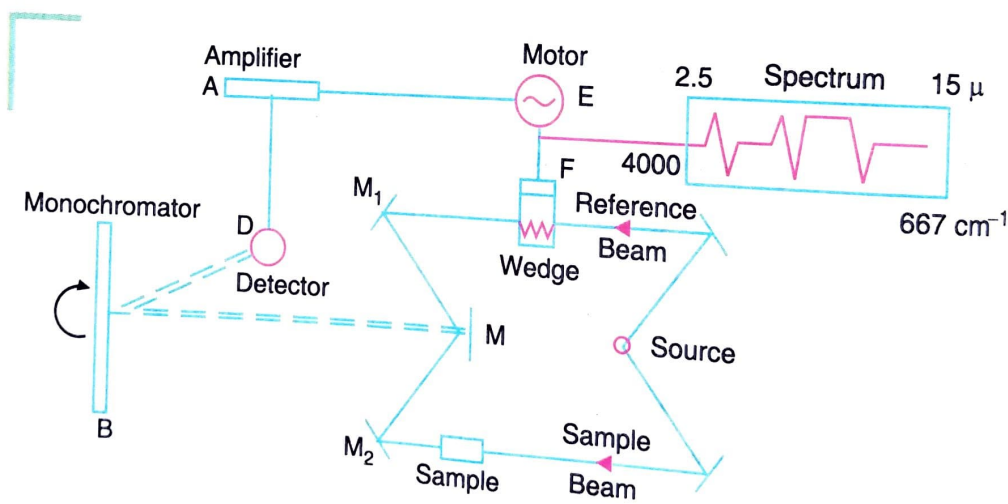

Fig. 3.11. Infra-red Spectrometer.

The absorbance of the sample at a particular frequency can be calculated as:

$$A = \log (I_0/I)$$

Also transmittance, $\quad T = I/I_0$

or

$$A = \log (1/T)$$

Intensities of the bands can be recorded as a linear function T against the corresponding wa... number. Intensities of the two beams are converted into and measured as electrical energies ... the help of detector thermopile. For this we proceed as follows:

* It works on the thermopile principle—when two ends of the metal wire are attached with ... two ends of another metal wire, then a difference in temperature between the two ends cau... a current to flow in the wires. The intensity of radiation falling on the ... a current.

34. How will you explain that the carbonyl stretching frequency of an aldehyde is slightly higher than that of the corresponding methyl ketone ?

Ans. In case of methyl ketone (CH_3—CO—), the electron donating group is methyl which leads to more single bond character in carbonyl and hence $vC = O$ stretching is lowered.

35. The carbonyl stretching frequency in 2, 4, 6-cycloheptatrienone is exceptionaly low. Explain.

Ans. The exceptional low value of $vC = O$ str in 2, 4, 6-cycloheptatrienone is due to the conjugation effect. The cyclohepta trienyl cation (II) which is tropylium cation

I   II
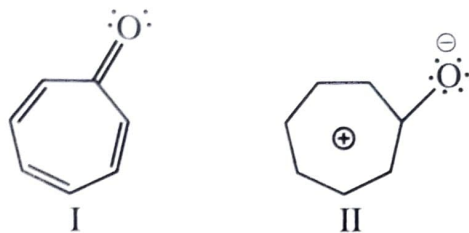
contains 6π electron cloud and its structure is stable. As a result of strong resonance contribution, the $vC = O$ str frequency is quite low.

36. Saturated aliphatic monocarboxylic acid, show carbonyl stretching near 1755 cm^{-1} whereas the saturated aliphatic ketones absorb near 1720 cm^{-1}. Explain.

Ans. In monocarboxylic acid, the carbonyl group is bound to oxygen atom. Now two opposing effect strongly influence the carbonyl frequency. These effects are inductive effect and mesomeric effect. Out of these, inductive effect dominates and thus absorption frequency in case of carboxylic acid is more.

3.16 Important Tips for Interpreting an Infra-red Spectrum

Following are some useful tips for interpreting an infra-red spectrum.

(i) Always place more reliance upon the negative evidence. The absence of a band in a particular region is a sure indication of the absence of group/groups absorbing in that region. For example if there is no absorption in the region 1900–1600 cm^{-1}, the carbonyl group $\left(>C=O \right)$ must be absent in the compound.

(ii) Always start from the higher frequency end of the spectrum. Mostly stretching vibrations occur in the region above 1500 cm^{-1} and are most informative. The region 1500–1000 cm^{-1} may be used for confirming esters, alcohols, ethers etc.

(iii) To distinguish between intermolecular and intramolecular hydrogen bonding, the spectra of the sample are scanned at two different concentrations. Various solvents may be used to study association effects.

(iv) For easy detection of the various groups present in the compound, the infra-red region (4000 to 667 cm^{-1}) may be visualised as consisting of the following portions:

Table T₃—15. Characteristic absorption frequencies of functional groups

Type of Vibration	Class of Compound	Frequency (cm^{-1})	Intensity
C – H Str	(i) Alkanes	2960-2850	(s)
C – H Str	(ii) Alkenes	3100-3010	(s)
C – H Str	(iii) Alkynes	~ 3300	(s)
C – H Str	(iv) Aromatics	3150-3020	(s)
C – H Str	(v) Aldehydes	~ 2820,	(w)
		2775-2720	(w)

C = C Str	(i)	Alkenes	1675-1600	(m,
C ⚌ C Str	(ii)	Aromatics	1600-1450	(m,
C ≡ C Str	(iii)	Alkynes	2260-2100	s
C = O Str	(i)	Aldehydes	1740-1720	(s)
C = O Str	(ii)	Ketones	1725-1705	(s)
C = O Str	(iii)	Carboxylic acids	1725-1700	(s)
C = O Str	(iv)	Esters	1750-1730	(s)
C = O Str	(v)	Amide	1680-1630	(s)
C = O Str	(vi)	Anhydrides	1850-1800 1790-1740	(s) (s)
C = O Str	(vii)	Acid chlorides	~ 1790	(s)
O – H Str	(i)	Alcohols and Phenols (dilute Solution)	3650-3580	(sharp,
O – H Str	(ii)	Alcohols, Phenols (Hydrogen bonded)	3550-3200	(b, s)
O – H Str	(iii)	Carboxylic acids	2700-2500	(b)
N – H Str	(i)	1°-amines, amides (Free) (Two bands)	~ 3500	(m)
N – H Str	(ii)	1°-amines, amides (H-bonded)	~ 3400	(m)
N – H Str	(iii)	2°-amines, amides Free-(one band)	3500-3300	(m)
N – H Str	(iv)	2°-amines, amides (Hydrogen bonded)	3310-3140	(m)
C ≡ N Str		Nitriles	2260-2220	(m)
$-\overset{+}{N}{\overset{O}{\underset{O}{\diagdown}}}^{\ominus}$ (Str)		Nitro compounds		
	(i)	Asymmetric	1620-1535	(s)
	(ii)	Symmetric	1375-1275	(v)
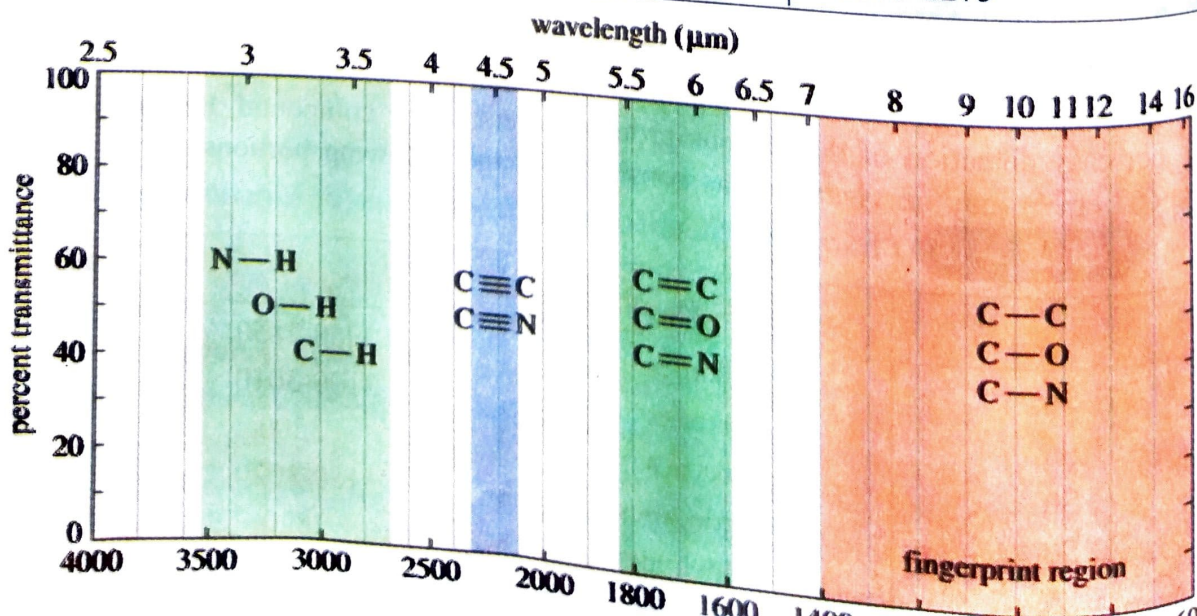
(a) **3600–3200 cm^{-1}**. The appearance of the bands in this region shows the presence of —OH, —NH$_2$, NH group in the compound. The position, intensity and the breadth of the bands tell whether the group is free, intramolecularly bonded or exhibit intermolecular hydrogen bonding. $\equiv$C—H str also shows a medium band near 3300 cm^{-1}.

(b) **3200–3000 cm^{-1}**. Absorptions due to C—H str and Ar—H stretching occur in this region. The sharp bands of weak to medium intensities are observed.

(c) **3000–2500 cm^{-1}**. The absorptions due to C—H stretching from methyl or methylene groups occur in this region. The asymmetric C—H stretching occurs at slightly higher wave number as compared to that of symmetric C—H str. A very broad band between 3000—2500 cm^{-1} is most characteristic of acids (—COOH group). Two weak bands, one at 2720 cm^{-1} and the other near 2820 cm^{-1} are most characteristic of C—H stretching in aldehydes. The higher frequency band is seldom observed.

(d) **2300—2100 cm^{-1}**. This is the region in which alkynes, cyanides, cyanates, isocyanates absorb. The bands observed are weak and variable. —C≡C stretching occurs between 2140–2100 cm^{-1}. —C≡N stretching shows a variable band between 2260–2200 cm^{-1}. Isocyantes show a strong band between 2280–2250 cm^{-1}.

(e) **1900–1650 cm^{-1}**. Strong bands due to C=O stretching occur in this region.

Anhydrides show two strong bands in the region 1850–1740 cm^{-1}. Esters, aldehydes, ketones, lactones, carboxylic acids, amides show strong bands due to C=O stretching in this region. Imides are also recognised by two strong bands (doublet) in the region around 1700 cm^{-1}. Following points regarding C=O stretching may be helpful.

(i) α, β-unsaturation lowers the frequency of absorption by 15–40 cm^{-1}. But in amides, a small absorption shift towards lower frequency is observed.

(ii) Increase in the ring strain in case of cyclic ketones raises $vC=O$ absorption.

(iii) Hydrogen bonding to the carbonyl compound lowers $vC=O$ absorption by 40–60 cm^{-1}.

(f) **1600–1000 cm^{-1}**. This region is very important for identifying nitro compounds and also confirming the presence of ethers, esters, primary, secondary and tertiary alcohols. The appearance of strong bands due to C—O stretching at 1300–1050 indicates (i) an ester provided C=O stretching is observed in the region 1750–1735 cm^{-1} and (ii) an alochol if O–H stretching free and/or bonded occurs between 3600–3200 cm^{-1}. Ethers show a strong band in the region 1150–1070 cm^{-1} due to C—O stretching in —C—O—C—. This region also helps to identify C—H str in aromatic compounds. For aromatic rings, medium bands around 1600 cm^{-1}, 1580 cm^{-1} and 1500 cm^{-1} are observed.

(g) **Below 1000 cm^{-1}**. This region is very useful in identifying the type of substitution on the aromatic ring:

(i) a strong band at 770–730 cm^{-1} (s) shows monosubstitution.

(ii) ortho and para disubstituted compounds show one band each. The latter absorbs at a higher wavenumber.

(iii) Meta-disubstituted compounds are usually recognised by two medium bands in the region 850–710 cm^{-1}.

3.17 Important Terms and Definitions in Infra-red Spectroscopy

1. **Infra-red region.** For structure elucidation, the Infra-red region is from 4000–667 cm^{-1}. Out of this, the high frequency region (4000–1300 cm^{-1}) is the functional group region and that from 1300–667 cm^{-1} is the finger print region.

2. **Infra-red spectrum.** I.R. spectrum of a compound represents its energy absorption pattern in the infra-red region. It is obtained by plotting percent absorbance/transmittance of the