

**Example 6.20.** How do distinguish a  $\pi \rightarrow \pi^*$  transition from  $n \rightarrow \pi^*$  transition? (P.T.U. Dec, 2004)

**Solution:** The  $\lambda_{\max}$  value of a  $\pi \rightarrow \pi^*$  transition is less as compared to that of  $n \rightarrow \pi^*$  transition.

**Example 6.21.** What is Hypochromic effect in UV spectroscopy? (P.T.U. May 2003)

**Solution:** Hypochromic effect is defined as the decrease in the intensity of absorption band i.e. a decrease in  $\epsilon_{\max}$  due to presence of certain groups. For example, on replacing a hydrogen atom in benzene by a chloro group hypochromic shift is produced.

**Example 6.22.** Arrange the following compounds in the increasing order of their UV absorption maxima: ethylene, naphthalene, anthracene, 1,3-butadiene.

**Solution:** The absorption maxima ( $\lambda_{\max}$ ) increases with the increase in the number of conjugated  $\pi$ -bonds. So the increasing order of  $\lambda_{\max}$  for the compounds is:



**Example 6.23.** What type of transitions will be obtained in the UV spectra of (a) acetone (b) aniline. (P.T.U. May 2005)

**Solution:** (a) acetone :  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$

(b) aniline :  $\pi \rightarrow \pi^*$ ,  $n \rightarrow \pi^*$ ,  $n \rightarrow \sigma^*$

**Example 6.24.** Which out of  $\text{CH}_3\text{COCH}_3$  and  $\text{CH}_2=\text{CHCOCH}_3$  exhibits higher value of  $\lambda_{\max}$  in UV spectroscopy?

**Solution:** Due to presence of conjugation,  $\text{CH}_2=\text{CHCOCH}_3$  exhibits higher value of  $\lambda_{\max}$  than  $\text{CH}_3\text{COCH}_3$ .

**Example 6.25.** How will you distinguish 1,3-pentadiene and 1,4-pentadiene by UV spectroscopy?

**Solution:** Due to presence of conjugated double bonds, 1,3-pentadiene shows a higher value of absorption maxima as compared to 1,4-pentadiene.

**Example 6.26.** Mention the type of transition occurring in the UV spectra of the following compounds: (a) benzene (b) methane (c) ethanol. (P.T.U. May 2005)

**Solution:** (a) benzene :  $\pi \rightarrow \pi^*$

(b) methane :  $\sigma \rightarrow \sigma^*$

(c) ethanol:  $n \rightarrow \sigma^*$ ,  $\sigma \rightarrow \sigma^*$

## 1.13. INFRARED SPECTROSCOPY

Infrared spectroscopy refers to the spectrum obtained due to vibrational transitions caused by absorption of infrared radiations by molecules.

It is also called vibrational spectroscopy as it involves the transitions between the vibrational energy levels of molecules. It is abbreviated as IR Spectroscopy.

The infrared radiations absorbed by molecules can induce transitions between vibrational energy levels as well as between rotational energy levels. So it is also called Rotational-Vibrational spectroscopy.

Infrared spectroscopy is a useful technique which gives important information about the structure of a compound. It is an important tool to confirm the structure of a known compound. The structure of a newly synthesized compound can be established with the help of Infrared spectroscopy.

### 1.13.1 Infrared Region

The Infrared radiations cause various bonds of molecules to vibrate. Depending on the energy of infrared radiations, the infrared region is divided in three major regions as shown in Table 1.3.

**Table 1.3 Wavelength and wavenumber of Infrared radiation**

Region	Wavenumber ( $\bar{\nu}$ ) range ( $\text{cm}^{-1}$ )	Wavelength ( $\lambda$ ) range ( $\mu\text{m}$ )
Near IR Region	12500 – 4000	0.8 – 2.5
IR Region	4000 – 667	2.5 – 15
Far IR Region	667 – 50	15 – 200

The most useful infrared region lies between  $4000 - 667 \text{ cm}^{-1}$ . The energy of the radiations in this region lies between 1 to 15 Kcal/mole. This energy is not sufficient to excite the electrons in a molecule. It can only cause the stretching or bending of the bonds of molecules. The region between  $12500 - 4000 \text{ cm}^{-1}$  is called near IR region and the region between  $667 - 50 \text{ cm}^{-1}$  is called far IR region.

The IR spectra of compounds are plotted as percentage transmittance against wavenumber. The percentage transmittance is plotted along y-axis and wavenumber is plotted along x-axis.

### 1.13.2 Fundamental Modes of Vibrations and Types

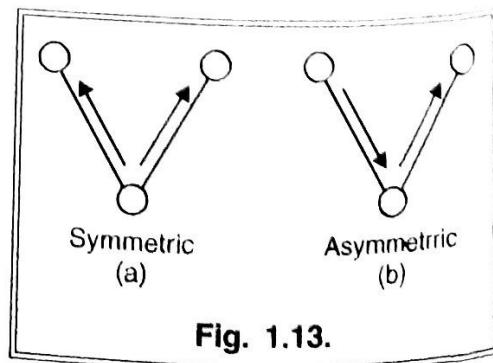
The atoms in a molecule are not held rigidly. The atoms are constantly vibrating about the inter-connecting bonds. These vibrations are called *molecular vibrations*. The two major types of vibrations which occur in molecules are stretching vibrations and bending vibrations, and these are explained below:

#### TYPE I : STRETCHING VIBRATIONS

In stretching vibrations the positions of the atoms change thereby producing changes in bond lengths without any change in the bond angles. Stretching vibrations are of following two types:

(i) **Symmetric stretching:** In symmetric stretching, the movement of the atoms with respect to a particular atom in a molecule is in the same direction [Fig 1.13(a)].

(ii) **Asymmetric stretching:** In asymmetric stretching, one atom moves away from the central atom and the other atom approaches the central atom [Fig 1.13(b)].

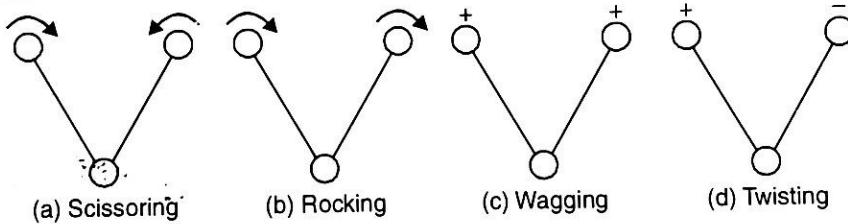


**Fig. 1.13.**

## TYPE II : BENDING VIBRATIONS

In bending vibrations the positions of the atoms change thereby producing changes in bond angles without any change in the bond length (Fig 1.14). The Bending vibrations are of following types:

- (i) **Scissoring:** In this vibration, the two atoms approach each other in the same plane.
- (ii) **Rocking:** In this vibration, the movement of atoms take place in the same direction and in the same plane.
- (iii) **Wagging:** This vibration involves the movement of two atoms up and below with respect to central atom.
- (iv) **Twisting:** This vibration involves the movement of one atom up the plane while the other atom moves down the plane with respect to central atom. In Figure 1.14, the positive sign on an atom indicates the movement of atom up the plane and negative sign on an atom indicates the movement of atom down the plane.



**Fig. 1.14. Bending Vibrations**

It may be pointed out here that more energy is required for the stretching of a bond and less energy is required for the bending of the bond. *Hence, in the infrared spectrum, the stretching absorption of a bond appear at high frequency (or low wavelength) as compared to the bending absorption of the same bond.*

### 1.13.3 Theory of Infrared Spectra

To record the I.R. spectra of a molecule, infrared radiation is incident on the molecule. The molecule will absorb the infrared radiation if the molecular vibrations caused by the infrared radiation produce a change in the dipole moment of the molecule.

*Only those molecules show infrared spectra which undergo a change in dipole moment on the absorption of Infrared radiation.*

Consider the following example of HCl :

The dipole moment ( $\mu$ ) for a molecule HCl is given by

$$\mu = \delta \times d \quad \text{H}^{\delta+} - \text{Cl}^{\delta-}$$

where ' $\delta$ ' refers to charge developed on H and Cl, and ' $d$ ' is the bond length

On absorption of infrared radiation, HCl molecule undergoes stretching vibrations producing a change in the bond length. Hence, the dipole moment of HCl will undergo a change on the absorption of infrared radiation. So, HCl molecule will show I.R. spectrum.

*The molecules which show infrared spectra are called I.R. active.*

Similarly, it can be shown that all the heteronuclear diatomic molecules can show infrared spectra and hence are I.R. active. CO, HBr, NO, HI are examples of I.R. active molecules. The individual bonds like O – H, N – H, C ≡ N, C = O are also I.R. active.

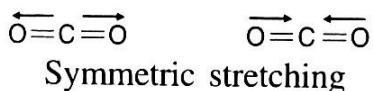
The homonuclear diatomic molecules can not show infrared spectra as they do not have permanent dipole moment and hence are called I.R. inactive. H<sub>2</sub>, Cl<sub>2</sub>, O<sub>2</sub> are examples of I.R. inactive molecules.

**Example of Carbondioxide:** The I.R. spectra may be shown by those molecules which do not have any permanent dipole moment ( $\mu = 0$ ) but which on the absorption of infrared radiation undergo a change in the value of dipole moment from the initial zero value.

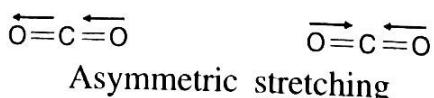
CO<sub>2</sub> has no permanent dipole moment as the instantaneous dipole of two (C = O) bonds is in opposite direction and hence cancel each other.



On symmetric stretching of CO<sub>2</sub> molecule, no change in dipole moment occurs as both the C = O bonds undergo stretching or contraction of equal extent. So, the individual dipole of two C = O bonds is equal and cancel each other. So, *symmetric stretching mode of CO<sub>2</sub> molecule is I.R. inactive*.



The asymmetric stretching of CO<sub>2</sub> causes stretching of one C = O bond and contraction of other C = O bond. Now, both the C = O bonds will have different value of dipole and will not be able to cancel each other. So, asymmetric stretching produces a change in the dipole moment of CO<sub>2</sub> molecule from the original zero value. Hence, *asymmetric stretching mode of CO<sub>2</sub> molecule is I.R. active*.



#### 1.13.4 Vibrational Frequency and Energy Levels

A diatomic molecule consisting of two atoms joined by a bond vibrates as a one dimensional *simple harmonic oscillator*. The value of stretching vibrational frequency of a bond can be calculated using the Hook's law which is represented as follows

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \dots(1.10)$$

where  $\nu$  is the fundamental frequency of vibration.

$k$  is force constant of bond and relates to strength of bond

$\mu$  is reduced mass of molecule and is explained below :

For a diatomic molecule XY, consisting of atom X having mass m<sub>1</sub> and atom Y having mass m<sub>2</sub>, the reduced mass  $\mu$  is given by

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}$$

Further, as  $c = \nu\lambda$

$$\Rightarrow \bar{\nu} = \frac{c}{\lambda} = c \bar{\nu} \quad \left( \because \bar{\nu} = \frac{1}{\lambda} \right)$$

Substituting this value of  $\mu$  in equation (1.10), we get

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \quad \dots(1.11)$$

The energy of a vibrational energy level is given by

$$E_{\text{vib}} = \left( v + \frac{1}{2} \right) h\nu \quad \dots(1.12)$$

where  $v$  is the vibrational quantum number and  $\nu$  is the fundamental vibrational frequency.

The energy of lowest vibrational energy level ( $v = 0$ ) is

$$E_0 = \left( v + \frac{1}{2} \right) h\nu = \left( 0 + \frac{1}{2} \right) h\nu = \frac{1}{2} h\nu$$

This means that molecule possesses energy even at zero vibrational level and it is called **zero point energy**.

Similarly, the energy of first vibrational energy level ( $v = 1$ ) is

$$E_1 = \left( v + \frac{1}{2} \right) h\nu = \left( 1 + \frac{1}{2} \right) h\nu = \frac{3}{2} h\nu$$

So, the energy of any vibrational level can be calculated by equation (1.12). These energies are shown in Figure (1.15) where energy is plotted against internuclear distance.

In order to raise a molecule from the level  $v$  to  $v + 1$ , the energy required is given by

$$\begin{aligned} \Delta E &= E_{v+1} - E_v \\ &= \left( (v + 1) + \frac{1}{2} \right) h\nu - \left( v + \frac{1}{2} \right) h\nu = h\nu \end{aligned}$$

The vibrational energy levels are equally spaced with a spacing of  $h\nu$ .

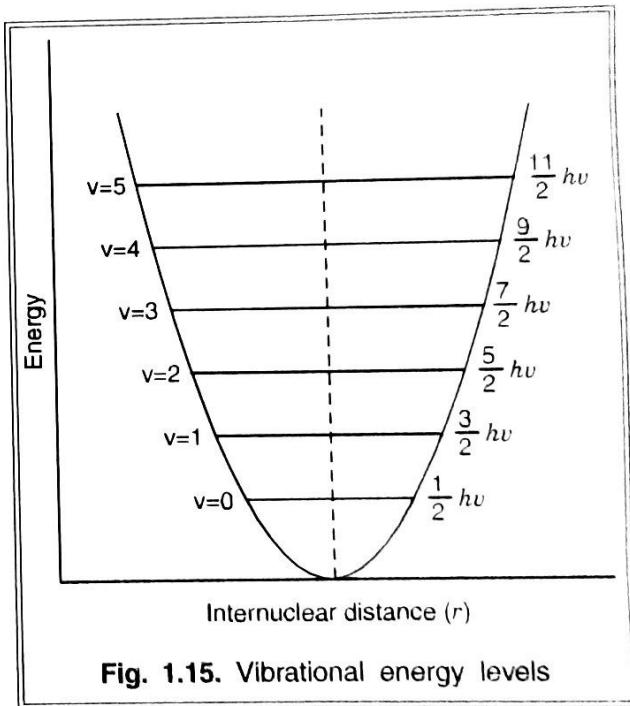
### 1.13.5. Anharmonics

A molecule vibrating as a simple harmonic oscillator is represented by a parabolic potential energy curve (Fig. 1.15). The potential energy is given by Hook's Law :

$$V(r) = \frac{1}{2} k (r - r_e)^2$$

where  $r_e$  is equilibrium bond length.

However, a molecule does not always vibrate as a simple harmonic oscillator. At high vibrational excitations, the large amplitude of vibrations allows the molecule to explore



**Fig. 1.15.** Vibrational energy levels

regions of the potential energy curve which are not parabolic. This motion is called anharmonic.

In anharmonic motion, the restoring force is no longer proportional to displacement. The potential energy of an anharmonic oscillator is given by :

$$V(r) = D_e [1 - e^{a(r-r_e)}]^2$$

where 'a' is a constant and  $D_e$  is the dissociation energy of the molecule.

The frequency (in  $\text{cm}^{-1}$ ) for the vibrational transition in anharmonic oscillator is given by

$$\bar{v} = \left(v + \frac{1}{2}\right) w_e - \left(v + \frac{1}{2}\right)^2 w_e r_e$$

where

$w_e$  = equilibrium vibrational frequency

$r_e$  = anharmonicity constant

$v$  = vibrational quantum number

As  $w_e r_e \ll w_e$ , hence, due to anharmonicity, the vibrational energy levels are lowered. The spacing between levels goes on decreasing with increase in vibrational quantum number.

The vibrational transitions follow the selection rule  $\Delta v = \pm 1$ . The transition from  $v = 0$  to  $v = 1$  is most intense because the ground energy level is most populated. It is called fundamental transition. However, due to anharmonicity, sometimes the transitions from  $v = 0$  to  $v = 2$  or from  $v = 0$  to  $v = 3$  are also observed. These are called overtones. These are less intense as they violate the selection rule (Fig. 1.16).

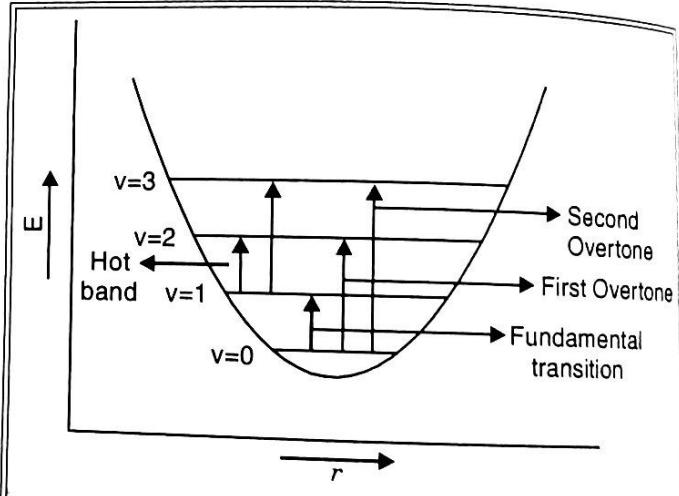


Fig. 1.16. Vibrational transitions

At higher temperature, the molecules are present in higher vibrational energy levels. So, there is probability of transitions from  $v = 1$  to  $v = 2$  or from  $v = 1$  to  $v = 3$ . These transitions are called hot bands as they take place at high temperature.

## Solved Numericals

**Numerical 1.1.** Calculate the force constant of HCl if the fundamental frequency of vibration is  $8.667 \times 10^{13} \text{ s}^{-1}$ .

**Solution:** Mass of hydrogen atom,  $m_H = \frac{1.008}{6.02 \times 10^{23}}$

$$= 1.67 \times 10^{-24} \text{ g} = 1.67 \times 10^{-27} \text{ Kg}$$

Mass of chlorine atom,  $m_{\text{Cl}} = \frac{35.5}{6.02 \times 10^{23}} = 5.89 \times 10^{-23} \text{ g} = 5.89 \times 10^{-26} \text{ Kg}$

Reduced mass of HCl is given by

$$\frac{1}{\mu} = \frac{1}{m_H} + \frac{1}{m_{Cl}}$$

Substituting the values of  $m_H$  and  $m_{Cl}$ , we get

$$\mu = 1.6277 \times 10^{-27} \text{ kg}$$

Given: frequency of vibration  $\nu = 8.667 \times 10^{13} \text{ s}^{-1}$

As,

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

So, force constant

$$\begin{aligned} k &= 4\pi^2 \nu^2 \mu \\ &= 4 \times (3.142)^2 \times (8.667 \times 10^{13})^2 \times 1.6277 \times 10^{-27} \\ &= 483.1 \text{ N m}^{-1} \end{aligned}$$

**Numerical 1.2.** If the force constant of CO molecule is  $1840 \text{ Nm}^{-1}$ . Calculate the fundamental frequency of vibration in  $\text{cm}^{-1}$ .

**Solution:** Mass of carbon atom,  $m_C = \frac{12}{6.02 \times 10^{23}} = 19.9 \times 10^{-24} \text{ g} = 19.9 \times 10^{-27} \text{ Kg}$

Mass of oxygen atom,  $m_O = \frac{16}{6.02 \times 10^{23}} = 26.6 \times 10^{-24} \text{ g} = 26.6 \times 10^{-27} \text{ Kg}$

Reduced mass  $\mu$  of CO is given by

$$\frac{1}{\mu} = \frac{1}{m_C} + \frac{1}{m_O}$$

Substituting the values of  $m_C$  and  $m_O$ , we get

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

Force constant of CO molecule,  $k = 1840 \text{ Nm}^{-1}$

Velocity of radiation  $c = 3 \times 10^8 \text{ m sec}^{-1}$

Fundamental frequency of vibration in  $\text{cm}^{-1}$  (or wave number)

$$\begin{aligned} \bar{\nu} &= \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \\ &= \frac{1}{2 \times 3.142 \times 3 \times 10^8} \sqrt{\frac{1840}{1.138 \times 10^{-26}}} = 2.132 \times 10^5 \text{ m}^{-1} \\ &= 2.132 \times 10^5 \times 10^{-2} \text{ cm}^{-1} = 2132 \text{ cm}^{-1} \end{aligned}$$

**Numerical 1.3.** The force constant of HF molecule is  $970 \text{ Nm}^{-1}$ . Calculate the frequency of vibration in  $\text{cm}^{-1}$  required to excite the molecules from  $\nu = 0$  to  $\nu = 1$ .

**Solution:** Mass of hydrogen atom,  $m_H = \frac{1.008}{6.02 \times 10^{23}} = 1.67 \times 10^{-24} \text{ g} = 1.67 \times 10^{-27} \text{ kg}$

$$\text{Mass of fluorine atom, } m_F = \frac{19}{6.02 \times 10^{23}} = 31.56 \times 10^{-24} \text{ g} = 31.56 \times 10^{-27} \text{ kg}$$

Reduced mass  $\mu$  of HF is given by

$$\frac{1}{\mu} = \frac{1}{m_H} + \frac{1}{m_F}$$

Substituting the values of  $m_H$  and  $m_F$ , we get

$$\mu = 1.577 \times 10^{-27} \text{ kg}$$

Force constant of HF,  $k = 970 \text{ Nm}^{-1}$

Velocity of radiation  $c = 3 \times 10^8 \text{ m sec}^{-1}$

Fundamental frequency of vibration in  $\text{cm}^{-1}$  (or wave number)

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

$$= \frac{1}{2 \times 3.142 \times 3 \times 10^8} \sqrt{\frac{970}{1.577 \times 10^{-27}}} = 415890 \text{ m}^{-1}$$

$$= 415890 \times 10^{-2} \text{ cm}^{-1} = 4158.9 \text{ cm}^{-1}$$

### 1.13.6 Modes of Vibrations of Polyatomic Molecules (IR Spectra of Polyatomic Molecules)

The number of vibrational absorption signals shown by a polyatomic molecule depends on the degrees of freedom of molecule.

*The degrees of freedom of a molecule is defined as the number of independent coordinates required to describe the position of the molecule completely.*

Consider a molecule containing  $N$  atoms. The position of an atom can be known completely by three coordinates  $x$ ,  $y$  and  $z$ . So, the total number of coordinates required to describe the position of  $N$  atoms is  $3N$ . Hence the degrees of freedom of a molecule are  $3N$ .

The total degrees of freedom of a molecule consist of translational degrees of freedom, rotational degrees of freedom and vibrational degrees of freedom.

So, for a molecule containing  $N$  atoms,

$$\begin{array}{ccc} \text{translational} & + & \text{rotational} \\ \text{degrees of freedom} & & \text{degrees of freedom} \end{array} + \begin{array}{c} \text{vibrational} \\ \text{degrees of freedom} \end{array} = 3N \quad \dots(1.13)$$

**For linear molecule:**

Translational degrees of freedom = 3

Rotational degrees of freedom = 2

So, from equation (1.13)

Vibrational degrees of freedom =  $3N - 3 - 2 = 3N - 5$

*These are also called normal modes of vibration.*

Hence, theoretically there will be  $3N - 5$  fundamental bands for a linear molecule.

**For non-linear molecule:**

Translational degrees of freedom = 3

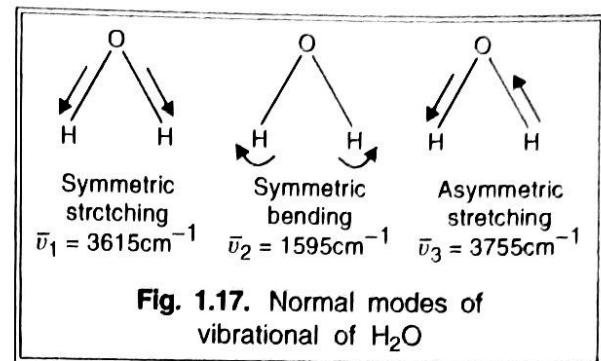
Rotational degrees of freedom = 3

So, from equation (1.13)

Vibrational degrees of freedom

$$= 3N - 3 - 3 = 3N - 6$$

So, a non-linear molecule will have

 $3N - 6$  normal modes of vibration.**Example of  $\text{H}_2\text{O}$  molecule:**  $\text{H}_2\text{O}$  is a non-linear molecule, soNormal modes of vibration of  $\text{H}_2\text{O}$ 

$$= 3N - 6 = (3 \times 3) - 6 = 3$$

The three normal modes of vibration of  $\text{H}_2\text{O}$  are shown in Figure (1.17).

As it is easy to bend a molecule than to stretch it, so the frequency of bending vibration is less than the frequency of stretching vibration ( $\bar{\nu}_2 < \bar{\nu}_1$ ). Also, it is easier to stretch a molecule symmetrically than to stretch it asymmetrically, so the frequency of symmetric stretching vibration is less than the frequency of asymmetric stretching vibration ( $\bar{\nu}_1 < \bar{\nu}_3$ ).

**1.13.7 Characteristic Signals of Infrared Spectrum**

The different functional groups undergo absorption at different values of wavenumber of infrared radiation. Each functional group is characterized by absorption signal at a typical value of wave number. These absorption signals for different functional groups are shown in Table 1.4.

**Table 1.4 IR absorption signals of different functional groups**

Functional group	Type of vibration	Wave number ( $\bar{\nu}$ ) ( $\text{cm}^{-1}$ )	
Alcohol	O – H	stretching	3200 – 3600
Alkane	C – H	stretching	2850 – 3000
	C – H	bending	1350 – 1470
Alkene	C = C	stretching	1620 – 1680
	= C – H	stretching	3010 – 3150
	= C – H	bending	675 – 1000
Alkyne	C ≡ C	stretching	2100 – 2200
	≡ C – H	stretching	3300 – 3350
Aromatic	C = C	stretching	1580 – 1650
	=C – H	stretching	3000 – 3100
Carbonyl	C = O	stretching	1680 – 1820
Ether	C – O	stretching	1000 – 1300
Amine	N – H	stretching	3300 – 3500
	N – H	bending	1600 – 1650
Nitrile	C ≡ N	stretching	2210 – 2280
Alkyl Halide	C – Cl	stretching	600 – 700

The typical absorption signals shown in table 1.4 may be conveniently studied by dividing the signals in the following four regions:

(i) **Hydrogen stretching vibrations region:** This region is in the range 2500-3700 cm<sup>-1</sup>. The IR signals in this region are shown by stretching vibrations of bonds like O-H, C-H, N-H. The high value of wave number for these bonds is due to the low mass of hydrogen. (as  $\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$ ).

(ii) **Triple bond region:** This region is in the range 2000-2500 cm<sup>-1</sup>. The triple bonds like C ≡ C and C ≡ N undergo absorption in this region. The high value of wave number in this case is due to the large force constants of triple bonds.

(iii) **Double bond region:** This region is in the range 1600-2000 cm<sup>-1</sup>. The IR signals in this region are shown by the stretching vibrations of C = C, C = O, C=N bonds.

(iv) **Single bond region:** This region is in the range 500-1600 cm<sup>-1</sup>. The IR signals in this region are shown by stretching and bending vibrations of single bonds of different molecules. This region is called *finger print region*.

### 1.13.8 Finger Print Region

The most useful region of infrared spectra lies between 4000 – 600 cm<sup>-1</sup>. The region 4000-1500 cm<sup>-1</sup> is called **functional group region** as most of the functional groups show their characteristic absorption bands in this region (Fig. 1.18). The presence of a functional group in a compound can be confirmed by analyzing the position of absorption bands in functional group region.

The region below 1500 cm<sup>-1</sup> is called **finger print region**. In the I.R. spectrum of a molecule, a number of absorption bands are obtained in the finger print region due to bending vibrations of the different bonds of molecule. The pattern of peaks obtained in finger print region is very complex (like the finger prints of human beings). These peaks are characteristic feature of a compound.

*No two compounds can have the same pattern of peaks in finger print region.*

The finger print region can be used for comparing spectra of unknown compounds with known compounds to establish the identity of the unknown compound.

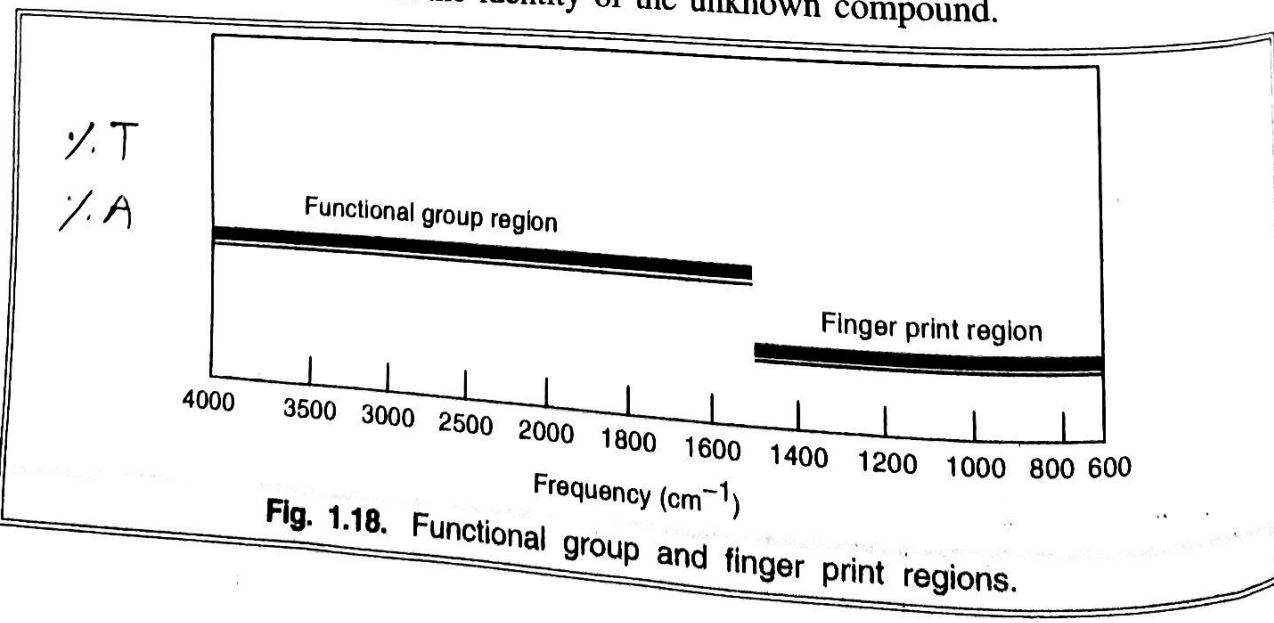
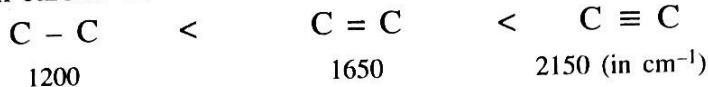


Fig. 1.18. Functional group and finger print regions.

### 1.13.9. Factors affecting Vibrational Frequency

The vibrational frequency of a molecule depends on the following factors :

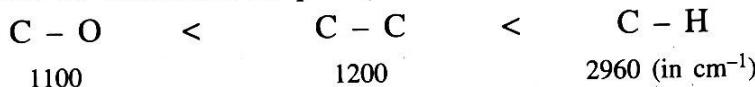
**1. Force Constant.** The vibrational frequency of a bond is directly proportional to the force constant of bond. For example, increasing order of stretching frequency of different types of carbon-carbon bonds is



**2. Reduced Mass.** The vibrational frequency of a bond is inversely proportional to reduced mass. So, higher the mass of bonded atoms, small is vibrational frequency. For example, the order of reduced mass of C – O, C – C, C – H bonds is :



Hence, order of vibrational frequency is :



**3. Hydrogen bonding.** As hydrogen bonding elongates a bond, so less energy is required for the vibration of that bond. Hence, the compound undergoing hydrogen bond formation give signal at lower vibrational frequency.

**4. Structure of Compound.** The vibrational frequency depends on the structure of compound. For example :

- (a) In Methane, the four hydrogen atoms vibrate symmetrically and there is no change in dipole moment of methane during vibration. Hence, methane does not absorb infrared radiation.
- (b) Carbonyl group ( $\text{C} = \text{O}$ ) has vibrational frequency in the range  $1650\text{-}1800 \text{ cm}^{-1}$  whereas ether group ( $\text{C} - \text{O} - \text{C}$ ) gives signal in the range  $1000\text{-}1250 \text{ cm}^{-1}$ .
- (c) 1-Hexyne, 1-hexene and hexane show typical infrared vibrational signal at  $3300 \text{ cm}^{-1}$ ,  $3095 \text{ cm}^{-1}$  and  $2850 \text{ cm}^{-1}$  respectively.

### 1.13.10 Applications of Infrared Spectroscopy

The following are the important applications of Infrared spectroscopy:

**1. Identification of functional groups:** Infrared spectroscopy is very useful in the identification of functional groups present in different compounds. Each functional group exhibits a characteristic absorption band in IR spectrum. For example, an aldehyde has an absorption signal at  $1710\text{-}1750 \text{ cm}^{-1}$ , an alcohol at  $3200\text{-}3600 \text{ cm}^{-1}$  and an alkyne at  $2100\text{-}2200 \text{ cm}^{-1}$ . Similarly, the absence of an absorption band in a particular region indicates the absence of that functional group in a compound.

**2. Detection of impurities:** A pure sample gives sharp and well resolved peaks. The presence of impurities reduces the sharpness of peaks and causes the appearance of extra peaks. This results in blurring of the spectrum. For example, if a compound does not contain any hydroxyl group ( $-\text{OH}$  group), but a peak is being shown by the compound in the range  $3200\text{-}3600 \text{ cm}^{-1}$ , then it indicates the presence of hydroxyl impurities in the compound.

**3. Structural determination of unknown compounds:** The structure of an unknown compound can be determined by comparing the absorption peaks of compound in finger print region with the peaks shown by a known compound. No two compounds can have identical IR spectra in finger print region. So by comparing the IR spectra of unknown compound and known compound it can be found if both these compounds are same or different.

**4. Distinction between inter and intra molecular hydrogen bonding:** As hydrogen bonding elongates a bond, so the absorption band of the compound having hydrogen bonding is obtained at lower value of wave number (i.e. lower energy). The dilution of a compound having intermolecular hydrogen bonding by a non-polar solvent decreases the extent of hydrogen bonding. Hence, the absorption band is obtained at higher value of wave number (i.e. higher energy). However, the intra molecular hydrogen bonding is not affected by dilution. So, the dilution of a compound having intra molecular hydrogen bonding produces no change in its IR spectrum.

**5. Kinetics of reactions:** The progress of a reaction can be analysed by IR spectroscopy. The functional groups present in a compound undergo rearrangement during the formation of products in a reaction. This is accompanied by a change in the position absorption band of compound. This change can be monitored by noting the IR spectra of the reaction mixture after regular intervals. For example, during the reduction of an alcohol to produce an aldehyde or ketone, the IR spectra of the reaction mixture after regular intervals will indicate the decrease in the intensity of the peak in the region  $3200 - 3600 \text{ cm}^{-1}$  (due to  $-\text{OH}$  group) and increase in the intensity of the peak in the region  $1700 - 1800 \text{ cm}^{-1}$  (due to  $\text{C} = \text{O}$  group).

## Solved Conceptual Problems

**Example 1.27. Why inverted peaks are obtained in the IR spectra of a compound?**

**Solution:** The IR signals are obtained when infrared radiation is absorbed by the compound. The IR spectrum is a plot of wavenumber of radiation vs transmittance. On the absorption of radiation, the intensity of transmitted radiation is decreased i.e. transmittance is decreased. This results in formation of inverted peaks in IR spectra.

**Example 1.28. Why ethylene does not show  $\text{C}=\text{C}$  stretching band in its IR spectrum?**

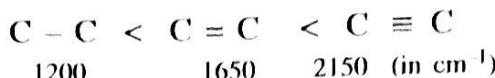
**Solution:** Since ethylene is a symmetrical molecule, so the stretching of  $\text{C}=\text{C}$  bond does not produce any change in the dipole moment of ethylene. So  $\text{C}=\text{C}$  stretching band is not obtained in its IR spectrum.

**Example 1.29. Using IR spectroscopy, how will you determine whether oxygen in a compound is present as a carbonyl, hydroxyl or ether group?**

**Solution:** In IR spectrum, carbonyl group will exhibit a strong absorption in the range  $1650-1800 \text{ cm}^{-1}$ . Thy hydroxyl group will show absorption in the range  $3100-3600 \text{ cm}^{-1}$  whereas ether will show band in the range  $1000-1250 \text{ cm}^{-1}$ .

**Example 1.30. Compare the relative stretching frequency of  $\text{C} - \text{C}$ ,  $\text{C} = \text{C}$  and  $\text{C} \equiv \text{C}$  bonds.**

**Solution:** As the frequency of vibration is directly proportional to the force constant of bond, so the increasing order of stretching frequency is



**Example 1.31.** What happens when a molecule absorbs infrared radiation?

**Solution:** Absorption of infrared radiation by a molecule induces transitions between the vibrational energy levels resulting in the formation of infrared spectrum.

**Example 1.32.** How can you distinguish between 1-hexyne, 1-hexene and 1-hexane on the basis of IR spectra? (P.T.U. Dec 2004, Dec 2006)

**Solution:** 1-Hexyne, shows a strong absorption at  $3300 \text{ cm}^{-1}$  due to terminal  $\equiv \text{C} - \text{H}$  stretching and a  $\text{C} \equiv \text{C}$  stretching absorption at  $2120 \text{ cm}^{-1}$ . IR spectrum of 1-hexene shows a band at  $3095 \text{ cm}^{-1}$  due to terminal  $= \text{C} - \text{H}$  stretching and a  $\text{C} = \text{C}$  stretching absorption at  $1640 \text{ cm}^{-1}$ . These typical signals are absent in hexane.

**Example 1.33.** When does a molecule absorb infrared radiation?

**Solution:** Infrared radiation is absorbed when the oscillating dipole moment of a molecule, due to molecular vibration, interacts with the oscillating electrical vector of infrared radiation. On absorption of radiation, the amplitude of that vibration is increased. This results in the vibrational transition and vibrational absorption spectrum is obtained.

**Example 1.34.** How would you distinguish between phenol and cyclohexanol using IR spectroscopy?

**Solution:** Both will show O–H stretching in the range  $3200\text{--}3400 \text{ cm}^{-1}$ . But C–H stretching of phenol would be obtained above  $3000 \text{ cm}^{-1}$  whereas cyclohexanol gives C–H stretching below  $3000 \text{ cm}^{-1}$ . Phenol also shows C–H bending vibration in the range  $650\text{--}1000 \text{ cm}^{-1}$ .

**Example 1.35.** What do you understand by IR spectra? (P.T.U. Dec 2004)

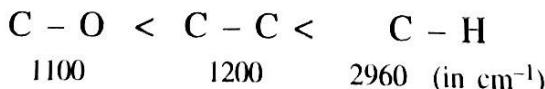
**Solution:** The IR spectra are obtained due to vibrational transitions caused by absorption of infrared radiations by molecules. It is also called vibrational spectroscopy as it involves the transitions between the vibrational energy levels of molecules.

**Example 1.36.** HCl is IR active but  $\text{H}_2$  and  $\text{Cl}_2$  are not. Explain.

**Solution:** HCl is a polar molecule having permanent dipole moment, so it is IR active. Both  $\text{H}_2$  and  $\text{Cl}_2$  are non-polar compounds having zero dipole moment and hence IR inactive.

**Example 1.37.** Arrange the following bonds in the increasing order of vibrational frequency:  $\text{C} - \text{H}$ ,  $\text{C} - \text{C}$ ,  $\text{C} - \text{O}$ .

**Solution:** The vibrational frequency is inversely proportional to the reduced mass, so as the mass of the atom bonded to carbon increases, the vibrational frequency decreases. So the increasing order of vibrational frequency is



**Example 1.38.** Why some fundamental vibrations are IR active and others are inactive?

**Solution:** IR radiation is absorbed only when a fundamental vibration produces a change in the dipole moment of molecule. Hence, only those fundamental vibrations are IR active which produce a change in the dipole moment whereas others will be IR inactive.