

# Chapter - 3

## 1.3 IR SPECTROSCOPY

### 1.3.1 Introduction

IR spectroscopy is an important analytical technique which helps in the chemical identification of a compound. IR radiations lie in the wavelength range of 1.2 - 400  $\mu$ m. IR spectroscopy is based upon selective absorption of IR radiations by the molecule which induces vibrational-rotational transitions within the molecule. These vibrational-rotational transitions produce closely packed absorption bands characteristic to the bonds and functional groups present in the molecule.

IR instruments are of two types namely, dispersive instruments (spectrophotometer) and Fourier transform infrared instrument (FTIR). The components of the instrument are similar to that of the UV-visible spectrophotometer except the radiation source and detector. The radiation sources used are incandescent lamp, Nernst glower etc. and the detector used are thermal and photon detectors.

IR spectrum of a compound is considered as fingerprint for its identification. Hence, it is used for identification and structural elucidation of the compounds. It can be used to study isomerism in inorganic compounds. It is also used to study the presence of water in the sample, symmetry of a compound etc.

### 1.3.2 Principle

IR spectroscopy is based upon the principle that, when a compound is exposed to IR radiations, it selectively absorbs the radiations resulting in vibration of the molecule of the compound. It results in closely packed absorption bands which are characteristic to the functional groups and bonds present in the compound. Thus an IR spectrum of a compound is considered as the fingerprint for its identification.

### 1.3.3 Theory

IR spectroscopy is one of the most widely used analytical technique for identification and determination of compounds. The IR region is divided into four sections.

| Region                                | Range ( $\mu$ ) |
|---------------------------------------|-----------------|
| Photographic region                   | Visible to 1.2  |
| Very near IR region (Overtone region) | 1.2 to 2.5      |
| Near IR region (Vibration region)     | 2.5 to 25       |
| Far IR region (Rotation region)       | 25 to 300 - 400 |

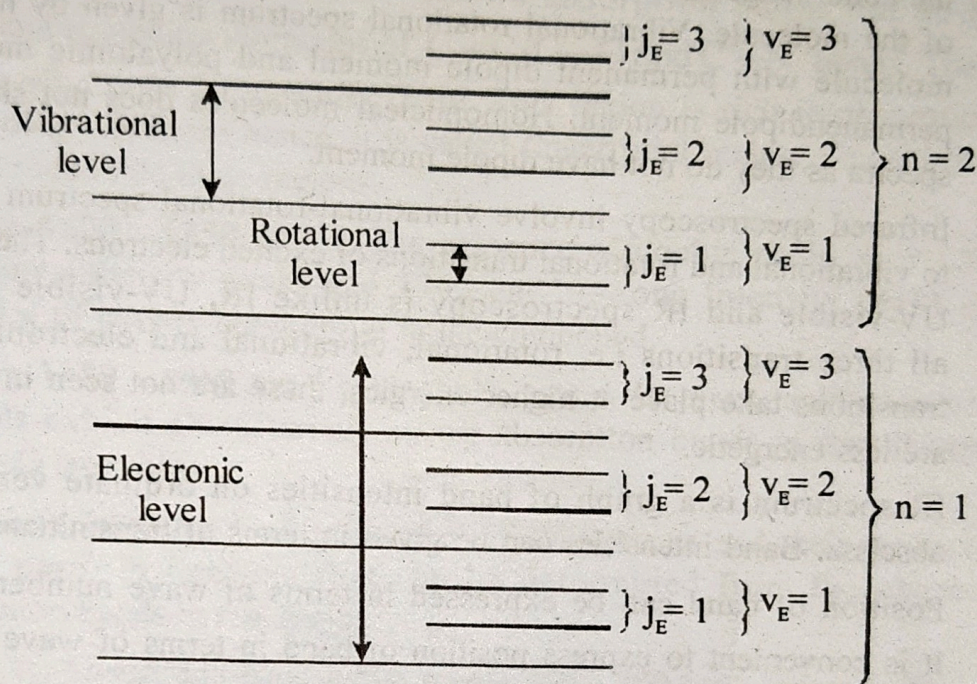


## IR Spectra :

A molecule in its ground state possesses three energy levels, electronic energy level ( $e_E$ ), vibrational energy level ( $v_E$ ) and rotational energy level ( $j_E$ ). The diagrammatic representation can be given as follows :

Figure :

Diagrammatic Representation of Different Energy Levels of a Molecule



When the molecule absorbs energy, electron jumps from lower energy level to the higher energy level. Depending upon the energy of incident IR radiations, various transitions may occur. When an electron absorbs less energy, rotational transition takes place. These transitions occur between the rotational quantum levels within the same vibrational level. As a result, changes take place in the rotational quantum number ( $j$ ). The spectrum observed is called rotational spectrum obtained in far IR region or rotation region (25 to 300 - 400  $\mu$ ).

When the electron absorbs still higher energy, vibrational transitions take place between the vibrational quantum levels within the same electronic level. As a result, changes take place in the vibrational quantum number ( $v$ ). The vibrational-transitions are accompanied with rotational transitions. The spectrum observed is called vibrational-rotational spectrum obtained in near IR region or vibration region (2.5 to 25  $\mu$ ).

When the transition of the electron occurs from  $v_E = 0$  to  $v_E = 1$ , the frequency of such resulting radiation is called fundamental vibrational frequency. When the transition of the electron occurs from  $v_E = 0$  to  $v_E = 2$ , the frequency of such radiation is called first overtone frequency. Similarly, transition from  $v_E = 0$  to  $v_E = 3$  gives second overtone frequency.



When the electron absorbs energy sufficient to cause electronic transitions which occur between the electronic quantum levels. ( $n = 1, 2, 3, \dots$  etc). As a result, changes take place in the principle quantum number ( $n$ ). These transitions are accompanied by both vibrational and rotational transitions. The spectrum observed is called electronic band spectrum obtained in visible and UV region.

Vibrational-rotational spectra helps in prediction of energy required to distort the bond length and bond angles from their equilibrium position and hence the flexibility of the molecule. Vibrational rotational spectrum is given by hetero molecular diatomic molecule with permanent dipole moment and polyatomic molecules with or without permanent dipole moment. Homonuclear molecules does not show vibrational-rotational spectra as they do not have dipole moment.

Infrared spectroscopy involve vibrational-rotational spectrum which occur mainly due to vibrational and rotational transitions of excited electrons. The basic difference between UV-visible and IR spectroscopy is unlike IR, UV-visible spectrum occurs due to all three transitions i.e, rotational, vibrational and electronic transitions. Electronic transitions take place at higher energies, these are not seen in IR because IR radiations are less energetic.

IR spectrum is a graph of band intensities on ordinate versus position of band on abscissa. Band intensities can be given in terms of transmittance ( $T$ ) or absorbance ( $A$ ). Position of band can be expressed in terms of wave number ( $\bar{\nu}$ ) or wavelength ( $\lambda$ ). It is convenient to express position of band in terms of wave number as these exists a direct relationship between wave number ( $\bar{\nu}$ ) and energy ( $E$ ).

$$E = \frac{hc}{\lambda}$$

where,

$E$  – Energy of radiation

$h$  – Planck's constant

$c$  – Velocity of light

$\lambda$  – Wavelength

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

IR spectrum is usually plotted using transmittance, hence, absorption band appears as dips rather than maxima. Each dip is called band or peak.

### Regions of IR Spectrum :

A molecule absorbs IR radiations of various wavelengths depending upon the nature of groups or bonds present in it and gives characteristic absorption bands. The presence of characteristic absorption band indicates the presence of a particular functional group. IR spectra is divided into two regions.



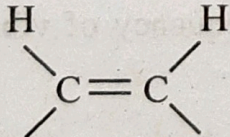
- (a) **Region 4000 - 1250  $\text{cm}^{-1}$**  : This region consists of absorption bands of vibrational states of various types of bonds present in the molecule.
- (b) **Fingerprint Region** : Region less than 1250  $\text{cm}^{-1}$  consists of **complex vibrational and rotational spectra of the complete molecule**. This region is useful for identification of the compounds since no two compounds can have identical IR spectra under identical conditions.

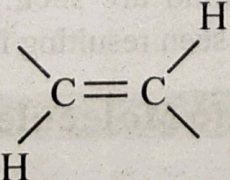
Region present below 1500  $\text{cm}^{-1}$  shows absorption bands due to bending vibrations and stretching vibrations of C - C, C - O and C - N bonds. The number of bending vibrations is generally more. This region is rich in absorption bands due to bending vibrations hence, it is called finger print region. Finger print region is further divided into three regions.

- (i) **Region 1500 - 1350  $\text{cm}^{-1}$**  : The presence of double peaks near 1380  $\text{cm}^{-1}$  (medium intensity peak) and 1365  $\text{cm}^{-1}$  (strong intensity peak) indicates presence of tertiary butyl group in the compound.
- (ii) **Region 1350 - 1000  $\text{cm}^{-1}$**  : Alcohols, esters, lactones, acid anhydrides and phenols exhibit characteristic strong absorption bands in the IR region due to C - O stretching.
- (iii) **Less than 1000  $\text{cm}^{-1}$**  : The number of substituents and their position (ortho, meta, para) in benzene ring can be determined from the characteristic absorption bands in this region.

*Example* : 1. Absorption band in the region 750 - 700  $\text{cm}^{-1}$  indicates the presence of mono substituted benzene.

2. Geometrical isomers of olefins can be distinguished in the region 970 - 700  $\text{cm}^{-1}$ . Higher wave number indicate that the hydrogen atoms in olefins are trans with respect to each other.

Cis-isomer  shows an absorption band at 700  $\text{cm}^{-1}$  (strong intensity

band) and trans isomer  at 970 - 960  $\text{cm}^{-1}$  (strong intensity band).

### 1.3.4 Criteria for Absorption of IR Radiation

- (i) **Wavelength of Incident Radiation** : The absorption of radiations by the molecule occurs only when the frequency of incident radiation is equivalent to natural frequency of vibration of the part of the molecule. The part of the molecule can be an atom or group of atoms. After absorption of characteristic radiations, the molecule vibrates with greater amplitude due to absorbed IR energy.

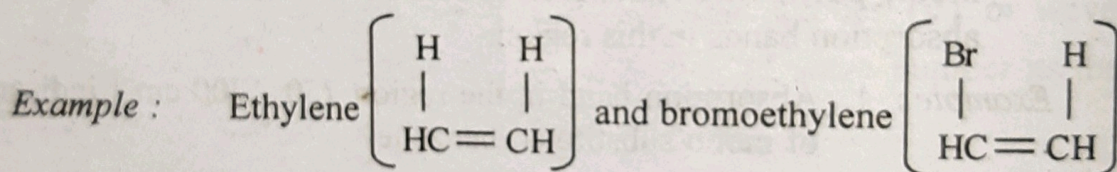


*Example:* HCl has vibrational frequency of  $8.7 \times 10^{13}$ /sec. When HCl sample exposed to IR radiations, it can be seen that only the radiations of frequency  $8.7 \times 10^{13}$ /sec. are absorbed and remaining are transmitted.

- (ii) **Dipole Moment and Symmetry of the Molecule:** A molecule will absorb radiation only when there is a change in dipole moment due to electric field of radiation. The electric charges +ve and -ve on the atoms of the molecule experience forces (due to the electric field of the IR radiations) in opposite directions. As a result, spacing between the charged atoms (electric dipoles) in the molecule also decrease. These charged atoms when vibrated absorb radiation. The amount of IR radiation absorbed by the molecule is proportional to the rate of vibration. If the rate of vibration in charged atoms is fast, they exhibit intense absorption and vice versa.

Symmetrical diatomic molecules ( $O_2$ ,  $N_2$ , etc) do not possess dipole moment and hence, cannot absorb IR radiations. Even though symmetrical compounds such as ethylene  $-C=C-$  exhibits dipoles, they do not show any change in dipole moment, upon  $C=C$  stretching.

If the symmetry of the compound is destroyed, it exhibits dipole moment and strong IR absorption.



Substitution of bromine for hydrogen of ethylene destroys the symmetry. Stretching of the double bond exhibits change in dipole moment and strong IR absorption takes place. If the atoms in the molecule are close to each other, the rate of change of electric dipole is fast. This increases the frequency of vibration and in turn increases the intensity of IR absorption.

When a polar molecule is exposed to IR radiations, stretching vibrations along the internuclear axis of the polar bond are seen. Hence, electron distribution changes and a change in dipole moment is seen resulting in absorption of IR radiations.

### 1.3.5 Vibrations In a Polyatomic Molecule

Polyatomic molecules give fundamental and overtone bands in IR spectra which are related to degrees of freedom in a molecule.

A polyatomic molecule contains ' $n$ ' number of atoms. Each atom has three degrees of freedom corresponding to three directions (coordinates X, Y and Z) which are perpendicular to each other. Since the number of atoms in a polyatomic molecule is ' $n$ ', Hence, the number of degrees of freedom will be  $3n$ .



The motion of a molecule can be described by considering three aspects. They are :

- (a) Translational Motion
- (b) Rotational Motion
- (c) Vibrational Motion

In a non-linear polyatomic molecule, three degrees of freedom describe translational motion and three describe rotational motion.

Degrees of freedom for translational motion = 3

Degrees of freedom for rotational motion = 3

Hence,

$$\begin{aligned} \text{Degrees of freedom for} & \quad \text{(Total number of degrees of} & \quad \left[ \begin{array}{cc} \text{Degrees of freedom} & \text{Degrees of freedom} \\ \text{vibrational motion of} & \text{freedom for a nonlinear} & - \left[ \begin{array}{cc} \text{for translational} & + \end{array} \right. \\ \text{nonlinear polyatomic molecule} & \text{polyatomic molecule)} & \quad \text{motion)} & \quad \text{for rotational} \\ & & \quad \text{motion)} & \quad \text{motion)} \end{array} \right] \\ & = 3n - (3 + 3) \\ & = 3n - 6 \end{aligned}$$

In a linear polyatomic molecule rotation about the bond axis is not possible. Hence, rotational motion is described by only two degrees of freedom. Further, 3 degrees of freedom describes the translational motion.

Therefore,

$$\begin{aligned} \text{Degrees of freedom for} & \quad \text{(Total number of degrees of} & \quad \left[ \begin{array}{cc} \text{Degrees of freedom} & \text{Degrees of freedom} \\ \text{vibrational motion of} & \text{freedom for a linear} & - \left[ \begin{array}{cc} \text{for translational} & + \end{array} \right. \\ \text{linear polyatomic molecule} & \text{polyatomic molecule)} & \quad \text{motion)} & \quad \text{for rotational} \\ & & \quad \text{motion)} & \quad \text{motion)} \end{array} \right] \\ & = 3n - (3 + 2) \\ & = 3n - 5 \end{aligned}$$

A normal mode is defined as  $(3n - 6)$  or  $(3n - 5)$  degrees of freedom of vibrational motion depending upon the non-linearity or linearity of the polyatomic molecule respectively. Normal modes of vibrations can be classified into two types :

**(a) Stretching Vibrations :**

- (i) Symmetric stretching vibrations
- (ii) Asymmetric stretching vibrations



**(b) Bending or Deformation Vibrations :**

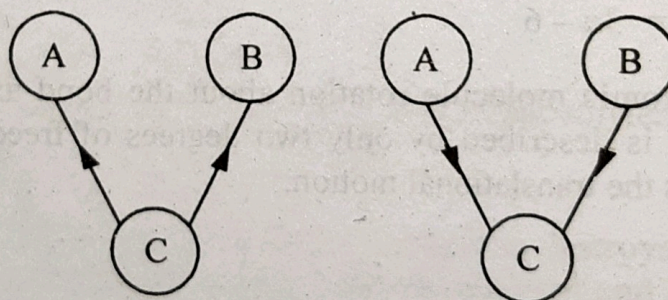
- (i) Scissoring deformation vibrations
- (ii) Wagging deformation vibrations
- (iii) Rocking deformation vibrations
- (iv) Twisting deformation vibrations

**(a) Stretching Vibrations :** These type of vibrations involve movement of atoms within the same bond axis such that the bond length changes without any change in bond angle at regular intervals. Symmetrical molecules like  $\text{O}=\text{C}=\text{O}$  are IR active because no change in dipole moment is observed upon stretching vibrations.

Non-cyclic systems show  $(n-1)$  stretching vibrations because, these vibrations describe one-dimensional motion. Bond angles change if acceleration due to gravity resist displacement.

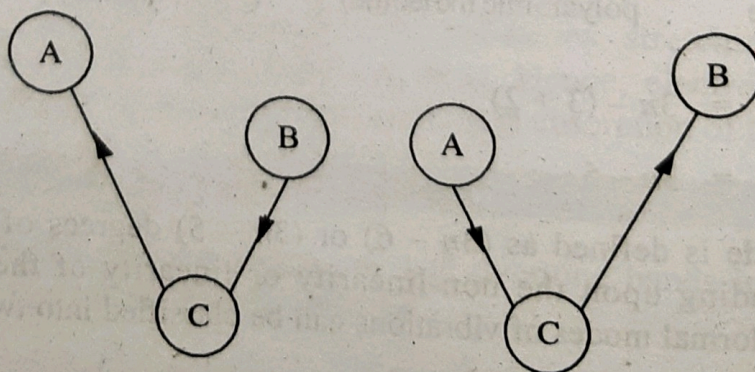
**(i) Symmetrical Stretching Vibrations :** In these type of vibrations, the atoms A and B, move away or towards the central atom, without any change in bond axis or bond angle.

**Figure :**  
Symmetrical  
Stretching  
Vibrations



**(ii) Asymmetrical Stretching Vibrations :** In these type of vibrations, the atoms A and B, move with respect to central atom such that one moves away and the other moves towards the central atom C.

**Figure :**  
Asymmetrical  
Stretching  
Vibrations

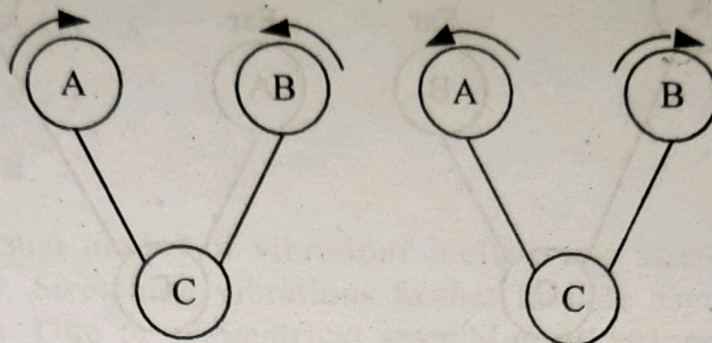


**(b) Bending or Deformation Vibrations :** These types of vibrations involve movement of atoms which are attached to a common central atom, such that there is change in bond axis and bond angle of each individual atom without any change in their bond lengths.



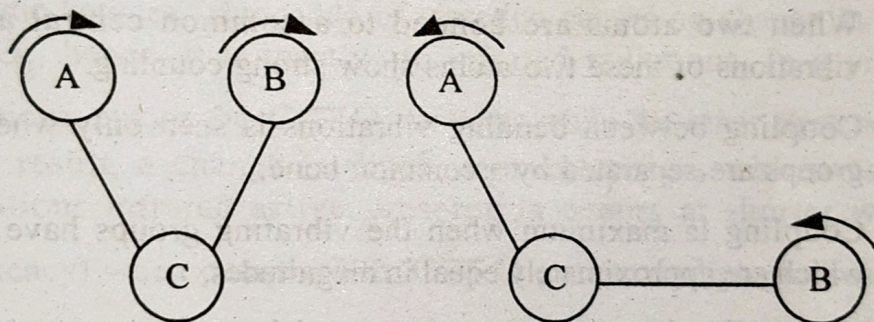
- (i) **Scissoring Deformation Vibrations** : In these type of vibrations, in plane bending of atoms occur wherein they move back and forth.

Figure :  
Scissoring  
Deformation  
Vibrations

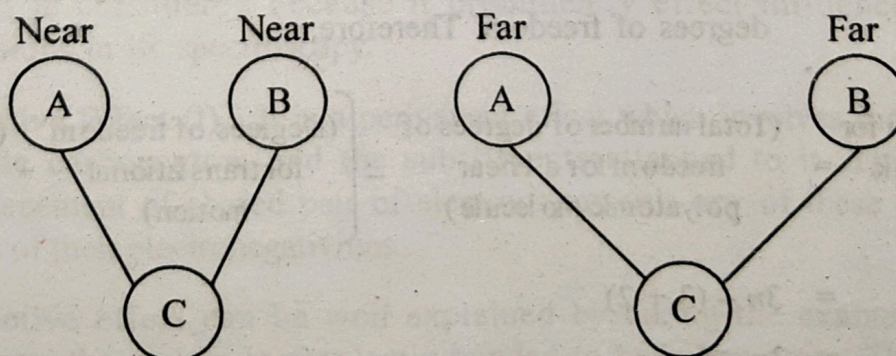


- (ii) **Rocking Deformation Vibrations** : In these type of vibrations, in plane bending of atoms occur wherein they swing back and forth with respect to the central atom.

Figure :  
Rocking  
Deformation  
Vibrations

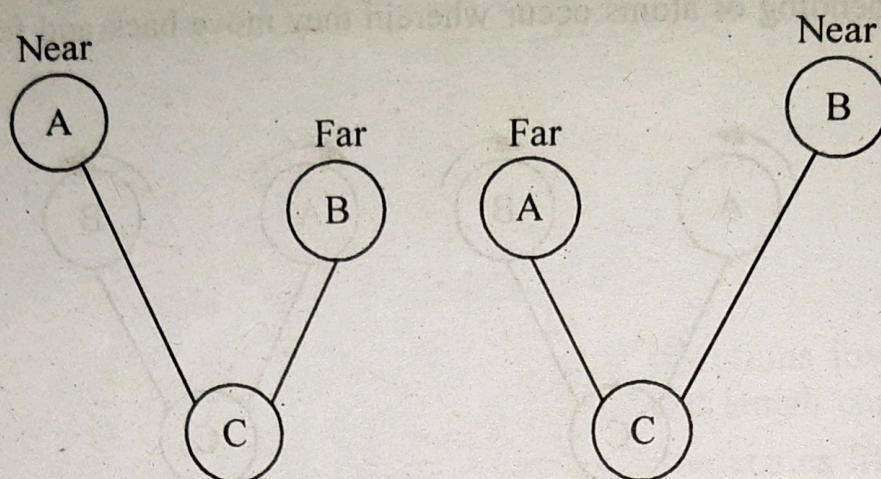


- (iii) **Wagging Deformation Vibrations** : In these type of vibrations, out of plane bending of atoms occur wherein they oscillate back and forth.



- (iv) **Twisting Deformation Vibrations** : In these type of vibrations, out of plane bending of atoms occur wherein they rotate around the bond which joins the central atom C of molecule.





### Factors Affecting Vibrational Frequency :

1. **Interactions Due to Vibrational Coupling :** Vibrational coupling involves interaction between two similar or different vibrating groups. Vibrational coupling depends upon various factors like :

- When two atoms are bonded to a common central atom, the stretching vibrations of these two atoms show strong coupling.
- Coupling between bending vibrations is seen only when the two vibrating groups are separated by a common bond.
- Coupling is maximum when the vibrating groups have individual energies which are approximately equal in magnitudes.
- If the vibrating groups are separated by two or more bonds, negligible or no coupling takes place.

*Example :* Vibration coupling can be best explained by taking an example of a triatomic molecule such as carbondioxide ( $\text{CO}_2$ ). As  $\text{CO}_2$  is a linear molecule (all the atoms lie on a single straight line) rotation about the bond axis does not take place. Thus, rotation is described by two degrees of freedom. Therefore,

$$\begin{aligned}
 \text{Degrees of freedom for a linear polyatomic molecule} &= (\text{Total number of degrees of freedom for a linear polyatomic molecule}) - \left[ (\text{Degrees of freedom for translational motion}) + (\text{Degrees of freedom for rotational motion}) \right] \\
 &= 3n - (3 + 2) \\
 &= 3n - 5
 \end{aligned}$$

$$\text{Normal Modes of Vibrations} = 3n - 5$$

where,

$n$  = Number of atoms



As  $\text{CO}_2$  is a triatomic molecule i.e.,  $n = 3$ , therefore normal modes of vibrations for a linear triatomic molecule ( $\text{CO}_2$ ) is given as :

$$= 3n - 5$$

$$= 3 \times 3 - 5$$

$$= 9 - 5$$

$$= 4.$$

These normal modes of vibrations include two stretching and two bending vibrations. Stretching vibrations further include asymmetric and symmetric vibrations. Due to symmetrical stretching vibrations (in phase stretching),  $\text{C}=\text{O}$  bond contracts. It is a known fact that stretching vibrations require more energy and hence occur at shorter wavelengths.

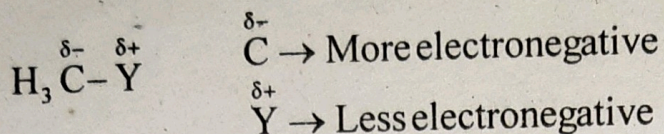
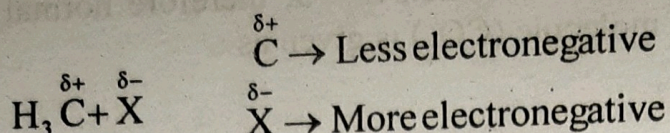
But due to coupling, absorption of symmetrical stretching vibrations occur at longer wavelengths (lower frequency) when compared to  $\text{C}=\text{O}$  group of aliphatic ketones. This mode of vibration causes no change in the dipole moment of  $\text{CO}_2$ , hence, it is inactive to infrared radiations. In asymmetric stretching vibrations, one of the  $\text{C}=\text{O}$  contracts while the other stretches out of the plane. As a result, a change in dipole moment occurs which makes this mode of vibrations infrared active. Absorption occurs at shorter wavelength (higher frequency) when compared to  $\text{C}=\text{O}$  group of aliphatic ketones. The variation in absorption frequency seen in  $\text{C}=\text{O}$  group of  $\text{CO}_2$  is due to strong interaction or coupling existing between the vibrating groups.

2. **Electronic Displacement Effects :** In organic molecules, the electron displacement takes place by four mechanisms namely, electromeric effect, hyperconjugation effect, inductive effect and mesomeric effect. Out of these, four only inductive effect is considered because it prominently effect influences the stretching vibrations in IR spectroscopy.

**Inductive Effect (I)** - It is a permanent effect which involves induction of polarity on the carbon atom and the substituents attached to it. This is seen due to displacement of shared pair of electrons towards any of these two atoms on the basis of their electronegativities.

Inductive effect can be well explained by taking the example of alkanes. In alkanes, the carbon is covalently bonded to hydrogen atom. The shared electron is symmetrically placed between carbon and hydrogen. Hence, inductive effect (I) is not observed. However, when one hydrogen atom of alkane is replaced by an electronegative atom X or Y with higher and lower electronegativity value respectively, inductive effect is observed.





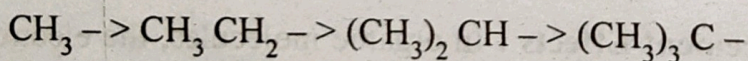
In first case i.e.,  $\text{H}_3\text{C}^+\text{X}$ , X is more electronegative or electron attracting than carbon atom.

Due to this, the shared electron pair is displaced towards more electronegative atom X and a small fractional charge is developed on the two atoms. Carbon atom (C) acquires positive charge and X acquires a negative charge. This effect is referred to as **negative inductive effect** or **-I effect**.

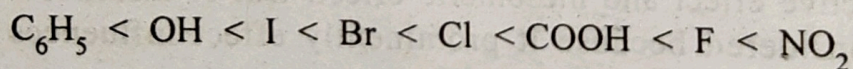
In the later case i.e.,  $\text{H}_3\text{C}^-\text{Y}$ , Y is less electronegative or electron releasing than carbon atom. As a result, the shared electron is displaced away from the less electronegative substituent (Y) towards the C-atom and a small fractional charge is developed. Carbon atom acquires a negative charge and Y acquires a positive charge. This effect is referred to as **positive inductive effect** or **+I effect**.

#### Examples of groups showing inductive effect :

- (a) Groups showing positive inductive effect (+I) or electron attracting groups.

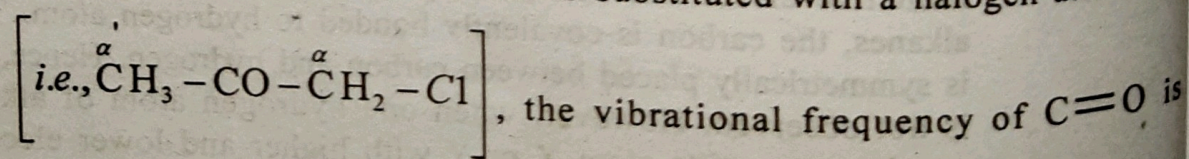


- (b) Groups showing negative inductive effect (-I) or electron releasing groups.



*Example:* Saturated aliphatic ketones such as acetone  $\text{CH}_3-\text{CO}-\text{CH}_3$  shows  $\text{C}=\text{O}$  stretching absorption at  $1715\text{ cm}^{-1}$ . The absorption frequency for other substituted aliphatic ketones varies from that of acetone due to the influence of inductive effect.

- (i) When  $\alpha$ -carbon atom of acetone is substituted with a halogen atom (Cl)



increased. As a result  $\text{C}=\text{O}$  absorption occurs at  $1725\text{ cm}^{-1}$ .



(ii) When both  $\alpha$  and  $\alpha'$  carbon atoms are substituted with two chlorine

atoms  $\left[ \text{i.e., } \overset{\alpha}{\text{Cl}} - \overset{\alpha}{\text{CH}_2} - \text{CO} - \overset{\alpha'}{\text{CH}_2} - \overset{\alpha'}{\text{Cl}} \right]$ , then a double negative inductive

effect is observed which gives rise to absorption of  $\text{C}=\text{O}$  at  $1740 \text{ cm}^{-1}$ .

In acetone  $\overset{\delta+}{\text{CH}_2} - \text{CO} - \overset{\delta+}{\text{CH}_3}$  the carbonyl group is bonded to two methyl group and hence positive inductive effect is observed which gives rise to  $\text{C}=\text{O}$  absorption at  $1715 \text{ cm}^{-1}$ . In acetaldehyde  $\text{CH}_3 - \text{CHO}$ , the carbonyl group  $\text{C}=\text{O}$  is bonded to first methyl group. Hence, the  $\text{C}=\text{O}$  absorption occurs at shorter wavelength i.e.,  $1730 \text{ cm}^{-1}$  when compared to acetone.

The above example infer that when inductive effect is more, frequency is greatly lowered i.e., more the inductive effect stretching vibrations occur at longer wavelengths.

**Mesomeric Effect :** It works along with inductive effect. In some cases, inductive effect dominates mesomeric effect or vice versa.

**Conjugation Effect :** Conjugation decreases the wave number of absorption. Oxygen atom of esters is more electronegative than nitrogen atom of amides. Hence, one pair of electron pair of nitrogen atom of amides participate more in conjugation thereby decreasing the absorption frequency of  $\text{C}=\text{O}$  group of amide.

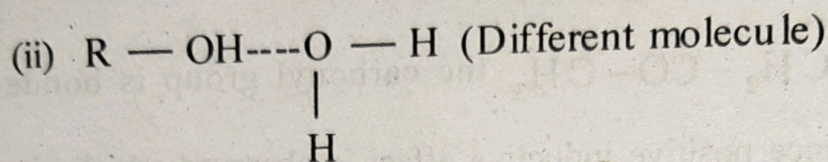
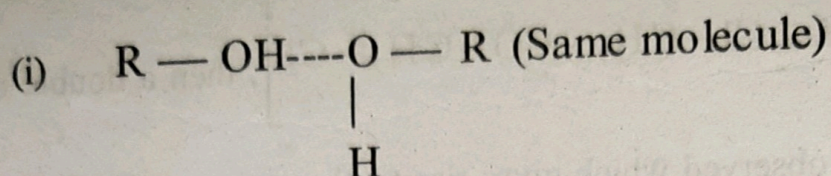
| Compound      | Wave number ( $\text{cm}^{-1}$ ) |
|---------------|----------------------------------|
| Benzamide     | 1663                             |
| Phenylacetate | 1730                             |

3. **Hydrogen Bonding :** Hydrogen bond is a type of electrostatic interaction between molecules that have hydrogen atoms and electronegative atoms like F, N, O etc.,. Bonding takes place when hydrogen atom is attached to an atom having more electronegativity and very small size. This interaction is nothing but a dipole-dipole interaction caused by the electron withdrawing properties of the electronegative atom. Hydrogen bonding is of two types.

(a) **Intermolecular Hydrogen Bonding :** The hydrogen bonding which takes place between molecules (same or different) is known as intermolecular hydrogen bonding.

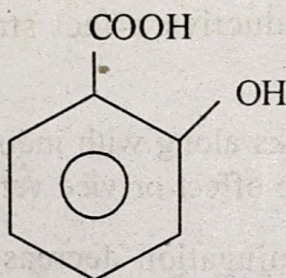


Examples :



(b) **Intramolecular Hydrogen Bonding** : The hydrogen bonding which takes place between different groups within a molecule.

Example : Salicylic acid - Bonding takes place between  $-\text{COOH}$  and  $-\text{OH}$  groups of salicylic acid.



For hydrogen bonding to occur, one molecule should be a proton donor and another should be a proton acceptor. Examples of proton donors are carbonyl ( $\text{C}=\text{O}$ ), hydroxyl amine ( $\text{NH}_2 - \text{OH}$ ), amide  $\text{CO}-\text{NH}_2$  etc. Examples of proton acceptors are oxygen (O), nitrogen (N), halogens (X) and ethylenic linkages ( $\begin{array}{c} | \quad | \\ -\text{C}=\text{C}- \end{array}$ ). Hydrogen bonding alters force constants of both the groups (proton donor and proton acceptor). As a result, the vibrational frequencies of these groups are also altered.

The solvent used in the preparation of the sample solution influences spectrum of the sample. This change occurs due to dipole-dipole interactions that exist within the solvent and also between solvent and solute. Therefore, solvents are selected with care. Solvents that exhibit hydrogen bonding are called **associating solvents**. (Examples : Acetone, benzene and alcohol etc). Solvents that do not exhibit hydrogen bonding are called **non-associating solvents**. (Examples :  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and  $\text{CS}_2$ ). These solvents are used commonly.

Groups such as hydroxyl ( $-\text{OH}$ ) and amine ( $-\text{NH}_2$ ) show characteristic vibrational frequencies when exposed to IR radiations. However, these frequencies are altered when the above groups exhibit hydrogen bonding.



Hydrogen bonding in alcohols ( $\text{—OH}$ ) is stronger than that in amines ( $\text{—NH}_2$ ) because, oxygen of alcohols is more electronegative than nitrogen of amines. Thus, vibrational frequency of ( $\text{—OH}$ ) group is lowered more in IR spectrum of alcohols when compared to ( $\text{—NH}_2$ ) group of amines.

Strength of hydrogen bonding is inversely proportional to the change in fundamental vibrational frequency of the compound involved in bonding. i.e., if the hydrogen bonding is strong, then, the fundamental vibrational frequency of the group involved in bonding is lowered and the absorption band obtained is broader and more intense and vice versa.

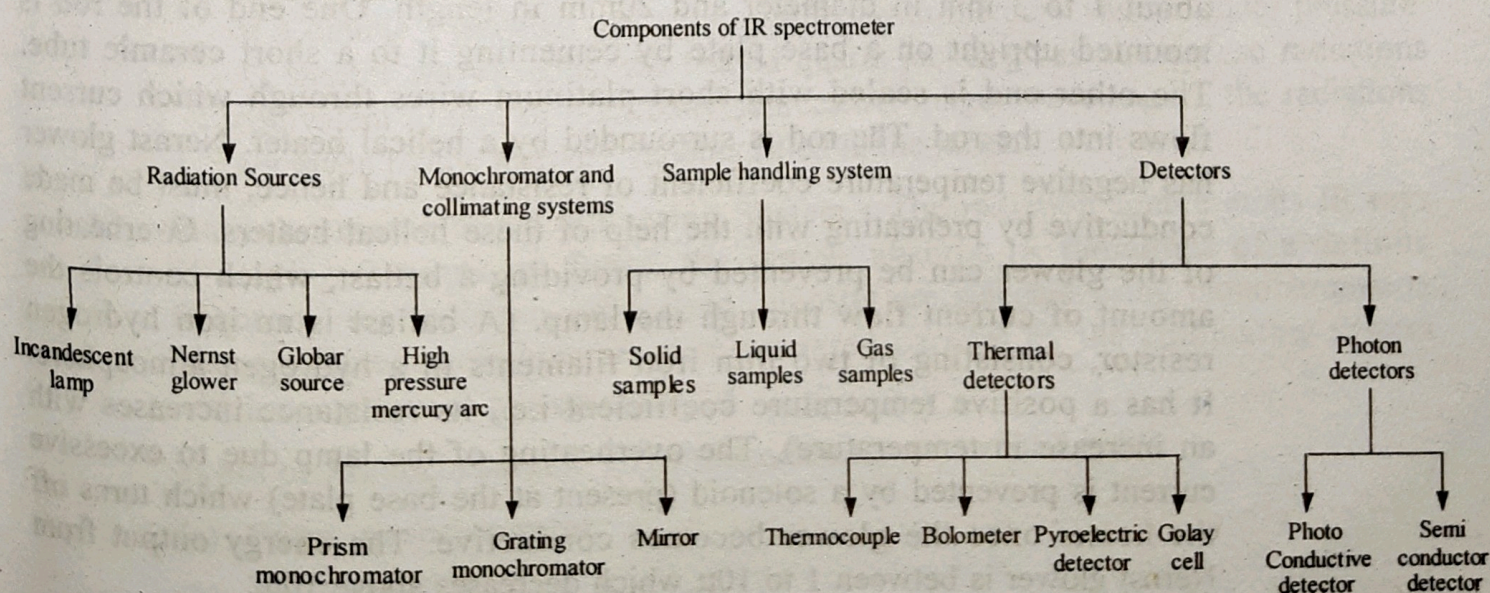
IR technique helps to distinguish inter and intramolecular hydrogen bondings. The IR spectrum of a compound involved in intermolecular hydrogen bonding shows hydrogen bonded absorption bands and unbonded absorption bands. In such compounds, the hydrogen bonded and unbonded absorption bands change with dilution of the compounds. Specifically, the frequency of hydrogen bonded absorption band is lowered and hence the absorption peak obtained is broader and more intense. The unbonded absorption band is increased (frequency is increased) and hence absorption band obtained is sharp as the dilution increases.

*Example :* In alcohols, upon dilution, some of the hydrogen bonds are broken and some remain intact. As a result, the bonded ( $\text{—OH}$ ) absorption decreases and sharp and well defined peak at  $3600\text{ cm}^{-1}$  is obtained due to unbonded ( $\text{—OH}$ ) groups. Dilution does not affect intramolecular hydrogen bonding.

In concentrated solution, hydrogen bonding is strong and hence **broad bonded absorption** band is obtained at lower frequency.

Intense hydrogen bonding is seen in chelates and enols because the bonds are not easily broken on dilution and free ( $\text{—OH}$ ) stretching is not seen. Therefore, broad and intense bands are observed at lower frequencies.

### 1.3.6 Instrumentation





1. **Radiation Sources** : Radiation sources used in IR spectroscopy are hot bodies whose emissions are equivalent to black body radiator. An ideal radiation source should have the following characteristics.

- (a) Intensity of incident light should be high.
- (b) It should emit continuous radiations.
- (c) Should be free from any fluctuations.
- (d) Should not show exhaustion on continuous usage.

**Types of Radiation Sources** : The various radiation sources used are as follows :

- (a) **Incandescent Lamp** : Incandescent lamp consists of a closely wound nichrome coil enclosed in a glass covering. Upon heating a black oxide film is formed on the nichrome coil which gives acceptable emissions of IR radiations. Temperature of about  $1100^{\circ}\text{C}$  can be obtained using nichrome coil incandescent lamp.

**Advantages :**

- (i) The incandescent lamp is simple, durable and does not show exhaustion.
- (ii) It is a reliable source for accurate determinations in inexpensive spectrometer or filter photometer and non-dispersive process analyzers.
- (iii) It can withstand a temperature of about  $1100^{\circ}\text{C}$  without requiring water cooling system.

**Disadvantages :**

- (i) As the nichrome coil is enclosed in a glass cover, it cannot give far IR radiations and has poor spectral emissions.
- (ii) The intensity of IR radiations emitted by the incandescent lamp is less compared to other radiation sources.

- (b) **Nernst Glower** : Nernst glower consist of a hollow rod made up of fused mixture of rare earth metal oxides like thorium, yttria and zirconia. The rod is about 1 to 3 mm in diameter and 20mm in length. One end of the rod is mounted upright on a base plate by cementing it to a short ceramic tube. The other end is sealed with short platinum wires through which current flows into the rod. The rod is surrounded by a helical heater. Nernst glower has negative temperature coefficient of resistance and hence, must be made conductive by preheating with the help of these helical heaters. Overheating of the glower can be prevented by providing a ballast, which controls the amount of current flow through the lamp. (A ballast is an iron hydrogen resistor, consisting of two thin iron filaments in a hydrogen atmosphere. It has a positive temperature coefficient i.e., its resistance increases with an increase in temperature). The overheating of the lamp due to excessive current is prevented by a solenoid (present at the base plate) which turns off the heater once the glower becomes conductive. The energy output from Nernst glower is between 1 to  $10\mu$  which decreases above  $10\mu$ .



**Advantages :**

- (i) The intensity of radiations emitted by Nernst glower is 3 times to that of nichrome coil incandescent lamp and global source.
- (ii) It emits wide range of radiations without any fluctuations in intensity over prolong period of time.
- (iii) It does not get oxidized by air.

**Disadvantages :**

- (i) Nernst glower are extremely fragile.
- (ii) They require heaters for preliminary heating to make them conductive in order to overcome the negative coefficient of resistance.

(c) **Globar Source :** It consists of a silicon carbide rod with a diameter of 6-8 mm and length 50 mm. It is enclosed in a brass tube which is provided with a water cooling system and a provision for emission radiations. It is electrically heated and does not require any preliminary heating like that of Nernst glower. It can be operated to a temperature of about  $1300^{\circ}\text{C}$  (temperature is controlled with a variable transformer). The radiations emitted by a globar source is equivalent to 80% of a black body radiator. The property of globar source lies between Nernst glower and incandescent lamp. Its intensity of radiation is less below  $10\ \mu\text{m}$  but high above  $15\ \mu\text{m}$ .

**Disadvantages :**

- (i) It undergoes exhaustion with time i.e., its resistance increases. This can be avoided by increasing the voltage of global source.

(ii) Less intense than Nernst glower.

(d) **High Pressure Mercury Arc :** Black body type radiators cannot be used in far IR region above  $50\ \mu\text{m}$ , as their radiations decreases with fourth power of wavelength. In this region, high pressure mercury arc is used which consists of a double - jacketed quartz lamp filled with mercury vapour under pressure. At shorter wavelengths, the heated quartz jacket gives out intense radiations equivalent to that of blackbody sources. At longer wavelengths, the radiations are given by the mercury vapours filled in the jacket.

2. **Monochromator and Collimating System :** The radiation source emits IR rays of varying frequencies. Since, the sample absorbs IR radiations of a definite frequency, the radiations of desired intensity are selected using monochromator. These selected radiations are then rendered parallel by the collimating system which comprises of mirrors and slits.

**Types of Monochromator :** The monochromators are of 2 types

- (a) Prism monochromator
- (b) Grating monochromator



## 1.60 [Unit - I]

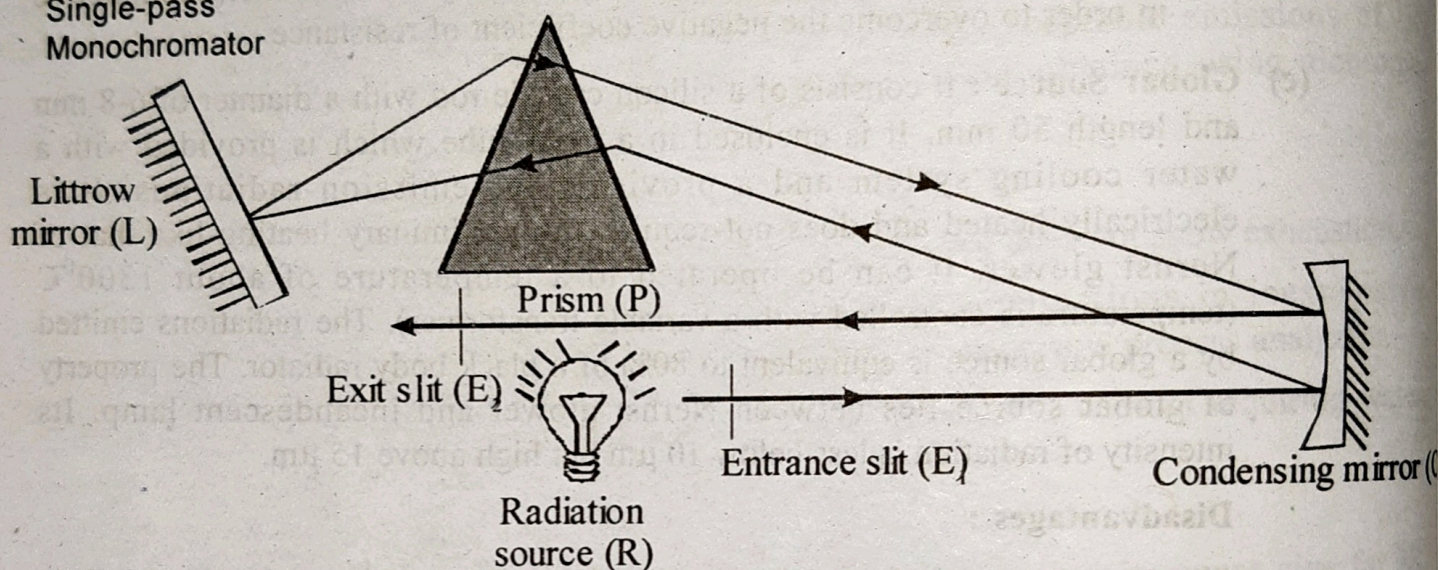
- (a) **Prism Monochromator** : Prisms made up of alkali metal halides like NaCl, KBr, etc., are used as they are transparent to IR radiations. Quartz prism can be used in near IR region  $10.8 - 3\mu$  only. Prism made up of lithium fluoride (LiF) can be used in near IR region ( $1 - 5\mu$ ). Crystalline NaCl prisms are widely used which shows high dispersion in the region between  $5 - 15\mu$  and satisfactory dispersion upto  $2.5\mu$ . They are used for mid IR region. Crystalline KBr and CsBr are used in far IR region ( $15 - 40\mu$ ).

Prism monochromators are of two types :

- (i) **Single-pass Monochromator** :

Figure :

Single-pass  
Monochromator



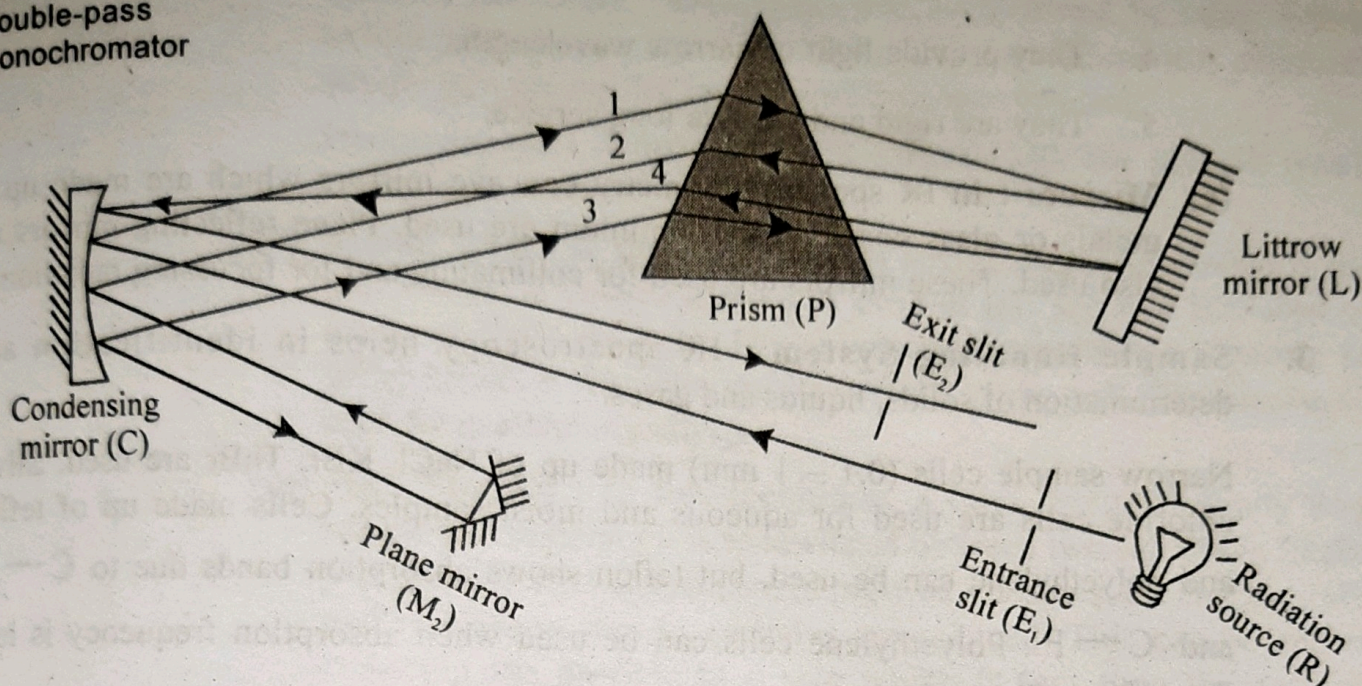
In a single-pass monochromator, a single beam of light from the radiation source (R) enters into the sample cell (not shown). After passing through the sample, it passes through the entrance slit (E) and strikes the condensing mirror (C), which directs the radiation to the prism (P). The prism disperses the radiation. This dispersed radiation strikes the Littrow mirror (L), and is reflected back to the condensing mirror via prism and finally exits through the exit slit (E<sub>2</sub>).

- (ii) **Double-pass Monochromator** : In a double-pass monochromator, a single light beam from the radiation source undergoes four passes (1, 2, 3, 4) through the prism as shown in the figure. The double pass of the light beam through the monochromator results in its better resolution before it reaches the detector thereby, producing fairly good results compared to single-pass monochromator.

**Precaution** : The prism material used in IR are water soluble alkali metal halides except quartz and are susceptible to scratching. They must be protected from moisture and kept in a desiccator.



**Figure :**  
Double-pass  
Monochromator



- (b) **Grating Monochromator** : Gratings consists of a series of parallel, equally spaced lines or grooves on a plane surface. They are made up of glass or plastic with highly polished surface of aluminium. When radiations strike, the surface of gratings, interference of light rays occur. The ability of gratings to resolve into individual spectral line depends upon the number of lines of grooves per inch. Dispersion power of grating is governed by law of diffraction. It is given by the equation :

$$n\lambda = d(\sin i \pm \sin r)$$

where,

$n$  – Order (numerical)

$\lambda$  – Wavelength of radiation

$d$  – Distance between two successive grooves.

$\sin i$  – Angle of incidence of IR radiation

$\sin r$  – Angle of diffraction

Grating having 20 grooves/ mm are used in far IR region. Gratings with different number of grooves or lines are used to cover wider wavelength range in order to minimize their overlap.

#### Advantages of Grating Monochromators :

1. Gratings give higher and linear dispersions compared to prism monochromators.
2. Grating monochromators are used over wide wavelength ranges.



3. Unlike prisms, gratings can be constructed with materials like aluminium which is resistant to atmospheric moisture.
4. They provide light of narrow wavelength.
5. They are rigid and provide long service.

(c) **Mirrors** : In IR spectrophotometry concave mirrors which are made up of metals or glass coated with aluminium are used. Plane reflecting mirrors are also used. These mirrors are used for collimating and for focussing radiations.

3. **Sample Handling System** : IR spectroscopy helps in identification and determination of solids, liquids and gases.

Narrow sample cells (0.1 – 1 mm) made up of NaCl, KBr, ThBr are used. Silver chloride cells are used for aqueous and moist samples. Cells made up of teflon and polyethylene can be used, but teflon shows absorption bands due to C—C and C—F. Polyethylene cells can be used when absorption frequency is less than  $600\text{ cm}^{-1}$ .

IR spectra varies with the physical state of the sample as molecular forces of attraction and absorption frequency is different for different physical states. It is therefore mandatory to indicate the state of sample in the IR spectra.

*Example* : IR spectra of stearic acid in solution shows broad peaks making it difficult to characterize them whereas IR spectra of stearic acid in solid film shows definite peaks.

**Precaution** : Sample cells made of alkali metal halides are polished with buffing powder to remove moisture absorbed by the sample cells.

- (a) **Solid Samples** : Solid samples can be analyzed using IR spectroscopy by the following ways :

- (i) Solution of solid
- (ii) Sample film
- (iii) Mull method
- (iv) Pressed pellet technique

- (i) **Solution of Solid** : In this technique, the solid sample is dissolved in an inert solvent and the solution is analyzed in liquid sample cell. As the solvents are not transparent to IR rays, therefore, they exhibit absorption band. Some of the solvents which are used in IR are  $\text{CCl}_4$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{COCH}_3$ , Cyclohexane etc. To avoid absorption band due to single solvent, two solvents having complimentary absorption regions are used.

*Examples* :  $\text{CCl}_4$  and  $\text{CS}_2$



For the organic compounds which are insoluble in  $\text{CCl}_4$  and  $\text{CS}_2$ , solvents like  $\text{CHCl}_3$ , acetonitrile and acetone can be used. Solvent and solute interaction must be taken into consideration especially for compounds having the property of hydrogen bonding.

**Disadvantage :** Solid sample may react with the solvent resulting in undesirable product.

(ii) **Sample Film :** In this technique, an amorphous solid sample is dissolved into a suitable volatile solvent. A drop of this solution is placed in a cell made of NaCl or KBr. The solvent is evaporated by gentle heating, which leaves a thin film on the surface of the cell. The resultant film is used for qualitative analysis.

(iii) **Mull Method :** In this technique, a thick paste of finely powdered sample and mineral oil is sandwiched between two salt plates (NaBr/KBr). The particle size of the sample must be chosen such that the reflections and refractions due to particles are reduced. This can be achieved by reducing the particle to a size which is less than the experimental wavelength or placing the particles in a medium whose refractive indices are close.

Mineral oil widely used is nujol oil but, it shows absorption maxima at  $2915\text{ cm}^{-1}$ ,  $1462\text{ cm}^{-1}$ ,  $1376\text{ cm}^{-1}$  and  $719\text{ cm}^{-1}$  which interferes with sample absorbance. This interference can be avoided using hexachlorobutadiene with nujol oil which absorbs in the regions of  $1630 - 1510$ ,  $1200 - 1400$  and  $1010 - 760\text{ cm}^{-1}$ , permitting recording of IR spectra of only the sample. This method is applied for qualitative analysis.

**Use :** Mull technique is used for crystalline compounds.

**Disadvantage :** Grinding of the crystalline sample may lead to degradation and polymorphic changes.

(iv) **Pressed pellet Technique :** In this technique, a tablet of  $x\text{ g}$  of finely powdered solid sample with  $100x\text{ g}$  of good quality KBr is prepared under pressure of about 25,000 psi. Alkali halides like CsI, CsBr are added to get longer wavelengths. Pressing of KBr is done in a mini press. The tablet formed have dimensions of 1 – 2 mm thickness and 1 cm diameter and are transparent to IR radiations.

**Use :** This technique can be applied in the quantitative analysis. The ratio of weight of sample to internal standard in each pellet gives accurate quantitative determination.

**Advantages :**

- (i) Absorption band due to mineral oil (mulling agent) can be avoided.
- (ii) KBr pellet can be stored and re-used.
- (iii) Spectrum obtained from this technique helps in easy characterization when compared to mull method.



**Disadvantages :**

- (i) The absorption spectrum always shows a band at  $3450\text{ cm}^{-1}$  due to hydroxyl (OH) group of the moisture which is present in the sample.
- (ii) Inorganic crystalline complexes may undergo decomposition or polymorphic changes due to exposure to heat and high pressure while forming a pellet.
- (iii) Bromide ion ( $\text{Br}^-$ ) of the KBr may substitute the ligand of the inorganic molecules.
- (iv) This technique can be applied to only those substances which can be powdered along with KBr.

**(b) Liquid Samples :** Liquid samples are freed from moisture and impurities and analyzed at room temperature. Appropriate concentration of the solution and cell length gives reproducible and accurate information about the shape and structure of the compound. The samples which are liquid at room temperature are directly introduced in sample cell such that the sample thickness is  $0.01 - 0.05\text{ mm}$  with transmittance of 15 and 20%.

High viscous liquids are sandwiched between two salt plates of NaBr or KBr as the sample cannot be introduced directly in a pre-assembled cell. (The sample thickness can be assessed by a spacer between the salt plates).

Various types of liquid sample cells available are :

- (i) Mountable cell
- (ii) Demountable cell
- (iii) Flow through cell
- (iv) Variable path length cell
- (v) Mini cell or cavity cell

**(i) Mountable Cell :** It consists of two salt plates (windows) separated by thin gaskets made up of teflon or metals like copper or lead. The metal gasket is wetted with mercury, so that, when it penetrates the metal, the gasket expands producing a tight seal. The windows and gaskets are held together by a clamp and permanently assembled in a stainless steel holder. The sample can be introduced in these cells with the help of hypodermic needle without disrupting the seal (tapered fitting cells). The path length of the cell is accurately measured with the help of interference fringes and labelled on the cell.

**(ii) Demountable Cell :** It consists of two salt plates and a teflon fitting to introduce the syringe. The teflon fitting provides a tight leak proof seal. This assembly (salt plates and teflon fitting) is introduced into a mount and screwed tightly. Unlike mountable cell, this cell is not fixed. It can be placed and removed from the cell assembly.



(iii) **Flow-through Cell** : These cells are helpful in continuous analysis of liquid samples. Flow through cells provides precision and ease of sample handling where repetitive sample analysis is required. IR spectrometers employing flow-through cells when coupled with column chromatograph can be used for determination of functional groups present in column effluent.

(iv) **Variable-path length Cell** : It consists of two salt plates arranged parallelly in a cylindrical stainless steel chamber and a scale. The above assembly is lined with teflon to provide a tight seal. The scale on the cell and the vernier scale can measure the cell thickness of  $\pm 0.005$  mm. The pathlength of the cell can be adjusted from 0.005 to 5 mm.

Variable-pathlength cell has two advantages :

(a) **Reference compensation and differential analysis** : Absorption bands due to solvent or reference can be avoided by adjusting the pathlength of reference beam of spectrometer (reference compensation). Small difference in concentration of two samples can be determined by adjusting the pathlength of variable cell. This help in analysing the minor sample components which cannot be analyzed using sample cells of fixed pathlength.

(b) Pathlength of the cell can be adjusted to get the proper intensity of weak absorption band.

The weak absorption signals of the liquid cannot be analyzed in the presence of strong absorption signals. Therefore, by adjusting variable pathlength cells, weak absorption signal intensity can be obtained from its exact IR absorption region.

The pathlength of the cell can be adjusted, thus, it does not require a number of cells having different thickness and fixed pathlength.

(v) **Mini Cell or Cavity Cell** : The mini cell consists of a fluted (threaded), two-piece plastic body and a pair of specially designed silver chloride ( $\text{AgCl}_2$ ) window disks. The windows are fitted into one of the pieces of the plastic body while the second piece is screwed with first one to form a tight seal.

The  $\text{AgCl}_2$  windows has a circular depression of about 0.025 mm or 0.1 mm, the circumference is inclined towards centre and the rim of the window is flat, thus providing an efficient seal.  $\text{AgCl}_2$  flows only under pressure providing a tight seal.

The pathlength of the cell can be varied by adjusting the windows in the following three ways :



- (a) The back of one salt window facing the back of another salt window for a conventional smear.
  - (b) One salt window is placed such that the back is facing the circular depression of the other plate giving a 0.025 mm pathlength.
  - (c) Both the plates are so arranged that the circular depression of each other giving a pathlength of 0.05 mm.
- (c) **Gas Samples :** Gas sample cells consist of a glass or metal cylinder made up of halogen salts such as NaCl, KBr etc. The cells are about 10 cm to 100 cm in length. Cells are equipped with internal gold-plated or stainless steel components and gold-surfaced mirrors. These components cause multiple reflection of the radiation thereby increasing effective pathlength of the cell several times longer than the actual cell length.

The gas sample is introduced into the cell through a stop cock under a pressure of 5 - 50 mm of Hg. Gas contains small number of analyte atoms and hence large sample cells which allow more number of molecules are used. Long pathlength cells allow analysis of substances in concentration of ppm or less.

**Advantages :**

- (i) Gas samples are used to determine the concentration range of pollutants in air, analysis of atmospheric gases, process instrumentation and impurities.
- (ii) The eluates from gas chromatograph can be analysed using IR spectroscopy by employing heated cells.

**Disadvantages :**

- (i) High pressure in the gas cell may cause broadening of absorption peaks.
- (ii) Analysis of gases by IR spectroscopy is less commonly employed due to its low sensitivity.
- (iii) Only dried gases can be analysed because the moisture content gives absorption bands which interfere with the analysis.

**4. Detectors : Types of Detectors**

- (a) Thermal detectors
  - (i) Thermocouple
  - (ii) Bolometer
  - (iii) Pyroelectric detector
  - (iv) Golay cell
- (b) Photon detectors
  - (i) Photo conductive detector
  - (ii) Semiconductor detector.

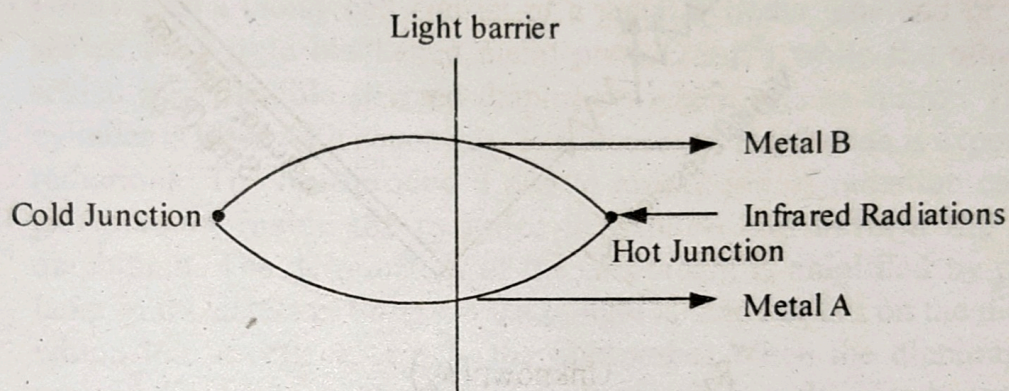


- (a) **Thermal Detectors** : When IR radiations fall on a thermal detector, its temperature increases due to heating. The increase in temperature produces potential difference which is proportional to the amount of radiations falling on the detector.

The properties which are measured in thermal detectors are expansion of solid, gas or fluid (Golay cell), electrical resistance (thermistor), voltage induced at the junction of two dissimilar metals (thermocouple and thermopile) and electric polarization (pyroelectric detectors).

(i) **Thermocouple** :

Figure :  
Thermocouple



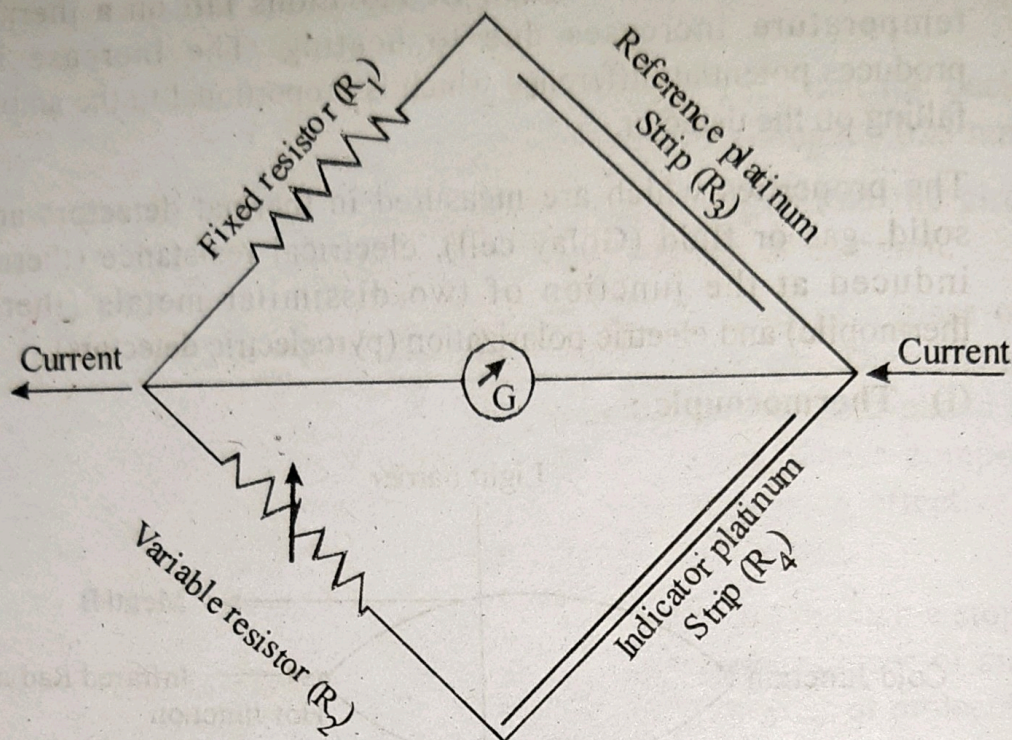
It is the most widely used detector in IR spectrophotometry. Its working is based on the fact that when two different semiconductor metal wires are connected and kept at different temperatures, a potential difference is developed between them which causes the flow of current. The thermocouple is enclosed in a steel casing which consist of a window made up of KBr or CsI. This is done to prevent the energy loss. The thermocouple consist of two wires of different metals A and B, welded together at both the ends. One end of the thermocouple is exposed to IR radiation and is called as hot junction. The other end is maintained at constant temperature (i.e., thermally insulated) and not exposed to the radiations, this end is called as cold junction. When the IR radiations fall on the hot junction its temperature increases which develops an electric potential difference between the two junctions. The magnitude of potential difference generated is proportional to the amount of IR radiation falling on the hot junction.

- (ii) **Bolometer** : Bolometer is based on the principle that for every one degree rise in temperature, electrical resistance of a metal increases. A bolometer is based on Wheatstone bridge arrangement. Wheat stone bridge has 4 arms. One arm of the bridge consists of a metal of unknown resistance and the resistance of other 3 arms is known. When the bridge is balanced no current flows through the galvanometer. When the bridge is unbalanced due to exposure of light or heat, current flows through the galvanometer due to change in resistance of the metal. The resistance of unknown can be determined by the formula,



1.68 [Unit - I]

Figure :  
Bolometer



$$\frac{R_2}{R_1} = \frac{\text{Unknown}(R_4)}{R_3}$$

In bolometer, two arms of the bridge are made up of platinum strips coated with lamp black. One arm is exposed to radiations (indicator strip) and the other arm is protected from radiations (reference strip). The two platinum strips are connected to a sensitive galvanometer, then to a battery in Wheatstone bridge arrangement. When radiations fall on the exposed platinum strip, the temperature of the strip increases, resulting in change in degree of resistance of the conductor and the bridge becomes unbalanced. Change in electrical resistance causes the current to flow through the galvanometer. The amount of current flowing through galvanometer is proportional to the amount of radiations falling on the exposed platinum strip. The response time of bolometer is 4 millisecond.

(iii) **Pyroelectric Detector** : Pyroelectric detector consists of a thin plate of pyroelectric crystal (crystals which show permanent dipole moment) of 0.25 to 12mm<sup>2</sup> in size. The crystal is placed between two electrodes which are connected to an external electric circuit. One of the electrode should be transparent to IR radiations. When the crystal is exposed to IR radiation, it absorbs the heat leading to change in its dipole moment. This change causes generation of electrical charges which are attracted towards the electrodes. Accumulation of charge at the electrodes create a potential hence, producing electric current in the external circuit. Various pyroelectric crystals are barium titanate, lead zirconate, lithium tantalate (LiTaO<sub>3</sub>), lithium niobate (LiNbO<sub>3</sub>), triglycine sulphate (TGS) and deuterated triglycine sulphate (DTGS).



**Use :** Pyroelectric detectors are increasingly used in Fourier transform spectrometer as they require rapid responses.

**Advantages :**

1. Pyroelectric detector has faster response time ( $10\mu$  sec.) when compared to other detectors.
2. These detectors response only to those radiations that have been suitably modulated or chopped but, unresponsive towards steady radiations.

(iv) **Golay Cell :** Golay cell consist of a metal cylinder, one end of which is sealed by a rigid blackened metal plate ( $2\text{mm}^2$ ) while the other end is sealed by a flexible silvered diaphragm which acts as mirror. The metal cylinder is filled with xenon gas. The blackened metal plate is exposed to IR radiations. The heat produced due to absorption of radiation causes the gas present inside the cylinder to expand and deform the flexible diaphragm. The deformation of the diaphragm is amplified by placing a lamp in the detector. From the lamp, light is made to fall on the diaphragm which inturn reflects it onto the phototube. When the diaphragm is at rest no light passes through it, however, when the diaphragm flexes varying amounts of light reaches the phototube. The resultant effect being the change in output of the detector. The signal received by the phototube is modulated according to the intensity of the radiation falling on the cell and is displayed on the readout device.

**Advantages :**

1. Golay cell can be used over wide wavelength range.
2. It has a faster response time (1 centisec) compared to bolometer and thermocouple.

**Disadvantage :** Due to expensiveness and bulkiness, it is less convenient.

(b) **Photon Detector :** These are based on the principle that when IR radiations fall on the semiconductor a proportional change in electrical property of conductor is seen. When photons from IR radiations fall on the semiconductor, the interaction produces electrons and holes (internal photoelectric effect). The energetic photons strike the electrons of semiconductor causing its excitation and renders it conductive from nonconducting state.

The semiconductors most commonly used are lead sulphate, lead telluride or germanium which do not conduct at low energy state. But, they conduct electricity when excited to high energy state.

(i) **Photoconductive Detector :** These are based upon the variation of electric conductivity of the cell when exposed to electromagnetic radiations. Photoconductive detectors are made up of photosensitive materials of the cadmium sulphide, lead sulphide etc.



When IR radiations fall on the detector, the electrical conductivity of the detector increases due to excitation of electron by the incident light. During the process, current is produced which is proportional to the amount of the incident IR radiations.

- (ii) **Semiconductor Detectors** : They are semiconductor of p-n junction type in which p-type material (in which holes carry current) is placed on n-type material (in which electrons carry current) in the form of a thin layer. Absorption of radiations by the device generates current voltage or both due to electron-hole pairs which are separated by internal electric field.

When the current supply is zero i.e., open circuit conditions, the terminal voltage increases with increase in light intensity. When the voltage is zero i.e., short-circuit condition, the current increases with increase in light intensity. When the current produced is negative and the voltage produced is positive, detector delivers a signal to the output or the readout system.

When a semiconductor detector is exposed to light, the current produced in it is proportional to the intensity of light incident on it, which is read from low impedance galvanometer or microammeter. Semiconductor detector is operated either in low impedance current or high impedance voltage amplifier. The highest sensitivity or lowest noise is obtained in short-circuit mode.

*Example* : Indium antimonide is a p-type material applied as a thin layer on a n-type material producing a diffused p-n junction in single crystal indium-antimonide. The sensitivity of detector is upto a wavelength of  $5.5\mu$ . Response time is less than  $1\mu\text{sec}$ . This semiconductor is mounted as an integral part of Dewar type vacuum bottle cooling unit in the conductor. The heat produced due to current can be prevented by the use of liquid nitrogen or Joule-Thomson coolers with compressed nitrogen gas.

The other semiconductor detectors are lead-tin telluride detector, mercury-cadmium telluride detector etc.

### 1.3.7 Types of IR Instruments

IR instruments can be classified as :

#### 1. Dispersive instruments

(a) Single beam IR spectrophotometer

(b) Double beam IR spectrophotometer

Non-dispersive instrument

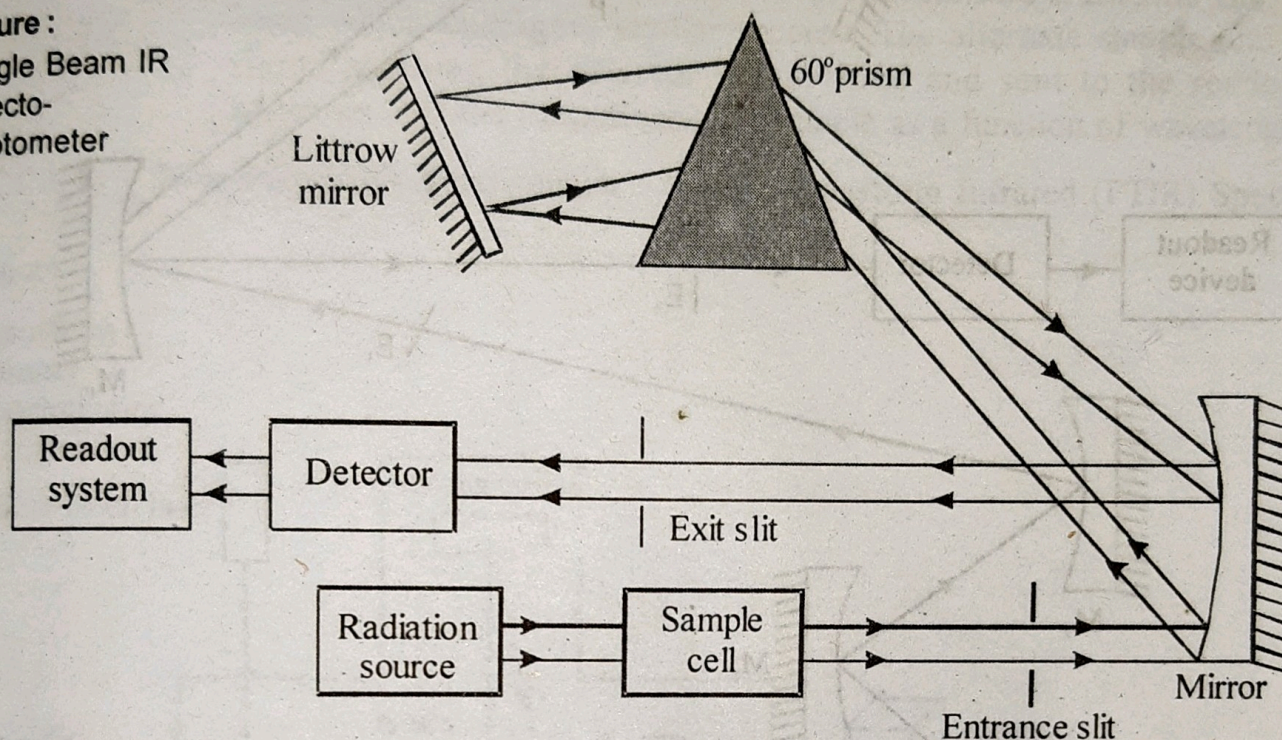
Fourier transform infrared (FTIR) spectrometer.



1. **Dispersive Instruments :** Dispersive instruments utilize prism or grating whereas non-dispersive instruments utilize interference filters, tunable laser sources or interferometer.

(a) **Single Beam IR Spectrophotometer :**

**Figure :**  
Single Beam IR Spectrophotometer



In single beam IR spectrophotometer, the radiation from the radiation source are allowed to fall on the sample cell. The sample absorbs the radiation and transmits some of it via the entrance slit onto the mirror. The radiation from the mirror are directed towards the prism and then to the littrow mirror. The littrow mirror reflects the incident beam back to the mirror and through the exit slit onto the detector. The detector sends signal to the readout device which gives the transmittance of the sample as a function of its wavelength.

**Disadvantages :**

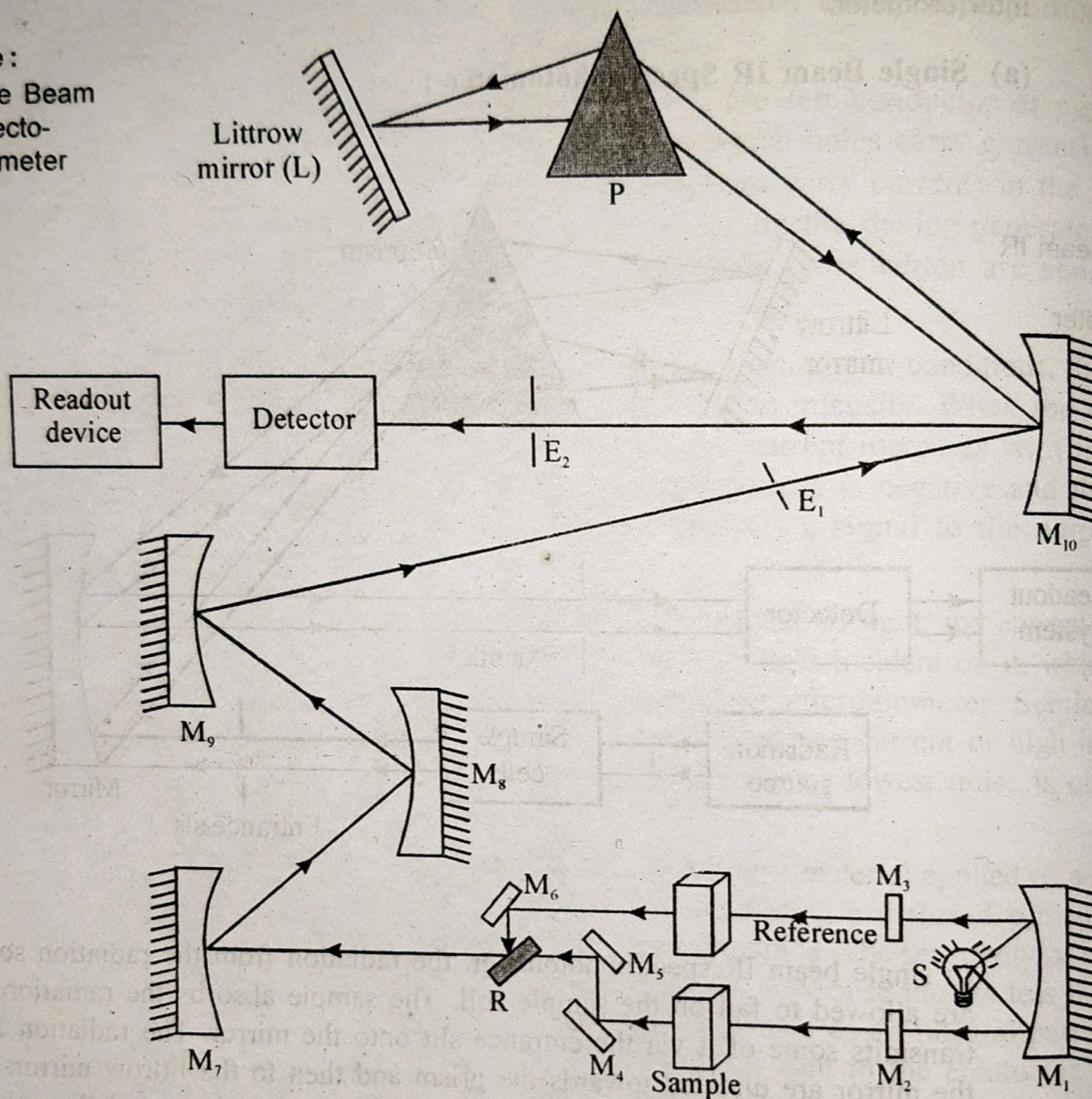
1. The emission intensity of radiation source is not uniform, the resultant effect being deformed IR absorption spectra.
2. The IR spectrum of the sample solution shows extra bands due to solvent. In such cases, the pure spectrum of the sample is obtained by subtracting the resultant spectrum from the spectrum of the solvent.

If the intensity of radiations emitted by the source is known, then the amount of radiations absorbed by the sample can be known with the help of detector reading.



## (b) Double Beam IR Spectrophotometer :

Figure :  
Double Beam  
IR Spectro-  
photometer



In double beam IR spectrophotometer, Nernst glower is used as a radiation source (S). The radiations emitted by it are split into two beams which are identical in their intensities. This identical beam pair is reflected by the mirror  $M_1$  on mirrors  $M_2$  and  $M_3$  where they undergo further reflection. After being reflected by mirror  $M_2$ , one of the beam passes through the sample cell while the other beam (reflected by mirror  $M_3$ ) passes through the reference cell. Two mirrors  $M_4$  and  $M_5$  reflects the transmitted light beam from the sample cell to the rotating sector mirror (R). On the other hand, the transmitted beam from the reference cell is also passed onto the rotating sector via mirror  $M_6$ . During one half of its rotation, the rotating sector mirror reflects the sample beam and blocks the reference beam. While in its other half rotation, the reference beam is reflected and the sample beam is blocked. As the two beams are of equal intensity, any change in their intensity would lead to an imbalance in the detector signal. The sample beam now undergoes reflection

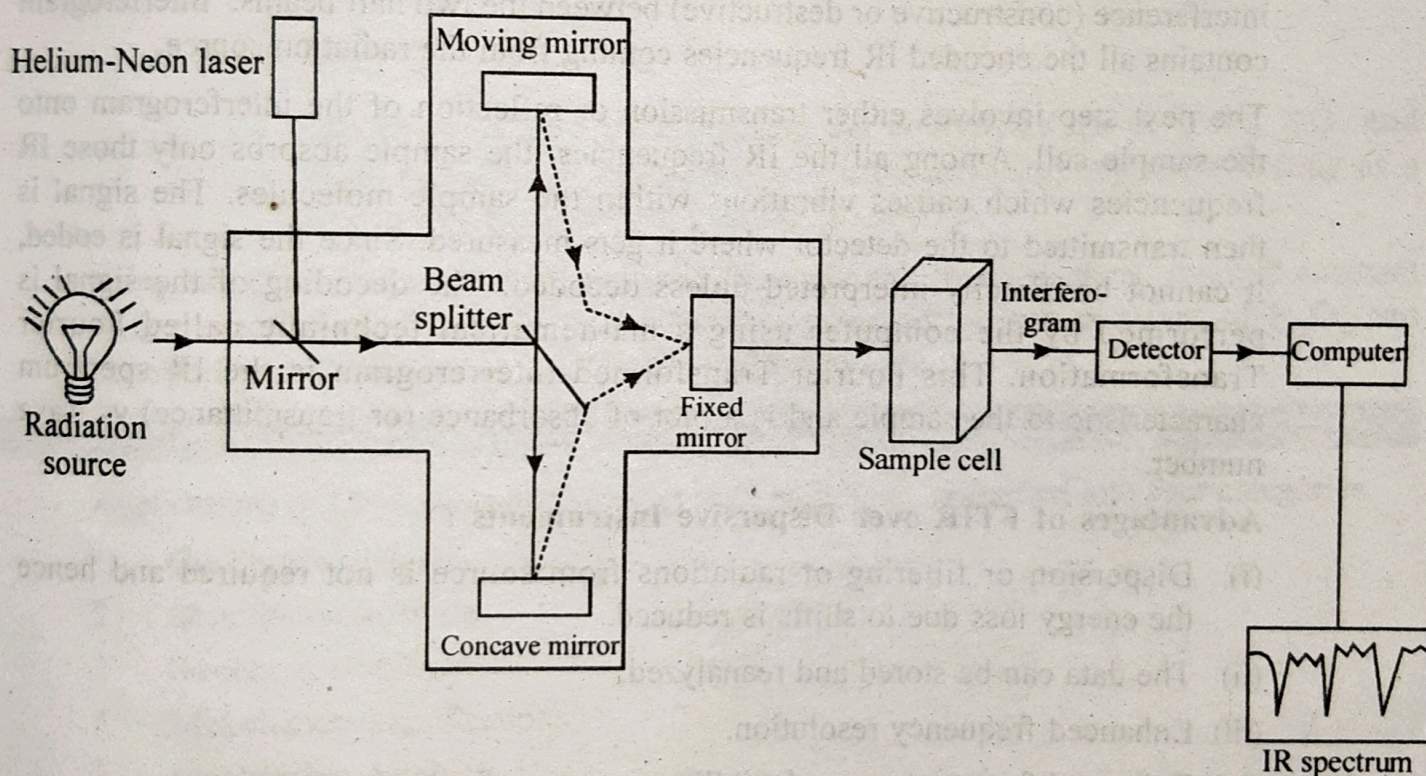


by mirrors  $M_7$ ,  $M_8$  and  $M_9$ . The beam is then passed through the entrance slit ( $E_1$ ) into the monochromator (consisting of mirror  $M_{10}$ , prism P and Littrow mirror L) where it undergoes dispersion. The dispersed beam is again reflected back to  $M_{10}$  which selects the beam of desired wavelength. The selected beam exits through the exit slit ( $E_2$ ) and falls on the detector. Signal from the detector is then passed onto the readout device. In the next rotation, the rotating sector blocks the sample beam and transmits the reference beam which undergoes similar process. The alternate sample and reference signal reaching the detector is amplified and sent to the readout device which records the transmittance of sample as a function of wavelength.

## 2. Non-Dispersive Instruments : Fourier Transform Infrared (FTIR) Spectrometer

Figure :

Transform  
Infrared  
Spectrometer



Fourier transform infrared (FTIR) spectrometer consist of the following components:

- |                         |                   |
|-------------------------|-------------------|
| (a) IR Radiation Source | (b) Beam Splitter |
| (c) Fixed Mirror        | (d) Moving Mirror |
| (e) Collimating mirrors | (f) Sample holder |
| (g) Helium-Neon laser   | (h) Detector      |