

## **Ultraviolet Spectroscopy (Electronic Spectroscopy)**

The range of UV region is 200nm to 400nm in the electromagnetic spectrum and it subdivided into (i) near UV 200-400nm (ii) Far UV <200 nm.

The UV radiation has sufficient energy to excite valence electrons in many atoms or molecules called electronic excitation.

### **Principle of UV-visible spectroscopy:**

When light is incident upon a homogeneous medium a part of the incident light is reflected, a part is absorbed by the medium and remaining part is allowed to transmit through. If  $I_0$  denotes the incident light,  $I_r$  the reflected light,  $I_a$  absorbed light and  $I_t$  transmitted light, Then,

$$I_0 = I_a + I_t + I_r \quad I_r \text{ is neglected as it is very small Hence } I_0 = I_a + I_t$$

**Lambert's Law:** When a beam light is allowed to pass through a transparent medium, the rate of decrease of intensity with the medium is directly proportional to the intensity of the incident light.

**Beer's Law:** The intensity of the transmitted decreases exponentially with the increase in concentration of the absorbing medium.

On combining these two laws and after a small derivation, we get an equation for the absorbance and it is called as Beer-Lambers law,

$$A = \epsilon c t$$

where A is absorbance of the medium,  $\epsilon$  is molar absorption coefficient, c is concentration of the medium and t is the thickness of the medium.

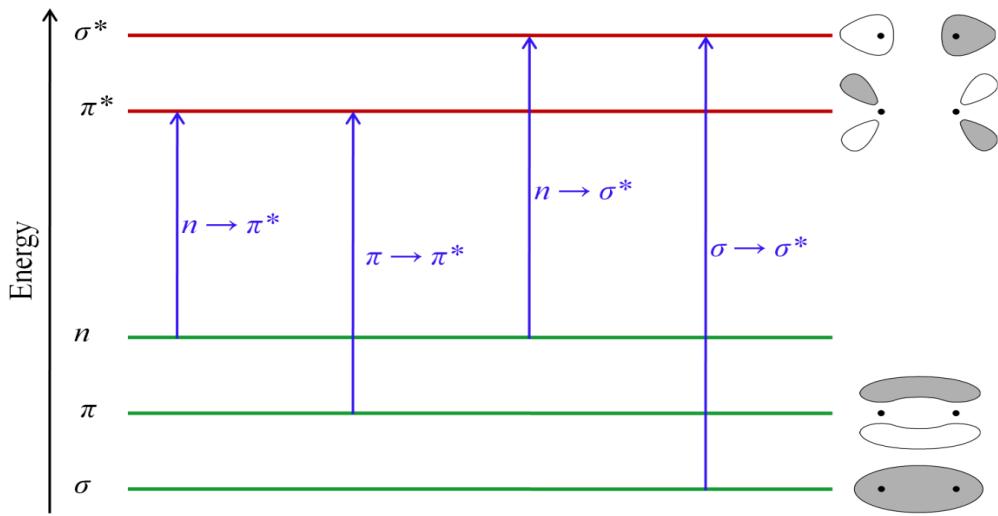
**Limitations of Beer-Lambers law:** Beer-Lambers law cannot be applicable in the following cases

- (1) Highly concentrated solutions.
- (2) If the coloured substance undergoes ionization, dissociation and polymerization in the solution.
- (3) Presence of impurities that fluoresce or absorb the light.
- (4) Colloidal suspensions.
- (5) If the structure of the substance changes with the concentration.

### **Types of Transitions in organic molecules**

The transitions in organic molecules involve three distinct types of electrons.

- (1)  $\sigma$ - electrons: These electrons are involved in saturated bonds or single bonds like in paraffins. The energy required to excite these electrons in  $\sigma$ -bonds is much more than the UV radiations.
- (2)  $\pi$ - electrons : These electrons are involved in unsaturated compounds with double and triple bonds.
- (3) n-electrons : these are the electrons which are not involved in the bonding and are present in those compounds that contain Nitrogen, Oxygen, Sulphur, halogens.



### 1. $\sigma \rightarrow \sigma^*$ Transitions

These transitions can occur in such compounds in which all the electrons are involved in single bonds and there are no lone pairs of electrons. These transitions take place in saturated compounds. These involve highest energy.

### 2. $n \rightarrow \sigma^*$ Transitions

Saturated compounds containing atoms with lone pairs (non-bonding electrons) undergo  $n \rightarrow \sigma^*$  transitions in addition to  $\sigma \rightarrow \sigma^*$ . These transitions usually need less energy than  $\sigma \rightarrow \sigma^*$  transitions. They can be initiated by light whose wavelength is in the range 150 - 250 nm. The number of organic functional groups with  $n \rightarrow \sigma^*$  peaks in the UV region is small.

Ex: in  $(\text{CH}_3)_3\text{N}$ , **two absorptions** at  $\lambda_{\max} = 227 \text{ nm}$  (due to  $n \rightarrow \sigma^*$ ) and at  $\lambda_{\max} = 99 \text{ nm}$  (due to  $\sigma \rightarrow \sigma^*$ )

### 3. $n \rightarrow \pi^*$ Transitions

these types of transitions are shown by unsaturated molecules which contain atoms such as O, N, S and halides. These transitions exhibit a weak band in their absorption spectrum.

Ex: Aldehydes and ketones exhibit these transitions (in the range 270-300 nm)

$n \rightarrow \pi^*$  Transition in pyridine disappears in acidic solution  
pyrazene shows a band at 300nm which is not shown by benzene

**4.  $\pi \rightarrow \pi^*$  Transitions:** promotion of an electron from a bonding  $\pi$  orbital to an antibonding  $\pi^*$  orbital of the conjugated systems results in these transitions.

Ex: Ethylene, and acetylene compounds exhibit these transitions.

**Chromophores:** Any group which exhibits absorption of electromagnetic radiations in the UV or visible region but may or may not impart colour to the compound is called as a chromophore.

Ex:  $>\text{C}=\text{C}<$ ,  $>\text{C}=\text{C}<$ ,  $>\text{C}=\text{O}$ ,  $-\text{NO}_2$ ,  $-\text{COOH}$

**Auxochrome:** Auxochromes are the chemical groups that result in a bathochromic shift when attached to a chromophore. The strongest auxochromes like  $-\text{OH}$ ,  $-\text{NH}_2$ ,  $-\text{OR}$ , etc. possess nonbonding electrons. They exhibit bathochromism by extending conjugation through resonance



**Bathochromic shift or red shift :** Shift of the absorption maximum towards longer wavelength due to the presence of certain groups such as OH and  $\text{NH}_2$  or by change of solvent.

**Ex:** Ethylene shows  $\pi \rightarrow \pi^*$  transition at 170nm whereas 1,3 butadiene shows at 217nm

**Hypsochromic shift or blue shift:** Shift of the absorption maximum towards shorter wavelength due to removal of conjugation or by change of solvent.

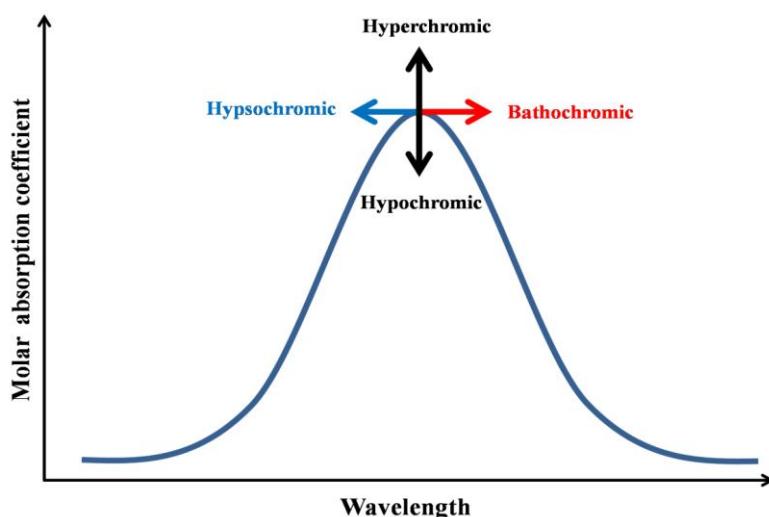
**Ex:** Aniline shows Abs. Max. at 280nm due to conjugation of pair of electrons with the benzene ring, **but** in acidic solutions Aniline shows Abs. Max. at 200nm because the pair of electrons on N atom are no longer preset to show conjugation effect.

**Hyperchromic Effect:** This effect involves an increase in the intensity of absorption and is brought about by an introduction of auxochrome

**Ex:** Introduction of methyl group in the position 2 of pyridine increases  $\epsilon_{\text{max}}$  ( $\lambda_{\text{max}} = 262$  nm) from **2750** to **3560** ( $\lambda_{\text{max}} = 262$  nm).

**Hypochromic Effect:** This effect involves the decrease in the intensity of absorption and is brought about by groups which distort the geometry of the molecule.

**Ex:** when methyl group is introduced in position 2 of biphenyl group, hyperchromic effect is observed due to distortion of symmetry.



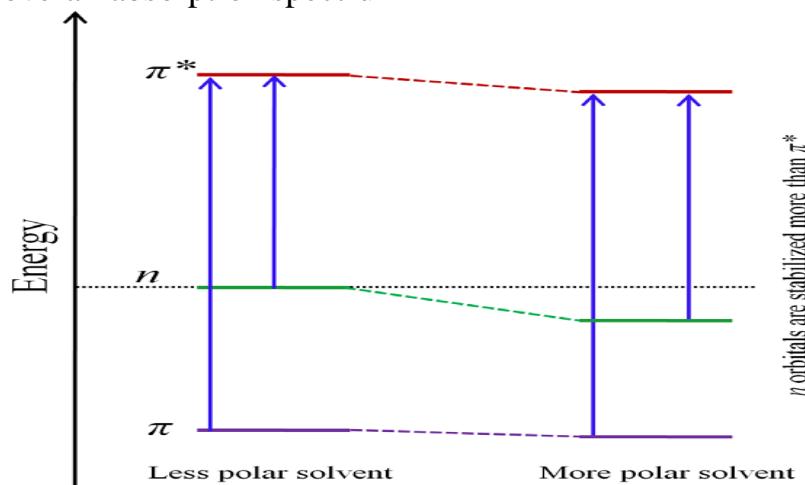
## Effect of solvent and extent of conjugation on $\lambda_{\text{max}}$

**Solvents:** The solvents used in any spectroscopic method should ideally be transparent (non-absorbing) to the electromagnetic radiation being used. Table 5.1 shows the wavelength cutoffs (the lowest working wavelength) of some of the solvents used in UV/visible spectroscopy.

### 5.1 Solvents commonly used in UV/visible spectroscopy

Solvent	Wavelength cutoff
Water	190 nm
Acetonitrile	190 nm
Cyclohexane	195 nm
Methanol	205 nm
95% ethanol	205 nm

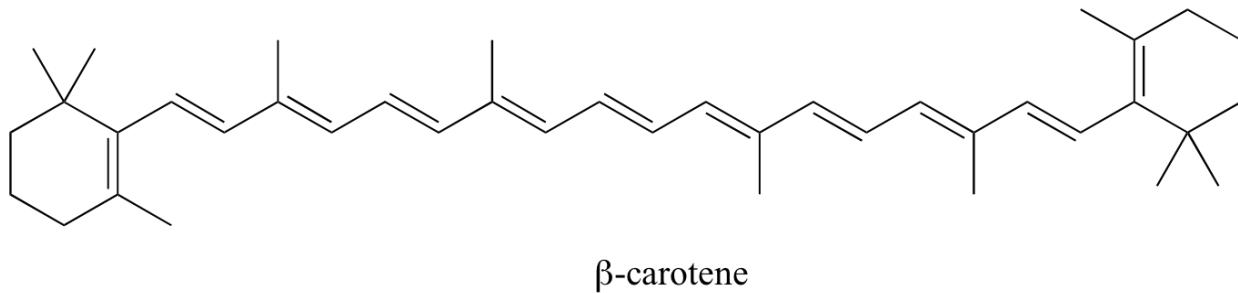
**Effect of solvent  $\lambda_{\text{max}}$ :** Polarity of solvents is an important factor in causing shifts in the absorption spectra. Conjugated dienes and aromatic hydrocarbons are little affected by the changes in solvent polarity.  $\alpha,\beta$ -unsaturated carbonyl compounds are fairly sensitive to the solvent polarity. The two electronic transitions  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  respond differently to the changes in polarity. Polar solvents stabilize all the three molecular orbitals ( $n$ ,  $\pi$ , and  $\pi^*$ ), albeit to different extents (Figure 5.4). The non-bonding orbitals are stabilized most, followed by  $\pi^*$ . This results in a bathochromic shift in the  $\pi \rightarrow \pi^*$  absorption band while a hypsochromic shift in  $n \rightarrow \pi^*$  absorption band. Shift to different extents of the two bands will result in the different shape of the overall absorption spectrum.



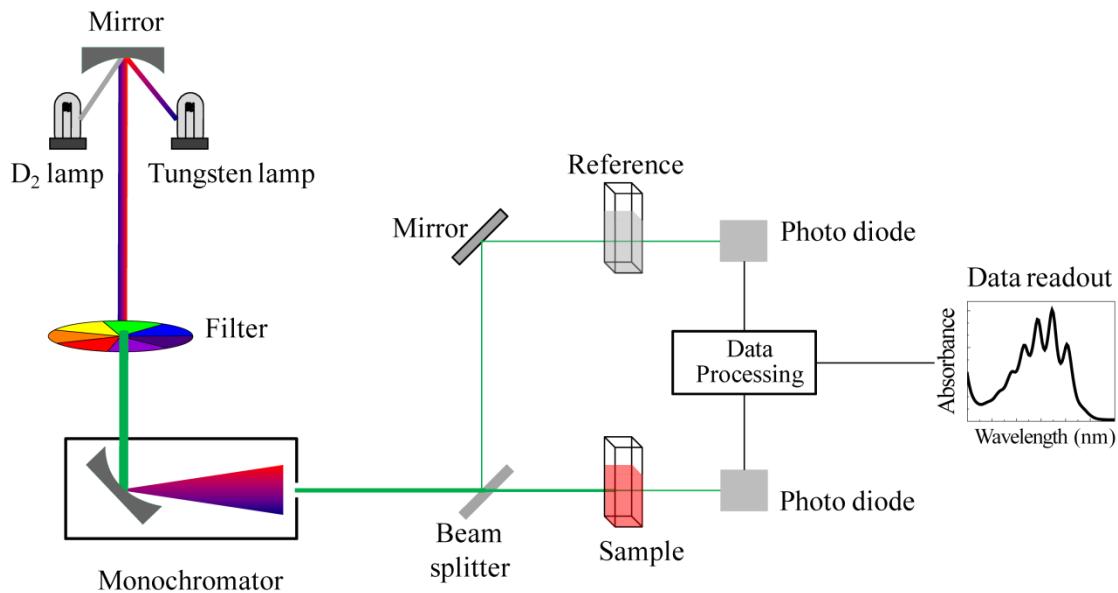
### **Effect of conjugation on $\lambda_{\text{max}}$ :**

1. Conjugation decreases the energy gap between HOMO and LUMO.
2. Hence less energy is required for electronic transitions.
3. Therefore transitions occur at longer wavelengths.
4. If a compound has enough double bonds it will absorb visible light and the compound will be coloured, e.g.  $\beta$ -carotene which is orange and is found in carrots and tomatoes has  $\lambda_{\text{max}} = 455\text{nm}$

Compound	Structure	$\lambda_{\text{max}}$	$\epsilon_{\text{max}}$
Ethylene	>C=C<	165	
1,3 butadiene	>C=C-C=C<,	217	20900
1,3,5,7 octatetraene	>C=C-C=C-C=C-C=<,	296	52000
$\beta$ -carotene		451	



### **Instrumentation of UV double beam spectrometer**



Instruments for measuring the absorption of U.V. or visible radiation are made up of the following components;

**1. Sources (UV and visible):** The electrical excitation of deuterium or hydrogen at low pressure produces a continuous UV spectrum. Both deuterium and hydrogen lamps emit radiation in the range 160 - 375 nm. Quartz windows must be used in these lamps, and quartz cuvettes must be used, because glass absorbs radiation of wavelengths less than 350 nm.

**2. Wavelength selector (monochromator):** monochromators contain the following  
An entrance slit, collimating lens, a dispersing device (usually a prism or a grating), a focusing lens and an exit slit.

Polychromatic radiation (radiation of more than one wavelength) enters the monochromator through the entrance slit. The beam is collimated, and then strikes the dispersing element at an angle. The beam is split into its component wavelengths by the grating or prism. By moving the dispersing element or the exit slit, radiation of only a particular wavelength leaves the monochromator through the exit slit.

### **3. Sample containers: Cuvettes**

The containers for the sample and reference solution must be transparent to the radiation which will pass through them. Quartz or fused silica cuvettes are required for spectroscopy in the UV region. These cells are also transparent in the visible region. Silicate glasses can be used for the manufacture of cuvettes for use between 350 and 2000 nm.

#### **4. Detectors**

The photomultiplier tube is a commonly used detector in UV-Vis spectroscopy. It consists of a photoemissive cathode (a cathode which emits electrons when struck by photons of radiation), several dynodes (which emit several electrons for each electron striking them) and an anode. The other detectors used are phototube, photocell, photodiode etc.,

**5. Recording system:** The signal from the photomultiplier tube is finally received by the recording system. The recording is done by recorder pen.

### **Applications of UVspectroscopy**

1. **Qualitative analysis:** compounds with n-bonding electrons, pi-electrons and single bonds can be identified by comparing with the spectra of known compounds by UVspectroscopy.
2. **Detection of impurities:** Peaks due to impurities are quite intense than the sample and hence can be easily detected.
3. **Quantitative analysis** can be done by calibration curve methods in order to know the concentration of the sample
4. **Molecular weight** of the sample can be determined by UV spectroscopy
5. **Dissociation constants** of the acids and bases can be determined.
6. **Chemical Kinetics: rate of the reacton can be studied by** UV spectroscopy
7. **Charge transfer transitions** in coordination complexes can be detected
8. Determination of the percentages of various keto and enol forms of the compound present in tautomeric equilibrium.
9. UV spectroscopy is used in the structural elucidation of organic and inorganic compounds

## Infrared spectroscopy

Infrared (IR) region of the electromagnetic spectrum lies between visible and microwave regions and therefore spans the wavelengths from  $0.78 - 250 \mu\text{m}$ . IR spectroscopy, therefore, is used to probe the vibrations in molecules and is also known as vibrational spectroscopy.

Infrared region is usually divided into three regions: near infrared, mid-infrared, and far infrared (Figure 10.1). IR spectroscopists use wavenumbers ( $\bar{\nu}$ ) to represent the IR spectra and we shall be following the same convention. Mid-IR region ( $\lambda = 2.5 - 25 \mu\text{m}; \bar{\nu} = 4000 - 400 \text{ cm}^{-1}$ ) is the region of interest for studying molecular vibrations.

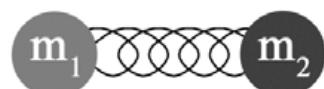
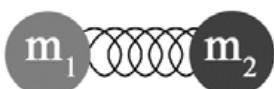
### Theory IR absorption:

For a molecule to absorb IR radiation, it has to fulfill the following requirements

- (1) The frequency of the IR radiation should be same as that of the vibrating molecule.
- (2) The molecule should have electric dipole moment.

### Frequency of vibration of the molecule:

We have seen that the bonds are not static but vibrating in different ways. A vibrating bond can therefore be considered a spring with its ends tethered to two atoms



If the masses of the atoms are  $m_1$  and  $m_2$ , the frequency of stretching vibration of the diatomic molecule can be given by the Hooke's law:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \dots \dots \dots \quad (10.1)$$

where,  $\nu$  is the frequency of vibration,  $k$  is the spring constant, and  $\mu$  is the reduced mass i.e.  $\frac{m_1 m_2}{m_1 + m_2}$

or

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

The spring constant,  $k$  is the measure of the bond strength. The stronger the bond, the higher the  $k$ , and consequently the higher is the frequency of vibration. This treatment implies that the diatomic molecule is a simple harmonic oscillator. The energy of a quantum harmonic oscillator is given by:

$$E = \left(n + \frac{1}{2}\right) h\nu \quad \dots \dots \dots$$

where,  $n = 0, 1, 2, \dots$  and  $h$  is the Planck's constant

$$E = \left(\nu + \frac{1}{2}\right) h\nu \quad \text{or} \quad E = \left(\nu + \frac{1}{2}\right) h c \bar{\omega} \quad \text{where } \bar{\omega} = \frac{c}{\lambda} = \frac{\nu}{2\pi} C$$

where,  $\nu = 0, 1, 2, \dots$  and  $h$  is the Planck's constant

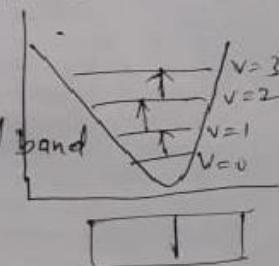
When  $\nu = 0$ , follow from the book  $E_0$  is given by

$E_0 = \frac{1}{2} h c \bar{\omega}$  is called zero point energy of the molecule. ie even at absolute zero, when translational and rotational motion cease, vibrational motion still exist.

Consider a transition from an upper vibrational level to lower vibrational level. Change in vibrational energy will

$$\Delta E = E_2 - E_1 = h c \bar{\omega}$$

transition from  $\nu=1$  to  $\nu=0$  gives fundamental band  
 $\nu=2$  to  $\nu=0$  gives first overtone.  
 $\nu=3$  to  $\nu=0$  gives second overtone.



## Absorption of infrared radiation

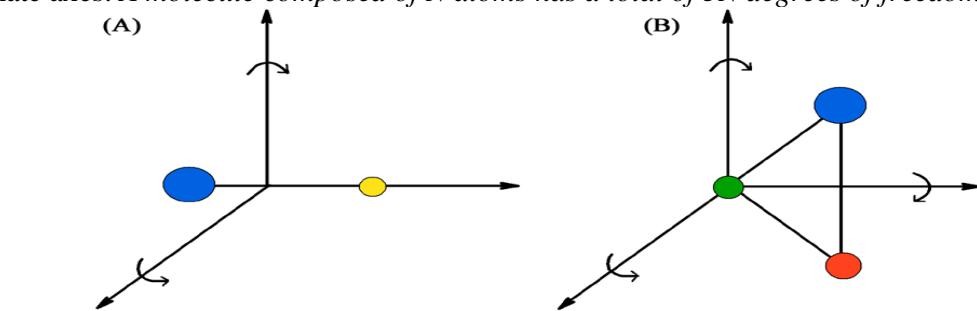
A molecular vibration is IR active i.e. it absorbs IR radiation if the vibration results in a change in the dipole moment. A diatomic molecule, that has one mode of vibration, may not absorb an IR radiation if the vibration does not accompany a change in the dipole moment. This is true for all the homonuclear diatomic molecules such as H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, etc. Vibration of carbon monoxide (C=O), on the other hand, causes a change in dipole moment and is therefore IR active. Vibration of a bond involving two atoms that have large electronegativity difference is usually IR active.

An IR active vibration of a particular frequency absorbs the IR radiation of same frequency. Let us calculate the position of absorption band for carbonyl stretching vibration (frequency =  $5.1 \times 10^{13}$  vibrations/second) in acetone.

$$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \text{ cm}^{-1}$$
$$\bar{\nu} = \frac{5.1 \times 10^{13} \text{ sec}^{-1}}{3 \times 10^{10} \text{ cm/sec}} = 1700 \text{ cm}^{-1}$$

## Degrees of freedom and molecular vibrations

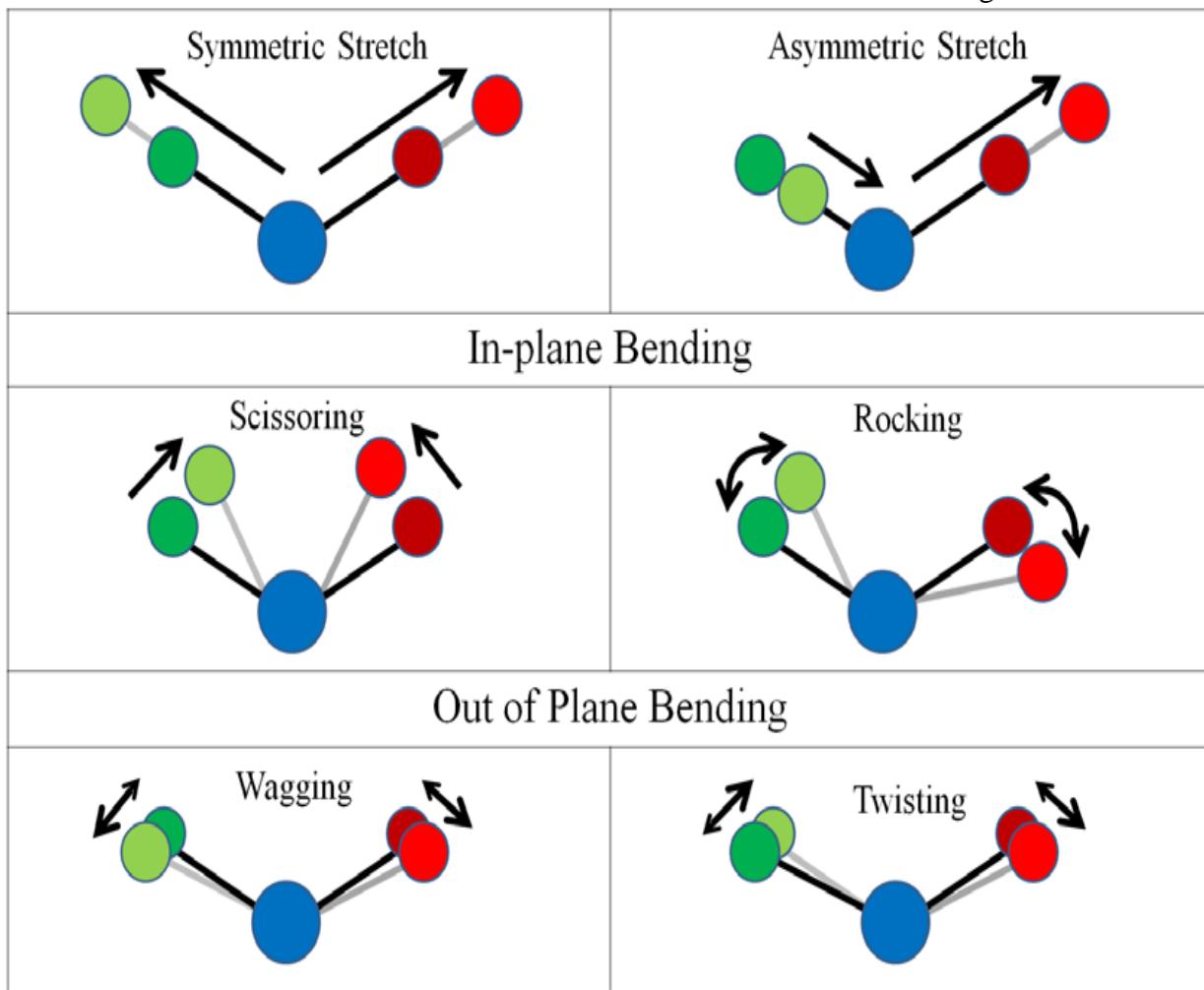
At non-zero temperatures, *i.e.* temperatures above 0 K, all the atoms in a molecule are in motion. The molecule itself also is in translational and rotation motion. In a three dimensional space, an atom in isolation has 3 degrees of freedom, corresponding to the motion along the three independent coordinate axes. A molecule composed of  $N$  atoms has a total of  $3N$  degrees of freedom (Figure 10.2).



Degrees of rotational freedom for a diatomic (A) and a triatomic (B) molecule

For a non-linear molecule, three of these  $3N$  degrees of freedom correspond to translational motion, three correspond to rotational motion while rest  $3N-6$  are the vibrational degrees of freedom. For a linear molecule, there are only two rotational degrees of freedom that correspond to the rotation about the two orthogonal axes perpendicular to the bond (Figure 10.2). A linear molecule, therefore, has  $3N-5$  vibrational degrees of freedom. Let us have a look at the degrees of freedom of a diatomic molecule. A diatomic molecule has a total of  $3 \times 2 = 6$  degrees of freedom. Three of these six degrees of freedom correspond to translational motion of the molecule; two of them define rotational degrees of freedom; while one corresponds to the vibration of the atoms along the bond. The  $3N-6$  vibrational degrees of freedom ( $3N-5$  for linear molecules) represent the true/fundamental modes of vibration of a molecule. The different types

of vibrations are shown in Figure 10.3.



**Figure 10.3 Stretching and bending vibrations in molecules**

## Fundamental modes of Vibrations / Normal modes of vibrations:

On a polyatomic molecule, each atom is having three degrees of freedom in three directions which are perpendicular to each other. Therefore a polyatomic molecule requires three times as many degrees of freedom as the number of atoms. Thus a molecule of  $n$  atoms has  $3n$  degrees of freedom.

For a nonlinear molecule, three degrees of freedom describe rotation and three describe translation, the remaining i.e.,  $3n - (3+3) = [3n - 6]$  degrees are fundamental vibrations.

For a linear molecule, only two degrees of freedom are required to describe rotation. Thus a linear molecule has  $3n - 5$  modes of fundamental vibrations.

These fundamental vibrations are further classified into

### Stretching vibrations

Symmetric stretching      Asymmetric stretching

### Bending vibrations (Deformation vibrations)

In-plane bending Vib<sub>rs</sub>      Out-of-plane bending  
Scissoring      Rocking      Wagging      Twisting

Stretching vibrations: In this, the atoms move along the bond axis so that the bond length increases or decreases periodically at regular intervals.

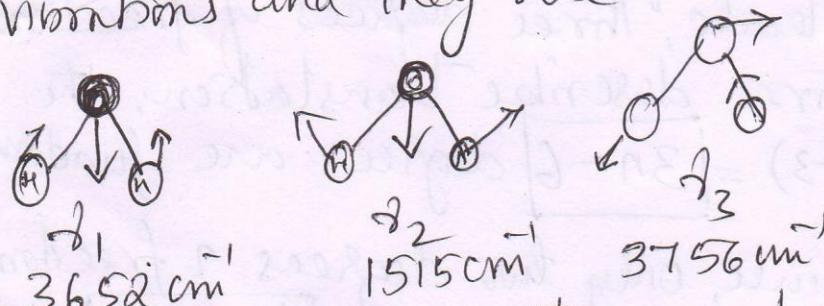
Symmetric stretching ( $\sigma$ ) and asymmetric stretching are denoted by  $\delta$  and are shown in the diagram.

Bending vibrations: In this, there is a change in the bond angle between bonds with a common atom, or the movement of a group of atoms with respect to the remainder of the molecule.

Bending vibrations occur at lower frequencies whereas stretching vibrations occur at higher frequencies.

Normal modes of vibrations for  $H_2O$  and  $CO_2$  molecules & their correspond absorption frequencies.

$H_2O$  is a bent molecule ∴ Normal modes of vibr are  $3n-4$  as  $H_2O$  is a triatomic bent molecule ∴  $3(3)-6 = 3$  mode of vibrations and they are



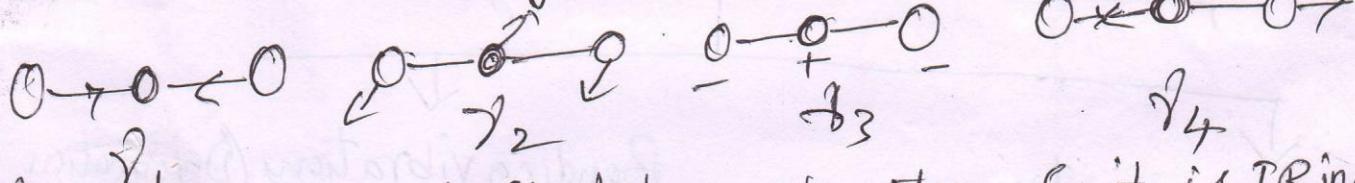
$\gamma_1$  is symmetric stretch  
 $\gamma_2$  is asymmetric stretch  
 $\gamma_3$  is bending vibration

$3652\text{ cm}^{-1}$

$1515\text{ cm}^{-1}$

$3756\text{ cm}^{-1}$

$CO_2$  is a linear triatomic molecule ∴ Normal modes of vibrations are  $3n-5 = 3(3)-5 = 4$  modes of vibrations and they are



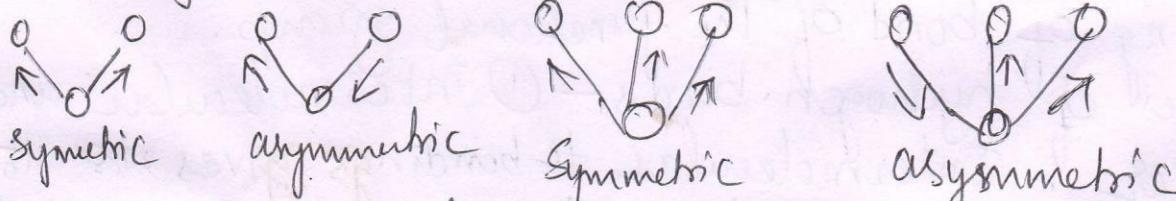
$\gamma_1$  is symmetrical stretching vibration & it is IR inactive as there is no change in the dipole moment.  $\gamma_4$  is asymmetric stretching and appear at  $2350\text{ cm}^{-1}$ .  $\gamma_2$  &  $\gamma_3$  are the bending vibrations & are of same frequency hence both will absorb at the same frequency i.e  $666\text{ cm}^{-1}$ . In the case of  $CO_2$  molecule though there are 4 modes of vibrations according to calculation, but only two absorption peaks are observed.

## Factors that influence the vibrational frequencies

The calculated value of the absorption frequency of particular group (in terms of wavenumber) is never exactly equal to the observed value. This is due to the influence of the structure of the molecule on that particular group in its immediate neighbourhood. Some of the factors that affect vibrational frequencies are

### 1. Coupled vibrations and Fermi resonance

The stretching absorption frequency of an isolated  $\text{CH}_3$  group is a ~~fixed~~<sup>one</sup> value, but in the case of methylene  $-\text{CH}_2-$  group two absorptions occur which correspond to symmetric & asymmetric vibrations. Asymmetric vibrations always takes place at higher wave numbers compared to symmetric vibrations. These are known as coupled vibrations as these occur different frequencies than that required for an isolated CH stretching. In  $\text{CH}_3$  group coupled vibrations occurs at different frequencies compared to  $\text{CH}_2$  gp.



Fermi resonance - whenever two fundamental modes of vibrations of same energy couple they produce two new modes of vibrations, with frequencies higher and lower than that of observed (in the absence of coupling) is called Fermi resonance.

Eg: In aldehydes C-H stretching ~~absorption~~ appears at a doublet at  $2820\text{ cm}^{-1}$  &  $2720\text{ cm}^{-1}$  due to the coupling of C-H fundamental mode with overtone of C-H bonding.

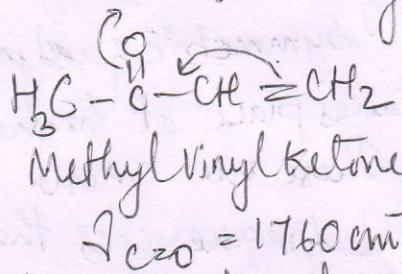
2. Electronic effects: The electronic effects are inductive effect, mesomeric effect, field effect, etc., <sup>conjugation</sup> changes the bond strength/force.

<sup>compd</sup>	$\nu_{C=O}$
Formaldehyde ( $HCHO$ )	$1750 \text{ cm}^{-1}$
Acetaldehyde ( $CH_3CHO$ )	$1745 \text{ cm}^{-1}$
Acetone ( $CH_3COCH_3$ )	$1715 \text{ cm}^{-1}$

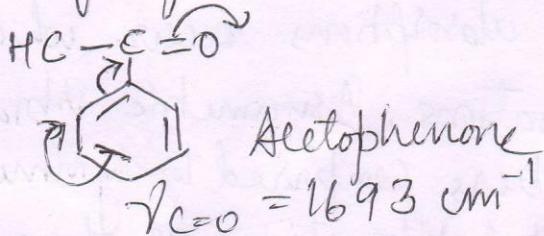
The  ~~$\nu_{C=O}$~~  decreases due to the introduction  $CH_3$  gp which causes +I effect which gives rise to the lengthening or weaken of the bond  $C=O$ .

Acetone ( $CH_3COCH_3$ )	$1715 \text{ cm}^{-1}$
Chloroacetone ( $ClCH_2COCH_3$ )	$1728 \text{ cm}^{-1}$
Dichloroacetone ( $Cl_2CHCOCH_3$ )	$1740 \text{ cm}^{-1}$

Introduction of electronegative atom causes -I effect which gives rise to shortening or strengthening of the  $C=O$  bond.



$$\nu_{C=O} = 1760 \text{ cm}^{-1}$$



$$\nu_{C=O} = 1693 \text{ cm}^{-1}$$

3. Hydrogen bonding: Hydrogen bonding shifts the absorption frequencies to lower wavenumber region due to weakening of bond of the functional group.

Two types of hydrogen bonds - ① Intermolecular and ② intramolecular. Intermolecular H-bonding gives rise to broad peaks whereas intramolecular hydrogen bonds gives rise to sharp and well defined peaks. Intermolecular H-bonds are concentration dependent whereas Intramolecular H-bonds are concentration depen-

Eg: ① Amines shows N-H stretching at  $3500 \text{ cm}^{-1}$  in dil solns but in concentrated solns N-H stretching is shown at  $3300 \text{ cm}^{-1}$

② Free OH stretching frequency is at  $3600 \text{ cm}^{-1}$  whereas Alcohols (intermolecular H-bonding) shows OH stretch at the range  $3400 - 3200 \text{ cm}^{-1}$

## Applications of IR Spectroscopy

1. Identification of compounds - Alkenes, Alkenes, alkynes, aromatics, alcohols, ethers, Carboxylic acids, esters, aldehydes, ketones, amines etc can be identified based on the frequency of absorption & the corresponding bands in the spectra.
2. Alcohols and phenols can be differentiated by IR Spectroscopy  
Though the stretching frequency of OH is same in both the cases, the position of C-O stretching is lesser than  $1200\text{cm}^{-1}$ . In the case of alcohols & is greater than  $1200\text{cm}^{-1}$  in phenols.
3. Aldehydes & Ketones can be identified by IR The  $\nu_{\text{C=O}}$  stretching frequency of ketones & aldehydes is around  $1700\text{cm}^{-1}$  & can vary slightly depending upon the nature of groups attached to the carbonyl group.
4. Carboxylic acids & its derivatives can be identified by observing the  $\nu_{\text{C=O}}$  &  $\nu_{\text{OH}}$  values
5. Determination of molecular structure
6. Studying the progress of the reaction
7. Detection of impurities: By comparing the spectrum of the ~~com~~ prepared compd with that of std pure compd.
8. Isomerism in Organic Chemistry: The geometrical isomers such as cis and trans can be easily identified by IR. cis isomers absorb at higher frequency and give much complex spectra than the trans isomers which are more symmetric.
9. Tautomerism in Organic Chemistry: Since tautomers have different chemical bonds they can be readily detected by IR.
10. The geometry of the coordination complexes can be determined

## Comparison of Fourier Transform and Dispersive IR

### Dispersive IR

- ① There are many moving parts resulting in mechanical damaging & wearing.
- ② Calibration against reference spectrum is required.
- ③ Only a radiation of narrow frequency range falls on the detector.
- ④ Stray radiation causes spurious readings.
- ⑤ The sample is subjected to thermal effect from the focussed beam.
- ⑥ Lesser resolution.
- ⑦ Less sensitive & less accurate.

### F.T. IR

- ① Only mirror moves so no wearing & mechanical damage.
- ② Not required.
- ③ All frequencies of radiation fall on the detector simultaneously.
- ④ Stray radiation does not affect all the signals are modulated.
- ⑤ The sample is free from thermal effects of the beam.
- ⑥ Higher resolution as its distance travelled is more.
- ⑦ More sensitive & accurate.

## Qualitative Analysis

IR spectroscopy is a great method for identification of compounds, especially for identification of functional groups. Therefore, we can use group frequencies for structural analysis. Group frequencies are vibrations that are associated with certain functional groups. It is possible to identify a functional group of a molecule by comparing its vibrational frequency on an IR spectrum to an IR stored data bank.

Here, we take the IR spectrum of Formaldehyde for an example. Formaldehyde has a C=O functional group and C-H bond. The value obtained from the following graph can be compared to those in reference data banks stored for Formaldehyde. A molecule with a C=O stretch has an IR band which is usually found near 1700 cm<sup>-1</sup> and around 1400 cm<sup>-1</sup> for CH<sub>2</sub> bend. It's important to note that this value is dependent on other functional groups present on the molecule. The higher 1700 cm<sup>-1</sup> indicates a large dipole moment change. It is easier to bend a molecule than stretch it, hence stretching vibrations have higher frequencies and require higher energies than bending modes. The finger print region is a region from 1400-650 cm<sup>-1</sup>. Each molecule has its own characteristic print and is often cumbersome to attach any values to this region.

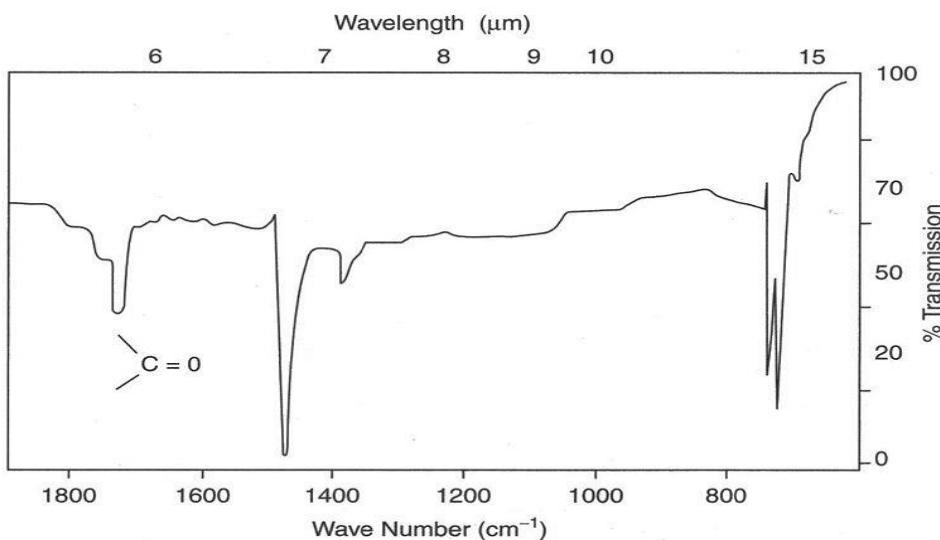


Figure 6 IR

## Spectrum of Formaldehyde

### Quantitative Analysis

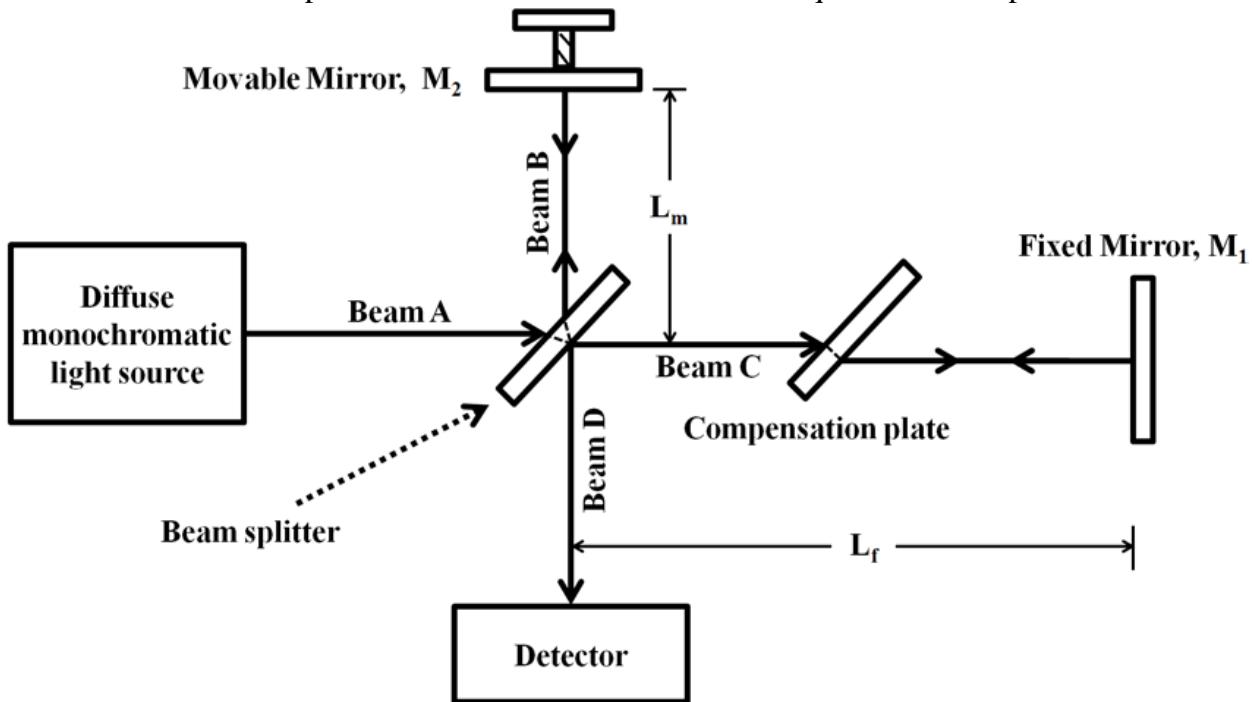
Infrared spectroscopy can also be applied in the field of quantitative analysis, although sometimes it's not as accurate as other analytical methods, like gas chromatography and liquid chromatography. The main theory of IR quantification is Beer's law or Beer-Lambert law, which is written as

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

Where A is the absorbance of the sample, I is the intensity of transmitted light, I<sub>0</sub> is the intensity of incident light, l is the path length,  $\epsilon$  is the molar absorptivity of the substance, and c is the concentration of the substance.

From the Beer's Law, we could figure out the relation between the absorbance and the concentration of the sample since the analytes have a particular molar absorptivity at a particular

wavelength. Therefore, we could use IR spectroscopy and Beer's Law to find the concentration of substance or the components of mixture. This is how the IR quantification operated.



#### **Box 10.1: Michelson interferometer**

A Michelson interferometer has a radiation source, a collimator, a beam-splitter, a movable mirror, a fixed mirror, a compensator, and a detector. The radiation coming from the source is collimated and focused on the beam-splitter. 50% of the radiation gets transmitted while 50% gets reflected. The mirrors reflect back the radiation towards the beam splitter that again allows 50% transmission and 50% reflection. This allows the beams, B and C to interfere and give the beam D. As the beam, B travels through the beam-splitter twice while beam C does not travel through it even once, a compensation plate of same material (un-mirrored) and thickness as the beam-splitter is, is placed between the beam-splitter and the fixed mirror. This allows the beams, B and C to travel the equal distance. The motion of the movable mirror,  $M_2$  causes the two beams to travel different distances thereby generating interference. Let us see what happens when a monochromatic radiation is used in the Michelson interferometer. If the beams, B and C travel the equal distance, they are in phase and will interfere constructively. If however, the  $M_2$  moves, say towards the beam-splitter by a distance of  $\lambda/4$ , the beam B travels a distance of  $\lambda/2$  less than that travelled by beam C. This allows a phase difference of  $180^\circ$  resulting in destructive interference. A continuous motion of the mirror  $M_2$ , therefore, will generate a sinusoidal signal through interference. The detector therefore detects a time domain signal. If a sample placed before the detector absorbs this radiation, the intensity of the light goes down. If a polychromatic light is used, the interference pattern generated carries all the wavelengths present in the polychromatic light. Absorption of any wavelength will result in a change in the interfering pattern. The interfering pattern, also known as interferogram is then Fourier transformed to obtain the frequency domain data

#### **Instrumentation of FTIR spectrometer**

**Radiation source---Sample source---Detector – Amplifier--- Recorder**

**Source:** Infrared radiation is produced by electrically heating a source, usually a Nernst filament or a Globar to 1000 - 1800°C. The Nernst filament is fabricated from a binder and oxides of

thorium, cerium, zirconium and yttrium. The Globar is a small rod of silicon carbide usually 5 cm in length and 0.5 cm in diameter. The maximum radiation for the Globar occurs in the 5500 - 5000 cm<sup>-1</sup> region. Nichrome wire, carbon arc, rhodium wire and tungsten filament lamp are also used as light source. In a commercial infrared spectrometer either a nichrome wire or a platinum filament contained in a ceramic tube is commonly used as infrared source for the range 4000 - 400 cm<sup>-1</sup>

#### **Detectors:**

There are (i) **pyroelectric detectors** based on ferroelectric materials such as lithium tantalate, generating a small electric voltage pulse in response to a temperature gradient caused by an incident light pulse. They can be used e.g. in optical energy meters for measuring the pulse energy of a Q-switched laser, including the pulse-to-pulse fluctuations.

#### **(ii) Bolometers**

A bolometer sensor contains a thin infrared-absorbing plate, made e.g. of amorphous silicon (Si) or vanadium oxide, which is suspended with two electrodes. One can then measure the temperature-dependent electrical resistance of the plate.

**Amplifiers and Recorders:** The radiant energy received by the detector is converted into measurable electrical signal and is amplified by the amplifiers. The amplified signal is registered by a recorder or a plotter. The recorder is driven with a speed which is synchronised with that of a monochromator, so that, the pen moving across the chart, records the transmittance of the sample as a function of the wave number.

#### **Sample handling techniques:**

A sample of a solid of low melting point can be melted on one plate and its spectrum may be obtained. A solid into small particles and suspend them in a viscous liquid that is placed in the light beam between KBr or NaCl plates. A liquid commonly used for this purpose is mineral oil - also called Nujol. The mixture of the solid particles suspended in the viscous liquid is called a mull.

Another popular method to use for solids is to form an intimate mixture by grinding the sample together with dry KBr. A measured amount of this finely ground powder is then pressed under several hundred kgs/cm<sup>2</sup> to form a transparent KBr disk about 1cm in diameter and less than 1mm thick. The KBr can, however, interact with some groups (such as - NH<sub>2</sub>) to cause distortion of the spectrum. In addition, water in the KBr can be hard to eliminate and the water absorption interferes with -OH and -NH<sub>2</sub> bands. A third approach is to deposit the solid as a film on a single KBr plate by allowing the solvent to evaporate from a solution of the sample.

In the case of liquids, a liquid is placed in the form of thin film, a complete spectrum of it may be obtained. A liquid can be spread as a film on an IR transparent plate if it is concentrated enough and will not evaporate. Otherwise, the liquid., is placed between two KBr or NaCl plates fixed in a holder and the corresponding spectrum can be obtained.