

## UNIT-II

### IR Spectroscopy

#### Principles of Infrared Spectroscopy:

\* The absorption of infrared radiations cause a excitation of molecule from a lower to that higher vibrational level.

\* All the bonds in a molecule are not capable of absorbing infrared light but only those bonds which are accompanied by a change in dipole moment with absorption in the infrared region.

\* The Infrared light is thus absorbed when the oscillating dipole moment interacts with the oscillating electric vector of the infrared beam.

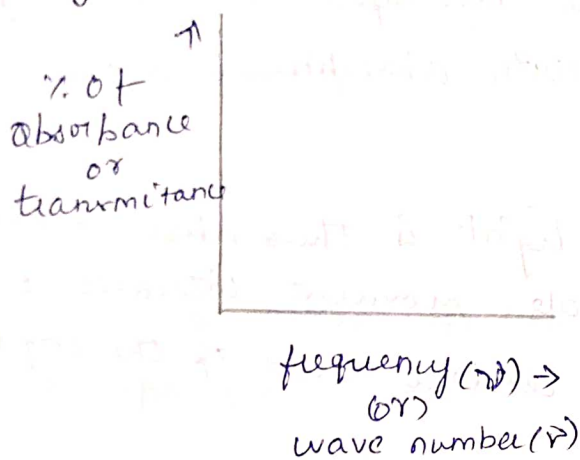
\* These vibrations absorb infrared radiation at certain quantized frequencies and give rise to characteristic bands. When infrared light of that frequency is incident on the molecule energy is absorbed and the amplitude of that vibration is increased.

\* Vibrational transitions which are accompanied by a change in dipole moment of the molecule are called Infrared active transition. On the other hand, vibrational transitions which do not involve change in dipole moment are not directly absorbed and these are Infrared inactive.

\* An infrared spectrum is obtained when the frequency of molecular vibration corresponds to the frequency of infrared radiation absorbed.

### Infrared spectrum:

Mostly infrared spectra are plotted as percentage of absorbance or transmittance against wave number or frequency.



### Normal modes of molecular vibrations:

When a molecule absorbs infrared radiation, it is set into vibration resulting in excitation of bond deformation either stretching or bending.

#### 1. Stretching vibration:

\* Stretching vibration is rhythmic movement where the distance between two atoms increases or decreases but the atoms remain in the same bond axis.

As this type of vibrations correspond to one-dimensional motion so there will be  $(n-1)$  stretching vibrations for non-cyclic

systems

stretching vibrations require higher energy and occur at higher frequency.

a) Symmetric stretching:

In symmetric stretching both the atoms move in and out simultaneously that is stretching and compression occur in a symmetrical fashion.

b) Asymmetric stretching:

In this mode one atom approaches the central atom while the other departs from it that is one bond is compressing while the other is stretching.

2. Bending vibrations:

The distance between the atoms remains constant but the position of the atom changes relative to the original bond axis.

Thus bending involves oscillation of the atoms perpendicular to the chemical bond.

At these vibrations describes two dimensional vibrations, there will be  $2n - 5$  bending vibrations for non-cyclic and linear molecule. Bending vibrations require lower energy and occur at lower frequency.

a) Scissoring:

Here the two atoms joined to a central atom move towards and away from each other with the deformation of the valence angle.

b) Rocking:

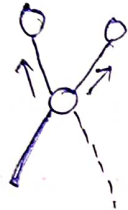
Here the structural unit swings back and forth in the plane of the molecule (in plane bending).

c) Wagging:

The structural unit swings back and forth out of the plane of the molecule. (out of plane bending)

d) Twisting:

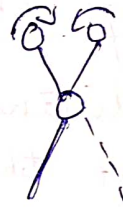
Here the structural unit's rotate about the bond which joins to the rest of the molecule (out of the plane bending)



Symmetric  
( $\nu_s \text{CH}_2$ )  
 $\sim 2853 \text{ cm}^{-1}$



Asymmetric  
( $\nu_{as} \text{CH}_2$ )  
 $\sim 2926 \text{ cm}^{-1}$



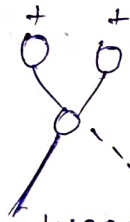
scissoring  
( $\delta_s \text{CH}_2$ )  
 $\sim 1465 \text{ cm}^{-1}$



Rocking  
( $\rho \text{CH}_2$ )  
 $720 \text{ cm}^{-1}$

stretching  
vibrations

Bending  
vibrations



wagging  
( $\omega \text{CH}_2$ )  
 $1350-1150 \text{ cm}^{-1}$



Twisting  
( $\tau \text{CH}_2$ )  
 $1350-1150 \text{ cm}^{-1}$

Various modes of vibrations of  $\text{AX}_2$  (eg  $\text{CH}_2$ ) gro

The + and - signs signify ~~the~~ vibrations perpendicular to the plane of paper.

## VIBRATIONAL FREQUENCIES:

We know that molecules vibrate for this they need energy. They get the necessary energy by absorbing light of suitable energy in the IR region. The position of the absorbed light in the spectrum can be specified in units of frequency. Such frequencies are called vibrational frequencies.

At ordinary temperature organic molecules are constantly vibrating each bond absorbs light of specific frequency and performs stretching and bending vibrations. Thus each bond has its characteristic stretching and bending frequency.

The stretching energy of a bond is greater than the bending energy. Thus stretching absorptions of a bond.

We can calculate the vibrational frequency of a bond using Hooke's law.

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

Where  $\nu$  = frequency :  $k$  = force constant of the bond &  $\mu$  is the reduced mass of the system.

Note:

In IR spectroscopy true frequencies ( $\nu$ ) are never used. Instead in majority of cases corresponding wave number ( $\bar{\nu}$ ) are used. Some times wavelength ( $\lambda$ ) are also used. Invariable we refer to a vibration as having a

frequency of  $\times \text{cm}^{-1}$  & so students are advised to be aware of this anomaly and they to avoid the confusion between  $\bar{\nu}$  and  $\nu$ .

## Calculation of force constant:

The force constant of a bond  $k$  in a diatomic molecule is related to the frequency of absorption according to the formulae.

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

Where  $R$  is the reduced mass of the system and can be calculated from the relation

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

Thus if  $\nu$  is measured from the

spectrum,  $k$  can be calculated.

## Factors influencing vibrational frequencies:

Main factor influence the frequency of a molecular vibration. It is not possible to pinpoint which factor is precisely responsible for the shift in vibrational frequencies. For example the  $C=O$  stretching frequency in  $RCOCH_3$  is lower than in  $RCOCl$ .

The reason may be:

- i) The difference in mass between  $CH_3$  and  $Cl$
- ii) The inductive or mesomeric influence of  $Cl$  on  $C=O$  (there is some coupling interaction between the  $C=O$  and  $C-Cl$  bonds)

(or)

iii) same steric effect which alters the bond angles we shall discuss here frequency shift which are brought about by structural changes in the molecule or by interaction between functional group.

Bond strength

$C-C$

$1200\text{cm}^{-1}$

$C=C$

$1610\text{cm}^{-1}$

As bond is a double frequency less double

As bond is a lower

bond character.

## 1. Bond strength

The vibrational frequency increases when the bond strength increases. E.g.  $C=O$  and  $C-O$  stretching will have higher frequencies than  $C-C$  and  $C-O$  stretching respectively. This is in accordance with Hooke's law.

## 2. Reduced mass:

The vibrational frequency increases when the reduced mass of the system decreases. E.g.,  $C-H$  and  $O-H$  stretching will have higher frequencies than  $C-C$  and  $C-O$  stretching respectively.

(This is also in accordance with Hooke's law.)

### Exceptions:

On the basis of mass we expect  $X-H$  stretching frequencies to fall along the order  $CH > NH > OH > FH$ ; in fact they rise mainly due to increasing electronegativity. There are also examples in which  $O-H$  stretching has lower frequency than  $O-O$  stretching against the expected higher value.

## 3. Vibrational coupling:

When two bonds vibrate with similar frequency, vibrational coupling takes place for this to happen the two bonds should be close to one another in the molecule. (E.g. we expect one

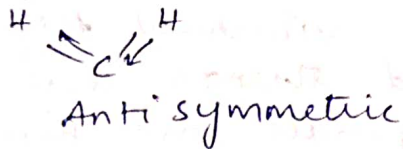
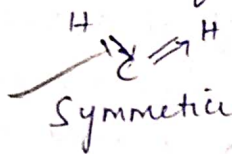
stretching absorption frequency for an isolated

$C-H$  bond: but in the case of methylene

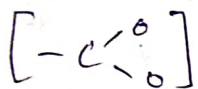
$(-CH_2)$  group two absorptions occur which

correspond to symmetric and antisymmetric

Vibrations follow:)



In such cases (antisymmetric vibrations always occur at higher frequencies while symmetric vibrations occur at lower frequency) these are called coupled vibrations since these vibrations occur at different frequencies than the required of an isolate C-H stretching. Similarly coupled vibrations of C=O group occur at different frequencies compared to -CH<sub>2</sub>- group. This vibrational coupling is a feature of other AX<sub>2</sub> groups exhibit two stretching bands. Example of another AX<sub>2</sub> type group is



#### Hydrogen bonds:

Hydrogen bonding brings about remarkable decrease in absorption frequencies. Stronger the hydrogen bonding greater is the absorption shift towards lower frequencies than the normal value.

Intermolecular hydrogen bonds.

i. Give rise to broad bands.

ii) Concentration dependent on dilution the intensities of bands decrease and finally disappear.

Intra molecular hydrogen bonds.

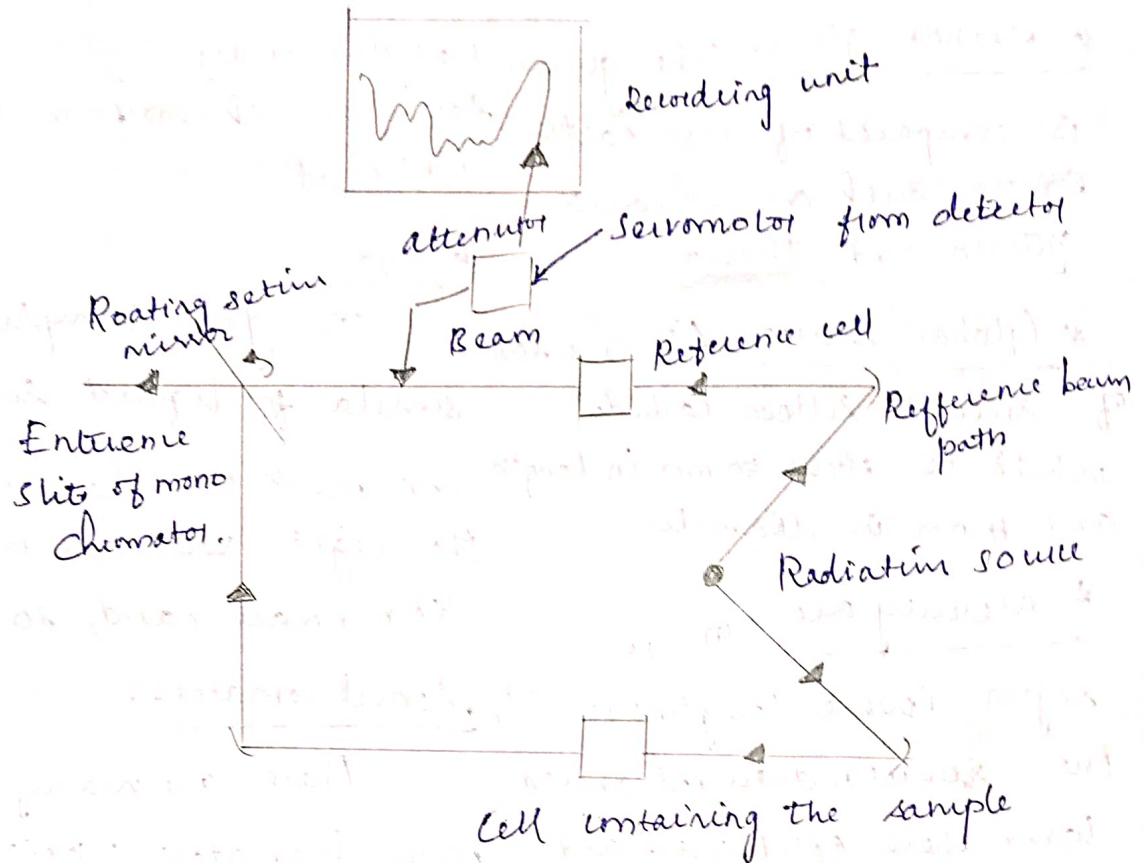
Give rise to sharp well defined bands.

Independent of concentration.



iii) The absorptivity frequency difference b/w free and associated molecule is large smaller.

### Instrumentation of IR Spectroscopy:



Double beam IR Spectrometer (Diagram)

The principal components of IR Spectrometer are.

- \* Radiation source.
- \* Sample cells and sampling of substance.
- \* Monochromators.
- \* Detector
- \* Recorders.

### IR radiation sources:

IR instrument require the use of a source of energy that emits IR radiation that must be constant and intense enough to be detected and extend to what is needed in the wave length.

Various popular sources of IR radiation are

\* Incandescent lamp: In the near IR instruments an ordinary incandescent lamp is used.

\* Nernst glower: The glower is composed of rare earth oxides such as zirconia, yttria and thoria.

\* Globar source: (It is a rod of sintered silicon carbide) which is about 50 mm in length and 4 mm in diameter.

\* Mercury arc: In IR region (wave length  $< 200 \text{ cm}^{-1}$ ) the sources described above have lower their effectiveness and special high pressure mercury arc lamps are used.

### Sample cells and sampling of substance

IR spectrum has been employed to characterize gas, liquid or solid sample.

\* Solid - A variety of methods are employed for the preparation of solid sample including the pressed pellet method, solid suspension, solution,

multitechnique solid films and soon

\* Liquid:

Liquid samples can be stored in the liquid sample cell that is composed of alkali halides. Only organic solvent such as chloroform can be utilized.

\* Gas:

The gas sample cell is similar for liquid samples or much as. The surface in the light path are made of KBr, NaCl, and so on.

### Monochromators:

There are many kinds of monochromators; prisms, gratings and filters. Prisms are constructed of potassium chloride; sodium chloride or cesium iodide. Filters are composed of lithium fluoride and diffraction gratings comprise alkali halides, alkali halides.

### Detectors:

Detectors can be used to measure the strength of IR radiation. They include thermocouple, Bolometers.

thermistors, Gokey cells, as well as pyroelectric detectors are employed. Bolometer is based upon the fact that electrical resistance of a metal increases with increase in temperature and thermocouple detectors based upon the fact that if two different metals are connected together with wire and a temperature differential exists between them.

### Recorders:

Recorders are devices used to capture all aspects of the IR spectrum.

### Double beam - IR spectrometer

From the diagram we know that

- \* The energy emitted by the radiation source is split by the instrument into two beams, which are energetically and optically identical. One of the beams passes through the sample and the other through the reference sample.

- \* The sample is placed in the sample beam and a reference material

such as the solvent used in the sample is placed in the reference beam. The two half beams are combined and passed along the optically path to the detector.

- \* When there is no sample in the sample cell the half beam travelling atom the sample beam is not absorbed and is equal to the reference beam when these two half beams recombine a steady signal reaches the detector.

- \* When the sample cell contains the sample the half-beam travelling through it undergoes a decrease in intensity and two half beams are recombined.

They produce an strong oscillating signal which is measured by the detector.

The signal from the detector is passed on to the recording unit through a servometer.

### Finger print region: not needed

The region b/w  $400\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$  is an IR spectrum is known as the

finger print region. It usually contains a large number of peaks, making it difficult to identify individual peaks. However, the finger print region of a given compound is unique and therefore can be used to distinguish b/w compounds.

IR spectra is called the fingerprint region because the absorbing pattern is highly complex but unique to each organic structure. The stretching vibrations for both the carbon-carbon and carbon-oxygen double bonds are easily identified at  $6.1 \mu\text{m}$  and  $5.8 \mu\text{m}$  respectively.

### Finger print Region:

\* One of the important functions of Infrared spectroscopy is to determine the identity of two compounds. Two identical compounds have exactly the same spectra when run in the same medium under similar conditions.

\* The region below  $1500 \text{ cm}^{-1}$  is rich in many absorptions which are caused by bending vibrations and those resulting from the stretching vibrations of C-C, C-O and C-N bonds.

\* In a spectrum, the number of bending vibrations is usually more than the number of stretching vibrations. The said region is usually rich in absorption bands and shoulders. It is called fingerprint region.

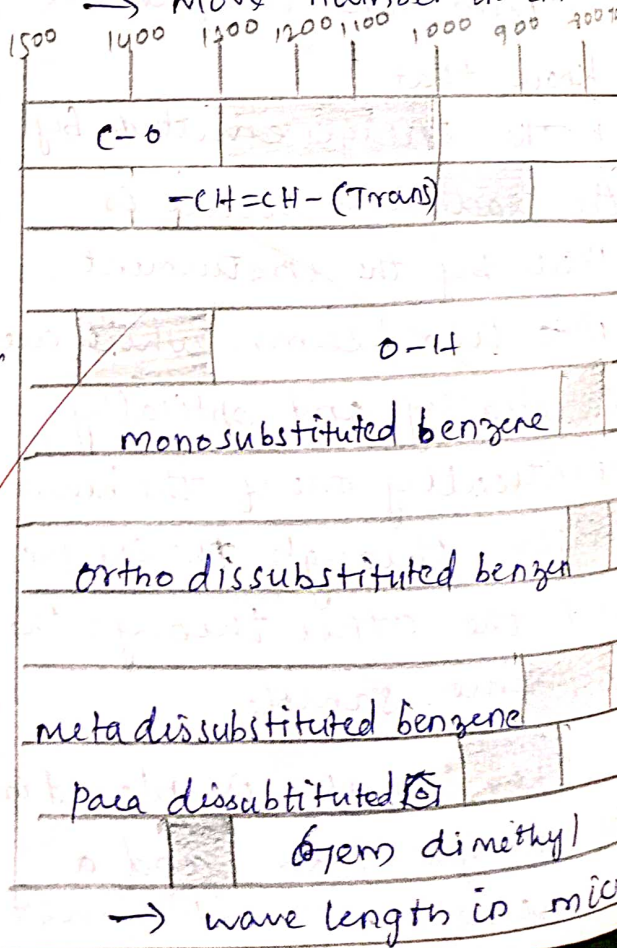
\* Finger print region can be subdivided into three regions as follows:

\*  $1500 - 1350 \text{ cm}^{-1}$

\*  $1350 - 1000 \text{ cm}^{-1}$  and

\* Below  $1000 \text{ cm}^{-1}$

→ wave number in  $\text{cm}^{-1}$



Characteristic absorptions in the fingerprint region

\* Some characteristic absorptions in each of the above regions are described below

\* Region : 1500 - 1350  $\text{cm}^{-1}$

The appearance of a doublet near 1380  $\text{cm}^{-1}$  and 1365  $\text{cm}^{-1}$

(s) shows the presence of tertiary butyl group in the compound.

\* Region : 1550 - 1000  $\text{cm}^{-1}$

All classes of compounds viz. alcohols, esters, lactones, and anhydrides show

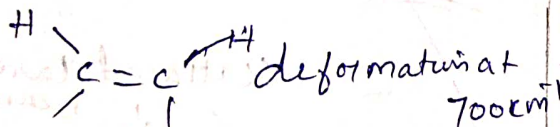
characteristic absorptions (Strong bands) in this region

10 C-O stretching primary alcohols form two strong at

1350 - 1260  $\text{cm}^{-1}$  and near 1050  $\text{cm}^{-1}$

phenols absorb near 1200  $\text{cm}^{-1}$

\* Region : below 1000  $\text{cm}^{-1}$



(s) and that at 970 - 960  $\text{cm}^{-1}$

(s) distinguishes between cis and trans alkenes. The higher value indicates that the hydrogen atom is

The alkenes are trans with respect to each other.

Characteristics absorption bands of various functional group

An absorption band is a range of wavelengths, frequencies or energies in the electromagnetic spectrum which are characteristic of a particular transition from an initial to final state in a substance.

Formula	Bond	Characteristic IR frequency range ( $\text{cm}^{-1}$ )
alcohol	C-H stretching	3200-3600 (broad)
Carbonyl	C=O stretching	1650-1750 (strong)
aldehyde	C-H stretching	~2800 and ~2700 (medium)
Carboxylic acid	C=O stretching O-H	1700-1725 (strong) 2500-3300 (broad)
alkene	C=C stretching vinyl C-H stretching	1620-1680 (weak) 3000-3080
Benzene	C=C stretching	~1600 & 1500 1430 (strong to weak)

Alkane	C-H stretching	2100-2950 cm <sup>-1</sup>
	terminal C-H	2850-2950
alkane	C-H stretching	2850-2950
amine	N-H stretching	3300-3500 cm <sup>-1</sup> (medium)

The scattering which occurs with a change in the frequency of the incident radiation is called Raman scattering. The phenomenon is called Raman effect.

$$\nu_i - \nu_s$$

If  $\nu$  is the frequency of the incident beam and  $\nu_s$  is given by the scattered light then the Raman frequency  $\nu_r$  is given by

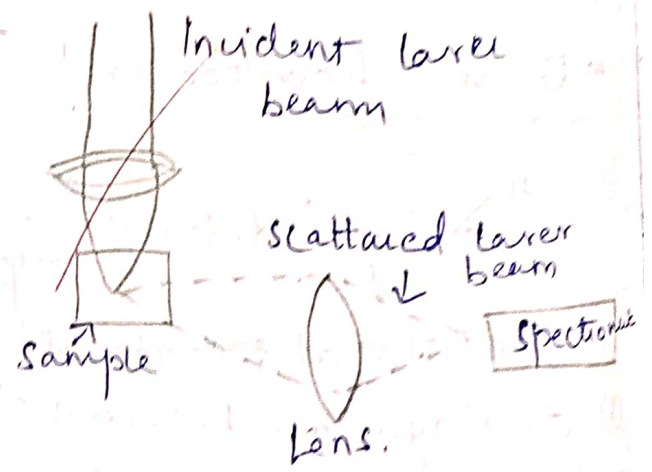
$$\nu_r = \nu_i - \nu_s \text{ or } \Delta E = h\nu_r$$

\* If a vibrational or rotational of molecule is to be active in Raman its polarizability must change during the vibration or rotation. This is the basic requirement or condition.

Raman Spectra:

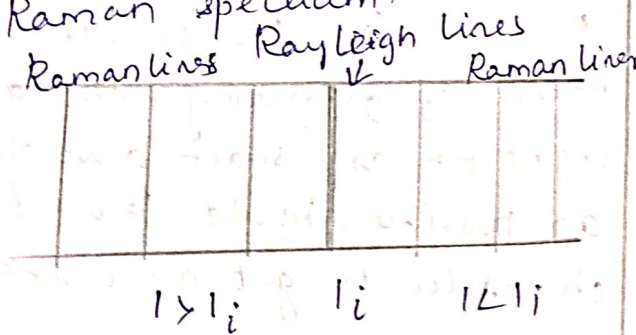
When an intense beam of light is passed through a liquid or gas, some of the light is scattered by the molecules of the medium. Most of the scattered light has the same frequency as the incident light. This type of scattering which occurs without a change in the incident frequency is termed Rayleigh scattering.

In 1928, Indian physicist Sir. C.V. Raman discovered that a very small fraction of the scattered light has frequencies higher or lower than the incident frequency.



The spectrum obtained from scattered radiations of sample can be observed with help of the apparatus in figure.

\* Laser beam is now used or light which gave weak spectral lines. The general pattern of spectrum recorded by scattered light is illustrated in figure. The sharp line in the middle corresponds to Rayleigh line Raman scattered light records a series of lines on either side of the Rayleigh lines. These are called Raman lines and constitute Raman spectrum.



Difference b/w Rayleigh & Raman scattering

Rayleigh scattering	Raman scattering
Elastic scattering ie the frequency of incident light and that of the scattered light are same	Inelastic scattering ie the frequency of the incident light and that of the scattered light are different

During the scattering the distance b/w the atoms in the molecules does not change

changes.

### Stokes and Anti-Stokes lines

The difference b/w the frequency of the incident light and the frequency of the scattered light is called the Raman frequency

$$\text{Thus is } \nu_R = \nu_i - \nu_s$$

The incident radiation may give up energy to the molecule on which it falls.

Then the frequency of the incident light will be more than that of the scattered light i.e.  $\nu_i > \nu_s$ . Then the Raman frequency.

$\nu_R$  is given by

$$\nu_e = \nu_i - \nu_s = \text{positive}$$

we get lines on the lower frequency side of the incident light

These are called Stokes lines.

On other hand. The incident light can also take up energy from the

molecule. Then the frequency of the incident light will be less than that of the scattered light

i.e.  $\nu_i < \nu_s$  then

$$\nu_R = \nu_i - \nu_s = \text{Negative}$$

We get lines on the higher frequency side they are called anti-stokes lines.

These Stokes and anti-stokes lines are generally called Raman line.

The intensities of Raman lines are in the following decreasing order.

Stokes lines > incident radiations > anti-stokes lines.

This is because the Stokes lines result from the absorption of energy of the incident light by the molecule. In this case the molecular energy increases. Therefore Stokes lines are more intense than the incident light.

On other hand anti-stokes lines result the emission of energy to the incident light by the molecule. In this case

The molecular energy decrease. Therefore anti-stokes lines are less intense than incident light. Totally Stokes lines are much more intense than the anti-stokes lines.

property	Anti-stokes lines	Stokes Line
Sign of Raman frequency $\nu_R = \nu_i - \nu_s$	Negative	Positive
Intensity	less intensity	high Intensity

We see that the intensity of Raman line changes with the frequency of incident radiation and has been found to be proportional to the fourth power of frequency. Hence a light of as short a wavelength as possible should be used in order to get as intense a Raman line as possible.

### Comparison of Raman Spectra and IR Spectra

Raman spectra	Infrared spectra
* It is due to the scattering of light by the vibrating molecules.	* It is the result of absorption of light by vibrating molecules.



* polarizability of the molecule will decide whether the Raman spectra will be observed or not	* The presence of permanent dipole moment in a molecule may be regarded as a criterion of IR spectra	* Substances under investigation must be pure and colourless	* This condition is not rigid.
* It can be recorded only in one exposure	* It required separate runs with different prisms to cover the whole region of IR.	* In Raman effect vibrational frequencies of large molecules can be measured	* In this the vibrational frequencies of very large molecules cannot be measured.
* The method is very accurate but is not very sensitive	* This method is accurate and very sensitive	* As Raman lines are weak in intensity concentrated solution must be utilised to increase the intensity of Raman lines	* Generally dilute solution are preferred. Homonuclear diatomic molecules are not found to be active.
* Water can be used as a solvent	* Water cannot be used as a solvent because it is opaque to IR radiation	* Molecular diatomic molecules are often found to be active.	

* Optical system are made of glass or quartz	* Optical system are made of special crystals as $CaF_2$ , $NaBr$ etc.
* Some times photochemical reaction takes place in the regions of Raman lines and thus create different	* photochemical reaction do not takes place.

### Applications of Raman spectra

#### Structural diagnosis

- 1- Molecular structure:
  - a) Raman spectra have been widely used in deciding the constitution of organic compounds since Raman frequencies for single, double and triple bonds are available. Here there can be easily located.
  - b) Similar linear structure and non-linear structures can be identified.

2. Using Raman spectra we can study the strength and nature of force which are present in the crystal.
3. Centres of vibrational bands which do not appear in infra red spectra are produced a Raman spectra. Thus force constants and moments of inertia can be calculated from Raman spectra.

4. In inorganic chemistry we can determine the chemical constitution and the nature of the valence bonds. Isomers show different Raman lines. It is used in the study of complex compound, mixed molecules and water of crystallisation.

5. In organic chemistry aliphatic and aromatic compounds have different Raman spectra. Structure of organic compounds and isomerism can be studied with Raman spectra.

6. In physical chemistry amorphous state and crystalline states, electrolytic dissociation, hydrolysis etc, may be studied.