



## Shree H.N.Shukla College of Science Rajkot

B.Sc. (Sem- 5) (CBCS)

CHEMISTRY: [502]

### Unit-5 IR Spectroscopy

- **Spectroscopy** is branch of chemistry that deal with **EMR** interaction with **matter** interaction.
- When an EMR radiation irradiated on sample to some portion of **IR radiation** absorbed, change of **vibrational level** of molecule to transmitted light detect detector plot the spectrum Absorbance versus wave number or frequency.

#### Learning Objective

- Know spectroscopic basic tool and its application.
- Identify functional group present in organic compounds.
- Hooks law used in vibration of chemical bond.
- Know different type of band in IR spectroscopy
- Know dispersive & FT-IR instruments
- Different factor affect on IR spectrum.

#### Introduction

- Infrared spectroscopy(IR) is an important tool for organic chemist. It is one of the widely used tools for the detection of functional group in pure compounds as well as in mixture for the composition purpose Infrared refers to that part of the electromagnetic spectrum between the visible and microwave region. In a molecule, atoms, ions by covalent bonds are not fixed at one position but continuously vibration with each other. The energy associated with this motion corresponds to frequencies in the region of infrared wave which stretches from  $4000-400\text{ cm}^{-1}$

#### Range of infrared

- Range of infrared Infrared rays lies between ultra-violet visible and microwave radiation in electromagnetic radiation.



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→ Infrared radiation further divided into three different parts

Near IR 0.8 $\mu\text{m}$	Mid IR 2.5 $\mu\text{m}$	Far IR 15 $\mu\text{m}$	200 $\mu\text{m}$ $\lambda$
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→ The energy possess of near IR radiation 10 to 37 K.Cal/mole energy while middle IR and far IR radiation possesses 1 to 10 K.Cal/mole and 0.1 to 1 K.Cal /mole.

→ Middle Infrared region from 4000-400  $\text{cm}^{-1}$  region is more useful for organic chemist.

#### Theory of IR spectroscopy

- The molecule absorb the radiation in the range of infrared and organic molecule converted it into vibrational and rotational spectrum is obtained.
- For the study of vibrational spectroscopy being with a diatomic molecule as the model vibrator as a harmonic oscillator.
- The diatomic molecule (two atoms joint with each other by covalent bond) obey Hook's law Vibration are **to** and **fro** motion of atoms connected by a bond in molecule as well as its gravity centre.
- The elongation and compression of bond alternately resulting in the displacement of atom from their equilibrium position. Let the displacement be 'a' an external force 'F' is required for the displacement. A restoring force 'f' arises in the bond in opposite direction of the displacement, for the equilibrium position
- According to classical harmonic motion, the displacement of atom is directly proportional to the applied force.

$$F = -f \quad \dots\dots (1)$$

$$F \propto a \quad \dots\dots (2)$$

$$F = -ka \quad \dots\dots (3)$$



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→ 'k' is proportionality constant which measures the stiffness at bond, hence also known as force constant for the relevant bond.

#### Short Questions & Answer

Sr.No.	Questions	Answer
1.	What is full form of EMR?	Electromagnetic Radiation
2.	What is range of middle IR?	2.5-15 $\mu\text{m}$
3.	Which law IR spectra observed?	Hook's law
4.	IR region between _____ and _____	Visible & microwave

#### Hook's Law

- It is discovered by the English scientist Robert Hooke in 1660.
- It states that **for relatively small deformations of an object, the displacement or size of the deformation is directly proportional to the deforming force.**
- $V = \frac{1}{2} \pi \sqrt{k/\mu}$
- **Where k = force constant**
- For C-C  $5 \times 10^5$  dyne/cm
- C=C  $10 \times 10^5$  dyne/cm
- C=C(triple)  $15 \times 10^5$  dyne/cm

#### Fundamental mode of vibration in IR

- A molecule has as many degrees of freedom as the total degree of freedom of its total degree of freedom of its individual atoms.
- Each atom has 3 degree of freedom corresponding to be Cartesian coordinates(x, y, z) necessary to explain their relative position A molecule possesses **n** atoms therefore has **3n** degree of freedom.



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- For nuclear molecules, three degrees of freedom for rotation and three degree of freedom for translation (vibration) to avoid duplication for non-linear molecule, while linear molecule, only two degree of freedom are two;
- For Linear molecule
  - ✓ Degree of freedom =  $3n-5$
- For Non-linear molecule
  - ✓ Degree of freedom =  $3n-6$ .

There are two types of molecular vibrations:

(1) **Stretching**

(2) **Bending**

#### [1] **Stretching Vibration**

- A stretching vibration is movement of atoms along the bond axis such that inter atomic distance is increasing or decreasing According to the direction of stretching, it can be further divided into two parts:

##### (a) **Symmetrical stretching**

- In diatomic molecules both atoms of bond are coming near to central point (gravity centre) at the same time and goes far from the centre point at the same time is known as Symmetrical stretching vibration. These vibrations are generally IR inactive, because it does not bring change in dipole moment.

##### (b) **Asymmetrical stretching**

- In diatomic molecules out of the two atoms, when one atom comes near to central point while other goes away from the central point is known as "Asymmetrical stretching" vibration.
- These vibrations required higher energy as compare to symmetrical stretching vibration; and absorption occurs at higher frequency



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### [2] Bending vibration

- A bending vibration is correlated to change in bond angles between bonds with a common atom or the movement of group of atoms with respect to one another
- According to presence of atom in plane; bending vibration divided in to two groups.

#### (a) In plane bending

- During vibration, the position of atom changes in the same plane, then it is known as in plane bending vibration. On the basis of motion of atoms, it can be further classified into two groups:

##### (1) Scissoring

If atoms of the molecule come near to each other or far from each other without change in bond length as well as plane then it is known as scissoring vibration.

##### (2) Rocking

Whole molecules can vibrate just like rock, i.e. structural units swing back and forth within the plane.

#### (b) Out of plane bending

During the vibration the atom change their plane is known as out of plane bending vibration i.e. the atoms swing up & down of the plane of the paper. According to the motion of the atom, further further it can be divided in two classes.

##### (1) Wagging

The atoms associated with bond come forth and back in the plane is known as wagging deformation.



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### (2) Twisting

The atom associated with bond play like twisting of rope i.e. atom come forth and back alternate in opposite direction is known as twisting formation.

### Short Questions & Answer

Sr.No.	Questions	Answer
1.	What is 'k' in Hook's law?	Force constant
2.	Fundamental vibration for linear molecule	$3N-5$
3.	For linear molecule rotational modes are ____	two
4.	Give name of stretching vibration.	Asymmetric & symmetric
5.	What do you mean by '3N' in fundamental equation?	Degree of freedom

### Selection rules in IR spectroscopy

→ When subject irradiated with infrared rays, it is necessary to know that whether the interaction is allowed or forbidden. An extended use of Schrödinger wave equation gives rise to quantum selection rule as  $\Delta v = \pm 1$ . The equation of selection rule-1 obey to restrict transition if  $\Delta v = +1$  it represents absorption while  $\Delta v = -1$  emission of radiation by the molecule.

→ From the selection rule-1 it is clear that each allowed transition given rise to the same spectral frequency is vibrational level are equally different from each other. The second selection rule is based on the physical nature of the molecules. During vibration if dipole moment of molecule is change i.e. electrical vector of EMR interact with dipole moment vector of molecule resulting in resonance. molecule absorb the IR-radiation.



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### Types of IR band

#### [1] Fundamental band

Transition from the ground state (V-0) to the first excited state (V1) absorb light strongly and give rise to intense bands called the Fundamental bands.

#### [2] Vibration Coupling

We expect one stretching absorption frequency for isolated C-H bond.

- But in the case of the methylene (-CH<sub>2</sub>-) group, two absorptions occur, which correspond to symmetric and asymmetric vibrations.
- In this case asymmetric vibrations always occur at higher wave numbers compared with the symmetric vibration.
- These are called coupled vibrations, these vibrations occur at different frequencies than that required for an isolated C-H frequency.
- Acid anhydrides have two C=O stretching bands between 1850-1800 cm<sup>-1</sup> and 1790-1745 cm<sup>-1</sup>, explained by symmetric and asymmetric stretching.

#### [3] Combination band

- The combination band arises from the anharmonicity of vibrations which lead to an interaction of two fundamental bands in polyatomic molecules. Its intensity is weak compared to **fundamental** and **overtone**.



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### [4] Difference band

→ It is a negative combination of two fundamental bands and its intensity is also weak compare to fundamental band so it is negligible.

### [5] Overtone

→ If the vibration of molecule is completely harmonic then only fundamental band occurs. But in real molecule, it is not possible so due to unharmonic vibration overtone occur the fundamental vibrations corresponds to transition from the vibration level zero ( $v=0$ ) to the first ( $v=1$ )

→ The term overtones is used to apply to a multiple of fundamental vibration. The transition  $v_0$  to  $v_2$  and  $v_0$  to  $v_3$  the **first** and **second** overtones.

→ First and second overtones required radiation **twice** and **three** times than fundamental frequency.

→ **Example** Fundamental frequency of CO is appeared at  $1700\text{ cm}^{-1}$  then first overtone of CO group appeared at  $3400\text{ cm}^{-1}$

### Fermi Resonance

This phenomenon was first observed by **Enrico Fermi** in the case of carbon dioxide  $\text{CO}_2$ .

$\text{CO}_2$  is linear molecule and four fundamental vibrations are expected Symmetric stretching vibrations are IR inactive because of no change in dipole moment. For symmetrical stretching Raman spectrum shows as strong band at  $1337\text{ cm}^{-1}$

Frequency of banding vibration is  $667.3\text{ cm}^{-1}$ , and overtones of this is  $1334.6$





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$\text{cm}^{-1}$  ( $2 \times 607.3$ ), which is very close to  $1337 \text{ cm}^{-1}$

The mutual perturbation of  $1397 \text{ cm}^{-1}$  (fundamental) and  $1334.6 \text{ cm}^{-1}$  (overtone) gives rise to two bands at  $1285.5 \text{ cm}^{-1}$  and  $1388.5 \text{ cm}^{-1}$  having intensity ratio of **1:09**

Interaction coupling can also occur between fundamental vibration and overtone or combination band vibration. During these type of coupling energy sharing take place between overtone and fundamental or combinational tone, is known as **Fermi-resonance**. As a result of this interaction intensity of overtone is increasing while intensity of fundamental band is decreasing.

Fermi resonance is also appeared in aldehyde molecule C-H bending vibration is appeared at  $1890 \text{ cm}^{-1}$  and its first overtone occur at  $2750 \text{ cm}^{-1}$  while C-H stretching seen absorption at  $2872 \text{ cm}^{-1}$ . So coupling take place between fundamental band and overtone, asymmetrical double is observed at  $2830$  &  $2695 \text{ cm}^{-1}$  i overtone extent their intensity while fundamental loses their intensity

### Finger print region

The region from the right  $4000\text{-}1600 \text{ cm}^{-1}$  to the left has great impact for the study of fundamental group. The absorption occurs in that region is due to stretching vibrations.

The region to the right of  $1600 \text{ cm}^{-1}$  to  $600 \text{ cm}^{-1}$  to the left is usually complex due to the both stretching and bending modes give rise to absorption here. However, each organic compound has its own identical absorption in this region. This region of infrared therefore known as '**finger-print region**'. Although the region of higher frequency may appear the same for similar molecule but the pattern display in finger print region seen a complete super impossibility of infrared spectra.

It is necessary to mention here that aromatic compound often display numerous



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hands in finger print region as compared to their aliphatic parts.

The patterns of finger print region are identical and sensitive even minor chemical difference or stereo chemical changes. The finger print region is an unique for comparison purpose.

#### Short Questions & Answer

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1.	IR transition depend on ___	Selection rule
2.	What is allowed Transition?	Obeys selection rule
3.	Which first molecule in Fermi resonance?	CO <sub>2</sub> molecule
4.	What is overtone?	Multiple of fundamental band
5.	What is region of finger print?	1600-600 cm <sup>-1</sup>

#### Instrumentation of IR spectrometer

[1] **The conventional IR spectrophotometer:** The important components of conventional under :

- Source of radiation
- Monochromator
- Sample handling
- Detector
- Recorder

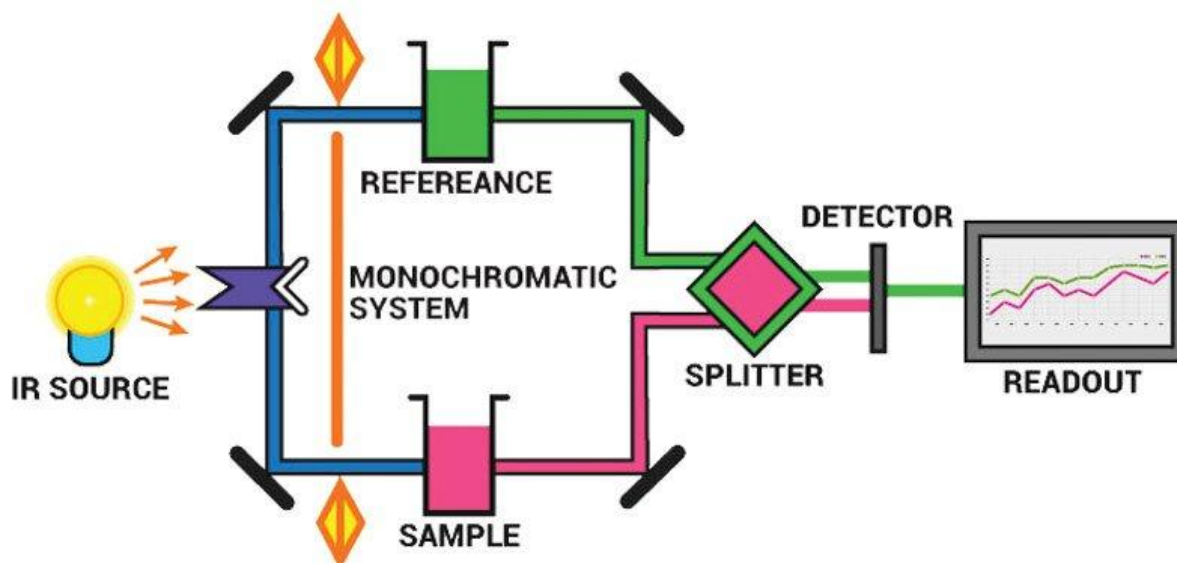


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#### (a) Source of Radiation

IR radiation is produced by electrical heating of Nernst Filament or Globar at 1000-1800 °C. The Nernst filament is made up from Zirconium Thorium and Cerium oxide. While Globar is a small rod of silicon carbide.

#### (b) Monochromator

It will disperse or resolve poly-chromatic light into mono chromatic light.

It consist of following parts

1) **Entrance slit** : It will sharply define the incoming beam of radiation.

2) **Disperse device**: It will disperse the radiation, When sharp beam of light is allowed to pass through filter.

3) **Prism or grating**: Type disperse device are employed in infrared work. Generally priam made of alkyl halide is favoured because of their whole range IR inastive and simplicity Priam made up from potassium bromide oftenly used in IR spectrophotometer

Grating device contains series of number of parallel equal distance lines drown on a plane surface. Approximately 10,000 to 15,000 line/inch is drown on highly polished surface of



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glass. Each groove acts as a scattering centre.

#### (c) Sample handling system

The method used for sample preparation depends upon the nature of sample.

#### 1. Gaseous Sample:

The scanning of gases or low boiling liquids by expansion of the sample into an evacuated cell. Gas cells are available in length of few centimetres to 40 meter in coil form.

#### 2. Liquid sample:

Liquid may be scanned between two salt plates without spacer. Pressing liquid sample between flat plates produces a film of 0.01mm or less in thickness.

#### 3. Solid sample:

Solid samples are usually examined by using mull technique, thin pressed disc or powder method.

Mulls are prepared by thoroughly grinding 2-5 mg of solid with Nujole. The mixture is examined between two salt plates.

In thin film method make a solution of sample in volatile solvent and press between two salt plates then after heat it to remove solvent and make a thin film on salt plates

In press disc method. Grind 1 mg sample with 99 mg KBr and make it fine powder then insert into "die" and press for 5 to 10 min. with 1000-1500 psi. So powder converts into transparent disc which can be examined.

#### (d) Detector

Gratings rotate slowly and send individual frequencies from monochromator to detector and it converts an infra red energy into electric energy.

#### (e) Amplifier and Recorder

Amplifier amplifies the signal and recorder records the plot of wavelength versus absorption,



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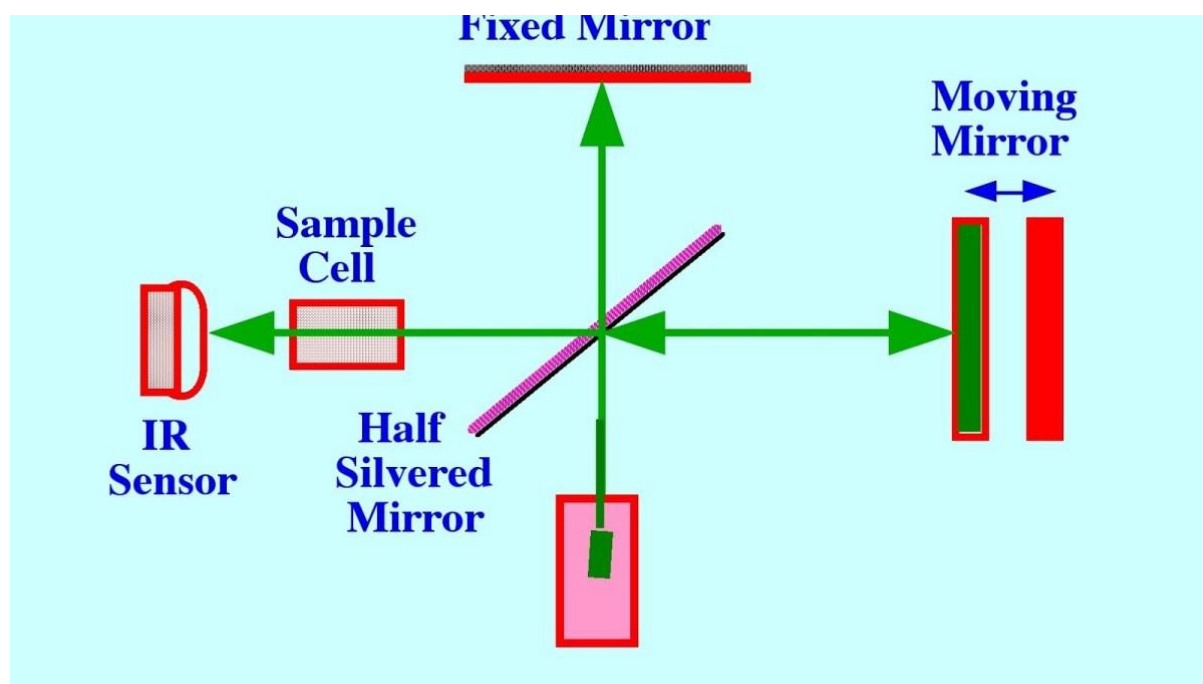
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#### [2] Fourier Transform Infrared spectrometer(FT-IR)

A beam containing the entire infrared wavelength passes through a sample at once in FT-IR. The result getting after absorption also passes all wavelengths in one beam. The information contain in resulting beam is converted into frequency dominated spectra by a microprocessor.

The FT-IR uses an interferometer causes two beam of IR radiation to interfere with one another, out of this two beam, one is variable. After reflection to their relative mirrors back to the beam splitter and recombine.



#### Advantages

Speed and sensitivity is better due to the scanning of all frequency at ones. It require less time as compare to dispersive method. Resolution and accuracy are also improved.

#### Factor affecting on IR spectrum

The variation in absorption frequency is depends on the following factors:

#### [1] Bond strength:

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We know Hook's Law, force constant ( $k$ ) increases as wave number also increasing.

#### **[2] Atomic weight:**

As per hook's law, mass of the molecule is inversely proportional to the frequency  
Therefore wave-number is decrease with increasing in atomic mass.

#### **[3] Inductive effect (I):**

Electron donating effect of any functional group produce +ve induction which increase the electron density on "C" atom and make bond weaker as a result force constant is decrease and also decrease the frequency of absorption.

If electron withdrawing effect of any group produces -Ve induction which decrease the electron density on "C" therefore bond is more polar which increase the absorption frequency.

#### **[4] Hydrogen bonding**

Due to the formation of hydrogen bond the electron density on oxygen is decrease which makes O-H band less polar as a result frequency is decrease.

#### **[5] Ring sizes**

By increasing the ring size, decrease the ring strain which make the ring the

$>C=O$  bond less polar due to the delocalization of electron, so frequency also decreases.

#### **[6] Resonance:**

If  $>C-O$  group is in conjugation of  $>C=C<$  group: make it resonance as result stability is increase and force strength decrease . Therefore IR absorption shift towards lower frequency.

#### **[7] % S character:**

% S character increases as wave frequency also increasing.



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#### Short Questions & Answer

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1.	Which source used in IR instrument?	Globar
2.	KBr pellet method used for _____ sample	Solid
3.	Which instrument more prefer IR over FT-IR?	FT-IR
4.	Nernst glover is _____	Oxide of lanthanides
5.	Which factor is affect on IR ?	Reduced mass & force constant

#### Learning outcome

- We able to predict which functional present in organic compounds.
- We understand basic principle and instrument of IR spectrometer.
- Able to determine fundamental vibration mode and know about overtone, combination band, difference band.
- We able to determine structure of compounds.
- We able to conformational analysis of molecule.



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