



“बेटी बचाओ, बेटी पढ़ाओ”

**JAYOTI VIDYAPEETH WOMEN'S UNIVERSITY, JAIPUR**  
**FACULTY OF PHARMACEUTICAL SCIENCE**

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**Course** : B. Pharm (5<sup>th</sup> sem)  
**Session** : Instrumental method of analysis –  
(IR Spectroscopy)

**Academic Day starts with–**

- Greeting with saying ‘Namaste’ by joining Hands together following by 2-3 Minutes Happy session, Celebrating birthday of any student of respective class and National Anthem

**IR Spectroscopy**

**IR Spectroscopy:**

Infrared spectroscopy is used in identification of functional groups in pure compounds.

- Infra-red (IR) does not have sufficient energy to induce electronic transition as seen in UV spectroscopy. When molecule absorbed electromagnetic radiation in IR region, undergoes vibrational or a rotational transitions which causes net change in the dipole moment in the molecule (IR active, for example HCl, CO etc), if dipole moment does not change in molecules then they are IR inactive (for example: O<sub>2</sub>, H<sub>2</sub>,

N<sub>2</sub> etc.) means they does not absorb IR radiation. IR region ranges from 4000-400 cm<sup>-1</sup>

- If the frequency of IR radiation matched with the vibrational frequency of molecule, then molecule absorb radiation.
- IR spectroscopy based on Hooke's law, suppose two atoms or masses are connected through spring (bond), then frequency of vibration can be represented by following equation

$$\nu = \frac{1}{2\pi} \sqrt{\kappa \mu} \text{ or}$$

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

Where,  $\kappa$  is force constant of the bond,

$\bar{\nu}$  is wave-number (cm<sup>-1</sup>),  $\nu$  is the frequency,

$c$  is speed of light and

$\mu$  is reduce mass ( $m_1$  and  $m_2$  are the masses of atoms)

$$\mu = \frac{m_1 \times m_2}{(m_1 + m_2)}$$

- Stronger the bond, greater the value of force constant ( $\kappa$ ), higher the frequency vibration or wave-number (cm<sup>-1</sup>).
- For example, C – C C = C C ≡ C
- force constant 5 x 10<sup>5</sup> 10 x 10<sup>5</sup> 15 x 10<sup>5</sup> ( dynes cm )
- wavenumber (cm<sup>-1</sup> ) 1200 1650 2100
- IR spectrum is divided mainly into two region as follows;

## FUNDAMENTAL VIBRATION

These vibrations are arising when molecule promoted from ground state to lower excited state. The fundamental vibrations for linear and non-linear molecules are determined by following way:

Molecule	Degree of freedom
Linear	$3n-5$
Non-linear	$3n-6$

The vibrations discuss below are fundamental vibrations.

a) **Stretching vibration:** Distance between two atom increase and decrease but bond angle remains constant. Types of stretching vibrations

i) **Symmetric stretching vibration:** In this case both the atoms stretched or compressed in same direction.

ii) **Asymmetric stretching vibration:** In this vibration one atom undergoes stretching and other atom undergoes compression and vice versa.

b) **Bending vibrations :** Distance between two atom remains constant but bond angle changes. These vibrations can occur either in plane or out of plane. Types of bending vibrations

1) **In plane bending vibrations:**

i) Scissoring: both the atom move towards each other just like scissor.

ii) Rocking: both the atoms move in same direction, either in left side or right side.

2) **Out of plane bending vibrations:**

i) Wagging : both the atom move up and down with respect to central atom.

ii) Twisting: one atom move up and other atom move down with respect to central atom.

## **OVERTONES AND COMBINATION BANDS**

When molecule absorbed electromagnetic radiation in IR region, and then molecule promoted from ground state to second, third or even fourth vibrational excited state. These bands are known as Overtones. The intensity of these bands is very weak. It is helpful in characterization of aromatic compounds.

When two fundamental vibrational frequencies ( $\nu_1 + \nu_2$ ) in a molecule couple to give rise to a new vibrational frequency within the molecule, it is known as combination band.

## **COUPLED VIBRATIONS**

The coupled vibrations are observed in group like  $-\text{CH}_2$ ,  $\text{NH}_2$  etc. In these groups same atoms are attached to the central atom. When  $-\text{CH}_2$  undergoes vibration by the absorption of IR radiation, due to internal perturbation, energy of one C-H bond is transfer to neighboring C-H bond which enhance its vibrational frequency. Therefore two stretching vibrational frequencies for  $-\text{CH}_2$  group is observed at  $2950\text{ cm}^{-1}$  (asymmetric stretching) and  $2860\text{ cm}^{-1}$  (symmetric stretching).

## **FERMI RESONANCE**

When fundamental vibration coupled with overtones or combination band, the coupled vibration is called Fermi resonance or when molecule absorb IR radiation then it transfers its energy or intensity from fundamental vibration to overtones, then Fermi resonance is observed. As we know that the intensity of overtones band is very weak as compare to fundamental vibrations. But, due to transfer of energy, the strong band is observed for overtones along with the fundamental frequency. Fermi resonance is generally observed in carbonyl groups. For example, in benzoyl chloride  $-\text{C}=\text{O}$  stretching vibration observed at  $1790\text{ cm}^{-1}$  and  $1745\text{ cm}^{-1}$ . The lower frequency band at  $1745\text{ cm}^{-1}$  is observed due to combination of overtones of CH bending vibration at  $875\text{ cm}^{-1}$  with the fundamental vibration of C=O stretching.

The region from 1500-600  $\text{cm}^{-1}$  in IR spectrum is known as Fingerprint region. In this region number of bending vibration is more than the number of stretching vibration.

Number of molecules contains same functional group & show similar peak above 1500  $\text{cm}^{-1}$  but they show different peak in finger print region. Therefore we can say that each and every molecule have unique peak or band which is observed in finger print region, it is just like the finger print of human.

Factor affecting vibrational frequency

**a) Conjugation:**

As the conjugation increase, stretching frequency decreases, because force constant decrease due to conjugation

**Inductive effect and resonance effect:**

Oxygen is more electronegative than nitrogen, therefore nitrogen easily donate electron or lone pair of nitrogen undergoes delocalization with C=O bond. Due to delocalization double bond of C=O changes into partial double bond therefore force constant decreases which decrease the C=O stretching frequency

**Hydrogen bonding:**

Intermolecular hydrogen bonding weakens the O-H bond, thereby shifting the band to lower frequency. For example, in neat solution O-H stretching vibration of phenol observed in the range from 3400-3300  $\text{cm}^{-1}$  . When solution is dilute then O-H frequency shifted towards higher frequency at 3600  $\text{cm}^{-1}$  .

Whereas in case of methyl salicylate, intramolecular hydrogen bonding lower down the stretching frequency of O-H at 3200  $\text{cm}^{-1}$  . Intramolecular hydrogen bonding does not change its frequency even in very dilute solution because upon dilution structure of compound does not change.

Ring strain: As the size of the ring decrease, vibrational frequency of C=O increase.

## **Application of IR Spectroscopy**

- a) Identification of different functional group.
- b) Distinction between intermolecular and intra-molecular hydrogen bonding.
- c) Identification of purity of the compound, if compound is impure then additional peaks are observed in the IR spectrum.
- d) Study of chemical reaction.

Identification of geometrical isomers (cis-trans).

## **FLAME PHOTOMETTTER**

Flame photometry (more accurately called Flame Atomic Emission Spectrometry) is a branch of spectroscopy in which the species examined in the spectrometer are in the form of atoms

A Flame Photometer is an instrument used in inorganic chemical analysis to determine the concentration of certain metal ions (mainly are sodium, potassium, calcium, lithium) Flame photometry is based on measurement of intensity of light emitted when a metal is introduced into the flame. –

### **Classification of Atomic Spectroscopic Methods:**

As mentioned earlier, in atomic spectroscopy, the elements present in a sample are converted to gaseous atoms or elementary ions in a process called atomisation. This process can be accomplished in a number of ways, using any of the following. 1 • Flame • Electrothermal (or furnace) method • Inductively coupled argon plasma • Direct current argon plasma • Electric arc Atomic Spectroscopic Methods-I: These methods accomplish the atomisation process in different temperature ranges. Once in the vapour phase, the atoms of the elements interact with radiation and provide information about themselves. You would recall from Unit 1 that the interaction of radiation and matter can manifest itself in terms of absorption, emission or fluorescence emission. Accordingly, we have atomic absorption, emission or fluorescence spectroscopies. Let us learn about the basic principle of these methods.

- **Next Topic-**
- Instrumental method of analysis – (Instrumentation)
- **Academic Day ends with-**  
National song 'Vande Mataram'