

LECTURE NOTES  
ON  
INFRARED SPECTROSCOPY  
**ENGINEERING CHEMISTRY**

B.Tech 1<sup>st</sup> year

By

**Dr. Ranvijay Pratap Singh**

**Assistant Professor**



**Faculty of Engineering & Technology**  
**University of Lucknow**

## INFRARED (IR) SPECTROSCOPY

OR

## VIBRATIONAL 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:

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

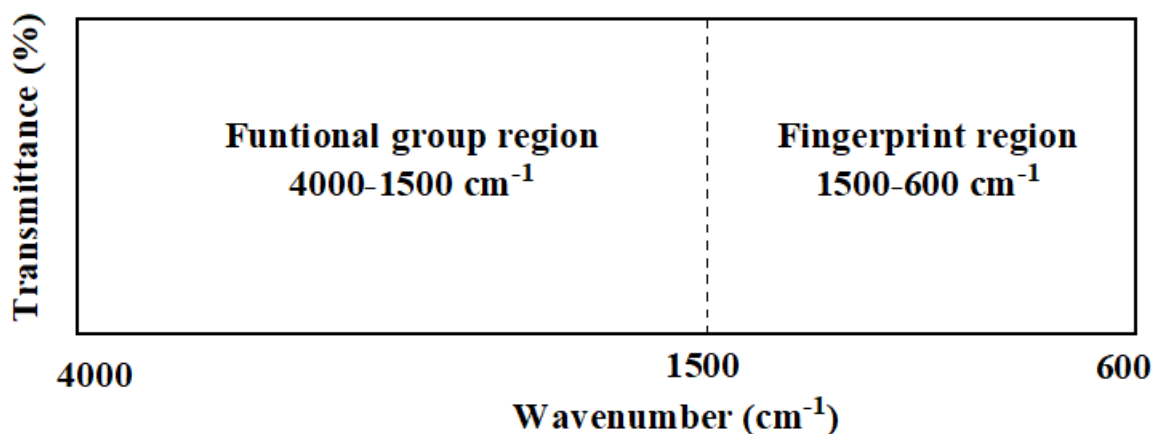
Where,  $\kappa$  is force constant of the bond,  $\bar{\nu}$  is wave-number (cm<sup>-1</sup>),  $\nu$  is the frequency,  $c$  is speed of light and  $\mu$  is reduce mass ( $m_1$  and  $m_2$  are the masses of atoms)

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

- 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> ( $\frac{\text{dynes}}{\text{cm}}$ )
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	$3n-6$

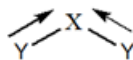
Where, 'n' is number of atom present in the molecule

The vibrations discuss below are fundamental vibrations.

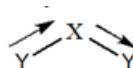
- a) Stretching vibration: Distance between two atom increase and decrease but bond angle remains constant.

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.

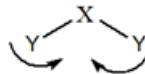


- b) Bending vibrations: Distance between two atom remains constant but bond angle changes. These vibrations can occur either in plane or out of plane.

## Types of bending vibrations

### 1) In plane bending vibrations:

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

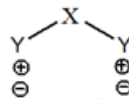


- ii) Rocking: both the atoms move in same direction, either in left side or right side.

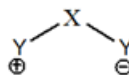


### 2) Out of plane bending vibrations:

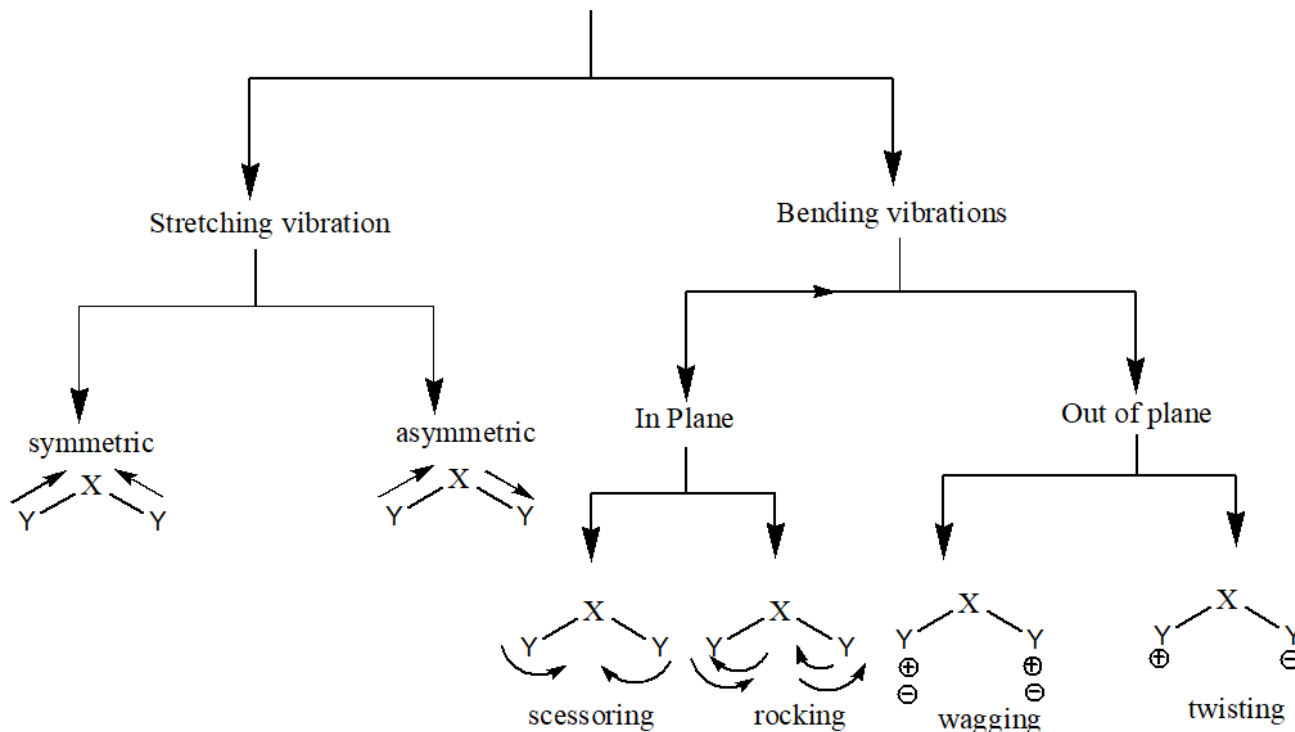
- i) Wagging: both the atom move up and down with respect to central atom.



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

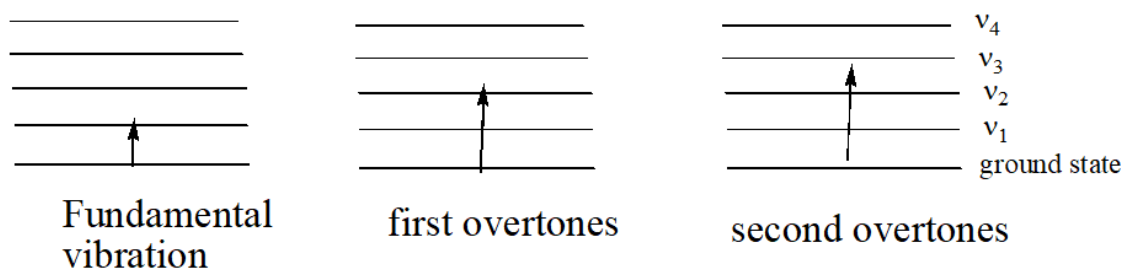


## Fundamental Vibrations in $XY_2$ molecule



## 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.

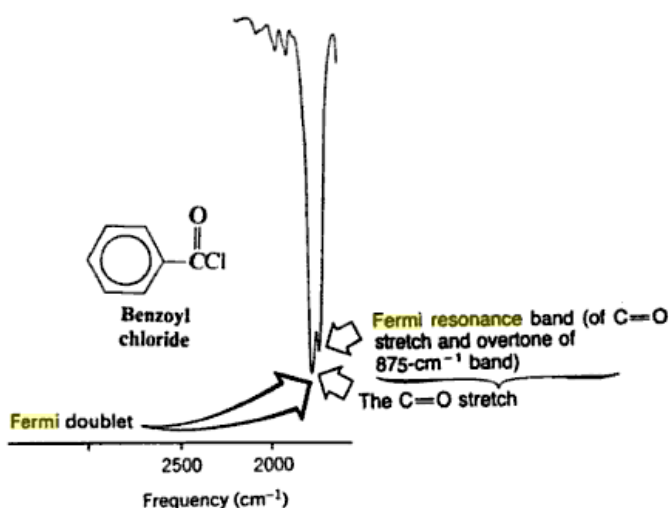
## COUPLED VIBRATIONS

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

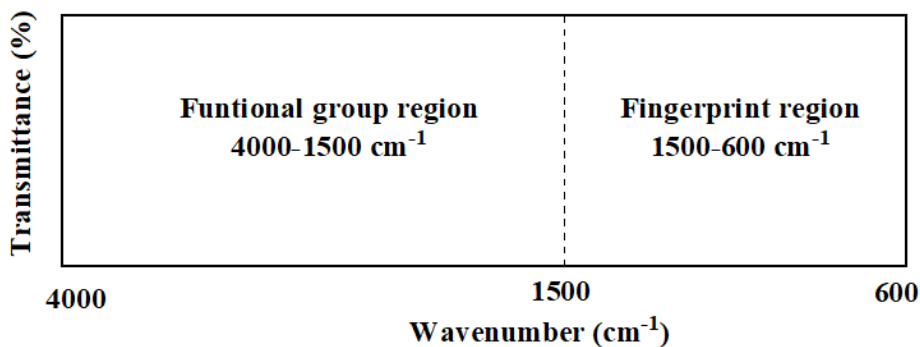
When fundamental vibration coupled with overtones or combination band, the coupled vibration is called Fermi resonance or when molecule absorb IR radiation then it transfers its energy or intensity from fundamental vibration to overtones, then Fermi resonance is observed. As we know that the intensity 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

overtone of CH bending vibration at  $875\text{ cm}^{-1}$  with the fundamental vibration of C=O stretching.



### FINGERPRINT REGION

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



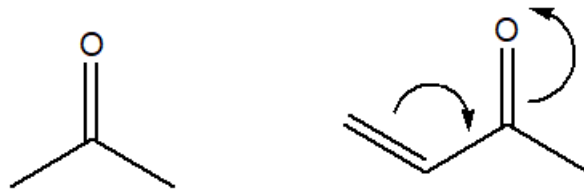
Number of molecules contains same functional group & show similar peak above  $1500\text{ cm}^{-1}$  but they show different peak in finger print region. Therefore we can say that each and every molecule have unique peak or band which is observed in finger print region, it is just like the finger print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

## IR correlation chart

Types of vibration		Frequency (cm <sup>-1</sup> )
Alkane	C-C stretching	1200
	C-H stretching	3000-2840
	-CH <sub>2</sub> bending	1465
	-CH <sub>3</sub> bending	1375
	CH <sub>2</sub> rocking	720
Alkenes	C=C stretching	1650
	=C-H stretching	3095-3010
	=C-H bending	1000-650
Alkynes	C≡C stretching	2100
	≡C-H stretching	3300
	≡C-H bending	700-600
Aromatic	C=C stretching	1600, 1500, 1450
	=C-H stretching	3040-3010
	=C-H bending	Below 900
C=O stretching	Amide	1680
	Carboxylic acid	1710
	Ketone	1715
	Aldehyde	1725
	Ester	1735
	Acid chloride	1800
	Anhydride	1760 (I), 1810 (II)
C-O	Stretching	1300-1000
O-H	Alcohol, phenol	
	Free	3600
	H-bonded	3400-3200
	Carboxylic acid	3400-2400
Amine	-N-H stretching	3440 (as), 3350 (s)
	-N-H bending	1650-1580
	C-N stretching	1350-1000
Amide	-N-H stretching	3370 (as), 3150 (s)
	-N-H bending	1650-1560
Nitriles	C≡N	2250
Imines	C=N	1690-1640
Nitro group (NO <sub>2</sub> )	N=O	1550 (as), 1350 (s)
Alkyl halide (C-X)	C-F	1350
	C-Cl	750
	C-Br, C-I	<660

## Factor affecting vibrational frequency

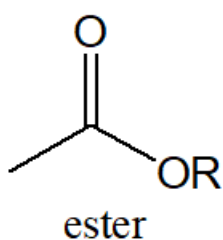
- a) Conjugation: As the conjugation increase, stretching frequency decreases, because force constant decrease due to conjugation.



$$\text{C}=\text{O} (\text{s}) = 1720 \text{ cm}^{-1} \quad \text{C}=\text{O} (\text{s}) = 1680 \text{ cm}^{-1}$$

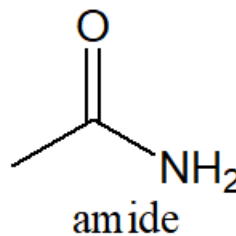
- b) Inductive effect and resonance effect:

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.



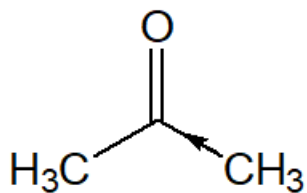
$$\text{C}=\text{O} (\text{s}) = 1735 \text{ cm}^{-1}$$

-I effect of -OR



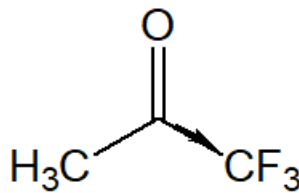
$$\text{C}=\text{O} (\text{s}) = 1690 \text{ cm}^{-1}$$

+R effect of -NH<sub>2</sub>



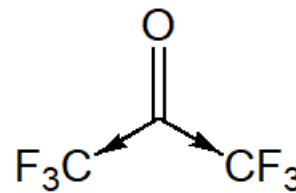
$$1720 \text{ cm}^{-1}$$

+I effect



$$1760 \text{ cm}^{-1}$$

-I effect



$$1790 \text{ cm}^{-1}$$

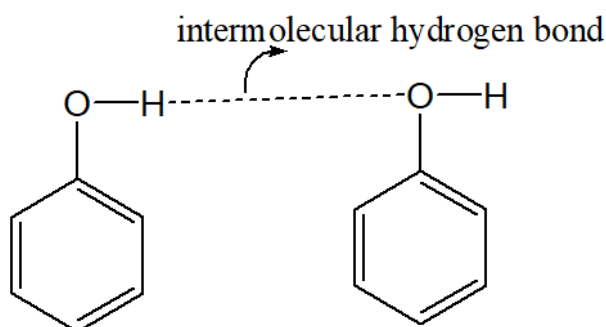
-I effect

- c) 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

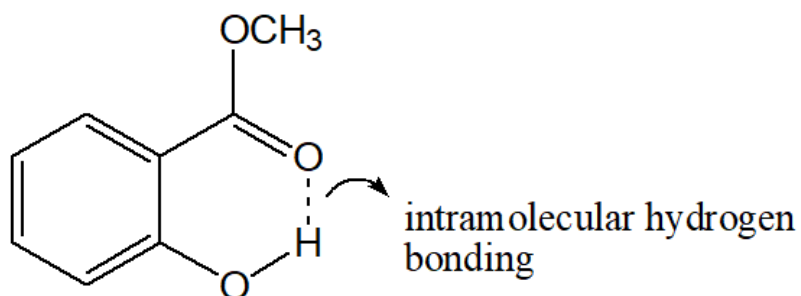


vibration of phenol observed in the range from  $3400\text{-}3300\text{ cm}^{-1}$ . When solution is dilute then O-H frequency shifted towards higher frequency at  $3600\text{ cm}^{-1}$ .



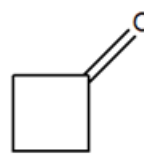
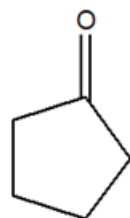
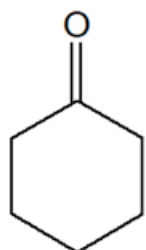
O-H frequency =  $3400\text{-}3300\text{ cm}^{-1}$

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.



O-H frequency centered at  $3200\text{ cm}^{-1}$

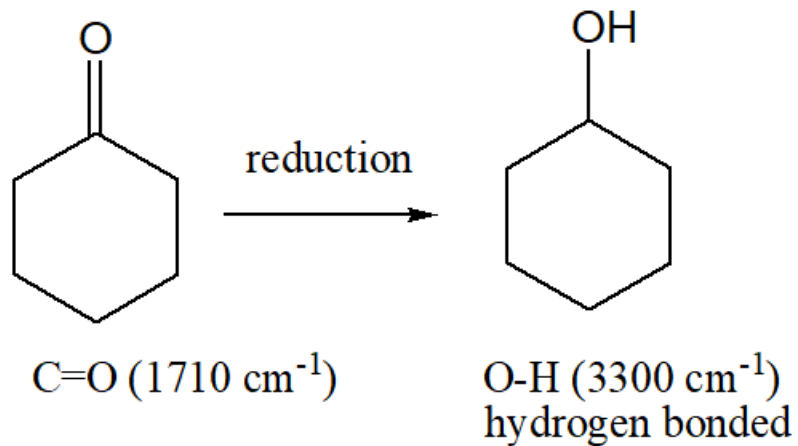
d) Ring strain: As the size of the ring decrease, vibrational frequency of C=O increase. For example.



### 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:



- e) Identification of geometrical isomers (*cis-trans*).