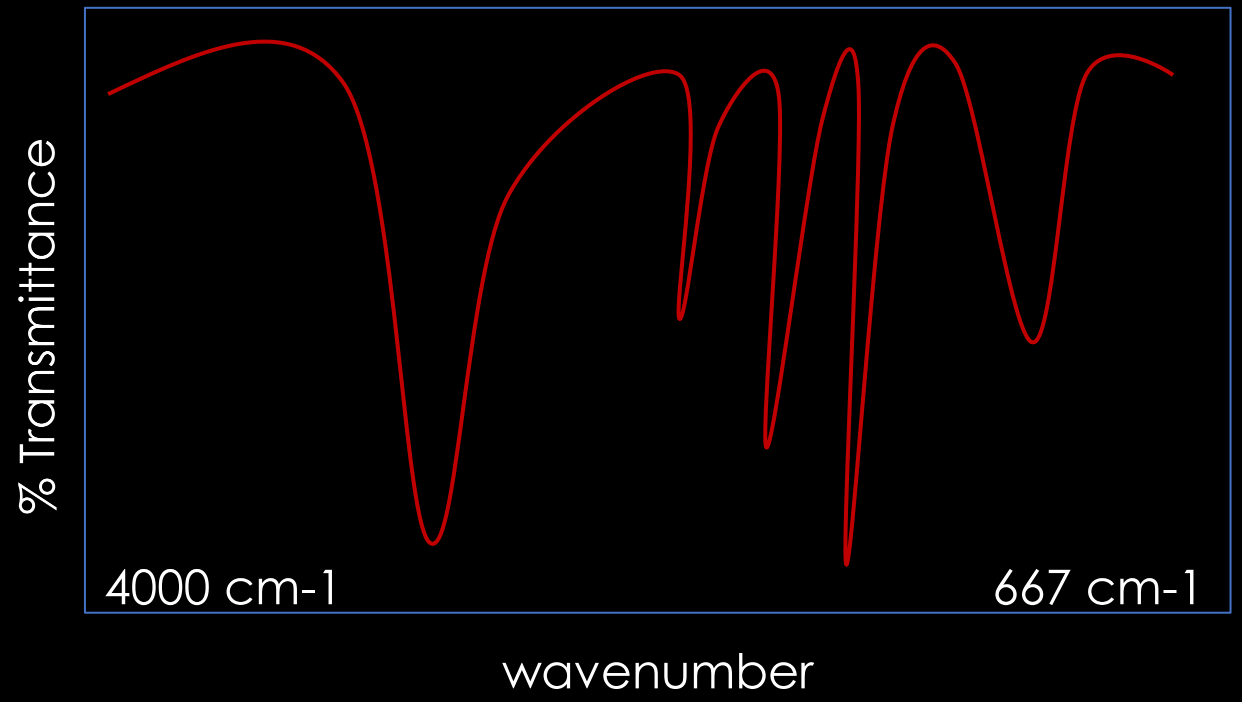
IR-Spectroscopy

(Part- 01)

- ✓ Basic Introduction
- ✓ Principle & Theory
- ✓ Fundamental Equations



Spectroscopy
Instrumental Analysis

IR-SPECTROSCOPY

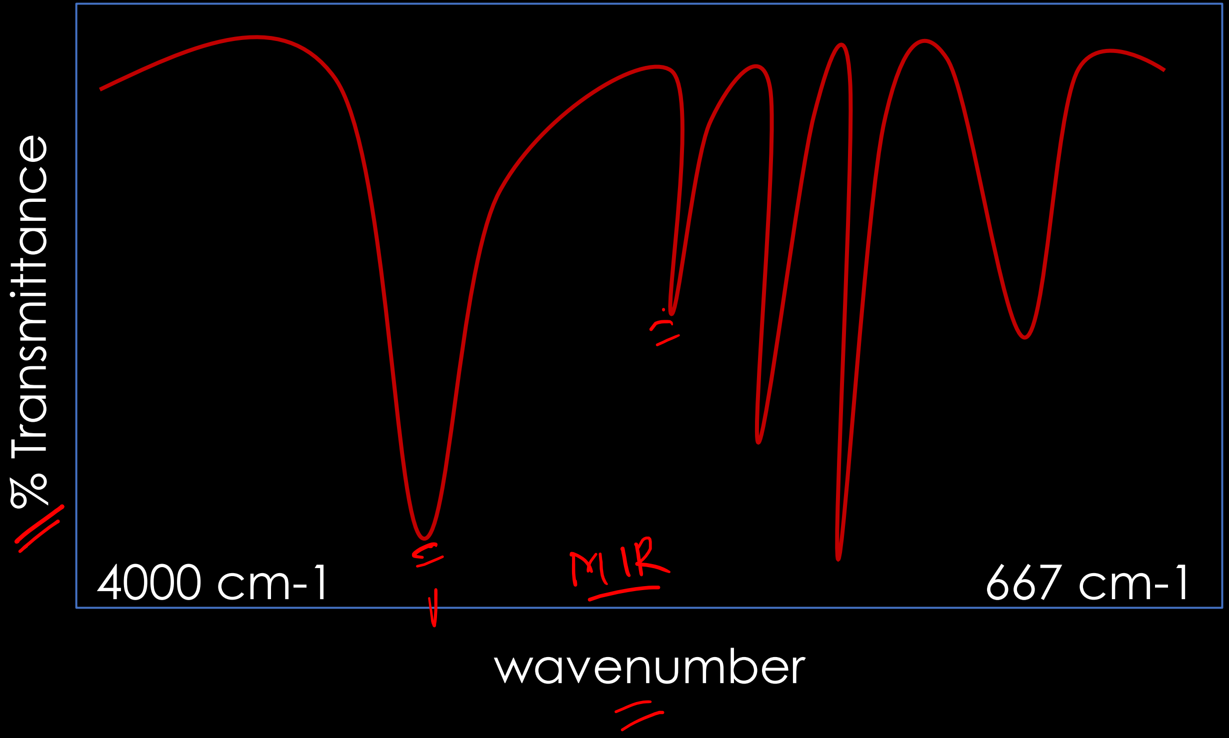
- InfraRed (IR) Spectroscopy is concern with the study of absorption of IR radiation.
- Absorption of IR can change in Vibrational energy, so also called Vibrational Spectroscopy
- It also change in Rotational energy
- The IR spectroscopy gives the significant information about functional group of the structure

#GPAT

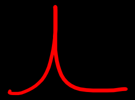
$\bar{\nu} = \frac{1}{\lambda}$

	In um λ	In cm-1 $\bar{\nu}$	
Infra Red	0.8-200 µm	12500-52 ✓	
Far IR	15-200 µm	667-50	Vibrational fundamental or rotational ✓
Mid IR	2.5 – 15 µm 25	4000-667	Vibrational fundamental
Near IR	0.8 – 2.5 µm	12500-4000	Vibrational (overtones)

IR-SPECTROSCOPY



$(A = \log_{10} \frac{1}{T})$



- Wave number (cm^{-1}) = 1/ wavelength in cm

$\bar{V} = \frac{1}{\lambda}$

cm^{-1} $\bar{V} = \frac{1}{\mu m \times 10^{-4}} = \frac{10000}{\lambda c}$

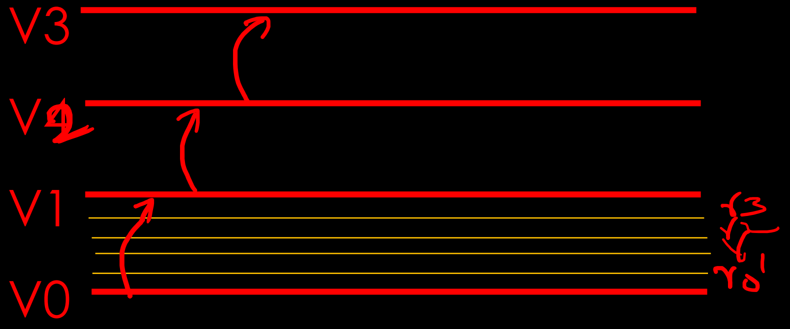
$V = \frac{\overset{4000}{\cancel{10000}}}{\cancel{2.5}} = 4000\ cm^{-1}$

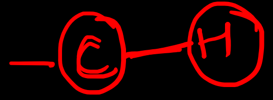
- $\Delta E = hv = hc/\lambda$

IR-SPECTROSCOPY

PRINCIPLE OF IR SPECTROSCOPY

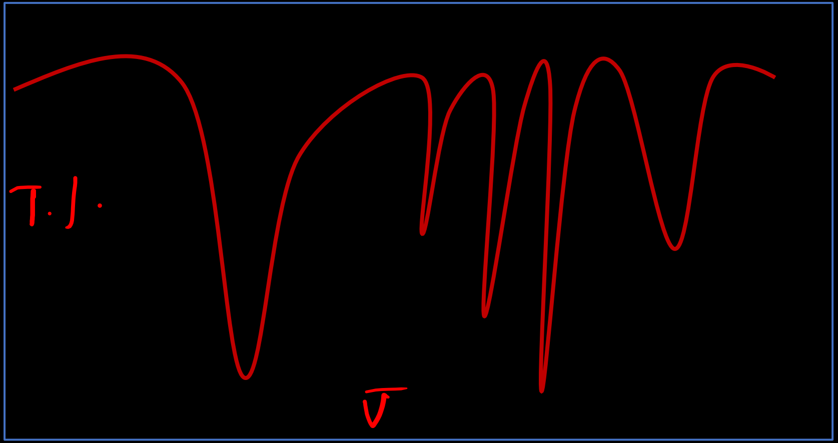
- Absorption of IR energy causes an excitation of molecules from lower to higher vibrational level, which is associated with a number of closely spaced rotational level.
- So IR spectra is considered as vibrational-rotational spectra
- The bonds in a molecule, which are accompanied by a changes in dipole moment will absorb in the IR region and such vibrational transitions is called IR active transition
- IR inactive – carbon- carbon bonds in symmetrical alkenes (C=C) and alkynes (C≡C)
- IR Active- C-H, C=O, C≡N, N-H, O-H, etc





IR-SPECTROSCOPY

PRINCIPLE OF IR SPECTROSCOPY



- The various bands seen in the IR Spectrum are due to characteristic functional groups and bonds present in a substance.
- Thus, IR Spectrum of a organic molecules is considered as a fingerprint and used for its identification
- ***No two compounds except enantiomers can have similar IR Spectra*
- Band position is expressed in wave number and Intensity is expressed in Transmittance

IR-SPECTROSCOPY

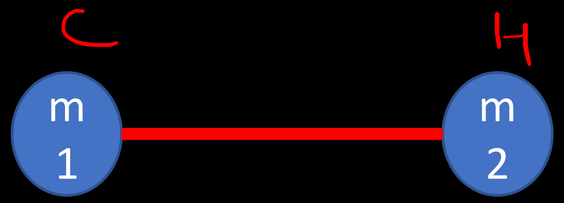
Theory and Fundamental of Molecular Vibration

$\lambda \downarrow \; E \; \bar{\nu} \; \nu \uparrow$

- Absorption of IR spectra is due to changes in vibrational and rotational level.
- $\bar{V}$ < 100 cm-1, Molecular rotational take place, a discrete line are formed in IR Spectra
- $\bar{V}$ = 10000 to 100 cm-1, Molecular vibration take place, a vibrational spectra appear as vibrational-rotational band in IR Spectra
- The vibrational energy is mainly depends on
  - Masses of atoms ✓
  - Strength of bond ✓
  - The arrangement of atoms ✓

$$\Delta E = h\nu = h\frac{c}{\lambda}$$

IR-SPECTROSCOPY



Theory and Fundamental of Molecular Vibration

- Hooke's Law can be applied to getting idea of vibrational energy/ Frequency

Vibrational frequency (υ) α $\sqrt{Bond\ strength/mass}$

$$\upsilon\ \alpha \sqrt{K/\left(\frac{m1m2}{m1+m2}\right)}$$

K- Force constant, single bond- $5x10^{5}$ gm sec $^{-2}$

m1, m2 – mass of atom (gm)

$$\boxed{\upsilon\ \alpha \sqrt{K/\mu}}$$

μ – reduce mass system

- $\boxed{\upsilon = 1/2\pi \sqrt{K/\mu}}$ ①
- $C/\lambda = \upsilon = 1/2\pi \sqrt{K/\mu}$

IR-SPECTROSCOPY

Theory and Fundamental of Molecular Vibration

Vibrational frequency (υ) α $\sqrt{Bond\ strength/mass}$

$$\upsilon\ \alpha \sqrt{K/\frac{m1m2}{m1+m2}}$$

C — H

$$\upsilon\ \alpha \sqrt{K/\mu}$$

$$\boxed{\upsilon = 1/2\pi \sqrt{K/\mu}} \text{ — ①}$$

$$\Delta E = h\upsilon \quad ✓$$

$$\bar{V} = \frac{1}{\lambda}$$

$$C/\lambda = \upsilon = 1/2\pi \sqrt{K/\mu}$$

$$C\bar{V} = \upsilon = 1/2\pi \sqrt{K/\mu}$$

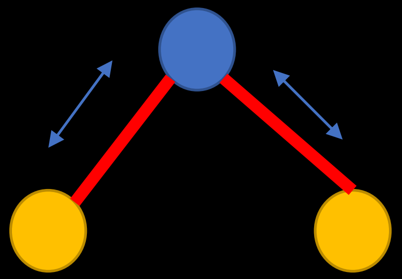
$$\boxed{\bar{V} = 1/2\pi c \sqrt{K/\mu}} \text{ — ②}$$

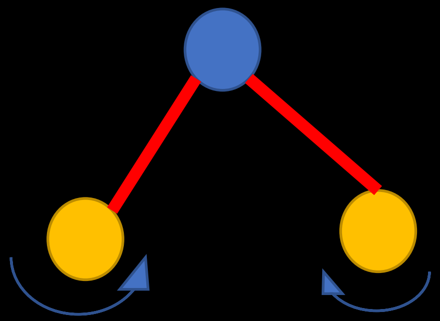
IR-SPECTROSCOPY

Theory and Fundamental of Molecular Vibration

- In the molecules, atoms or groups of atoms are connected by bonds
- These Bonds are similar as spring coil (not rigid in nature). They maintain some vibrations with some frequency, which is characteristics to every portion of the molecules. These is called "**Natural frequency of vibration**"
- If the applied IR frequency = Natural frequency of vibration; absorption of IR radiation take place and a peak is observed
- There are two type of Fundamental vibrations
  - Stretching
  - Bending
- Required energy; Stretching > Bending

$C-H$
$O-H$
$N-H$
$C=O$
$C\equiv N$


Stretching

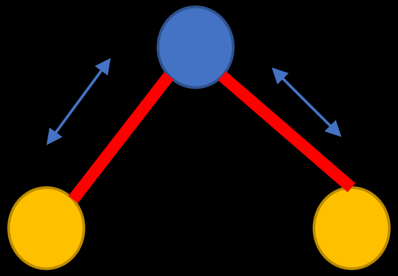

Bending

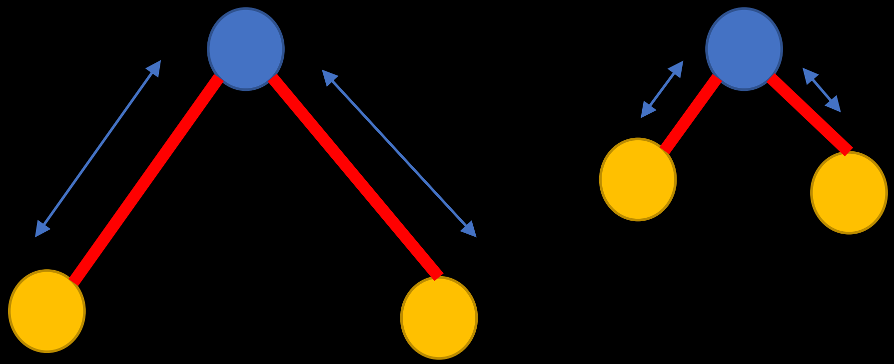
IR-SPECTROSCOPY

Theory and Fundamental of Molecular Vibration

A. Stretching

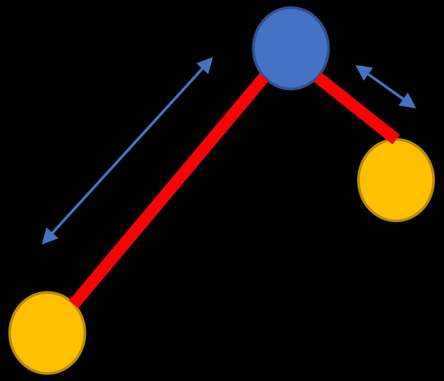
- The alteration (increase or decrease) in distance between two atom without changing in its bond axis.





1. Symmetrical Stretching

Stretching in same direction



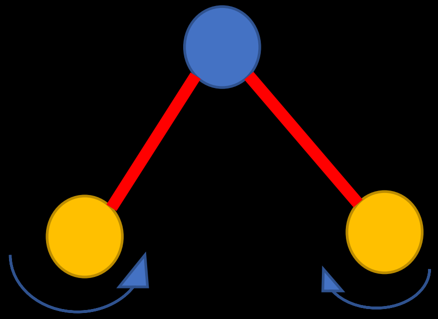
2. Asymmetrical Stretching

Stretching in opposite direction

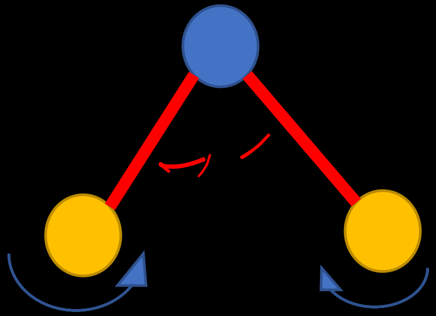
Theory and Fundamental of Molecular Vibration

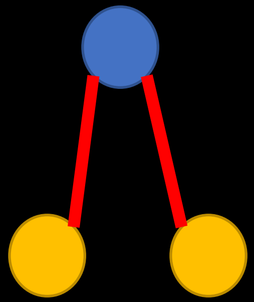
B. Bending

- The position of atom change with respect to the bond axis



In Plane





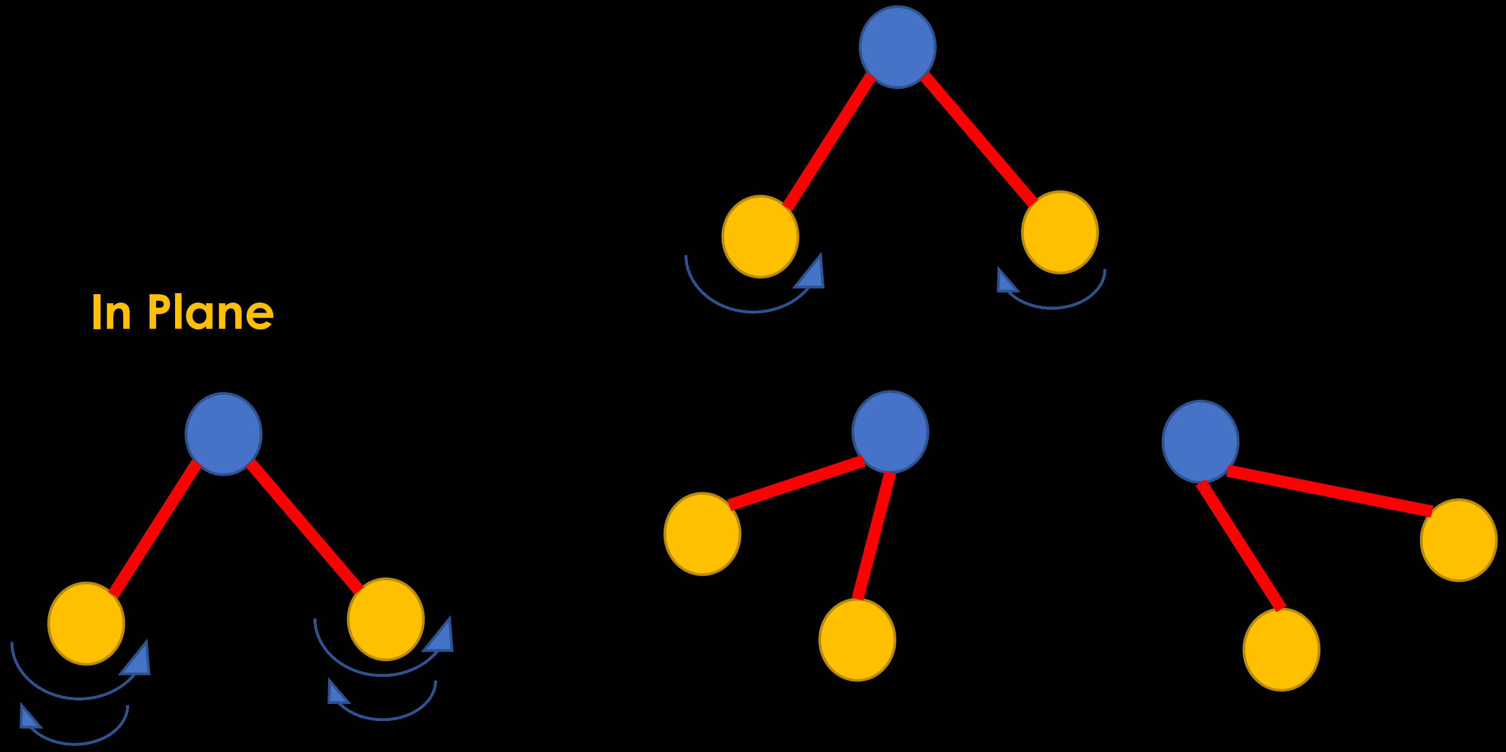
1. Scissoring

Two atom approach each other

Theory and Fundamental of Molecular Vibration

B. Bending

- The position of atom change with respect to the bond axis



2. Rocking

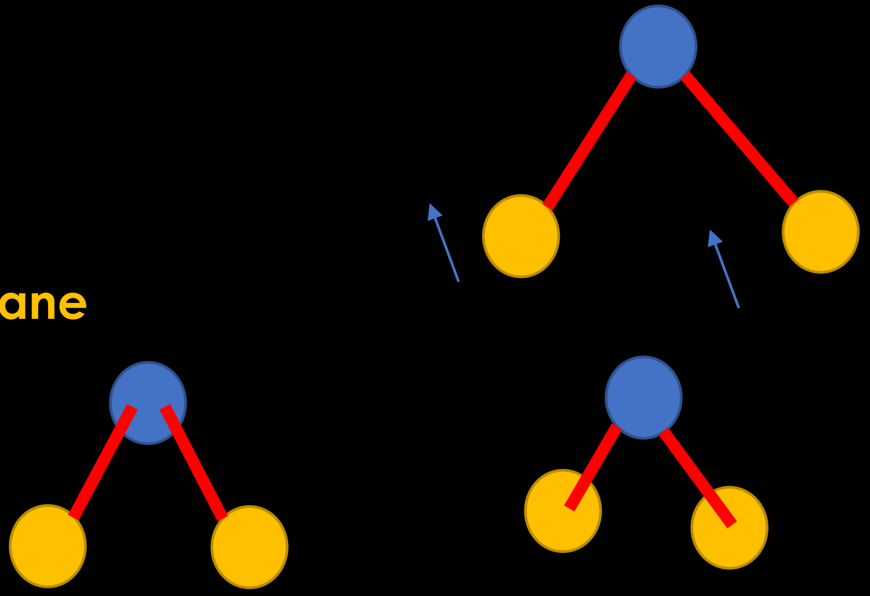
Movement of atom in same direction

Theory and Fundamental of Molecular Vibration

B. Bending

- The position of atom change with respect to the bond axis

Out Plane



3. Wagging

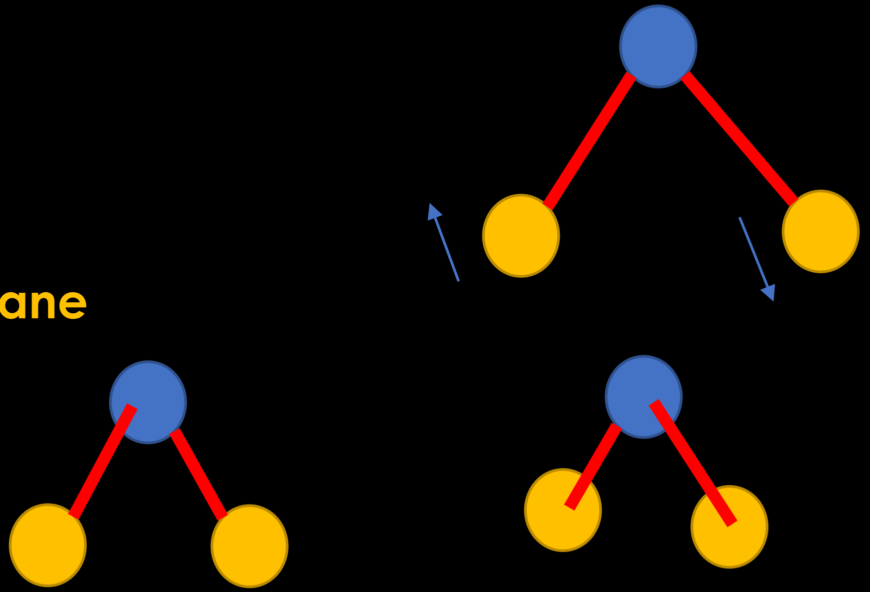
Two atoms move up and down the plane with respect to central atom

Theory and Fundamental of Molecular Vibration

B. Bending

- The position of atom change with respect to the bond axis

Out Plane



4. Twisting

One atoms move up and one atom move down the plane with respect to central atom

IR-Spectroscopy

(Part- 02)

- ✓ Hook’s Law Equation
- ✓ Numerical Questions

Spectroscopy
Instrumental Analysis

IR-SPECTROSCOPY

Hook's Law Equation

Vibrational frequency (υ) α $\sqrt{Bond\ strength/mass}$

$$\upsilon \propto \sqrt{K/\left(\frac{m1m2}{m1+m2}\right)}$$

$$\upsilon \propto \sqrt{K/\mu}$$

$$\boxed{\upsilon = 1/2\pi\sqrt{K/\mu}}$$

$$\checkmark\ \boxed{\Delta E = h\upsilon}$$

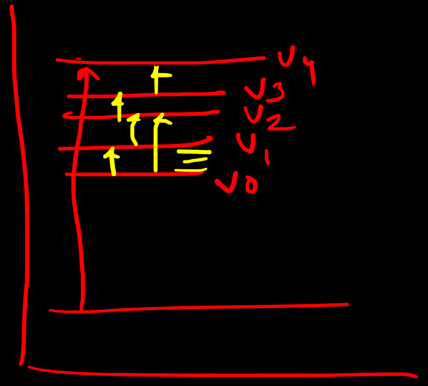
$$\bar{V} = \frac{1}{\lambda}$$

$$C/\lambda = \upsilon = 1/2\pi\sqrt{K/\mu}$$

$$C\bar{V} = \upsilon = 1/2\pi\sqrt{K/\mu}$$

$$\left(\bar{V} = 1/2\pi c\sqrt{K/\mu}\right)$$

$$\boxed{\bar{V} = 4.12\sqrt{K/\mu}}$$



UV

MIR = 2.5 – 15 μm

4000 – 667 cm^{-1} $\bar{V}$ (cm^{-1})

C = 12
H = 1
O = 16

IR-SPECTROSCOPY

Q.1 Calculate the wavenumber of C=C, if bond strength is 10 x 10^5 dynes/cm

$K = 5\times10^5$

$$\bar{V} = 1/2\pi c \sqrt{K/\mu}$$

$$\mu = \frac{m1m2}{m1+m2}$$

$$\bar{V} = \frac{1}{2\pi c}\sqrt{K/\frac{m_1m_2}{m_1+m_2}}$$

$$= \frac{1}{2\times3.14\times3\times10^{10}}\sqrt{\frac{10\times10^5}{\frac{\frac{12}{6.02\times10^{23}}\times\frac{12}{6.02\times10^{23}}}{\frac{12}{6.02\times10^{23}}+\frac{12}{6.02\times10^{23}}}}}$$

$\bar{V} = 1682\ cm^{-1}$

* Experimental Value = $\boxed{1650\ cm^{-1}}$

mass of C = 12 amu = $\frac{12}{6.023\times10^{23}}$ g

mass of H = 1 amu = $\frac{1}{6.023\times10^{23}}$ g

$$\bar{V} = 4.12\sqrt{K/\mu}$$

$$= 4.12\sqrt{\frac{10\times10^5}{\left(\frac{12\times12}{12+12}\right)}}$$

$$= 4.12\sqrt{\frac{10\times10^5}{6}}$$

$$= 4.12\times408.24$$

$$= 1682\ cm^{-1}$$

$$\mu = \frac{12\times12}{12+12} = \frac{144}{24} = 6$$

IR-SPECTROSCOPY

Q.2 Calculate the wavenumber of C-H, if bond strength is 5×10^5 dynes/cm

$$V = 1/2\pi c \sqrt{K/\mu}$$

$$\mu = \frac{m1m2}{m1+m2}$$

$$\bar{V} = 4.12 \sqrt{\frac{5 \times 10^5}{0.92}}$$

$$= 4.12 \sqrt{5.43 \times 10^5}$$

$$= 4.12 \times 736.88$$

$$= 3035\ cm^{-1}$$

* Exp. Value = $3000\ cm^{-1}$

$C\ (m_1) = 12$

$H\ (m_2) = 1$

$$\mu = \frac{12 \times 1}{12+1}$$

$$= \frac{12}{13} = 0.92$$

IR-SPECTROSCOPY

Q.3 Calculate the wavenumber of C=O, if bond strength is 10 x 10^5 dynes/cm

$$\bar{V} = 1/2\pi c \sqrt{K/\mu}$$

$$\bar{V} = 4.12 \times \sqrt{\frac{10\times10^5}{6.85}}$$

$$= 4.12 \times 382.08$$

$$= 1574 \text{ cm}^{-1}$$

$$\mu = \frac{m1m2}{m1+m2}$$

C (m_1) = 12

O (m_2) = 16

$$\mu = \frac{12\times16}{12+16} = \frac{192}{28} = 6.85$$

* C=O = 1600 – 1800 cm^{-1}

IR-Spectroscopy

(Part- 3)

Fundamental Modes of Vibrations in Polyatomic molecules

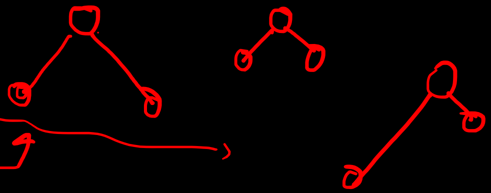
Spectroscopy
Instrumental Analysis

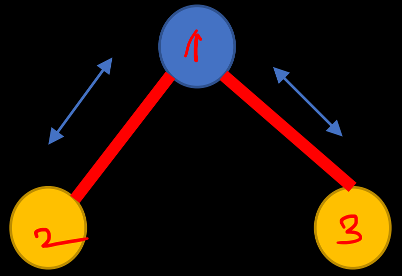
Types of Vibrational Modes

1. Stretching Vibrations: The alteration (increase or decrease) in distance between two atom without changing in its bond axis.

A. Asymmetrical

B. Symmetrical





Stretching

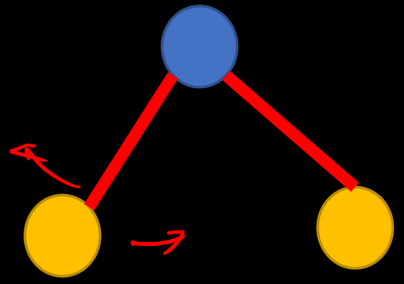
B. Bending Vibrations: The position of atom change with respect to the bond axis (also called Deformation Vibration). Required less energy than stretching.

A. Scissoring

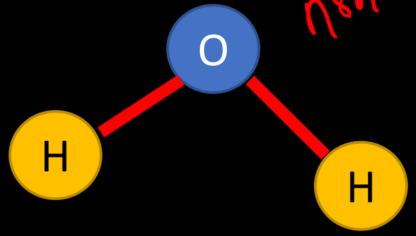
B. Rocking

C. Wagging

D. Twisting



Bending



non-linear

3

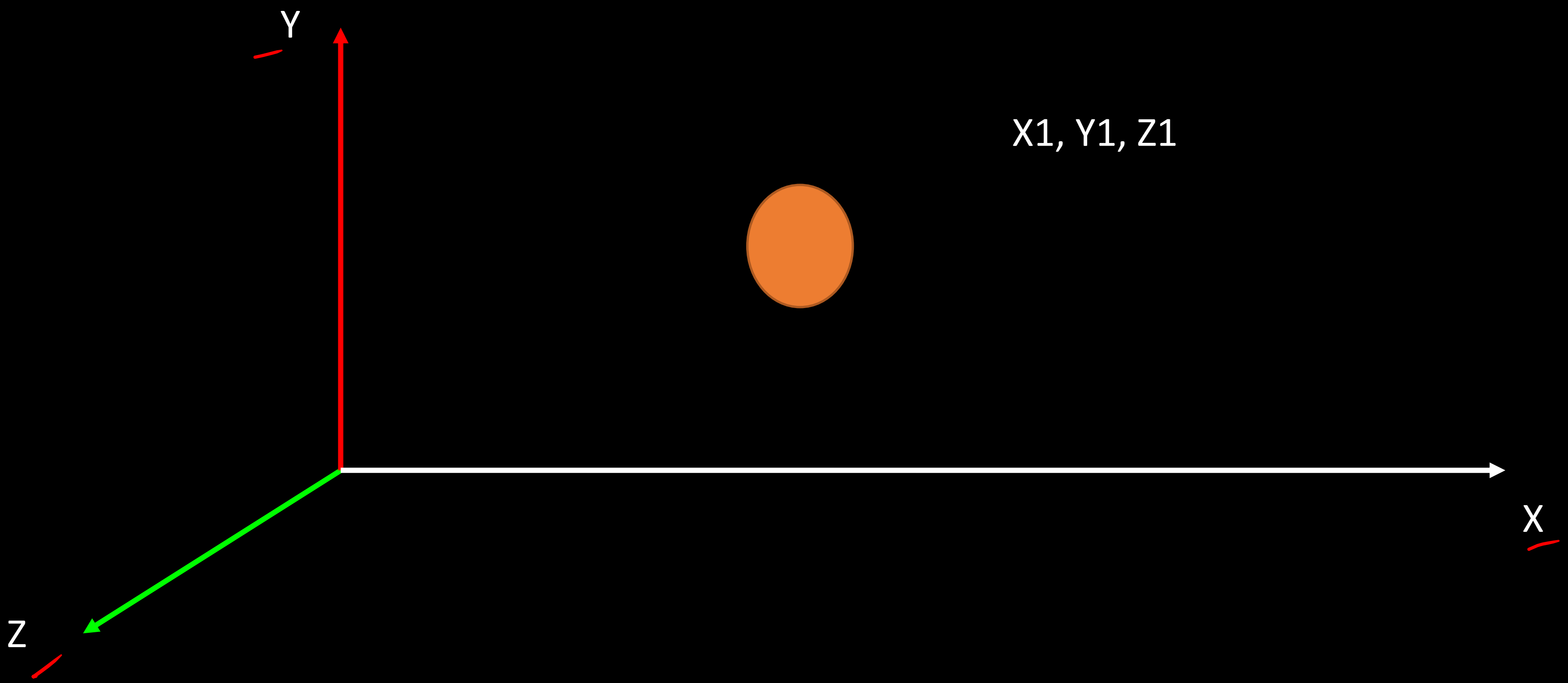
E.g. Water molecule has 3 vibrational mode

https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Spectroscopy/Vibrational_Spectroscopy/Vibrational_Modes/Number_of_Vibrational_Modes_in_a_Molecule

IR-SPECTROSCOPY

Degree of Freedoms (DF)

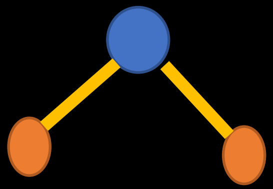
- DF of every atom – 3
- For Molecules with N atom- 3N



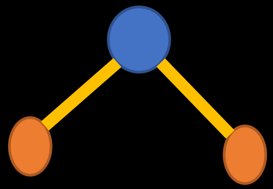
IR-SPECTROSCOPY

Modes of Movement of a molecules

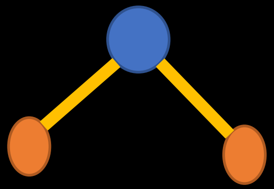
1. Translational ✓
2. **Vibrational** ✓
3. Rotational ✓



Translational



Rotational

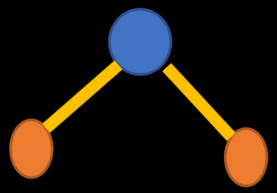


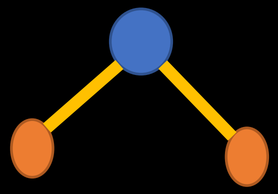
Vibrational

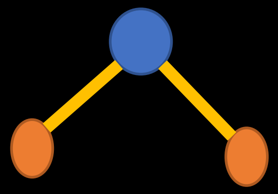
IR-SPECTROSCOPY

Modes of Movement of a molecules

1. Translational
2. Vibrational
3. Rotational


Translational

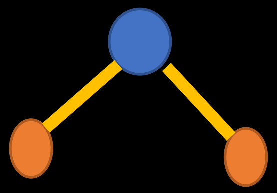

Rotational


Vibrational

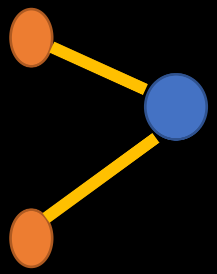
IR-SPECTROSCOPY

Modes of Movement of a molecules

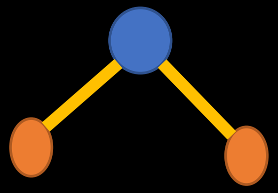
1. Translational
2. Vibrational
3. Rotational



Translational



Rotational

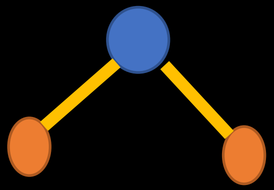


Vibrational

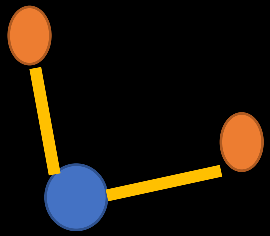
IR-SPECTROSCOPY

Modes of Movement of a molecules

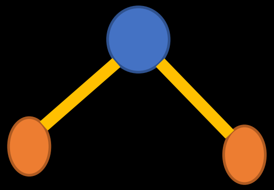
1. Translational
2. Vibrational
3. Rotational



Translational



Rotational

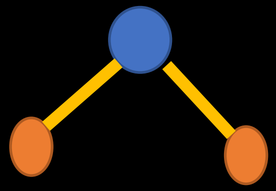


Vibrational

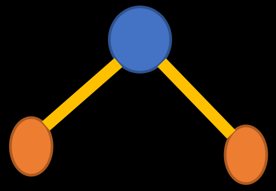
IR-SPECTROSCOPY

Modes of Movement of a molecules

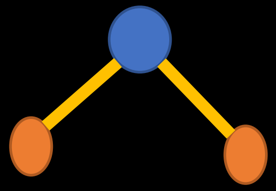
1. Translational
2. Vibrational
3. Rotational



Translational



Rotational

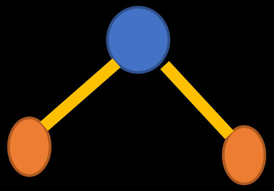


Vibrational

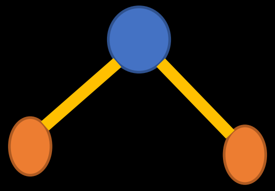
IR-SPECTROSCOPY

Modes of Movement of a molecules

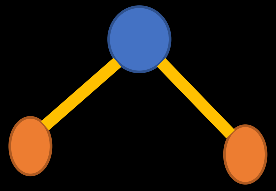
1. Translational
2. Vibrational
3. Rotational



Translational



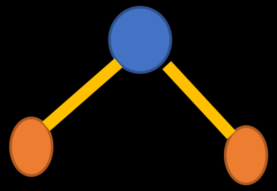
Rotational



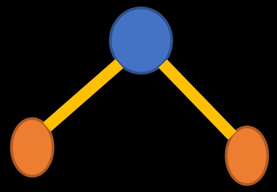
Vibrational

Modes of Movement of a molecules

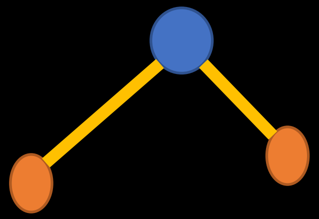
1. Translational
2. Vibrational
3. Rotational



Translational



Rotational

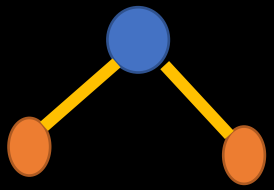


Vibrational

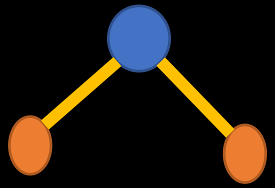
IR-SPECTROSCOPY

Modes of Movement of a molecules

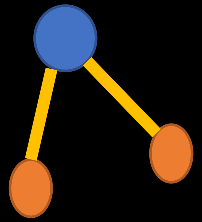
1. Translational
2. Vibrational
3. Rotational



Translational



Rotational

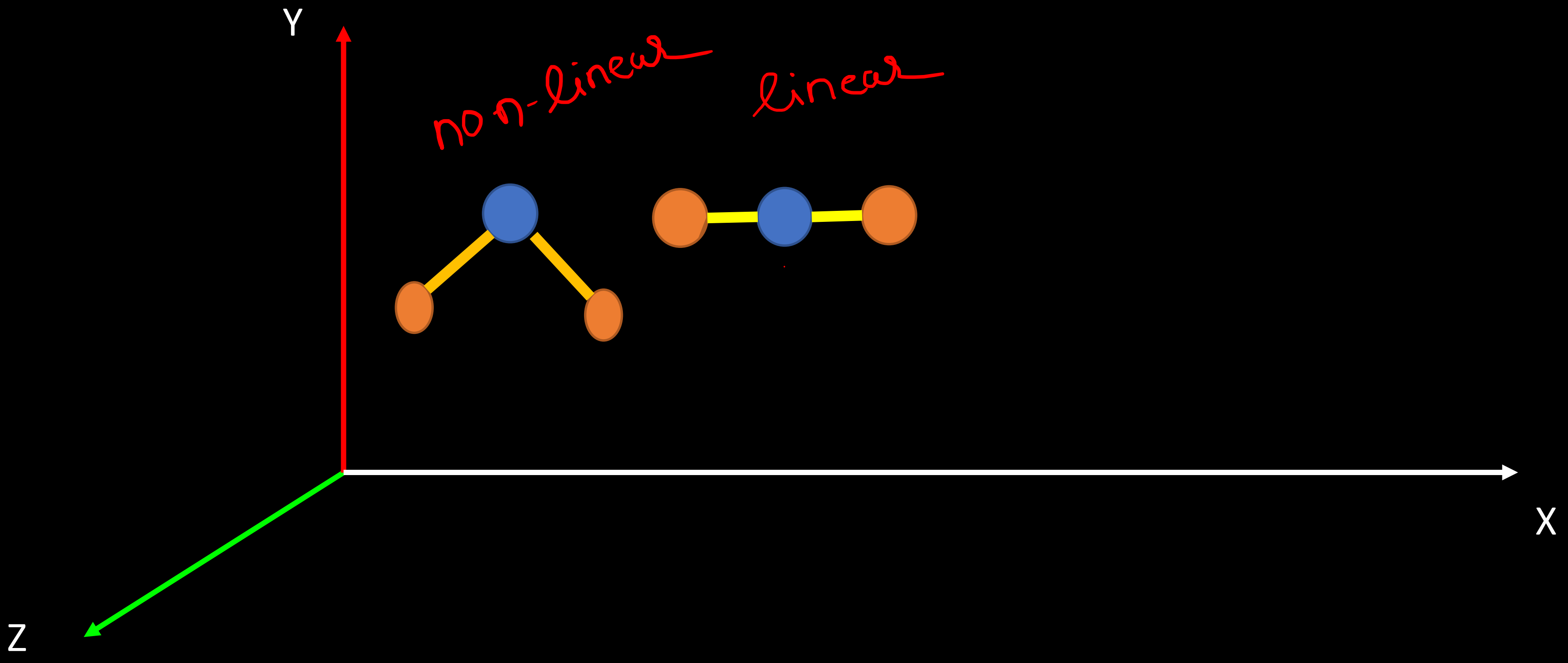


Vibrational

IR-SPECTROSCOPY

Modes

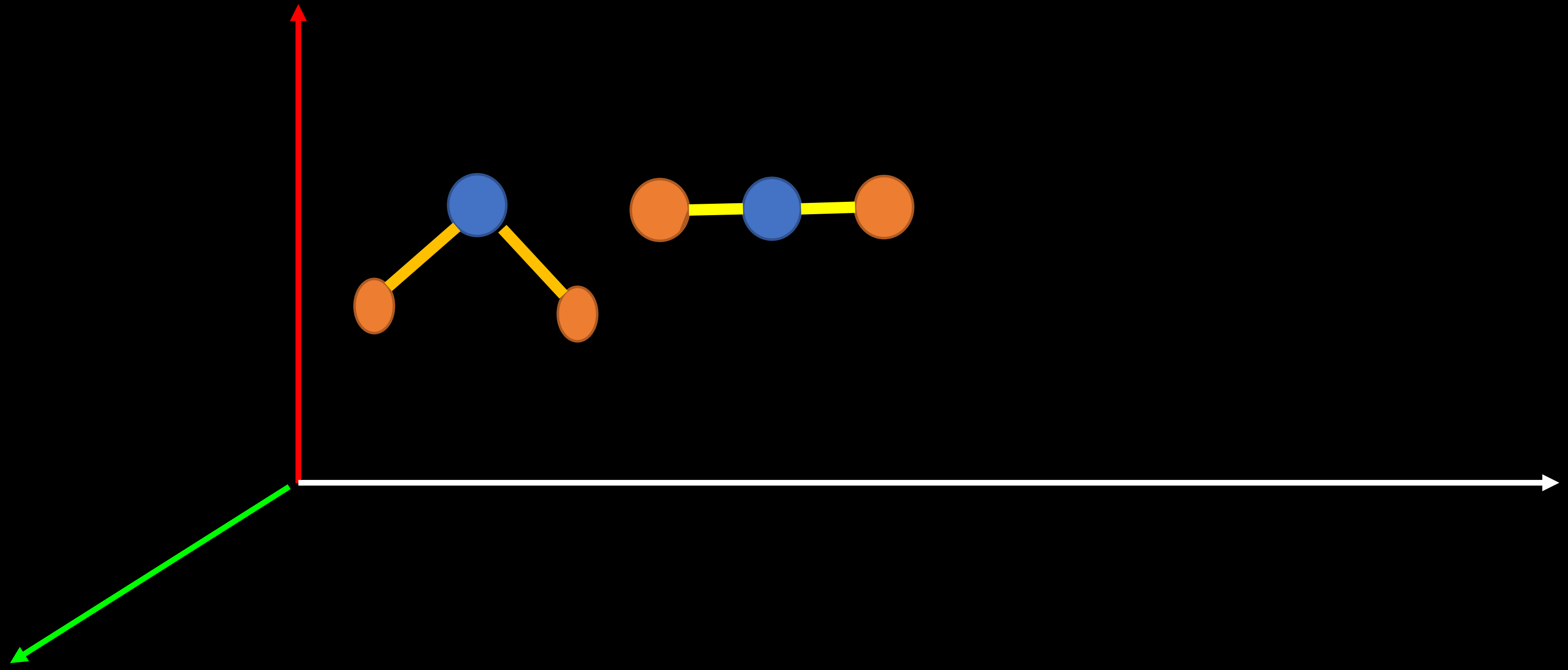
1. **Translational Mode = 3**



IR-SPECTROSCOPY

Modes

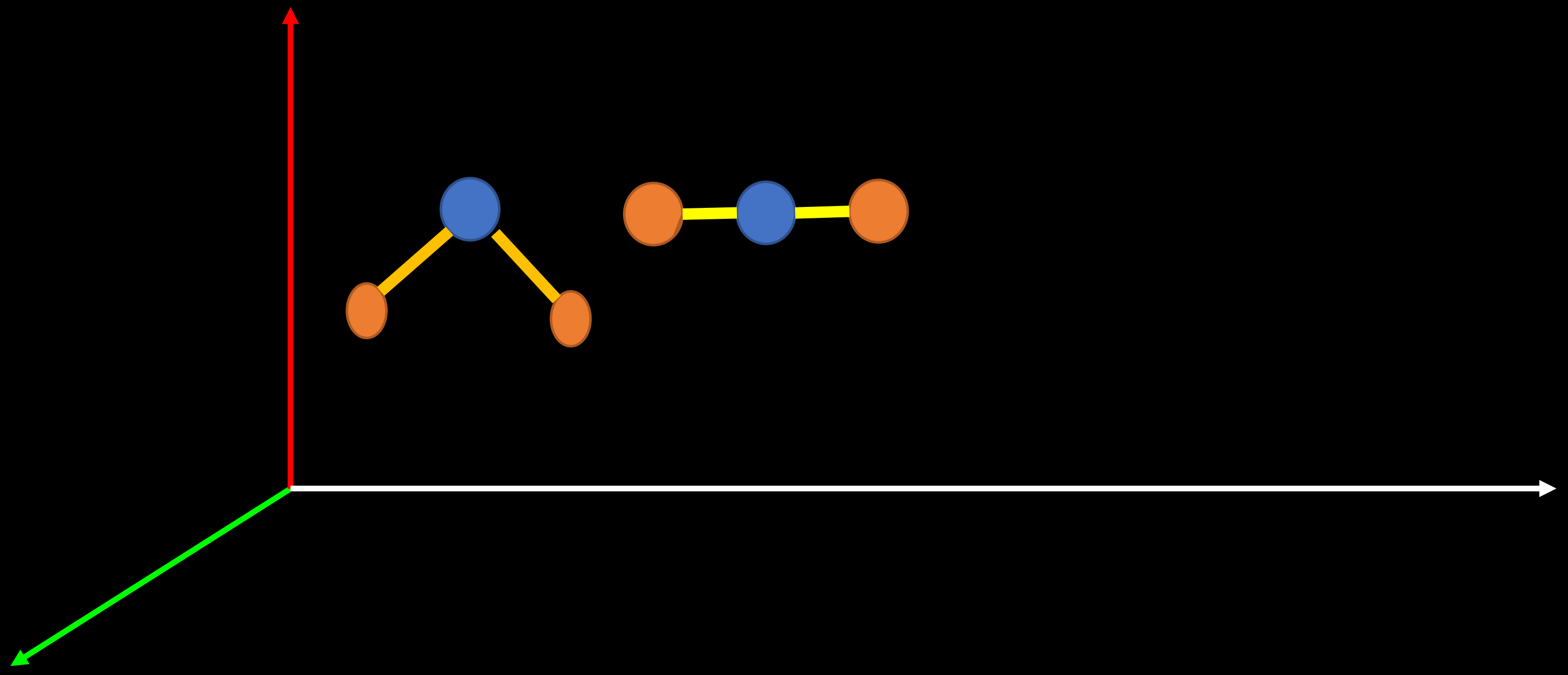
1. **Translational Mode = 3**



IR-SPECTROSCOPY

Modes

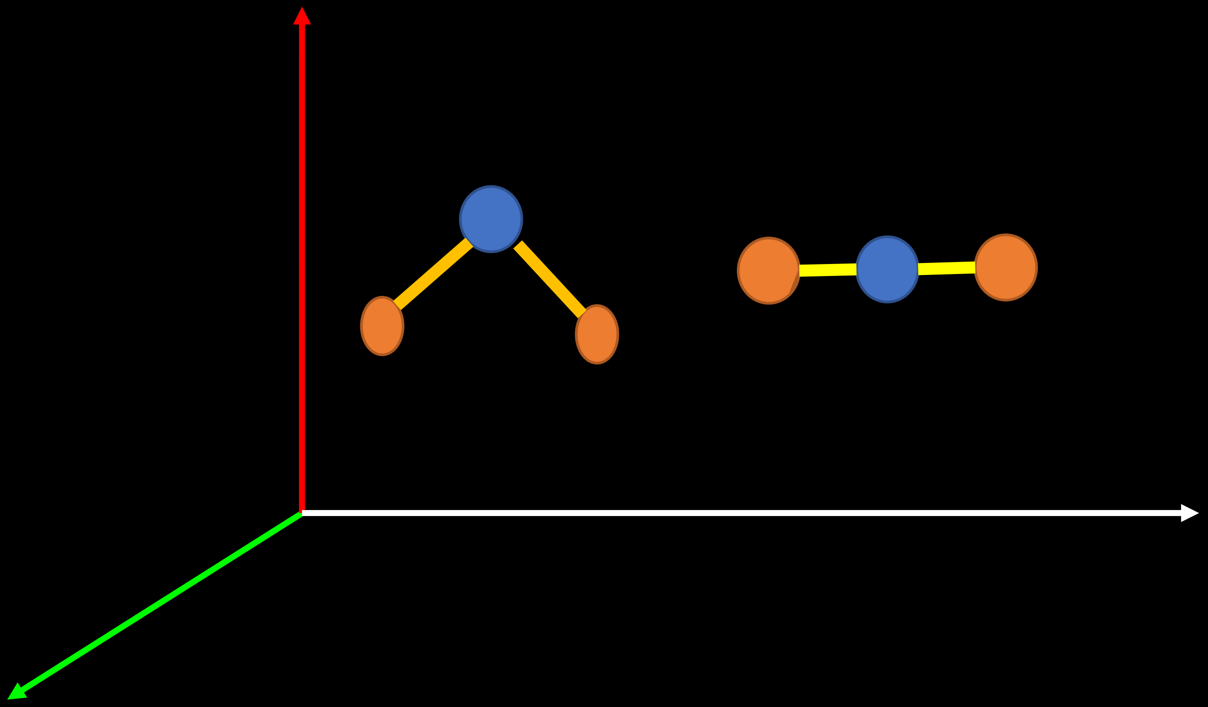
1. Translational Mode = 3



IR-SPECTROSCOPY

Modes

2. Rotational Mode = 3 (Non Linear Molecule) & 2 (Linear Molecules)



IR-SPECTROSCOPY

Vibrational Modes

1. Non Linear Molecules

DF of N Molecules = 3N

Translational Mode = 3

Rotational Mode = 3

Vibrational Mode **= DF – (TM+RM)**

$$\boxed{= 3N-6}$$

IR-SPECTROSCOPY

Vibrational Modes

2. Linear Molecules

DF of N Molecules = 3N

Translational Mode = 3

Rotational Mode = 2

Vibrational Mode = DF – (TM+RM)

$$\boxed{= 3N-5}$$

IR-SPECTROSCOPY

Calculation of Vibrational Modes

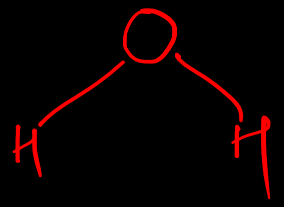
1. Water (H_2O)

Vibrational Mode = $\underline{3N-6}$

$= \underline{3}(3)-6$

$= 9-6$

$\boxed{= 3}$



non-linear

N = No. of atm prsnt in molecule

N = 3

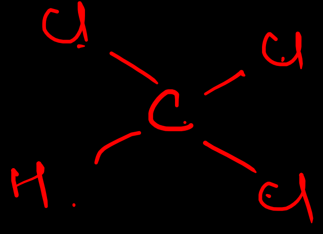
2. Chloroform ($CHCl_3$)

Vibrational Mode = $\underline{3N-6}$

$= \underline{3}(\underline{5})-\underline{6}$

$= 15-6$

$\boxed{= 9}$



Non-linear

N = 5

IR-SPECTROSCOPY

Calculation of Vibrational Modes

1. Carbon dioxide (CO2)

Vibrational Mode = 3N-5

= 3(3)-6

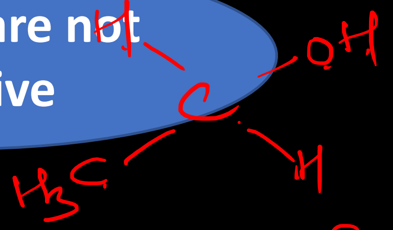
= 9-5

= 4

O = C = O linear

N = 3

All these are not IR Active



non-linear

N = 9

2. Ethanol (CH3CH2OH)

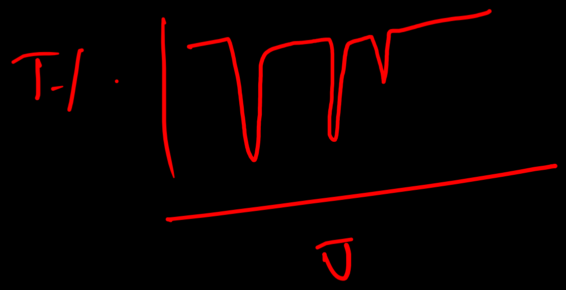
Vibrational Mode = 3N-6

= 3(9)-6

= 27-6

= 21

All these are not IR Active



IR-SPECTROSCOPY

Vibrational Modes

1. Non Linear Molecules

Stretching = N-1

Bending = 2N-5

2. Linear Molecules

Stretching = N-1

Bending = 2N-4

IR-Spectroscopy

(Part- 04)

Sample Handling Techniques

Spectroscopy
Instrumental Analysis

IR-SPECTROSCOPY

SAMPLE HANDLING

- **Sample**: Solids, Liquids, and Gases and solution
- The material containing the sample must be transparent to IR Radiation
- The Intramolecular forces of attraction are the most operative in solid sample and least in case of gaseous sample
- So substance of the same sample shows shifts in the vibrational frequency of absorption.
- So it is important to mention the sample state in IR spectra
- **Sample Cells-** Very narrow 0.01 to 1 mm

IR-SPECTROSCOPY

Solid Sample

1. Pressed Pellet Technique (KBr Pallet)
2. Mull Technique
3. Solid Film
4. Solid Run in Solution or Solution

1. Pressed Pellet Technique :

- In this technique some amount of finely ground solid sample is mixed with about 100 times its weight of powdered KBr . KBr will eliminate the problem of additional bands because it won't absorb infrared light in the "2.5µm to 15 µm region" and a complete spectrum of sample is obtained . The mixture is pressed under a high pressure(10000-15000 pounds/sq. inch) in a die to form a small pellet.

IR-SPECTROSCOPY

Solid Sample

1. Pressed Pellet Technique :

- The particle size of the grounded mixture (1-2 %w/w) should be <2um to avoid scattering
- #
- **Advantage:**
- 1.The KBr pellet can be stored for longer time. ✓
- 2. As the concentration of the sample can be suitably adjusted in the pellet, it can be used for quantitative analysis. ✓
- 3.The resolution of the spectrum in KBr is superior to that obtained with Nujol mull technique.

IR-SPECTROSCOPY

Solid Sample

1. Pressed Pellet Technique :

- **Disadvantage** :
- 1. It always has band at 3450cm-1 from the OH group of the moister present in the sample.
- 2.The high pressure involved in the formation of pellet may bring about polymorphic changes in crystallinity in the sample(specially for inorganic complexes) which causes complication in IR spectrum. In some causes even substitution of the ligand by bromide may be possible in inorganic complexes.
- 3.This method is not successful for some polymers which are difficult to grind with KBr.

IR-SPECTROSCOPY

Solid Sample

2. Mull technique :

- In this technique the finely ground solid sample is mixed with mulling reagents to make a thick paste or mull, which is then made to spread between IR transmitting windows. This is then mounted in a path of infrared beam and the spectrum is run. This method is good for quantitative analysis.
- Mulling Reagents: Nujol (mineral oil; mixture of liquid paraffinic hydrocarbon; commonly used), hexachlorobutadiene, or chloro-fluoro-carbon oil

GPAT

IR-SPECTROSCOPY

Solid Sample

2. Mull technique :

- **Disadvantages :**
- 1.It shows absorption of maximum at 2915 cm^{-1}, 1462cm^{-1}, 1376cm^{-1},
- 2.Polymorphic changes, degradation, and other changes may occur during grinding.

IR-SPECTROSCOPY

Solid Sample

3. Solid films :

- If a solid is amorphous in nature the sample is deposited on the surface of KBr or NaCl cell/disk by putting a drop of a sample and further evaporation of a solvent from the solid sample.
- Sample solution is made by using a volatile solvent up of evaporation of a solution of a solid.

#GPAT

- This method is useful for rapid qualitative analysis and become useless for carrying out quantitative analysis.
- E.g., Polymers, fats, and waxy material is commonly used in this techniques.

IR-SPECTROSCOPY

Solid Sample or Solution

D. Solid Run In Solution :

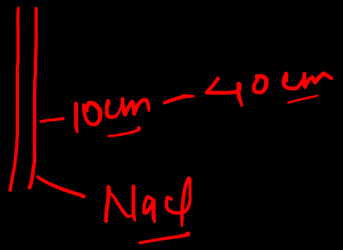
- The solid may be dissolved in a non-aqueous solvent (1-5 % w/v) provided there is no chemical interaction with the solvent and also the does not absorb in the studied range.
- The various solvent used are acetone, acetonitrate, benzene, CCl4 ,CS2, cyclohexane, terachloroethylene, methylenechloride. Among these only CCl4 , CS2 are ideal as they shows very few absorption band
- Sample cell made up of alkali halide (NaCl)

4

IR-SPECTROSCOPY

Sampling of gases:

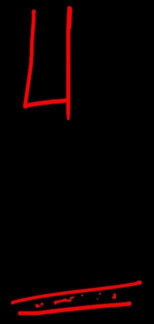
- Gas samples are examined in the IR spectrometer after removal of water vapour.
- The simplest gas cell consists of metal/gas cylinder of 10cm long and closed with a appropriate window (wall is made-up of NaCl).
- The gaseous sample is passed through a stopcock via a suitable gas handing apparatus and partial pressure of 5 to 15mmHG gives a reasonable level of absorption in most cases .
- The end wall of gas cell is made of NaCl and for low concentrated gases long path lengths are required.
- Multi reflection can be used to make effective path length as long as 40cm so that constituent of gas can be determind.



IR-SPECTROSCOPY

Sampling of liquid:

- Sample that are liquid at room temperature are usually put frequently with no preparation into rectangular cell made up of NaCl, KBr or ThBr and their IR spectra is obtained directly.
- Liquid can also make a thin film (0.1 to 0.3 mm) squezzed between NaCl plate. If the sample contains water cell made up of CaF2
- Sample cell – Sandwich cell, Matched cell or Demountable cell
- Some times the liquid samples can be dissolved in suitable solvents and scanned in IR region using any suitable cell.



IR-Spectroscopy

(Part- 05)

Factors Affecting Vibrational Frequency

- Bond Strength
- Molecular Mass
- Hybridization
- Molecular State
- Coupling Interaction
- Fermi Resonance
- Hydrogen Bonding
- Electronic Displacement Effects

Spectroscopy
Instrumental Analysis

IR-SPECTROSCOPY

Factors Affecting Vibrational Frequency

- Bond Strength ✓
- Molecular Mass ✓
- Hybridization ✓
- Molecular State ✓
- Coupling Interaction ✓
- Fermi Resonance ✓
- Hydrogen Bonding ✓
- Electronic Displacement Effects ✓
- Bond Angle ✓

IR-SPECTROSCOPY

Bond Strength

Vibrational frequency (υ) α $\sqrt{Bond\ strength/mass}$

For single bond K = $5x10^5$ gm sec $^{-2}$

For Double bond K = $10x10^5$ gm sec $^{-2}$

For Trible bond K = $15x10^5$ gm sec $^{-2}$

- Stretching vibration of Hydrocarbons

C≡C	>	C=C	>	C-C
2150 cm-1		1650 cm-1		1200 cm-1

IR-SPECTROSCOPY

Molecular Mass

Vibrational frequency (υ) α $\sqrt{Bond\ strength/mass}$

$m\uparrow$ $\nu\downarrow$

	C-H	>	C-C	>	C-O	>	C-Cl	>	C-Br	>	C-I
V (cm-1)=	3000		1200		1100		750		600		500

Hybridization

	SP	>	SP2	>	SP3
V (cm-1)=	3300		3100		2900

Molecular State

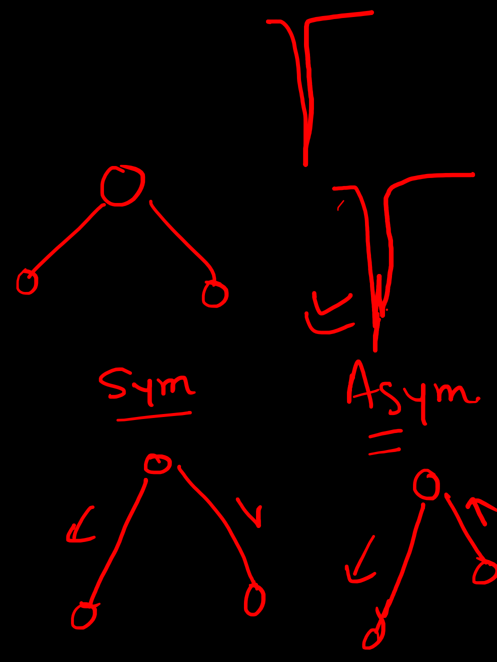
Vapor/Gas > Liquid > Solid

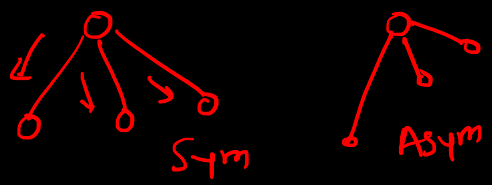
IR-SPECTROSCOPY

Coupling Interaction/Vibration

$-CH_2-$

- We except one stretching vibration for an vibrational C-H
- In Case of $-CH_2-$, two absorption occurs- Asymmetry and Symmetry
- V(Asymmetry) > V (Symmetry)
- These are known as coupled vibration due to occurs at different frequencies that isolated C-H stretching
- Similarly, coupled vibration of $-CH_3$
- Sometimes, it happens that two different vibrational levels have nearly the same energy.
- If such vibrations belongs to same species like –CH2- and –CH3 then a mutual perturbation of energy may occurs, resulting in the shift of one towards lower frequency and other towards higher frequency.

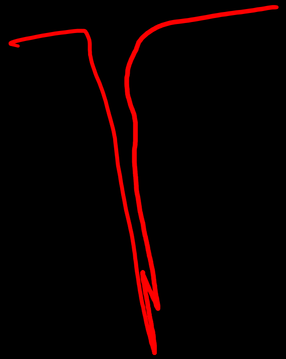




IR-SPECTROSCOPY

Coupling Interaction/Vibration

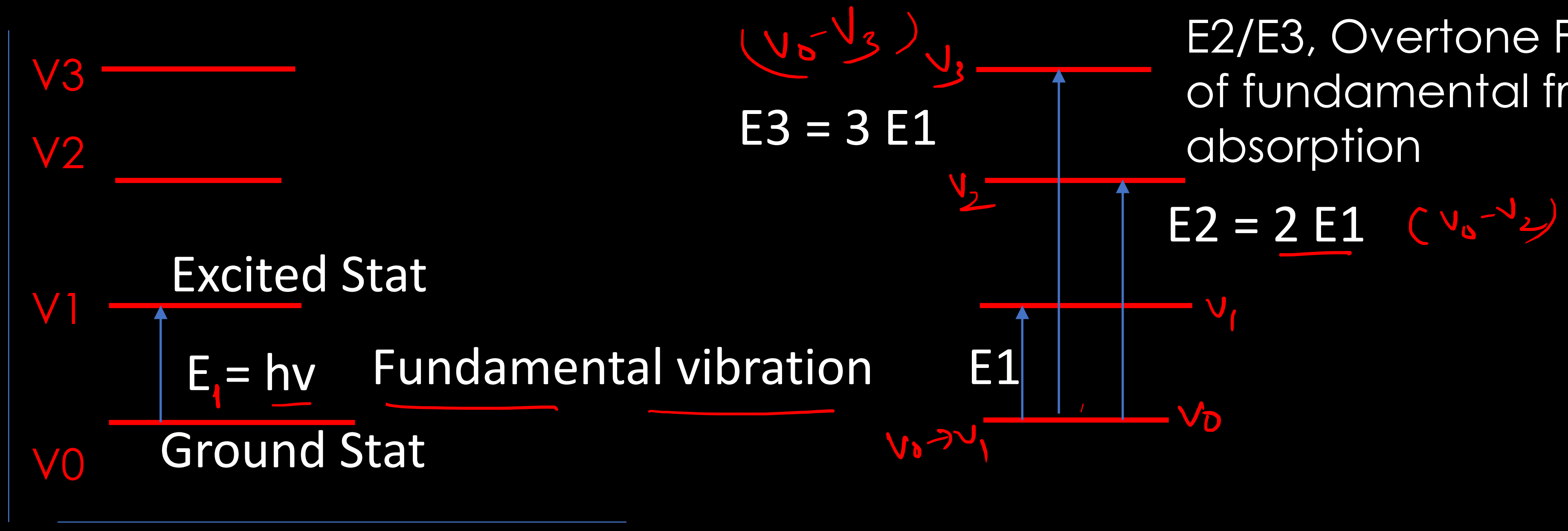
Examples	$\bar{V}$(asymmetry)	$\bar{V}$(symmetry)
$-CH_2-$	3000	2900
$-NH_2$	3400	3300
$-NO_2$	1550	1400
$-CO_2$	1600	1400



IR-SPECTROSCOPY

Fermi Resonance

- It occurs when a **fundamental vibration** couples with an **overtone** or **combination bands**



V3

V2

Excited Stat

V1

$E_1 = h\nu$ Fundamental vibration

V0

Ground Stat

$(V_0 - V_3)$ V_3

E3 = 3 E1

V_2

E2 = 2 E1 $(V_0 - V_2)$

V_1

E1

V_0

$V_0 \rightarrow V_1$

E2/E3, Overtone Frequency – multiples of fundamental frequency of absorption

IR-SPECTROSCOPY

- **Fermi Resonance**
- **Overtone**

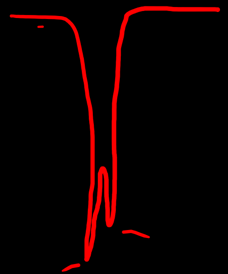
Fundamental Vibration- (V0→V1) –		1400 cm-1	E_1
First Overtone (V0→V2) –	$E_2 = 2E_1$	2800 cm-1	E_2
Second Overtone (V0→V3) -	$E_3 = 3E_1$	4200 cm-1	E_3
Third Overtone (V0→V4) -	$E_4 = 4E_1$	5600cm-1	E_4

$-CH_{str} = 3000 - \boxed{2800}$

$-CH_{def} = 1400$

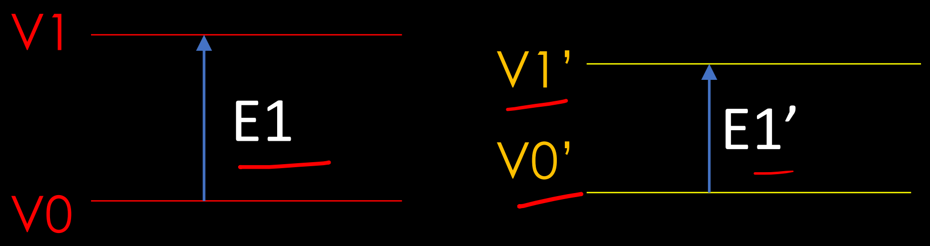
overtone $CH_{defor} = \boxed{2800}$

$CH_{str} = CH_{bend}$ overtone



IR-SPECTROSCOPY

- **Fermi Resonance**
- **Combination bands:** coupling of two fundamental vibrations
- $E2 = E1 + E1'$

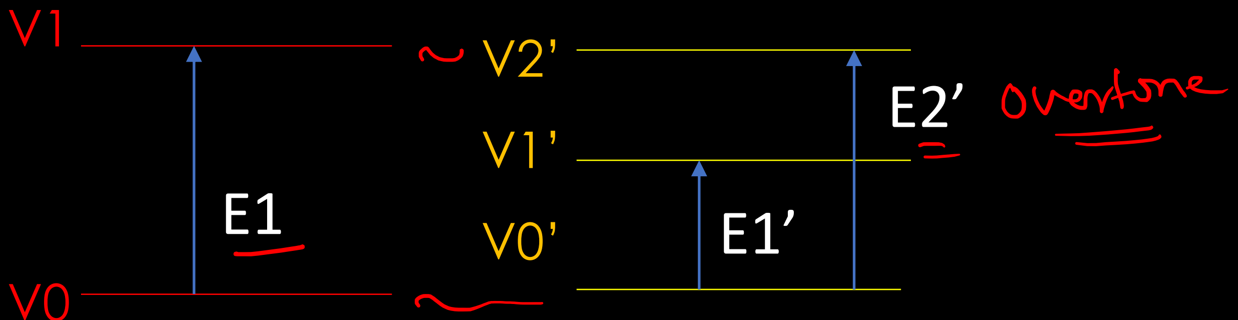


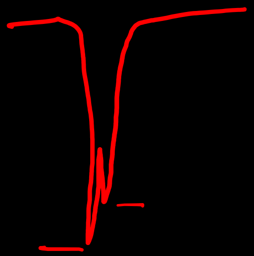
- 1400 cm-1- Fundamental Frequency (V0→V1)
- 750 cm-1 Fundamental Frequency (V0'→V1')
- 2150 cm-1 Combination bands $E2 = E1 + E1'$

IR-SPECTROSCOPY

- **Fermi Resonance**
- It occurs when a **fundamental vibration of one functional group** couples/rasonate with an **overtone** or **combination bands** of another functional group

or same





E1 = E2'

- 1400 cm-1- E1' Fundamental Frequency (V0'→V1')
- 2800 cm-1 E2' first overtone(V0'→V2')

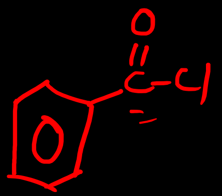
||

- 2790 cm-1 Fundamental Frequency (V0→V1)

IR-SPECTROSCOPY

Fermi Resonance

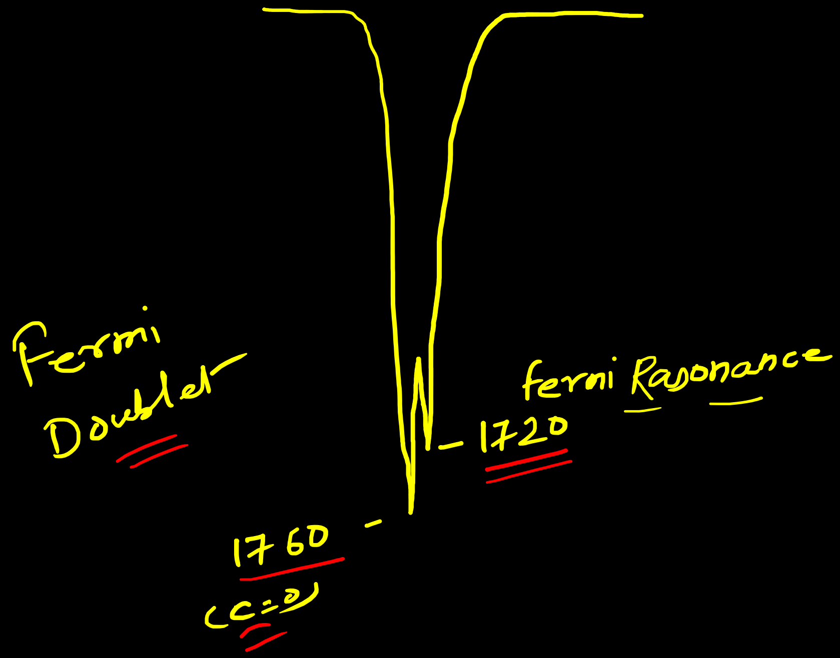
Ex 1. Benzoyl Chloride



1. Out of Plane C-H bend – 865 cm-1 Fundamental

- 1730 cm-1 Overtone

2. C=O str - 1710-1740 cm^{-1}



IR-SPECTROSCOPY

Fermi Resonance

Ex 2. Aldehyde

E_2'

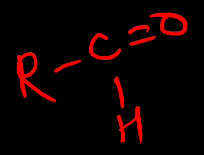
1 C-H bend = 1390 cm-1 Fundamental & 2780 cm-1 overtone

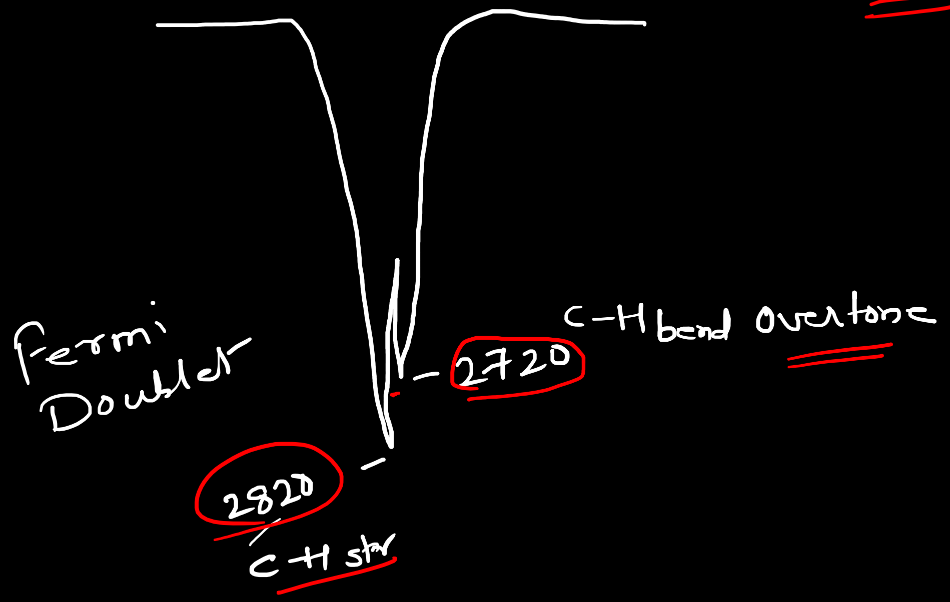
2. C-H str = 2800 cm-1 (Fundamental) E_1

$E_1 \approx E_2''$

3. Fermi Resonance – at 2820 & 2720 cm-1

$100 cm^{-1}$





IR-SPECTROSCOPY

$\bar{\nu}\downarrow$ H-bond

- **Hydrogen Bonding**
- Hydrogen bonding gives rise to downward frequency shift
- Stronger H-bonding, greater absorption shift towards the lower wave number from normal value
- Intramolecular H-Bond- sharp and well defined
- Intermolecular H-Bond- Broad Bands and conc. Dependent, on dilution such bands are decrease and finally disappear

$\bar{\nu}$ $\bar{\nu}\downarrow$ H-bond

- E.g., Amine (NH) – 3500 (dil conc) & 3300 (conc.)
  Alcohol (OH) – 3650 (dil conc.) & 3350 (Conc)

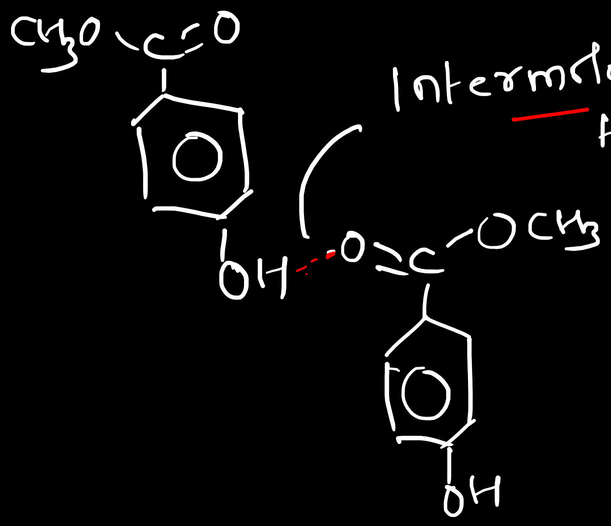
$\bar{\nu}\downarrow$ H-bond

IR-SPECTROSCOPY

①

p-hydroxy methyl benzoate

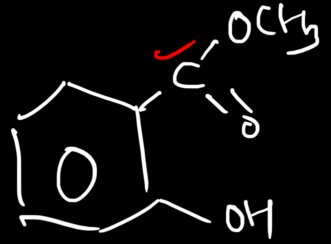
→



Intermolecular H-bond

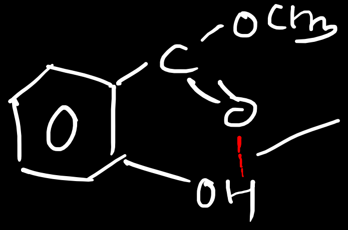
1710 cm^{-1} $\bar{\nu}\downarrow$

②



o-hydroxy methyl benzoate

→



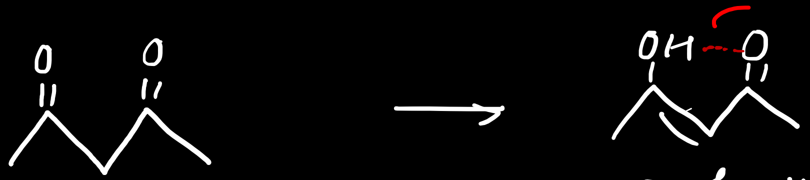
Interamolecular H-bond

1680 cm^{-1}

Normal - 1740-1780 cm^{-1}

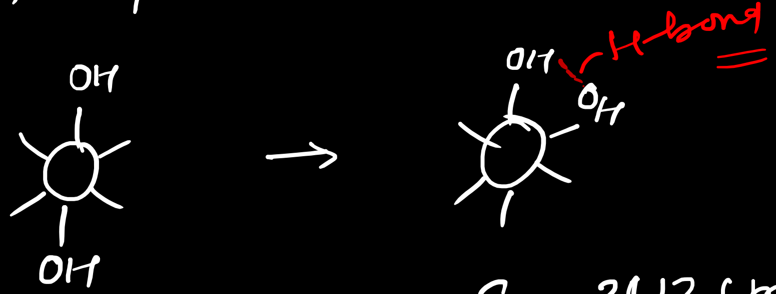
IR-SPECTROSCOPY

②



Keto 1725 cm⁻¹ Enol 1630 cm⁻¹ ↓

③ Ethylene Glycol



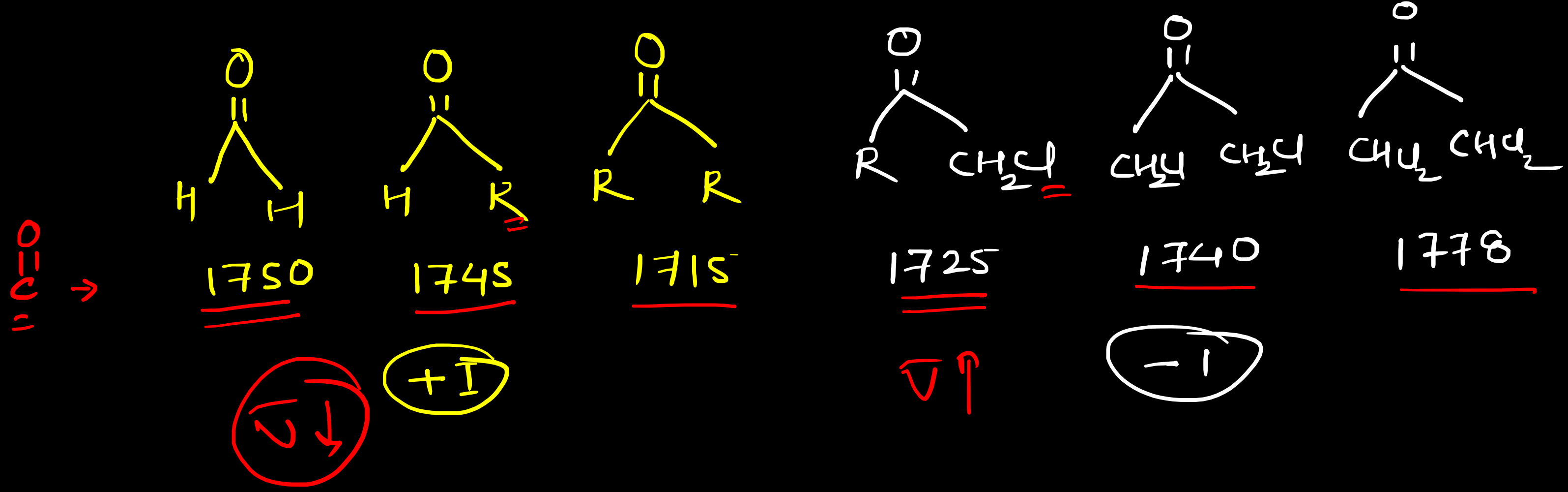
Anti 3644 cm⁻¹ Syn 3612 cm⁻¹ ↓

IR-SPECTROSCOPY

- **Electronic Displacement Effects**
- Depending on the attaching group, electron donating or electron withdrawing and depends on-
  - Inductive effects ✓
  - Mesomeric effects ✓
  - Field effects ✓
  - Conjugation ✓
- Under these effects the force constant (K) or bond strength may be alter and shift the vibrational frequency

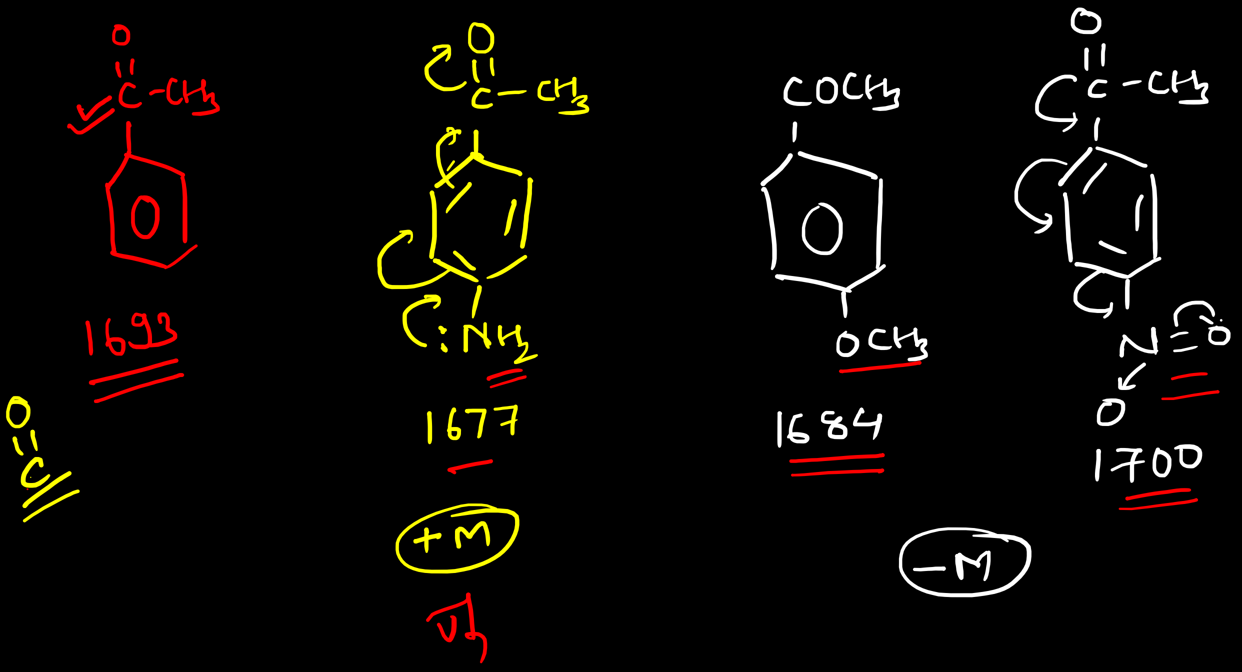
IR-SPECTROSCOPY

- **Electronic Displacement Effects**
- **Inductive Effects**
- +Inductive effects- decrease [↑bond length, ↓K, ↓$\bar{V}$]
- -Inductive effects- increase [↓bond length, ↑K, ↑V]



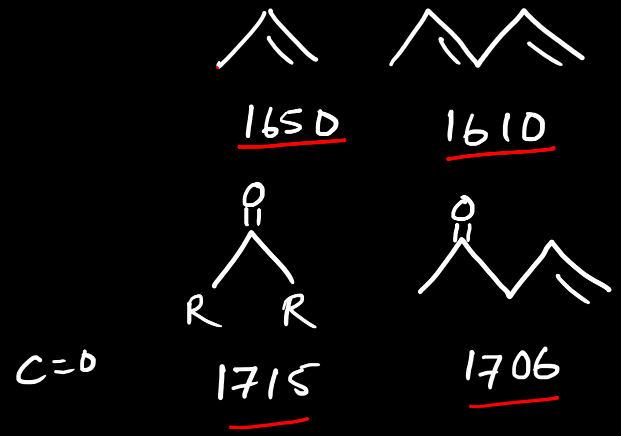
IR-SPECTROSCOPY

- **Electronic Displacement Effects**
- **Mesomeric Effects**
- +Mesomeric effects- Electron Donating Group (-NH2, -OH)- Decrease V ↓
- -Mesomeric effects- Electron Withdrawing group (-NO2, -C=O)- Increase V ↑



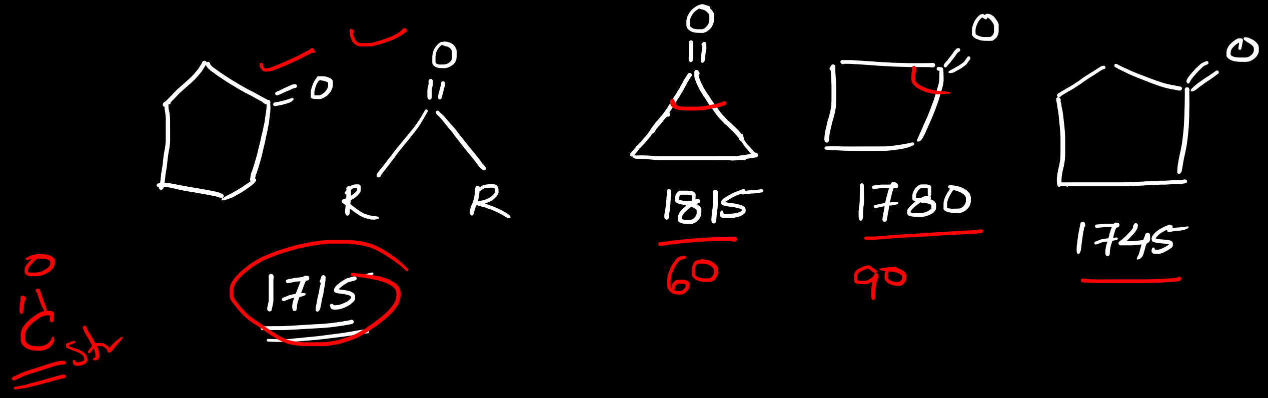
IR-SPECTROSCOPY

- **Electronic Displacement Effects**
- **Conjugation Effects**
- Conjugation increase the wavelength so decrease the wavenumber



IR-SPECTROSCOPY

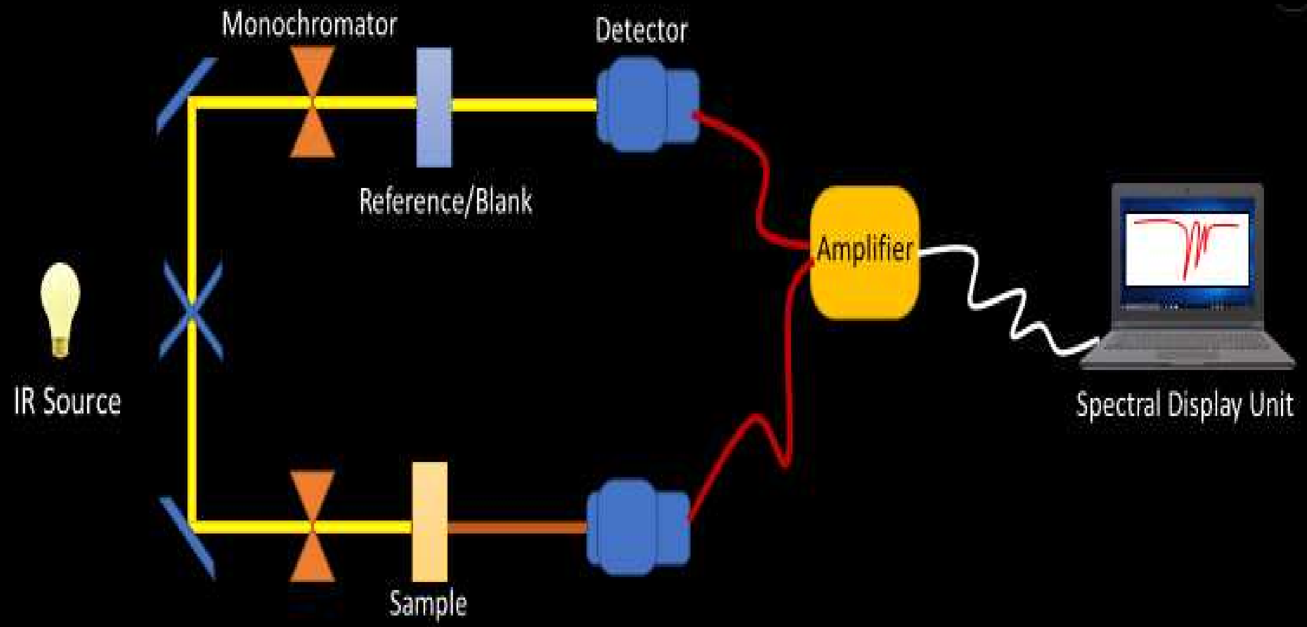
- **Bond Angle**
- Change in the bond angle can also alter the absorption band



Instrumentation of IR Spectrophotometer

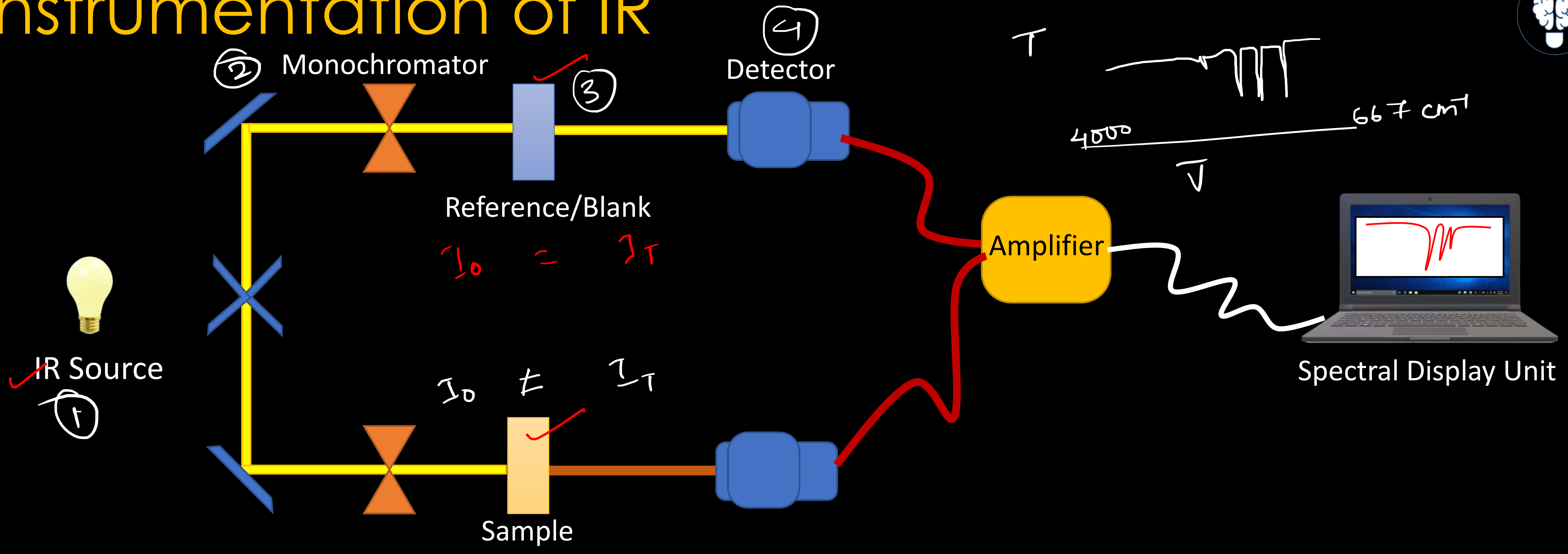
IR-Spectroscopy

(Part- 07)



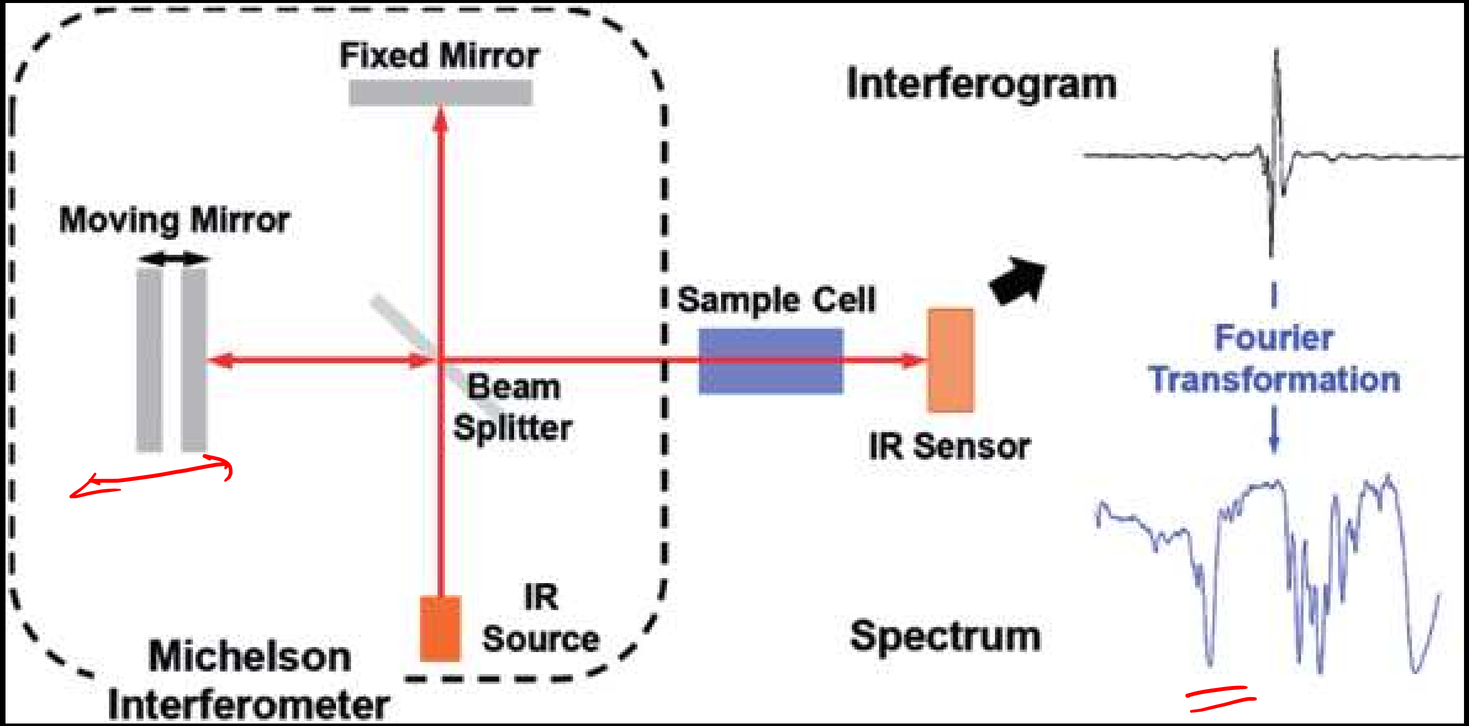
Spectroscopy
Instrumental Analysis

Instrumentation of IR



- Single Beam IR Spectrophotometer ✓
- Double Beam IR Spectrophotometer ✓
- FT-IR (Fourier Transform) IR Spectrophotometer ✓

Instrumentation of IR (FT-IR)



- Rapid ✓
- More Sensitive ✓
- Accuracy ✓
- Most Widely Used ✓

IR-SPECTROSCOPY

A. IR Radiation Source

GPAT

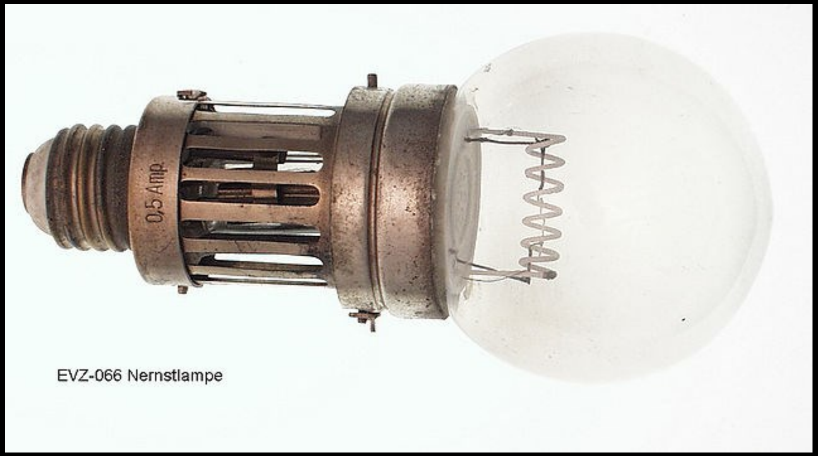
- IR radiation which must be steady, intense enough for detection and extend over the desired wavelength
- For Near IR (0.8-2.5 um or 12500-4000 cm-1)
  1) Tungsten lamp
  2) Nichrome wire
  3) Rhodium Wire
- For MID IR (2.5 to 15 um or 4000-667 cm-1)
  1) Nernst glower ✓
  2) Glober source ✓
- For Far IR (15-200 um or 667-50 cm-1) ✓
  1) Mercury arc
  2) Carbon dioxide laser

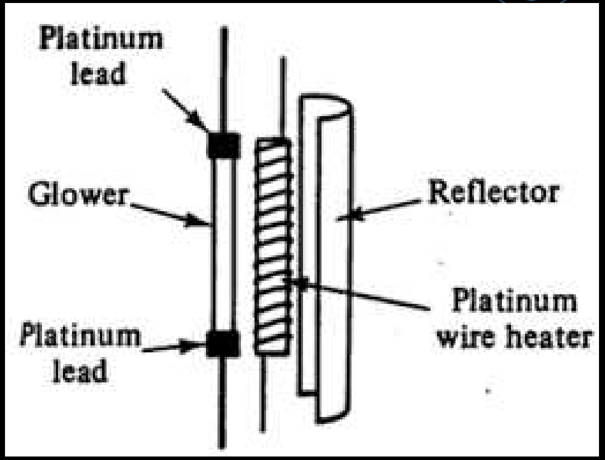
4000 — 1350 — 667

"Finger print" Region

IR-SPECTROSCOPY

Mid IR Radiation Source





1. Nernst glower

- Nernst Glower consists of a rod or hollow tube about 2 cm long and 1 mm in diameter , made by sintering a mixture of oxides of "Cerium, Zirconium , Thorium and Ytterium".
- Nernst glower is a "non conducting at room temperature" and must heated external means to bring conducting state. It should be heated at 1000 to 1800 ^{0}C
- It is maintained at higher temperature by making use of electrical heating and can be operated in air, since it is not subject to oxidation.

IR-SPECTROSCOPY

Mid IR Radiation Source

1. Nernst glower

- **Disadvantages**
- Mechanical failure
- Its energy is concentrated in visible and near infrared region of spectrum.
- The Nernst Glower has a large negative temperature coefficient of electrical resistance, and it must be heated externally (1000-1800 oc) to a dull red heat before the current is large enough to maintain the desired temperature.

IR-SPECTROSCOPY

Mid IR Radiation Source

4000 - 667

1. Glober Source

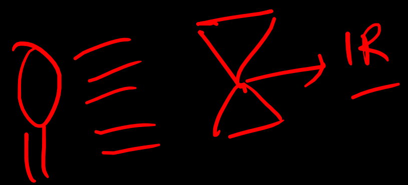
#

- Globar is a silicon carbide rod usually about 5cm in length and 0.5cm in diameter.
- It has an advantage of positive co-efficient of resistance. When heated to temperature between 1300-1700oc, it strongly emits radiation in IR region.
- Unlike Nernst Glower, the globar source is self starting and can be controlled conveniently with a variable transformer .
- The disadvantage is its less intense source than nernst glower. It is more satisfactory because it is worth at wave length longer than 650cm-1.

IR-SPECTROSCOPY

B. Monochromator

- Used to emit desired frequencies from the radiation source and reject the others.
- There are many kinds of monochromators: prisms, gratings, and filters.
- Prisms are constructed of Potassium bromide Sodium chloride, or Caesium Iodide. # GPAT-
- Filters are comprised of Lithium Fluoride, and
- Diffraction gratings comprise alkali Halides.
- **Components:**
  1) Entrance slit (to get narrow source)
  2) Collimator(to render the light parallel)
  3) Grating or Prism (to disperse radiation)
  4) Collimator(to reform the image of entrance slit)
  5) Exit slit (to fall on sample cell)



IR-SPECTROSCOPY

C. Detectors

- Detectors can be used to measure the strength/intensity of the infrared radiation. They include thermocouples, Bolometers, thermisters, Golay cells, as well as pyroelectric detectors are employed.
- For Near IR- lead sulfide photoconductive
- For Mid IR- Thermopile, Themistor or Pyroelectric
- For Far IR- Golay, pyroelectric

- At the shorter-wavelength end , below about 1.2 microns, the preferred detection methods are the same as those used for visible and U V radiation

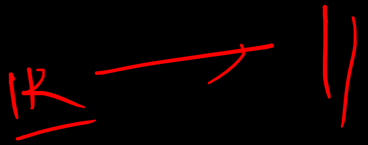
IR-SPECTROSCOPY

C. Detectors

- For Longer wavelength there are two types of detectors
- 1. Thermal detectors; in which the infrared radiation produces a heating effect that alters some physical property of detector
- 2. Photon detectors, which use the quantum effects of the IR radiations to change the electric properties of a semiconductor

IR-SPECTROSCOPY

C. Detectors



1. Bolometer;

- A bolometer is based upon the fact that the electrical resistance of a metal changes with increase of temperature. It is consists of a resistors made up of sintered oxides of manganese, cobalt and nickel, which have high temperature coefficient of resistance.
- The constructed metal or semiconductor that exhibits a large change in electrical resistance as a function of temperature. When radiation falls on the bolometer, its temperature changes and hence the resistance of conductor also changes. The degree of changes in resistance is a measure of amount of radiation falls on the bolometer
- Advantage: 1) response time is 4 milliseconds. 2) high sensitivity
- Disadvantage : Highly fragile

IR-SPECTROSCOPY

C. Detectors

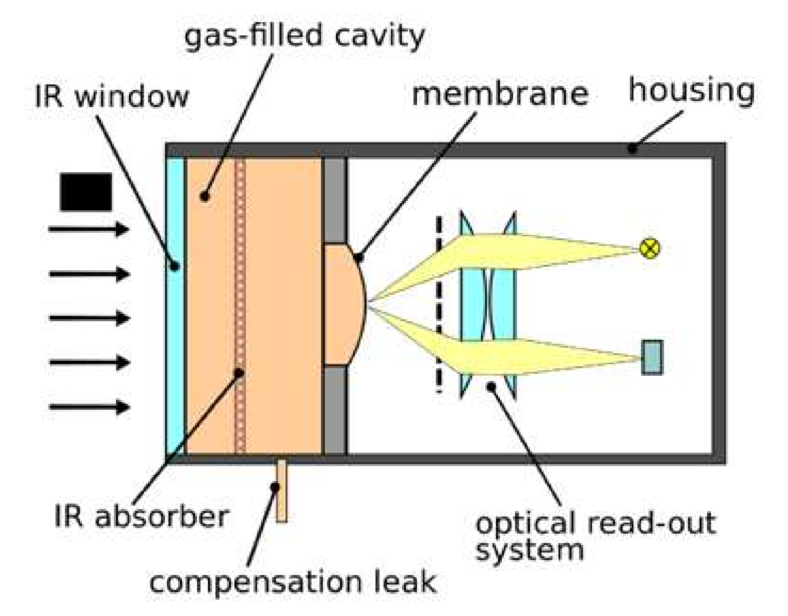
2. Thermistor

- It is a resistor made by fusing together several metallic oxides of manganese, cobalt and nickel which have a high temperature coefficient of resistance.

3. Golay cell

- It uses the expansion of a gas as the measuring device. The unit consists of a small metal cylinder closed by a rigid blackened metal plate at one end and by a flexible silvered diaphragm at other end. The chamber is filled with xenon. The radiation passes through a small IR transmitting window and is absorbed by the blackened plate. Heat conducted to the gas causes it to expand and deform the flexible diaphragm (mirror).

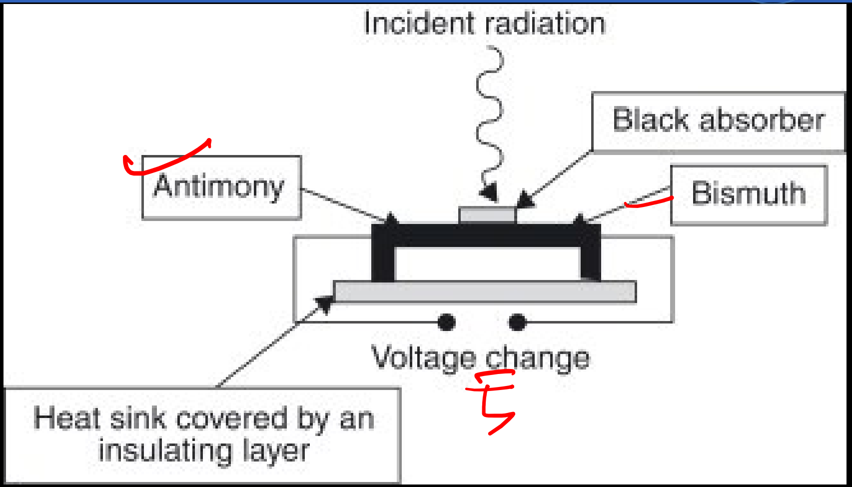
Golay cell →



IR-SPECTROSCOPY

C. Detectors

4. Thermocouple



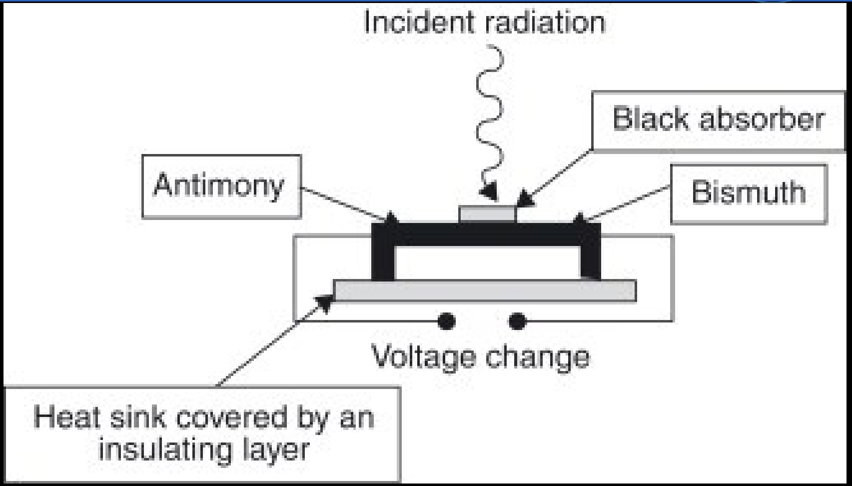
- This is most widely used in error detection. It is based on fact that an electric current will flow in two dissimilar metals (like bismuth And antimony).
- Wires are connected together at both ends, a small voltage is produced proportionally to the temperature differential exists between the two ends. Several thermocouples like this connected in series forms a thermopile so that their voltage adds
- The end exposed to IR radiation is called the hot junction (blackened gold foil in order to increase the energy gathering efficiency). It is a usually a black body. The other connection, the cold junction and is thermally insulated and carefully screened from stray light.

IR-SPECTROSCOPY

C. Detectors

4. Thermocouple

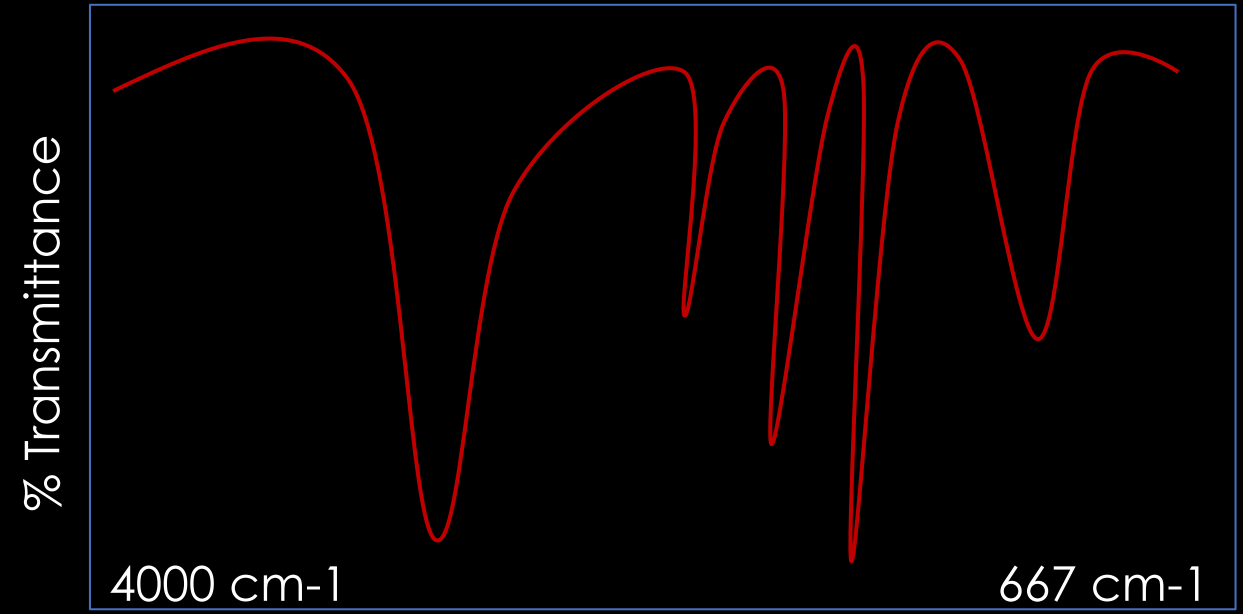
- The electricity which flows is directly proportional to the energy differential between two junctions.
- A thermocouple is closed in a evacuated steel casing with a IR transmitting window, KBr to avoid losses of energy by convection. The thermopiles offer the simplest and most direct means for converting radiant energy into electric signal.



Application of IR Spectrophotometer

IR-Spectroscopy

(Part- 08)



Spectroscopy
Instrumental Analysis

IR-SPECTROSCOPY

Application of IR Spectroscopy

1. Structural elucidation/Functional Group Detection/ Qualitative analysis of Functional Group

- Group Frequency Region- 4000 to 1350 cm-1
- Finger Print Region- 1350-667 cm-1.
- Functional group of present in molecules shows specific IR spectra

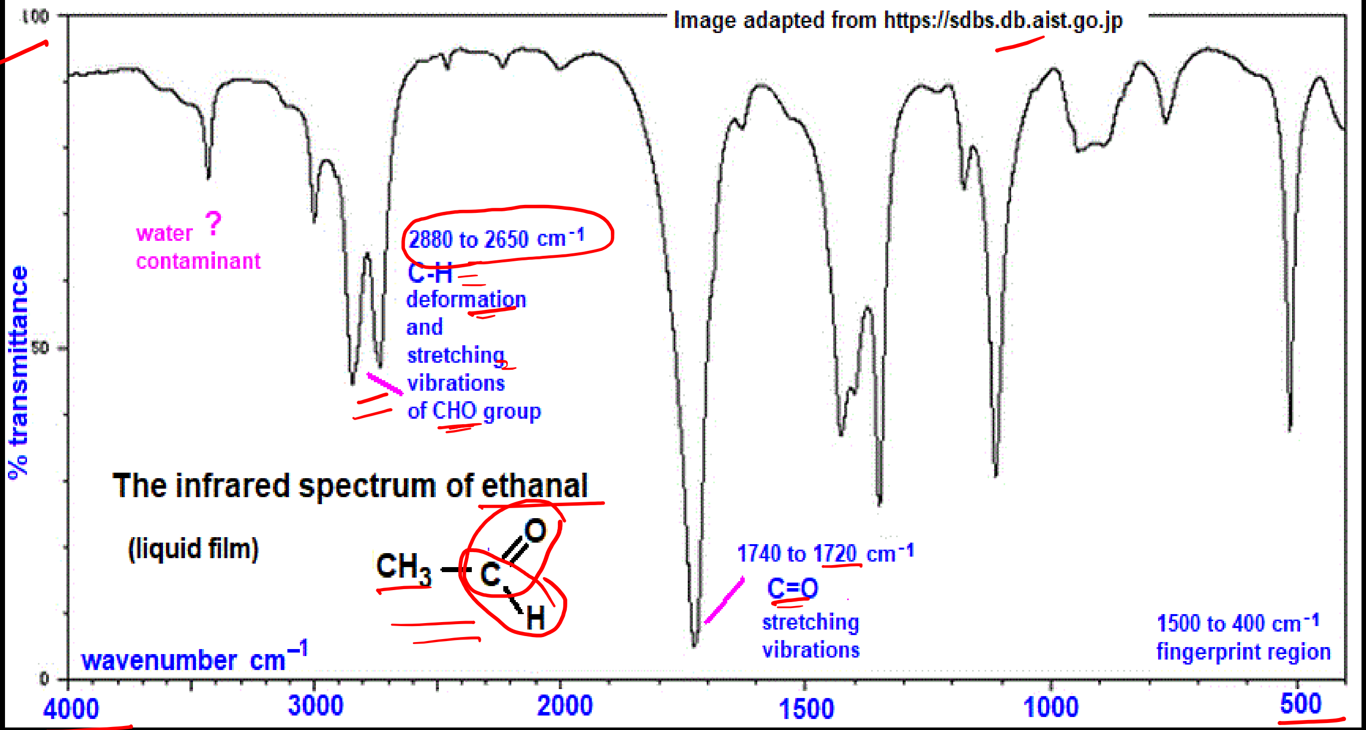


Image adapted from https://sdbs.db.aist.go.jp

The infrared spectrum of ethanal

(liquid film)

water ? contaminant

2880 to 2650 cm^{-1} C-H deformation and stretching vibrations of CHO group

1740 to 1720 cm^{-1} C=O stretching vibrations

1500 to 400 cm^{-1} fingerprint region

$\bar{\nu}$

$1500-700\ cm^{-1}$

https://www.sigmaaldrich.com/IN/en/technical-documents/technical-article/analytical-chemistry/photometry-and-reflectometry/ir-spectrum-table

IR-SPECTROSCOPY

Application of IR Spectroscopy

SN	Functional group	Org. Compound	IR Frequency	
1	O-H Str	Alcohol	3700-3585	free
			3550-3200	Intermolecular Bonding
			3200-2700	Intramolecular Bonding
		Carboxylic Acid	3300-2500	
2.	N-H Str	Aphetic P Amine	3400-3300	
		Sec. Amine	3350-3310	
3.	C-H Str	Alkane	3000-2840	
		Alkene	3100-3000	
		Alkyne	3333-3267	
		Aromatic	3030	
		Aldehyde	2830-2695	doublet
4.	C-H bend	Aromatic	2000-1650	overtone
5.	C=O Str	Aldehyde	1740-1720	
		Ketone	1725-1705	

IR-SPECTROSCOPY

Application of IR Spectroscopy

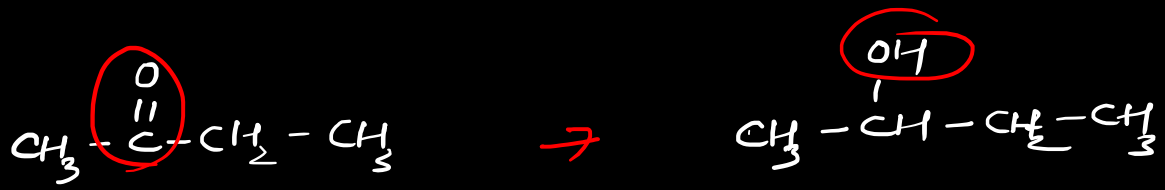
2. Distinction between H-Bonding ✓ → $\bar{\nu}$ ↓

3. Identification of Drug Substance ✓

4. Study of Chemical Reaction

Butan-2-one $\xrightarrow{\text{Red}}$ Butan-2-ol

(C=Ostr-1710 cm-1) (O-H str- 3300 cm-1)

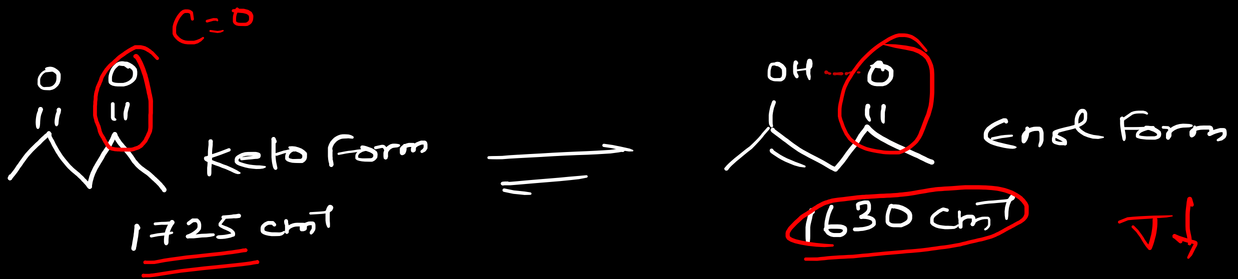


$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \rightarrow CH_3-\overset{\overset{OH}{|}}{CH}-CH_2-CH_3$$

IR-SPECTROSCOPY

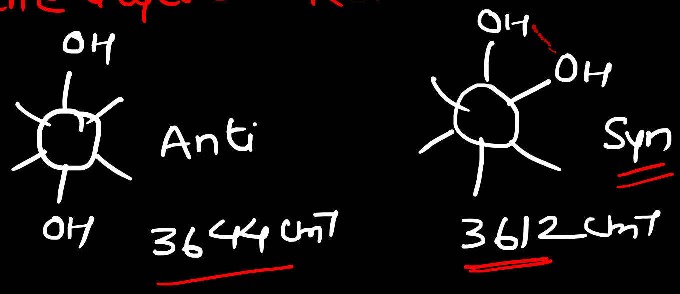
Application of IR Spectroscopy

5. Study of Keto-Enol Tautomerism

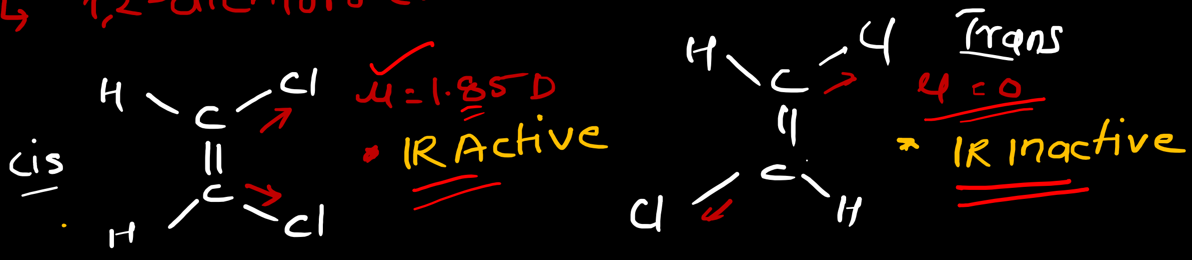


6. Study of Isomerism

↳ Ethylene Glycol - Rotational Isomerism



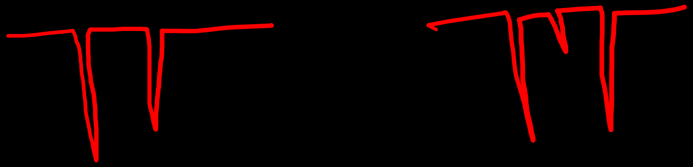
↳ 1,2-dichloro Ethane



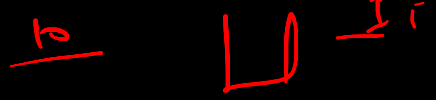
IR-SPECTROSCOPY

Application of IR Spectroscopy

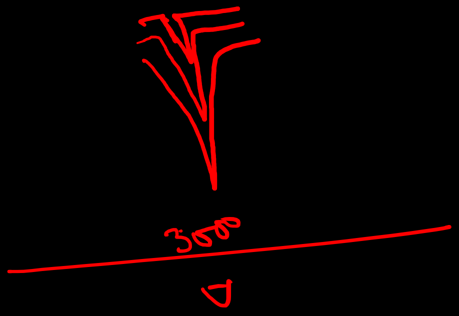
7. Determination of impurities



8. Quantitative Estimation of organic compounds by using peak Intensity or optical density or Abs



$$\boxed{A = \log \frac{1}{T}}$$



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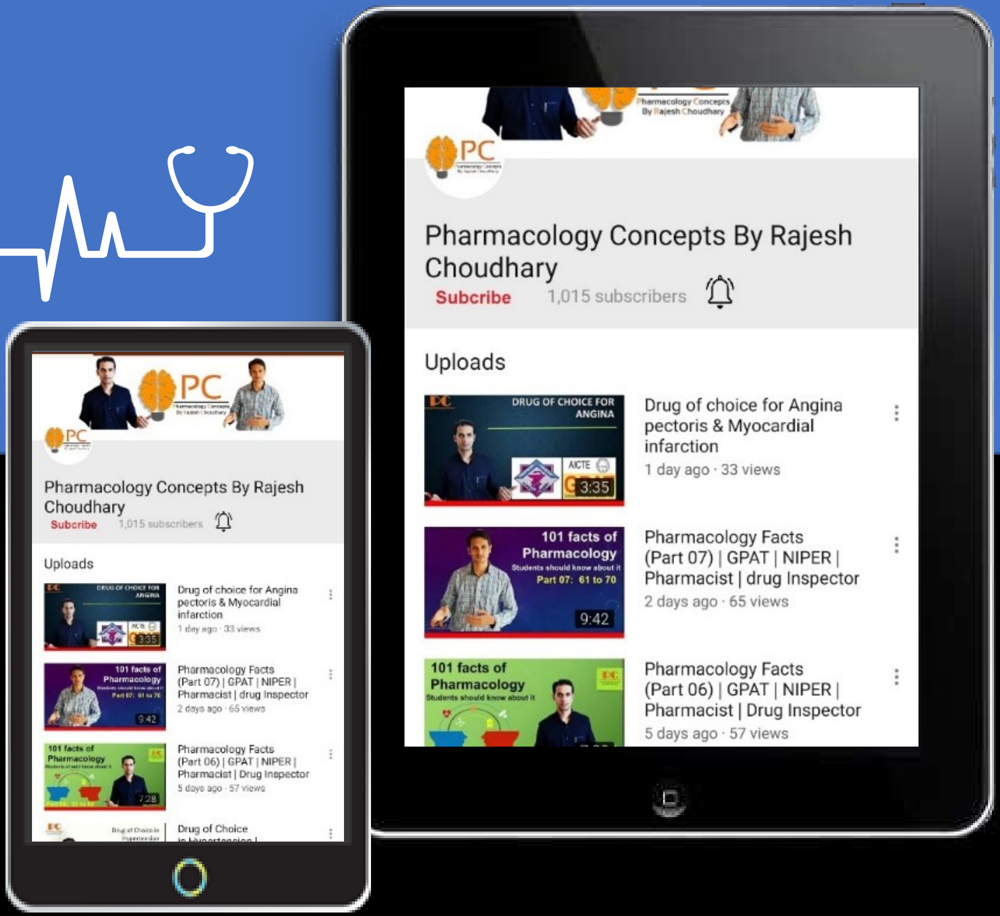

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