

# Spectroscopy

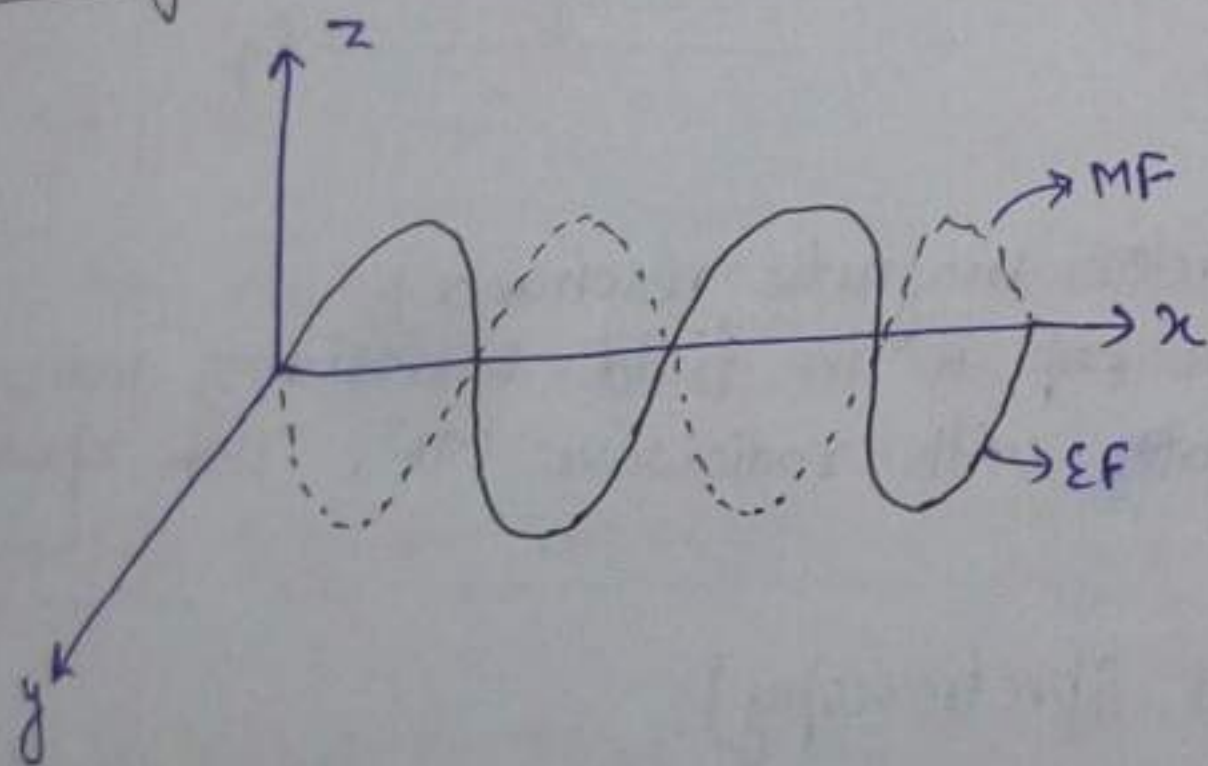
spectro → radiation, copy → measurement

→ Branch of chemistry which deals with the measurement of radiation. It helps to determine the structure of compd by interaction of electromagnetic radiation with matter.

Advantage of spectroscopy:-

- i) Very less quantity of sample required.
- ii) To obtain the result, usually less time is required.
- iii) The sample can be reused again.
- iv) Results obtain are reliable (i.e. less error)

Electromagnetic radiation:-



- wave length → Dist. b/w two consecutive crest or trough (m/cm)
- Wave number → The no. of waves passing through a unit length.
- frequency → The no. of waves passing through a point in one sec (hz)

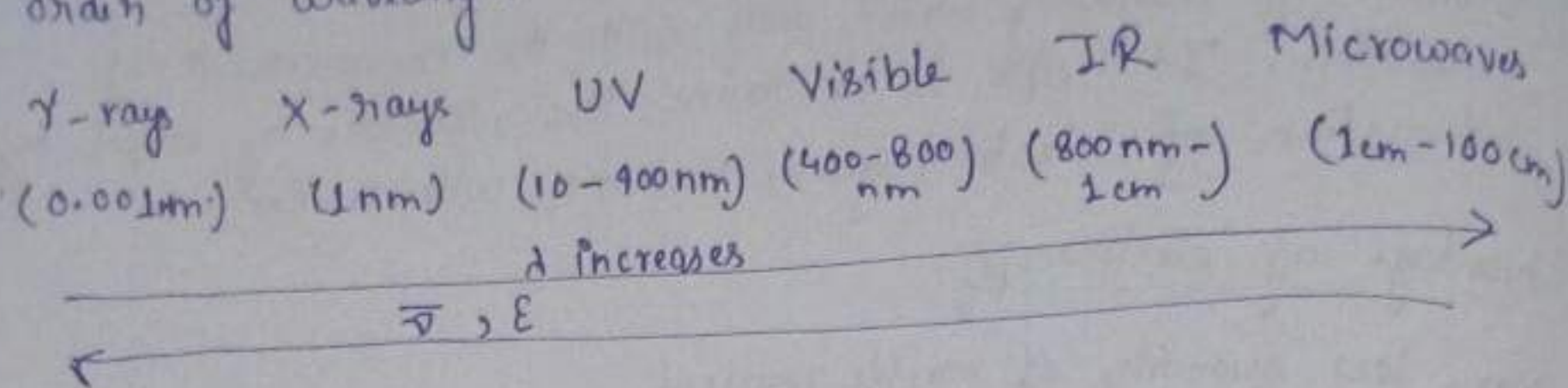
$$E = \frac{hc}{\lambda}$$

$$E \propto \nu \propto \frac{1}{\lambda} \propto \bar{\nu}$$



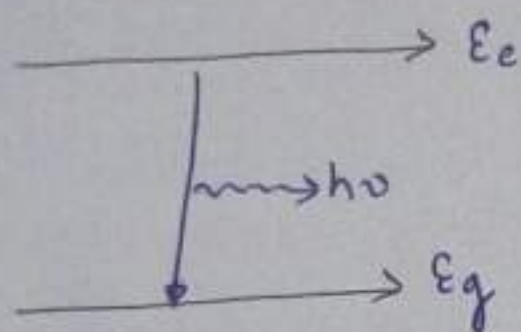
## Electromagnetic Spectrum:-

The orderly arrangement of electromagnetic radiation in increasing order of wavelength.

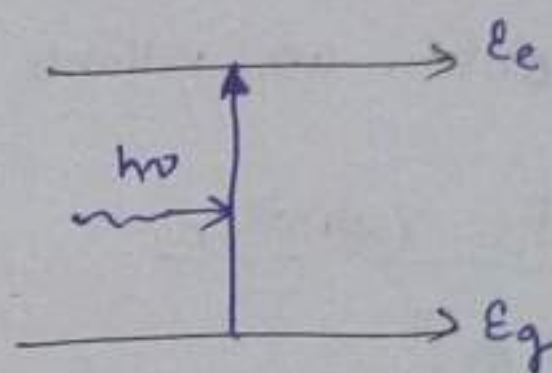


• Spectrum are of two types :-

1) Emission Spectrum



Absorption spectrum



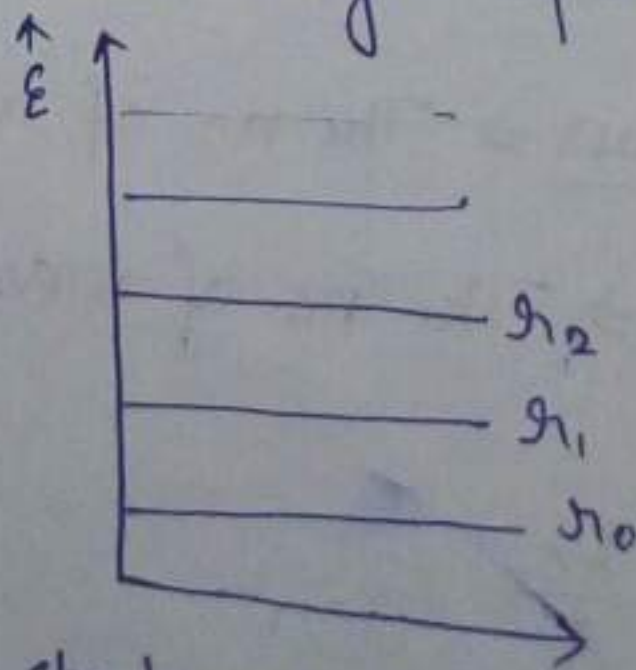
1) Radiowave:- NMR (nuclear magnetic resonance)

In a compound, when we keep it in field containing radiowaves then nucleus MF resonate with radiowave MF. Then spectrum so obtained is NMR.

2) Microwave:- (Rotational Spectroscopy)

If a microwave is passed through any molecule, the molecule starts rotating. We can find bond length of a molecule with this spectroscopy.

The energy gap b/w 2 energy levels is  $0.2\text{ KJ/mol}$ .



3) Infrared:- (Vibrational rotational spectroscopy)

We can find out the f.g. present in any compound when IR is passed in any compd, rotation & vibration starts in it.



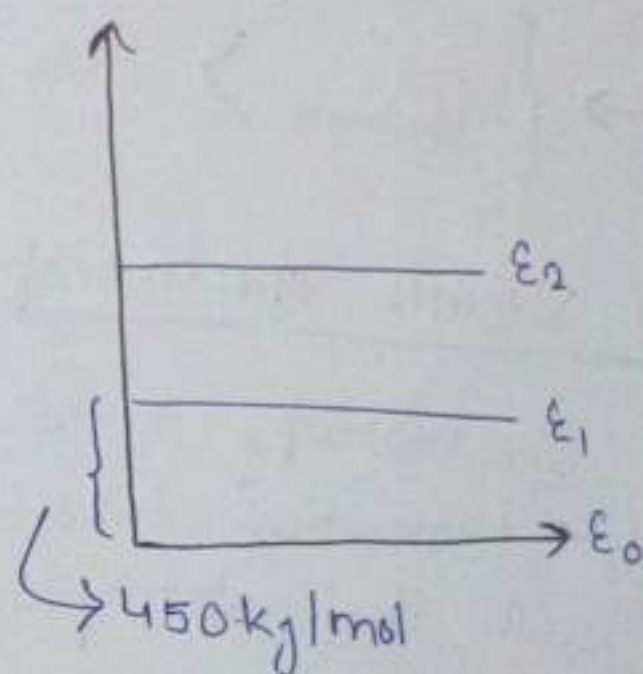
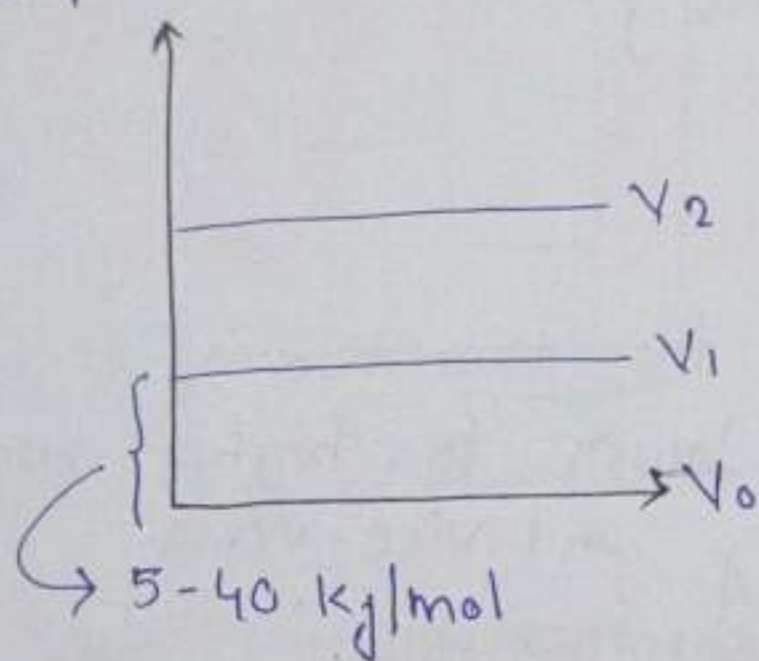
in increasing  
microwaves  
1cm - 100cm

## UV-Visible :- (electronic spectroscopy)

In this we observe transition of  $e^-$  from one energy level to other.

UV  $\rightarrow$  200 - 400 nm } use in electronic spectroscopy  
Visible  $\rightarrow$  400 - 800 nm }

It detect the no. of double bond, conjugated double bond. 200 - 400 nm is the region for unsaturated compound so this range is preferred.  $\leftarrow$  below 200 nm is the range of saturated compound.



radio wave  
spectrum

Transition occur at atomic level is atomic spectroscopy and at molecular level is molecular spectroscopy.

## • Different type of molecular energy :-

① Translational Energy :- Energy associated with the uniform motion of molecule as whole.

$$E_{\text{trans}} = \frac{3}{2} KT$$

{ Avg energy in a particular direction =  $\frac{1}{2} KT$  }

② Rotational Energy :- Energy due to rotation of molecule.

$$E_{\text{rot}} = \frac{1}{2} I \omega^2$$

③ Vibrational energy :-

$$E_{\text{vib}} = \left( v + \frac{1}{2} \right) h \nu_0$$



Energy due to vibrations of atoms in the molecule about its equilibrium position is known as vibrational energy.

→  $V$  is the vibrational quantum no. (may have value 0 or +ve)  
 $\epsilon_0$  is the vibrational energy.

⑥ Electronic Energy:- Electronic energy is the energy associated with the transition of electron or due to motion of electron or due to various electronic arrangement.

$$\rightarrow \{E_{\text{electronic}} > E_{\text{vib}} > E_{\text{rot}} > E_{\text{trans}}\}$$

→ UV Visible spectroscopy:-

This spectroscopy is associated with the transition of  $e^-$  in which transition takes place from lower to higher energy level with the absorption of energy and vice-versa.

This is also known as electronic spectroscopy

↓  
as it involves transition of electrons within a molecule or ions from a lower to higher electronic energy level or vice-versa by absorption or emission of radiations falling in the UV visible range of electromagnetic spectrum respectively.

UV VIBGYOR

UV		VIBGYOR	
Far UV region	near UV region	Visible	
100 nm	300 nm	400 nm	800 nm

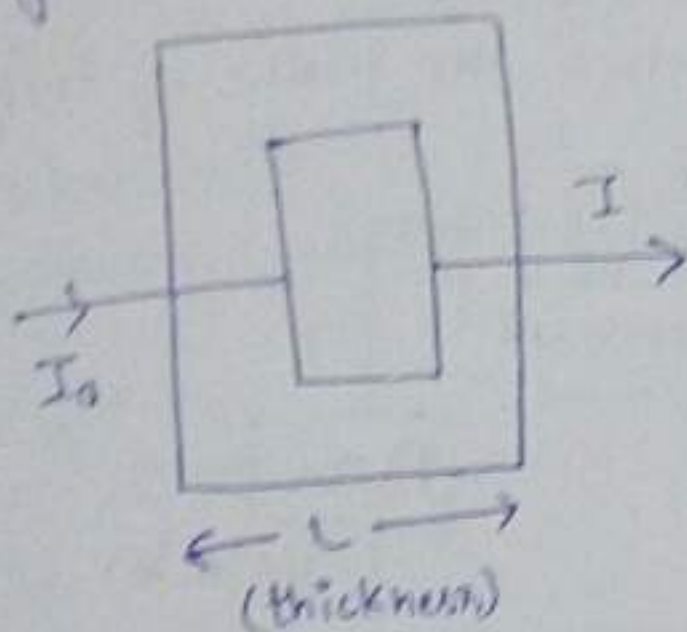
With the help of this spectroscopy we can find kinetics of certain reactions, no. of conjugated double bonds as well as aromatic conjugation, dissociation constant of acids & bases, molecular wt., detect impurities.



There are two laws known as laws of absorbance →

### Lambert's Law :-

It states that when a beam of monochromatic light is passed through an absorbing medium of certain thickness, the rate of intensity of light is directly proportional to the intensity.



$$-\frac{dI}{dL} \propto I$$

$$\frac{dI}{dL} = -kI$$

$$\int_{I_0}^I \frac{dI}{I} = -\int_0^L k dL$$

$$\log \frac{I}{I_0} = -kL$$

$$\Rightarrow \boxed{I = I_0 e^{-kL}}$$

$$\log \frac{I}{I_0} = \frac{-k}{2.303} L$$

$$\boxed{\log \frac{I}{I_0} = \epsilon L}$$

$\epsilon$  = absorption coefficient of absorbing medium  
 $= \frac{-k}{2.303}$

$\log \frac{I}{I_0}$  is absorbance and represented as  $A$

$$\Rightarrow \boxed{A = \epsilon L}$$

$$\text{Also, } I = I_0 10^{-at} ; a = \frac{k}{2.303}$$

$a$  = extinction coefficient of absorbing medium

① Beer's Law :- It states that when a beam of monochromatic light is passed through an absorbing medium of certain thickness, the rate of intensity of light is directly proportional to the intensity as well as the conc. of sol<sup>n</sup>.



15 Sept 2022

$c$  is in  $\text{mol/L}$

$$\frac{-dI}{dL} \propto I \cdot c$$

$$\Rightarrow \int_{I_0}^I \frac{dI}{I} = \int_0^L -kc dL \Rightarrow \left[ \log \frac{I}{I_0} = \frac{-k}{2.303} cL \right]$$

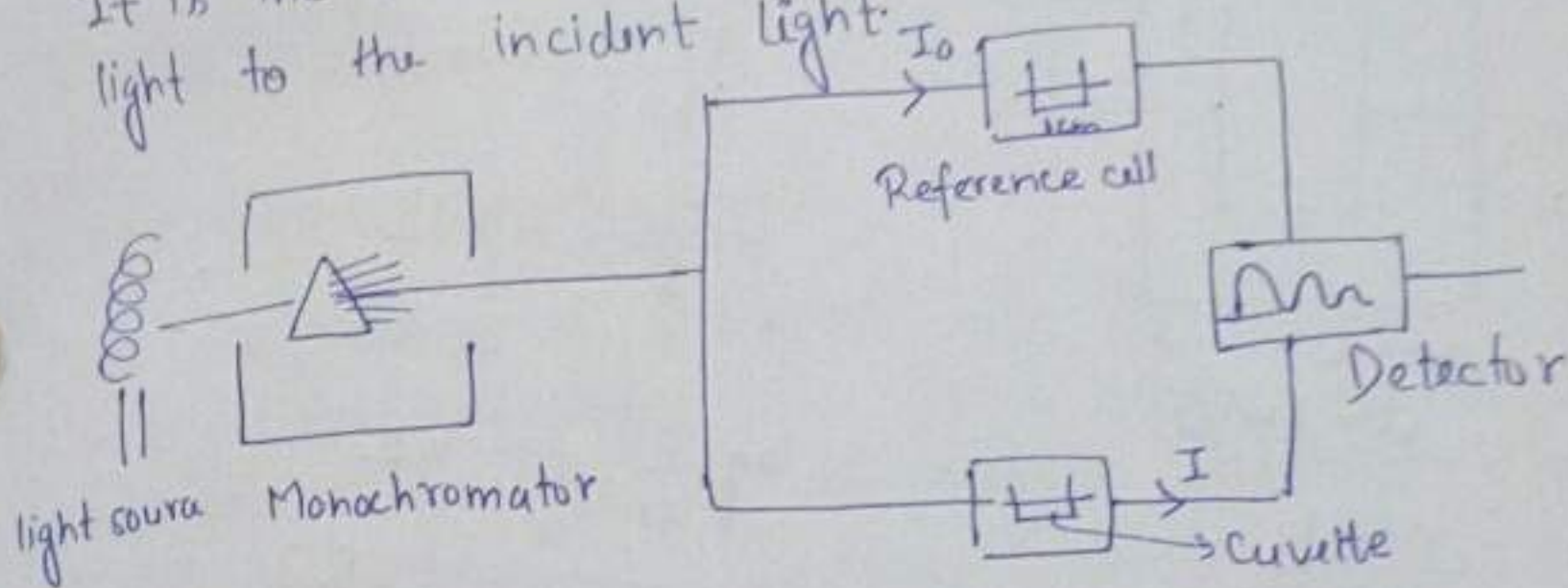
$$\Rightarrow \boxed{A = \epsilon \cdot c \cdot L}$$

$$\left| \begin{array}{l} \ln \frac{I}{I_0} = -k c L \\ I = I_0 e^{-k c L} \end{array} \right|$$

$\epsilon$  = molar absorption coefficient

### UV Visible Spectrometer:-

It is the instrument which measures the ratio of transmitted light to the incident light.



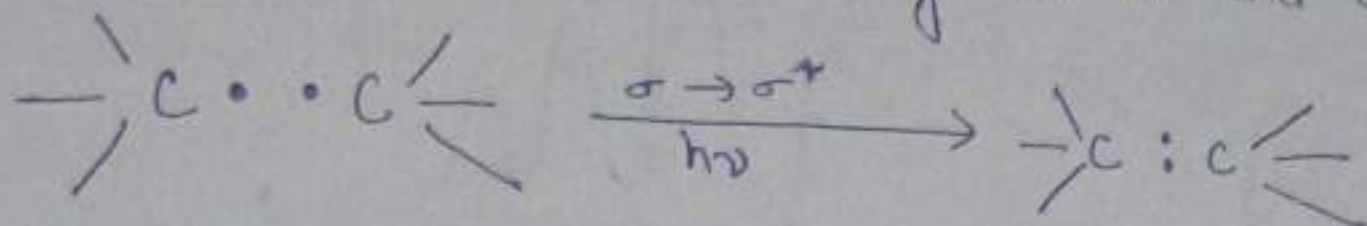
- light source can be of tungsten filament lamp (emit radiation of 375 nm or Deuterium discharge lamp (emit radiation of above 375 nm), so that we can get UV visible rays.
- Since the light splits in two beams so it is called double beam spectrometer.
- Cuvette :- It is made of silica and quartz and used to take sample so that it doesn't absorb light (only sample will).
- Take 1 mg of sample and dissolve it in any solvent. Make it upto 100 ml and from that take 1 ml and put that in cuvette.
- First pass the light through solvent only no light will be absorbed.
- Then through sample solution  $\Rightarrow$  some light will be absorbed (due to double bond) and a light of particular wavelength will be absorbed & rest radiated which pass through detector & form spectrum.



$$I_{\text{abs}} = I_0 - I = I_0(1 - e^{-kL})$$

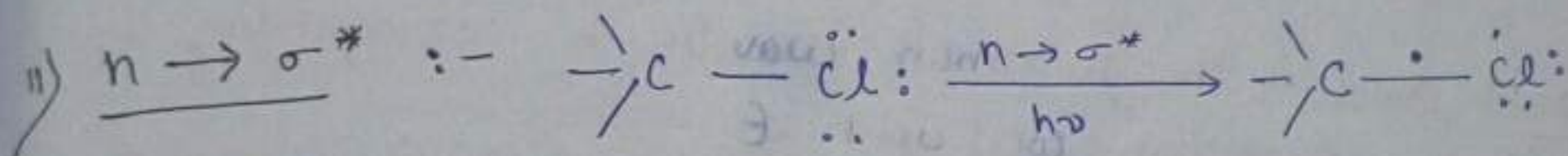
Types of electronic transitions:-

i)  $\sigma \rightarrow \sigma^*$  It is formed by end to end overlapping

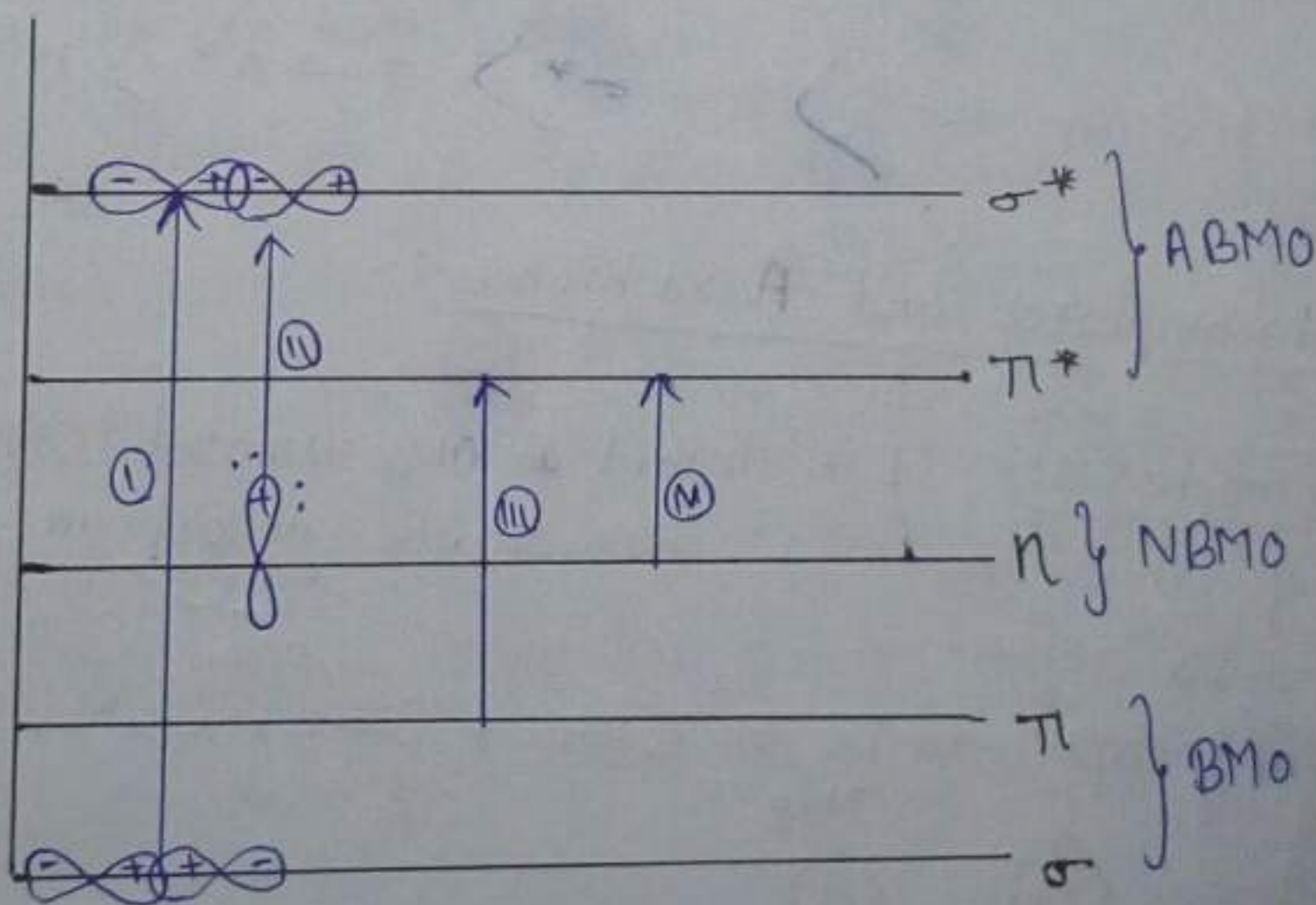


The  $e^-$ s moves from gs to es.

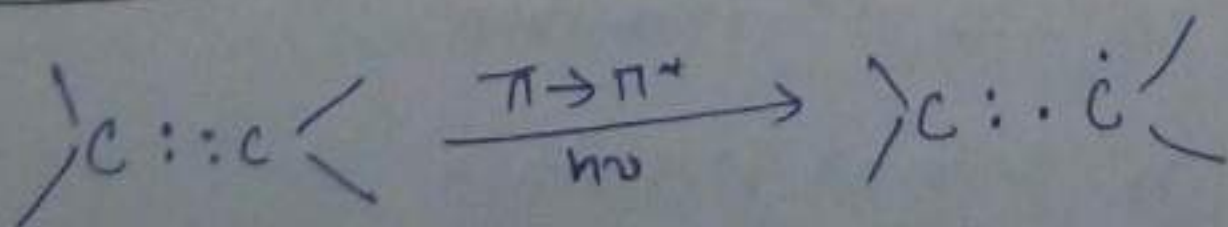
This takes place in case of saturated compounds. It consists of wavelength range (120 - 150) nm.



Energy Level Diagram:-



iii)  $\pi \rightarrow \pi^*$  :- It takes place in unsaturated compound.



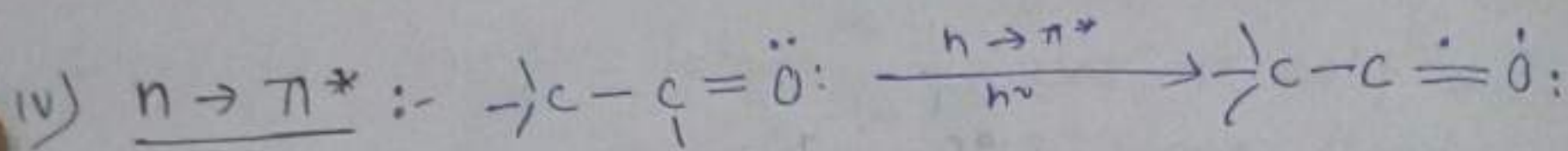
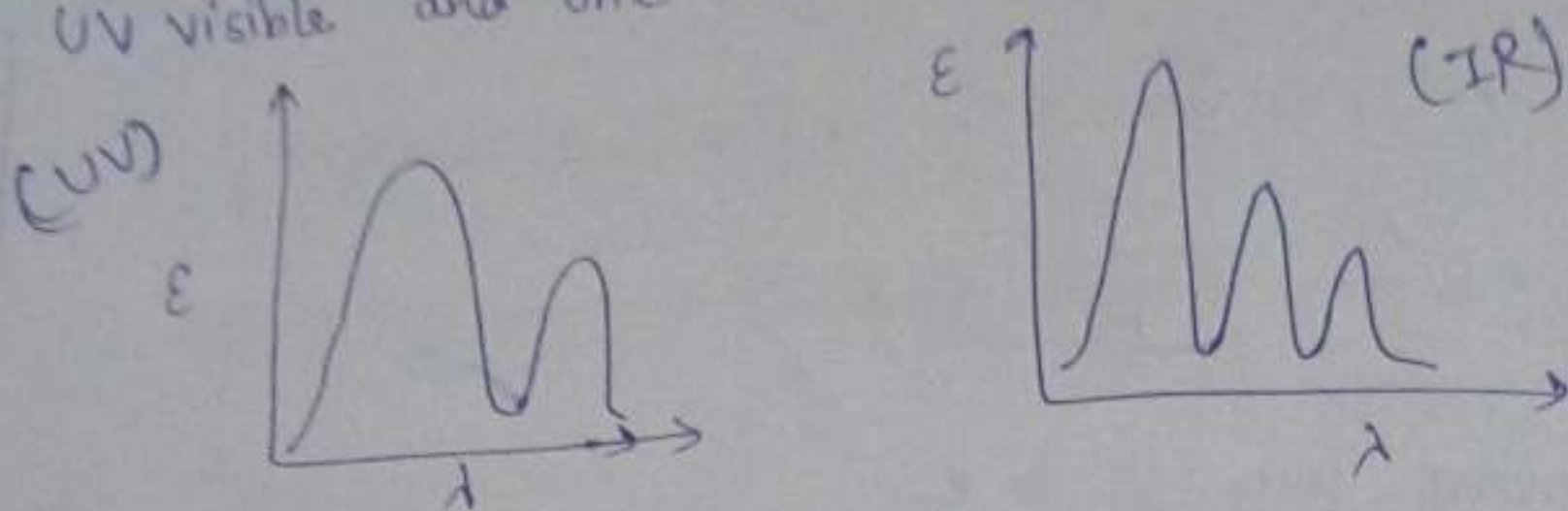
for double bond  $\rightarrow \sim 185 \text{ nm}$

for conjugated system  $\rightarrow \sim 200 \text{ nm}$

wavelength



Peak in UV visible spectroscopy is broader than IR spectroscopy because multiple transitions are taking place simultaneously in UV visible and one transition at a time in IR.



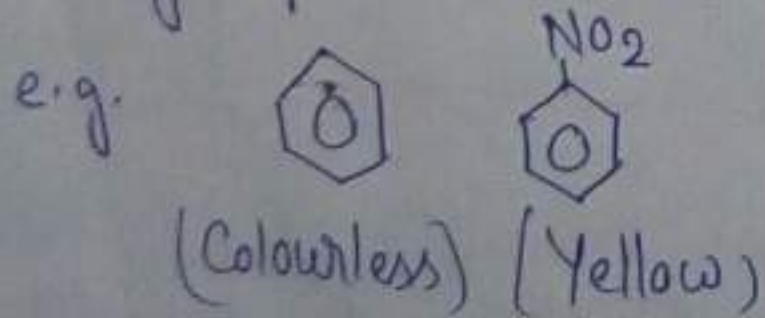
\*  $\lambda_{\text{max}}$  :-  $\lambda_{\text{max}}$  is the maximum wavelength corresponding to maximum absorption coefficient  $\epsilon$ .

Order of energy :-  $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$

\* Chromophores and Auxochromes :-

Chromophores :- It is defined as any isolated covalently bonded group that shows a characteristic absorption in the UV or visible region.

These groups can be  $\rightarrow \text{C}=\text{C}$ ,  $\text{C}\equiv\text{C}$ ,  $\text{C}\equiv\text{N}$ ,  $\text{C}=\text{O}$ ,  $\text{N}\equiv\text{N}$



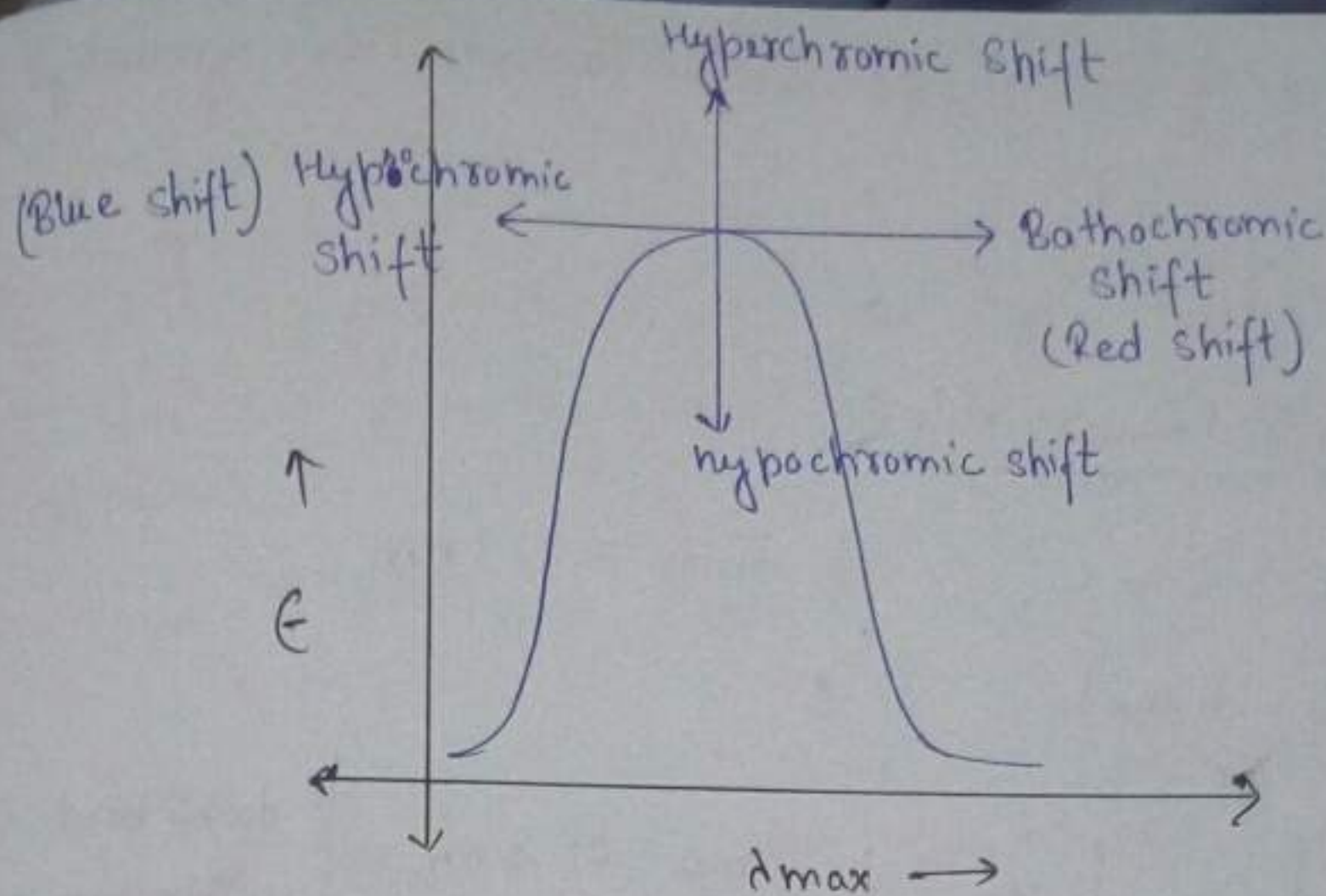
It is of 2 types  $\rightarrow$  ①  $\pi \rightarrow \pi^*$  transition  
②  $n \rightarrow \pi^*$  transition

Auxochromes :-  $\rightarrow$  They are not self chromophores but their presence will increase the intensity of absorption.  
enhancing colour  
e.g.  $-\text{OH}$ ,  $-\text{OR}$ ,  $-\text{SH}$ ,  $-\text{NR}_2$



spectroscopy  
usually in

21 Sept/2018



i) Bathochromic shift:- Shift of absorption maxima towards longer wavelength is called bathochromic shift. It is due to the presence of auxochromes.

ii) Hypsochromic shift:- If we decrease the polarity of solvent (strength of double bond dec.) or double bond break into single bond ( $\lambda = \text{bond} > \lambda - \text{bond}$ ), this lead to blue shift. (Due to this, molecule's symmetry get distorted)

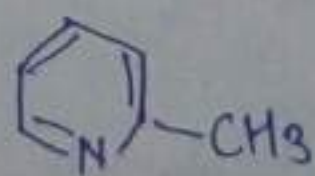
iii) Hyperchromic shift:- It is the effect leading to increase in the intensity of absorption max i.e.  $\epsilon_{max}$ . The introduction of a auxochrome usually increase the intensity of absorption maximum.



(Pyridine)

$\lambda_{max} = 257 \text{ nm}$

$\epsilon_{max} = 2750$



(methyl pyridine)

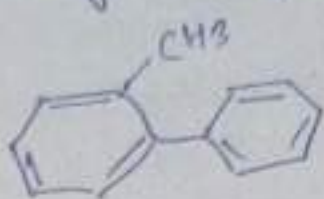
$\lambda_{max} = 262 \text{ nm}$

$\epsilon_{max} = 3560$

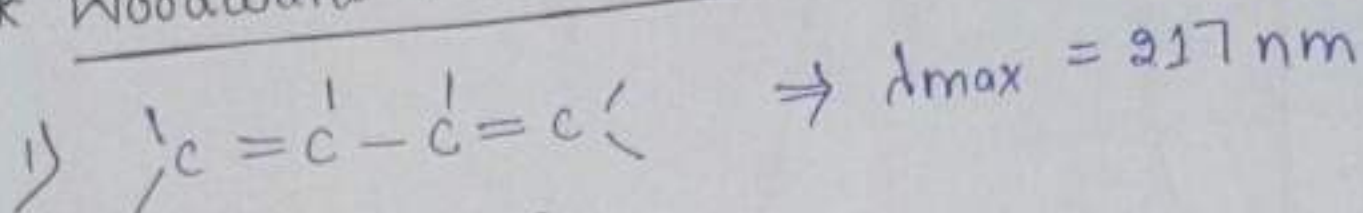
iv) Hypochromic Shift:- The decrease in intensity of absorption max ( $\epsilon_{max}$ ) is known as hypochromic shift.



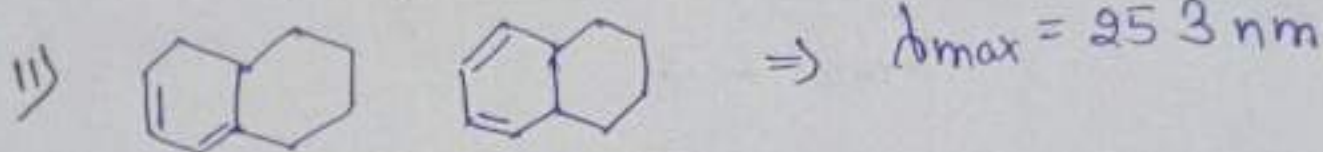
It is caused by the groups which distort the symmetry of the molecule.



### \* Woodward Fieser Rule :-

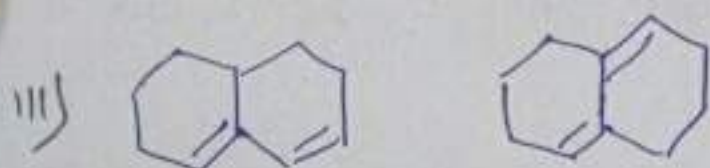


(acyclic diene)



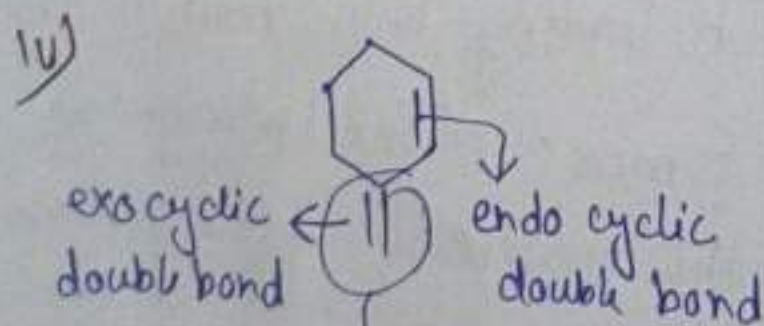
(Homocyclic diene)

(double bond in conjugated within same ring)

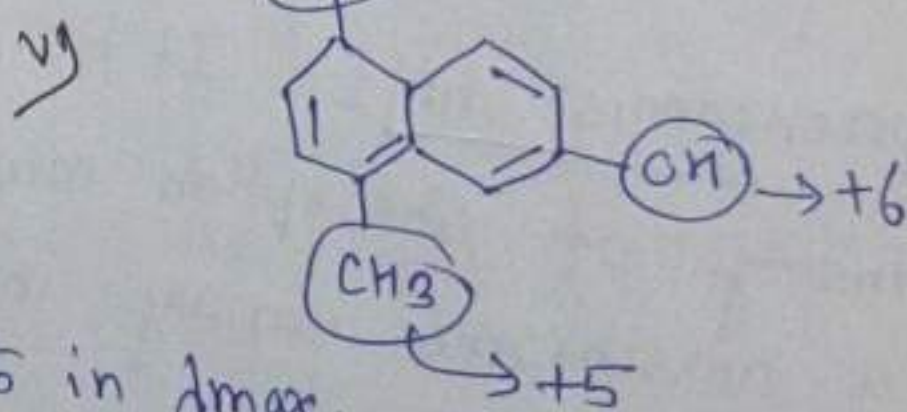


(Heterocyclic diene)

(conjugated double bond in different ring)

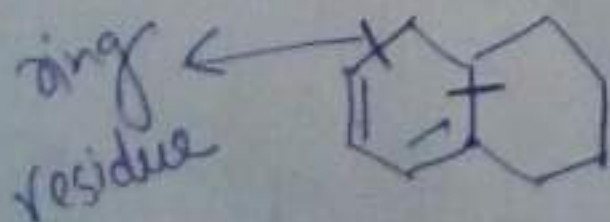


→ increment of +5 in  $\lambda_{\text{max}}$ .



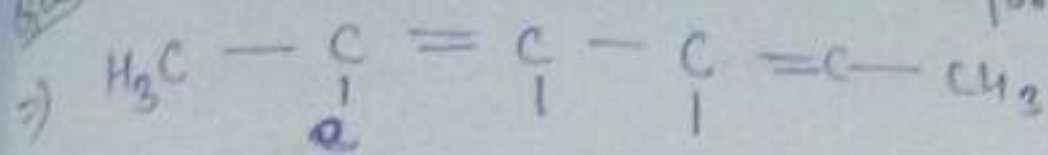
(group outside conjugated chain is not considered)

\* Single bond adjacent to double bond in conjugated chain is called ring residue. It produces an increment of +5.





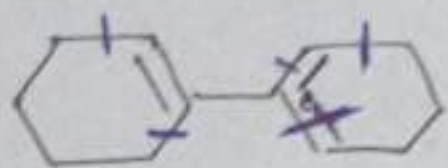
Ques:- Find the absorption max for 2,4 hexadiene



Since it is a acyclic diene, so the basic value = 217 nm  
But, due to 2 methyl substituents, increment of  $(2 \times 5) = 10$  nm appears.

$$\therefore \lambda_{\text{max}} = 227 \text{ nm} \text{ Ans.}$$

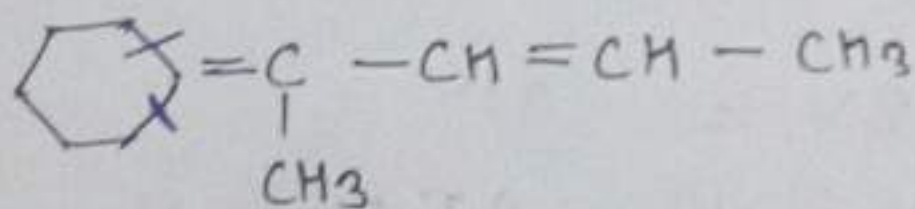
Ques:-



Since it is a heterocyclic diene, so basic value = 214 nm  
4 Ring residue  $(4 \times 5) = 20$  nm

$$\Rightarrow \lambda_{\text{max}} = 234 \text{ nm} \text{ Ans.}$$

Ques:-



Basic value = 217 nm

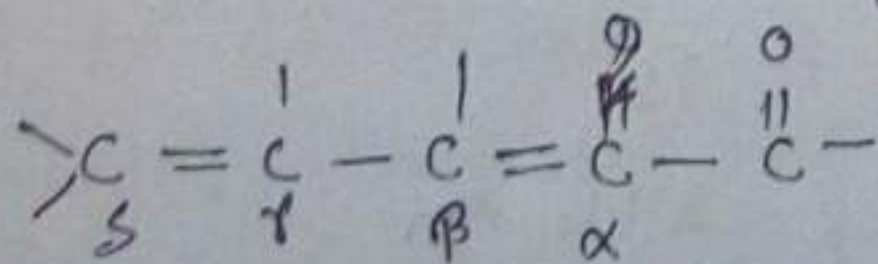
2 ring residue =  $(2 \times 5) = 10$  nm

1 exocyclic double bond = 5 nm

2 methyl substituents =  $(2 \times 5) = 10$  nm

$$\Rightarrow \lambda_{\text{max}} = 242 \text{ nm} \text{ Ans.}$$

\*  $\alpha, \beta$  unsaturated carbonyl compounds:- (Enones)



$$\lambda_{\text{max}} = 215 \text{ nm}$$

If methyl or ring residue is present at  $\alpha$  position,

then increment = +10 nm

$\beta$  = +12 nm

$\gamma, \delta$  = +18 nm

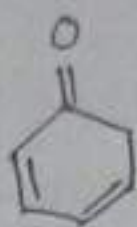


for exocyclic double bond = +5 nm  
 homo anular diene = +39 nm

Basic value = 215 nm

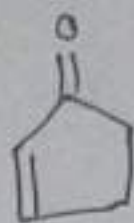
Homo anular diene = +39 nm

e.g.



BV = 215 nm

(6-membered ring)

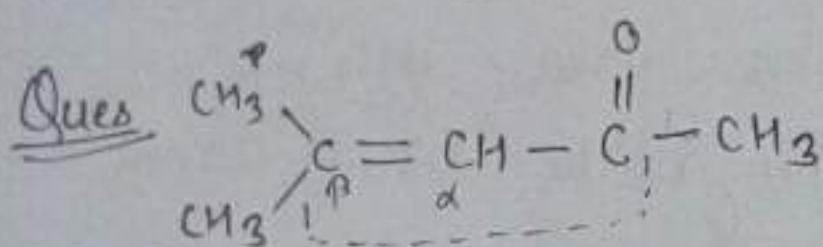


BV = 202 nm

(5-membered ring)

OH at  $\alpha$  = 35

OH at  $\beta$  = 30

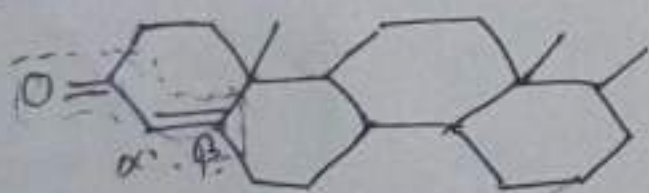


BV = 215

2 CH<sub>3</sub> gp at  $\beta$  =  $12 \times 2 = 24$

239  
 Ans

Que:-

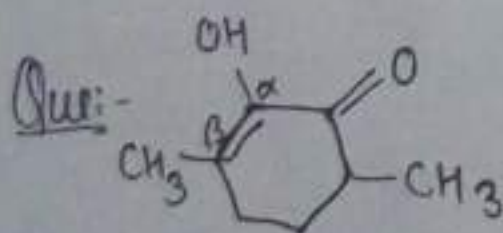


BV = 215

Ring residue at  $\beta$  position =  $2 \times 12 = 24$  nm

1 exo-cyclic double bond = +5 nm

244 nm



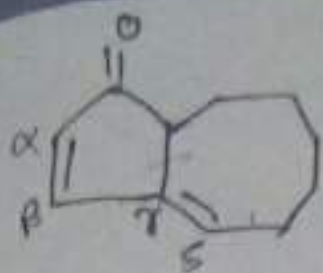
BV = 215 nm

ring residue at  $\beta$  = +12 nm

OH gp at  $\alpha$  = +6 nm 3.5 nm

CH<sub>3</sub> at  $\beta$  = 12,  
274 nm





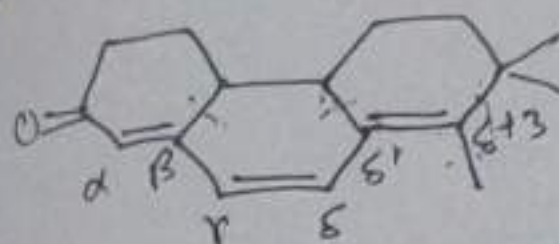
$$BV = 202 \text{ nm}$$

exo-cyclic at  $\gamma = +5 \text{ nm}$

1 Ring residue at  $\beta\gamma = +18 \text{ nm}$

1 ring " "  $\delta = +18 \text{ nm}$

1 double bond extended conjugation =  $+30 \text{ nm}$   
273



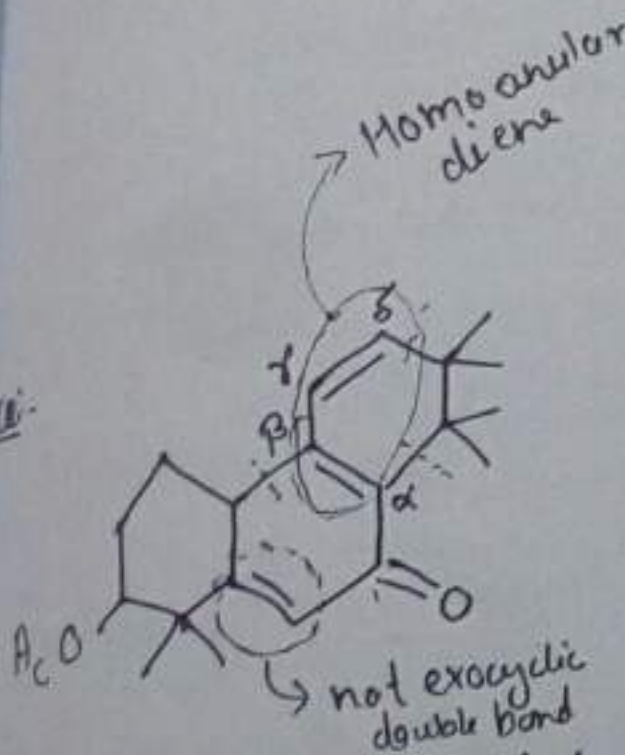
$$BV = 915 \text{ nm}$$

2 D.B. extended conj. =  $2 \times 80 = 60 \text{ nm}$

2 Ring residue + 1 chg at  $\delta + 3\delta + 2 = 3 \times 18 = 54 \text{ nm}$

2 exo cyclic =  $+5 \text{ nm} \times 2 = 10 \text{ nm}$

1 Ring residue at  $\beta = 12 \text{ nm}$   
354



Select most substituted chain

$$A \text{ B.V.} = 215 \text{ nm}$$

1. d.b. extending conj. =  $+30 \text{ nm}$

Ring residue at  $\delta \text{ C} = +10 \text{ nm}$

" " "  $\beta \text{ C} = +12 \text{ nm}$

" " "  $\delta \text{ C} = +18 \text{ nm}$

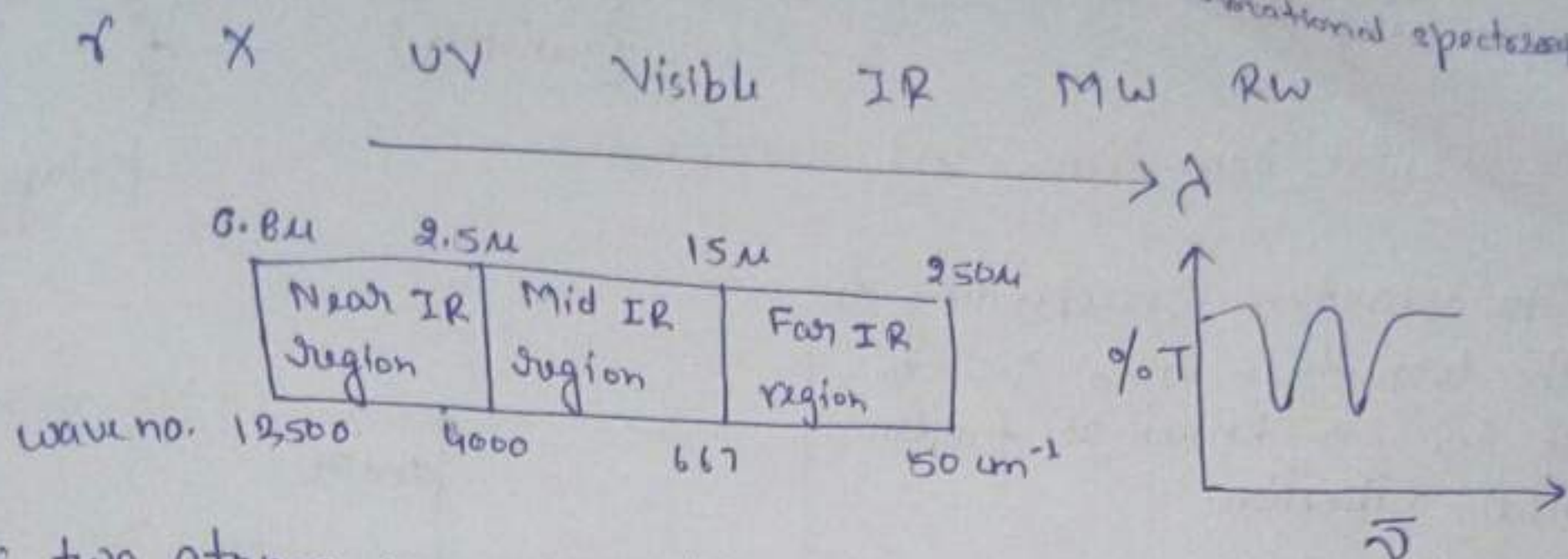
Homoanular diene =  $+39 \text{ nm}$   
+ 324 nm

A sol<sup>n</sup> of thickness 3 cm transmits 30% incident light  
 Calculate, the conc. of the sol<sup>n</sup> given extinction  
 coefficient  $\epsilon = 4000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ .

$$A = \epsilon \cdot c \cdot t \quad Tr = \frac{1}{A}$$

$$\frac{100}{30} = 4000 \cdot c \cdot 3$$



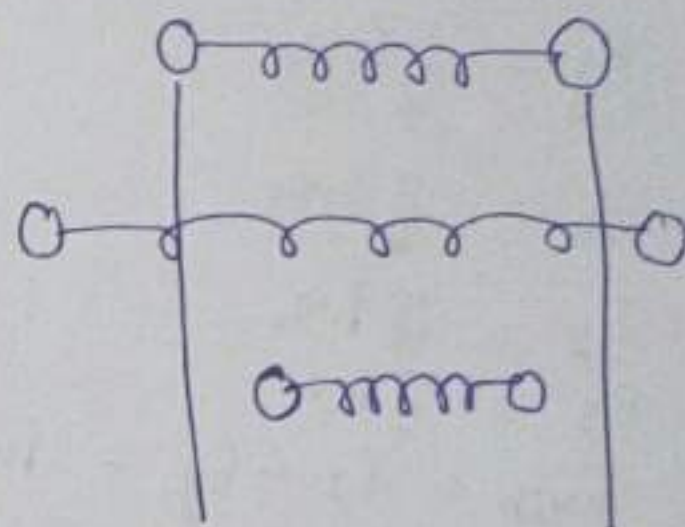


If two atoms are connected with string -

$$E = \frac{h}{2\pi} \sqrt{\frac{K}{\mu}} \quad ; \quad \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{K}{\mu}}$$

$K$  = spring constt / force constt

$\mu$  = reduced mass  $\frac{m_1 m_2}{m_1 + m_2}$

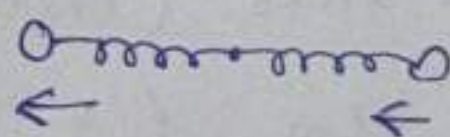
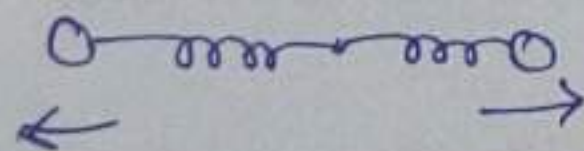


\* Two types of vibrations -

i) Stretching vibration (change in bl) ii) Bending vibrations (change in bond angle)

→ Symmetric (stretching in one direction)

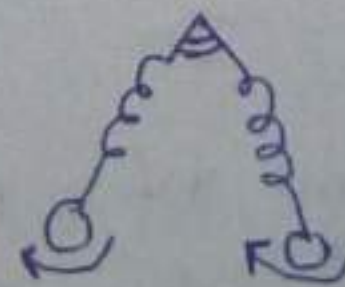
→ Asymmetric



Types of bending → (4)

i) Scissoring :- movement in opposite direction

ii) Rocking :- movement in same direction (angle remain constt).

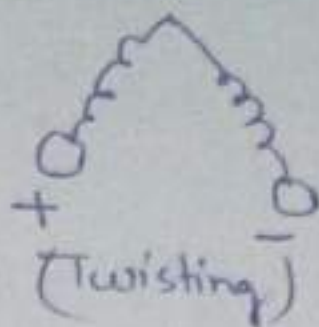


These take place in one plane

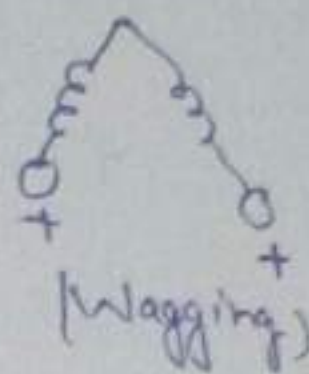
∴ In-plane bending vibrations.



i) Waggling } Out of plane  
 ii) Twisting } bending vibrations.



+ → above the plane  
 - → below



### \* Fundamental Vibrations and overtones:-

• The vibration corresponding to the transition from G.S. to 1st E.S. is known as fundamental vibration.

$$E_{vib} = (v + \frac{1}{2}) h\nu_0$$

$$E_g = \frac{1}{2} h\nu_0$$

$$E_1 = \frac{3}{2} h\nu_0$$

$$E_2 = \frac{5}{2} h\nu_0$$

$$E_3 = \frac{7}{2} h\nu_0$$

$$E_{vib} = E_1 - E_g = h\nu_0 \text{ (fundamental vibrational energy)}$$

• Any vibration other than fundamental vibration is known as overtone.

• Vibration corresponding to 2nd vibration stage from G.S. is known as 1st overtone.

$$E_{vib} = E_2 - E_g = 2h\nu_0 \text{ (Energy for first overtone)}$$

$$E_{vib} = E_3 - E_g = 3h\nu_0 \text{ ( " " 2nd overtone)}$$

⇒ Calculating no. of fundamental Vibrations :-

1) Non-linear polyatomic molecule:-

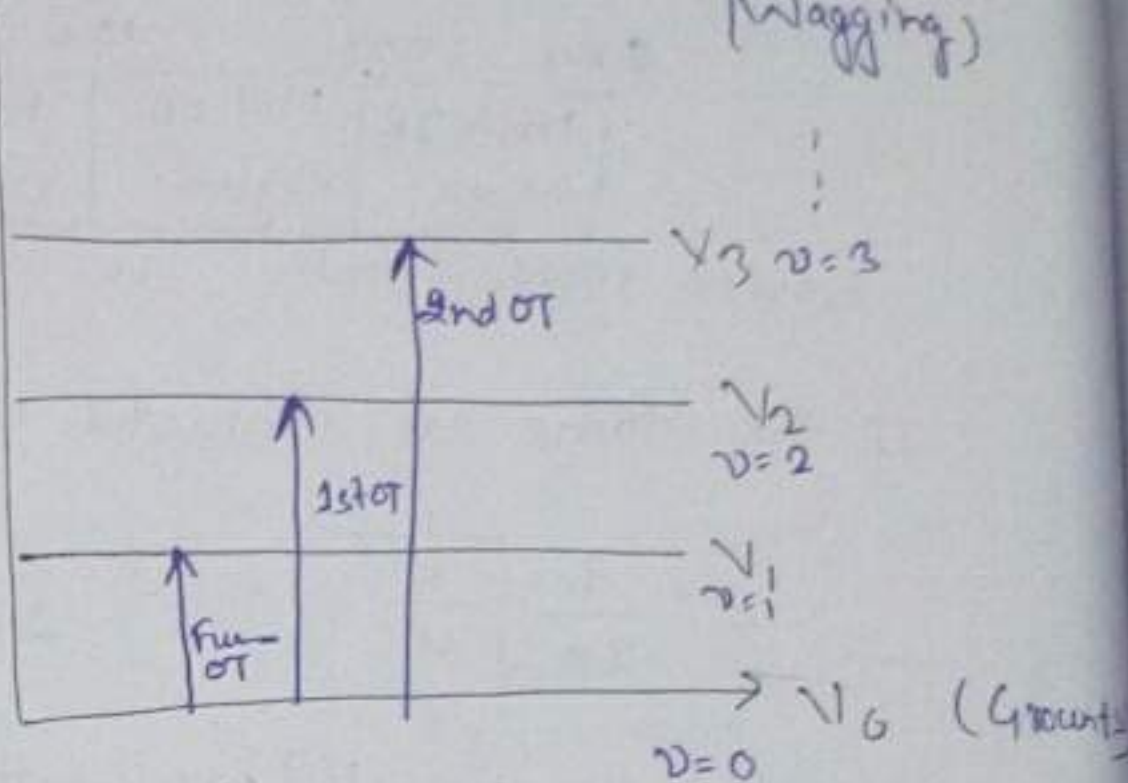
Let  $n$  be the no. of atoms in PA molecule

$$\Rightarrow \text{dof} = 3n$$

Translational dof = movement in straight line = 3

Rotational dof = 3

Vibrational dof = ?

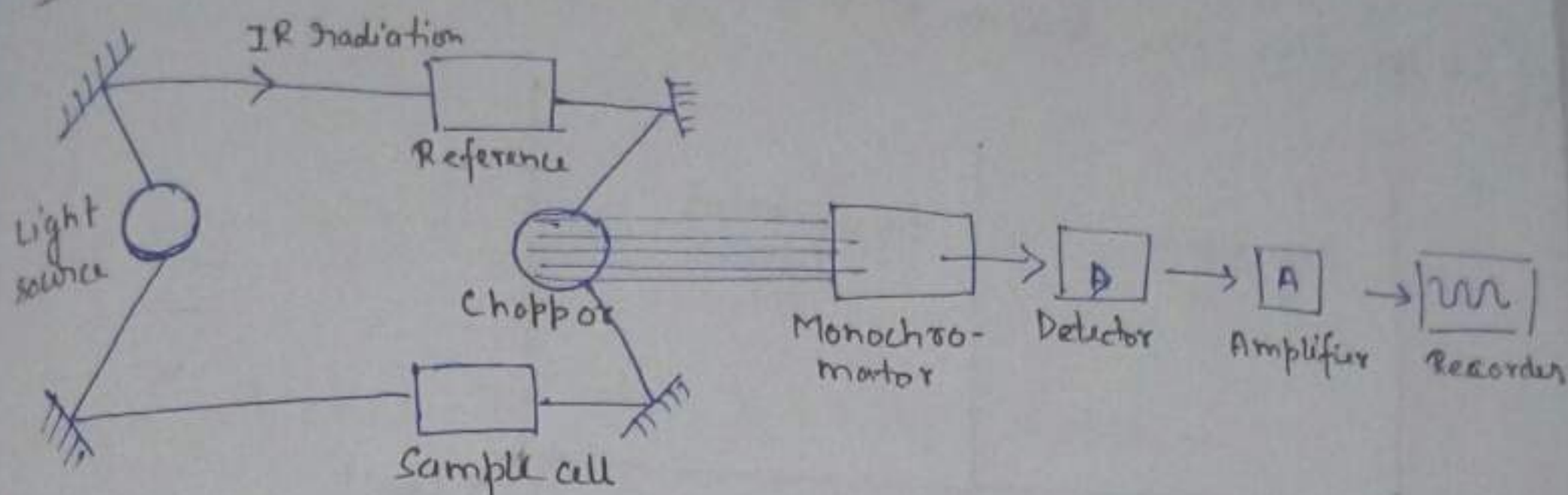




# Instrumentation :-

17 Nov 2018

## Schematic Diagram of IR Visible :-



Light source → ① Nernst Glower → • rod [Zr: Y: Erbium: 90: 7: 3]  
 • non conducting,  
 • emit IR radiation at 500°C.  
 • high intensity  
 ② Glower  
 ↓  
 • rod → SiC  
 • temp → 1300°C

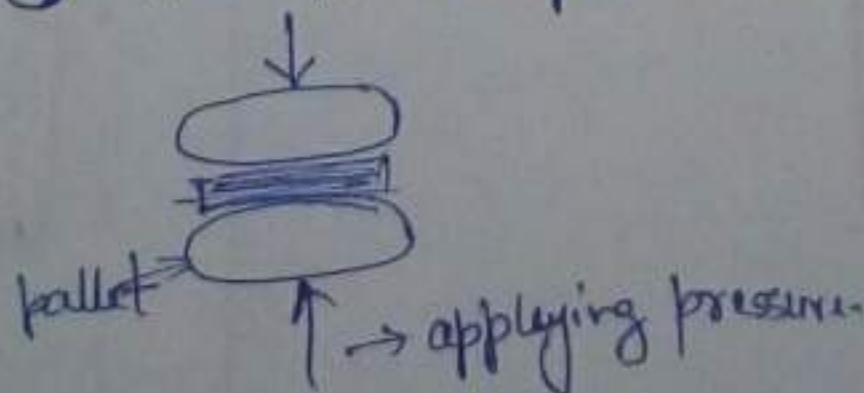
Detector → converts IR energy into electrical energy  
 Amplifier → inc. intensity of received electrical signal  
 Recorder → give IR spectrum.

## Sample preparation:-

There are 4 techniques for preparing solid samples:-

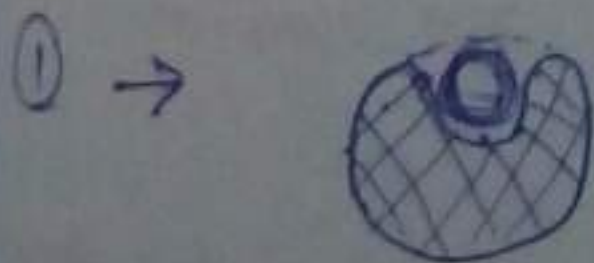
- ① Direct
- ② Pelletization
- ③ Mulling
- ④ Solution

② 1-2% sample + 99-98% of KBr



③ 1-2% sample + 95-98% KBr +

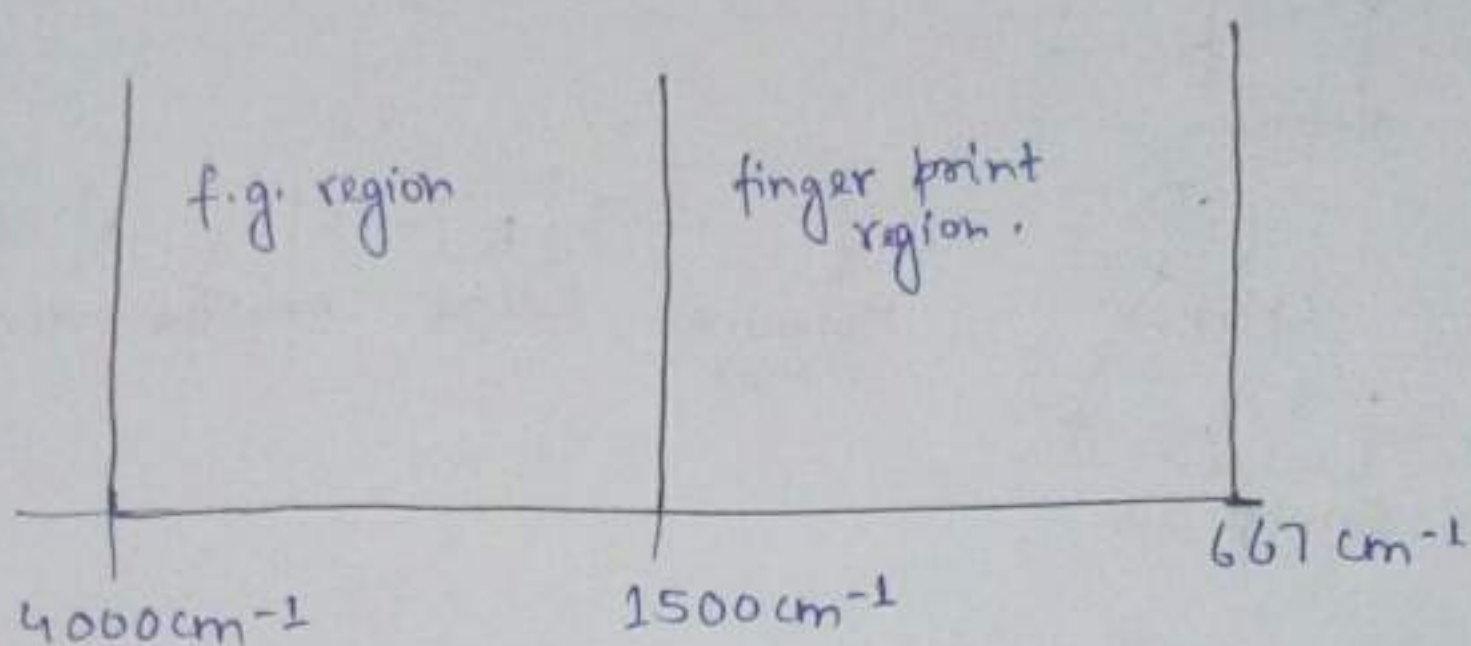
↓  
 make paste & put it b/w two pallets



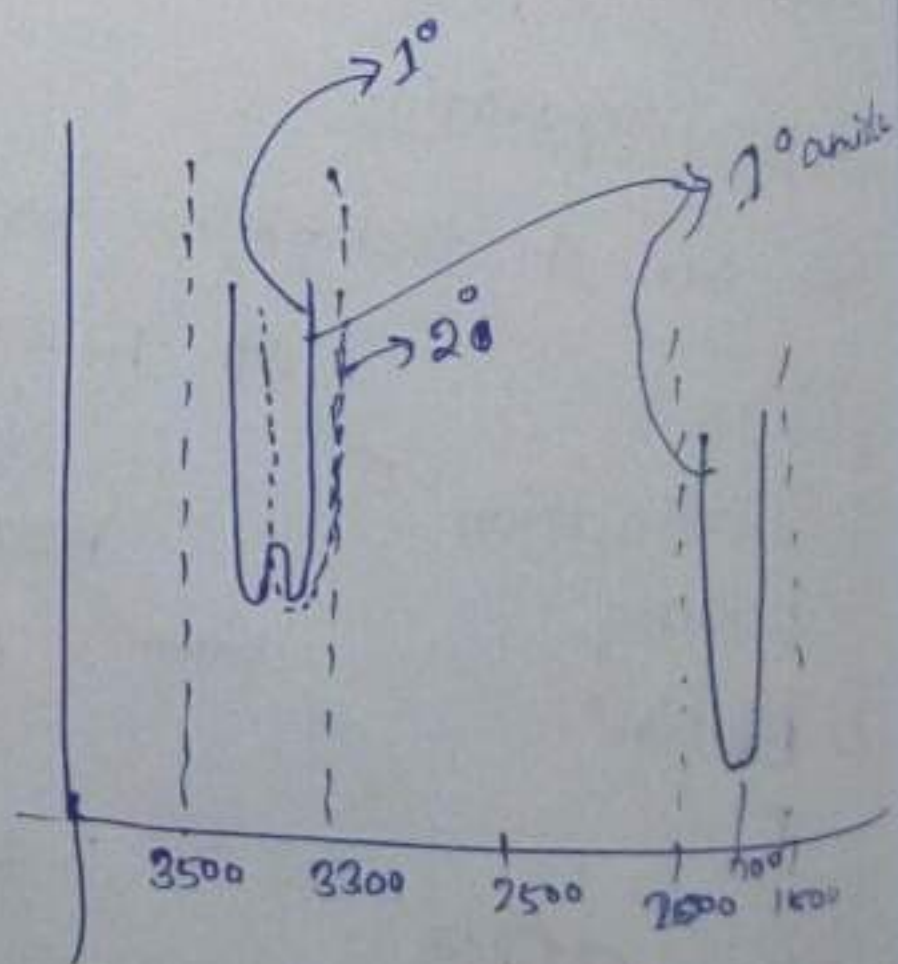
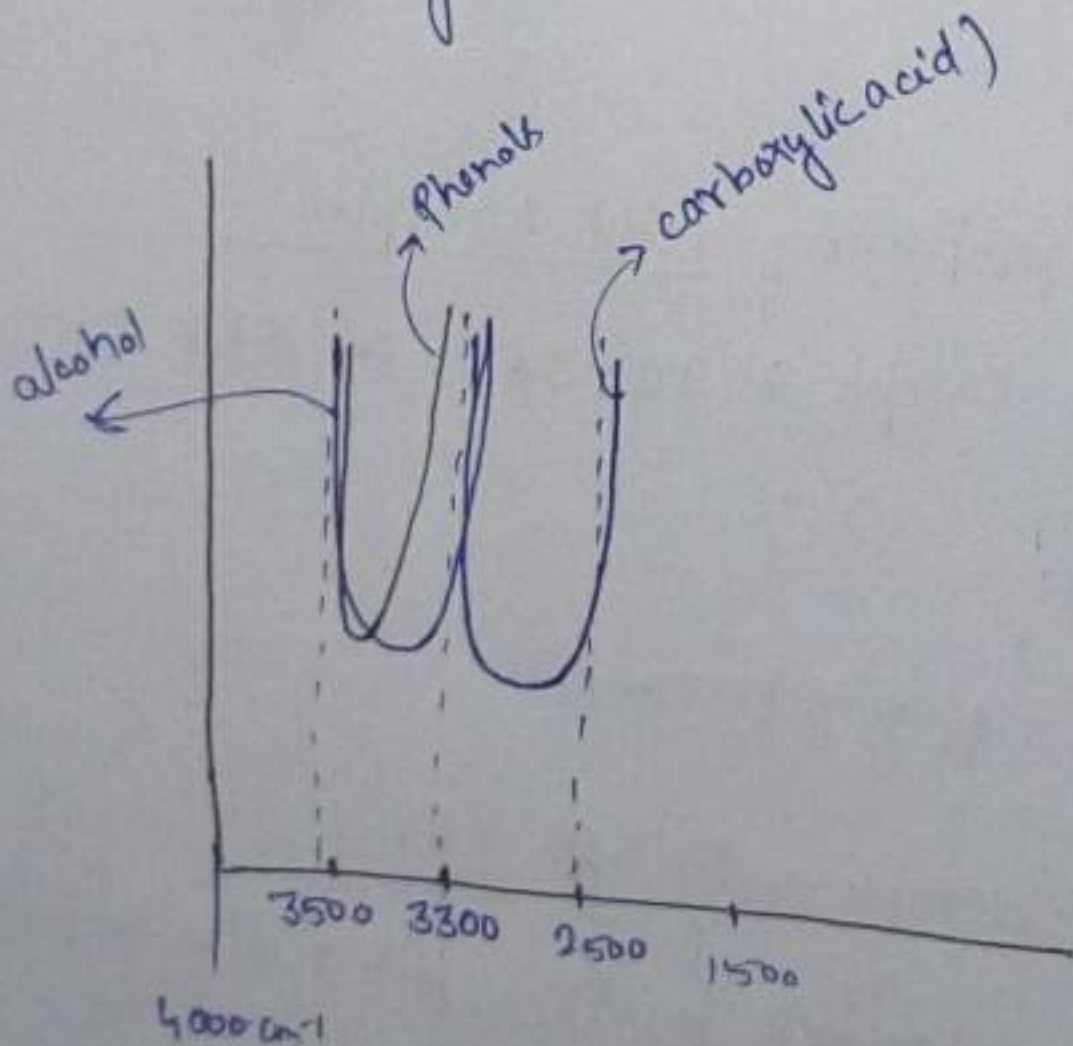
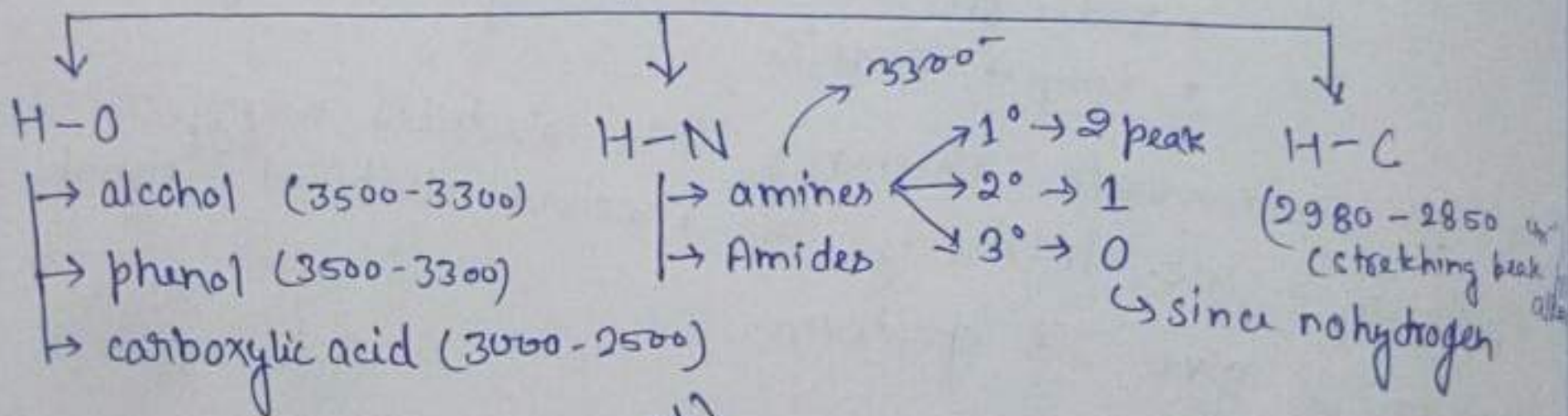


IR active molecules  $\rightarrow$  Net dipole moment have <sup>both</sup> (other than zero), e.g.  $H_2O$

(IR inactive are Raman active) e.g.  $O_2, CO_2$



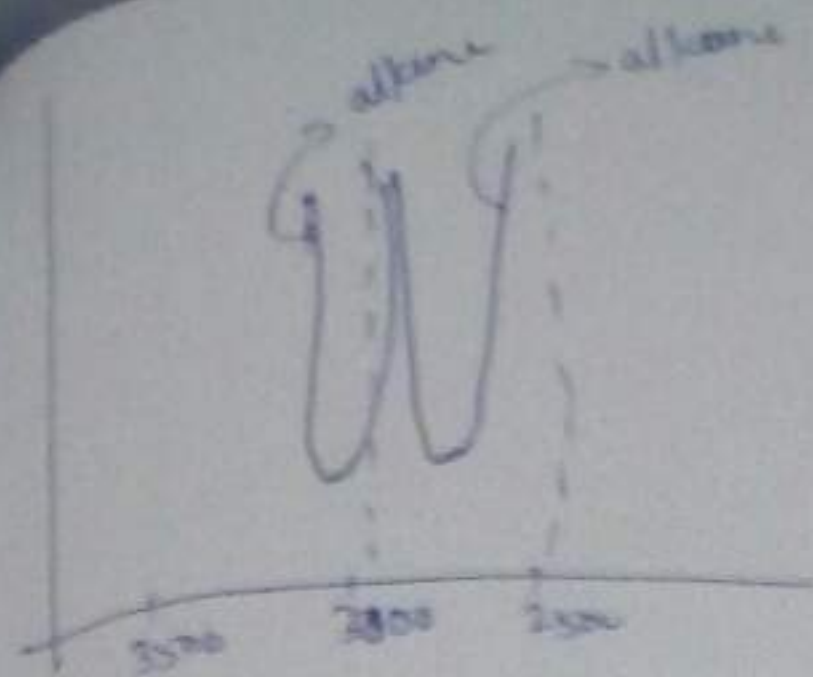
Hydrogen Attached to  $sp^3$  hybridized atom :-



In amide  $\rightarrow$  same as amines but <sup>also</sup> one additional peak <sup>at</sup>  $1700\text{ cm}^{-1}$  due to addition of carbonyl grp.



Acid value  
12.0

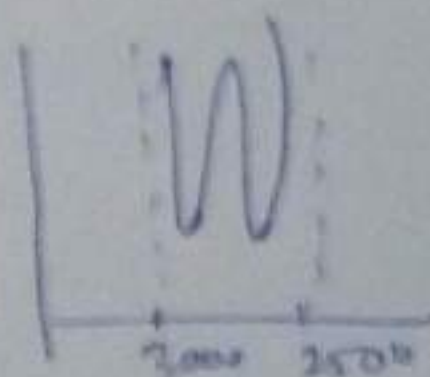
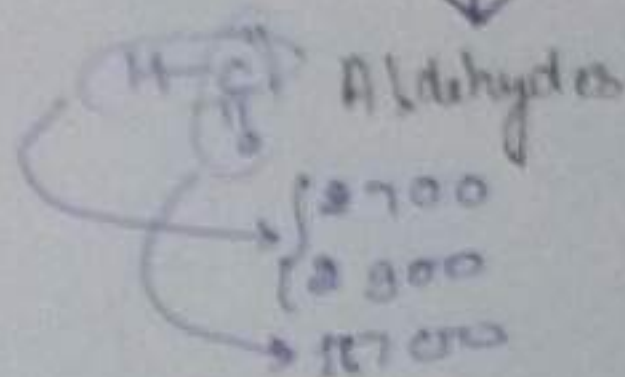


alkane stretching peak  
(Just below 3000) (2850-2850)  
banding peak  
1470-1350 cm⁻¹

Hydrogen attached to  $sp^2$  hybridized carbon -

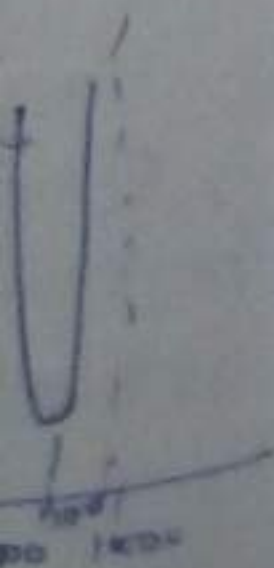
Alkenes  
(Just above 3000)  
stretching (3080-3010) cm⁻¹  
bending (1000-675) cm⁻¹

Aromatic  
 $\delta$  3100 cm⁻¹  
fingerprint 600-500 cm⁻¹



-2850 cm⁻¹  
stretching peak  
hydrogen

→ 2° amide



but along with  
additional