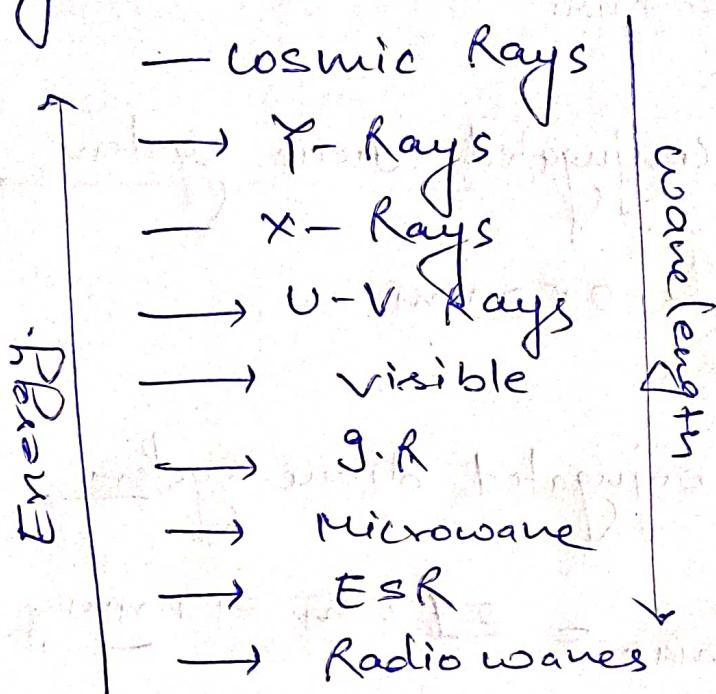


# Spectroscopy

It is the branch of science which deals with interruption of E.M. radiation with matter

Electromagnetic Radiation :- Every Rays which is coming from the outer-space



## U-V-visible Spectroscopy

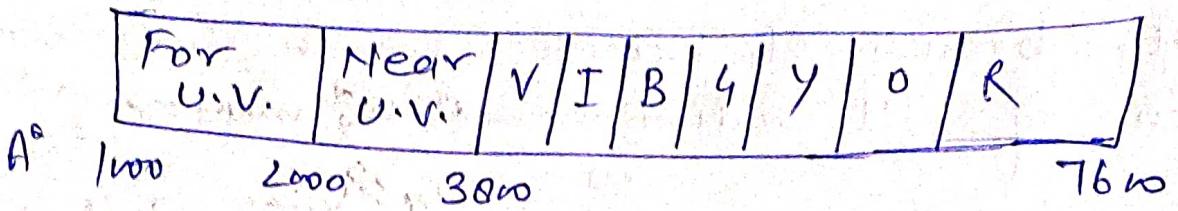
U-V-visible spectroscopy is commonly known as Electronic spectroscopy becz it involves the transition of  $e^-$  from  $(\sigma, \pi \& \pi^*)$   $e^-$  from the ground or lower energy state to the higher energy state.

## Range of U-V-Visible

For U.V.  $\rightarrow$  100 nm - 200 nm  
 $1000 \text{ } \text{\AA}^\circ - 2000 \text{ } \text{\AA}^\circ$

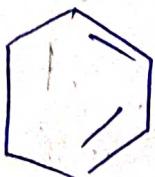
Near U.V.  $\rightarrow$   $2000 \text{ } \text{\AA}^\circ - 3000 \text{ } \text{\AA}^\circ$

Visible  $\rightarrow$   $3800 \text{ } \text{\AA}^\circ - 7600 \text{ } \text{\AA}^\circ$



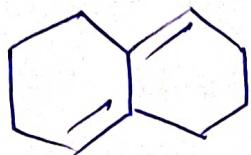
Wood Ward Fischer rule for calculation the value of  $d_{max}$   $\rightarrow$  max Absorption

### (i) Homo annular conjugated diene system



$$d_{max} = 253 \text{ nm.}$$

### (ii) Hetero annular conjugated diene system



$$d_{max} = \underline{\underline{217 \text{ nm}}} \quad \underline{\underline{217 \text{ nm}}} \\ = \underline{\underline{215 \text{ nm}}}$$

### (iii) conjugated Butadiene system

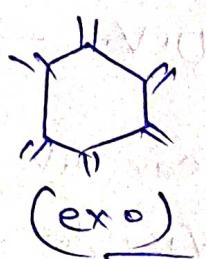


### Structural Increments

#### 1) Presence of Exocyclic D.B.

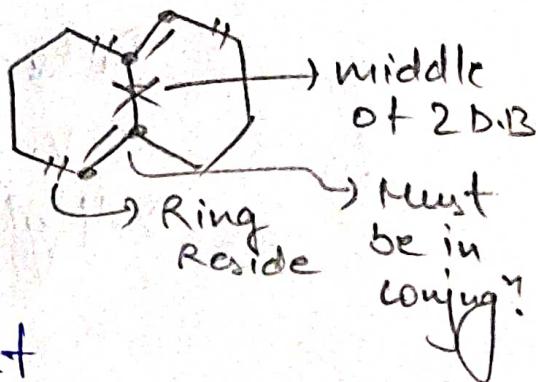
For each 1 exocyclic D.B. (+5nm) to

the Basic Value (B.V.)



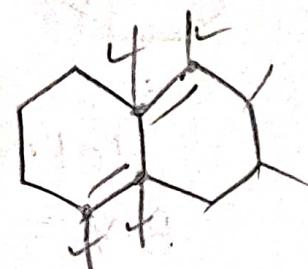
## 2) Presence of Ring Residue

For each ring Residue we add +5 nm to the Basic value.



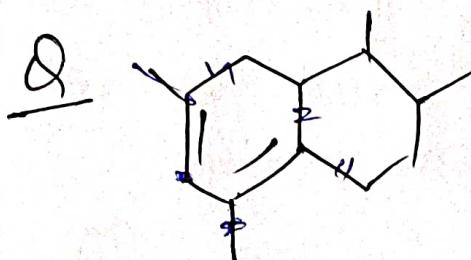
## 3) Presence of Alkyl Substituent

For each Alkyl Substituent we add +5 nm to its Basic value.



\* If homo and hetero both possible then prefer homo,

and if hetero double bond extends the conjugation then for each add (+30 nm) and also count Ring Residue and Alkyl subs. for that double bond.



System:- Homo annular

Basic value:- 253 nm

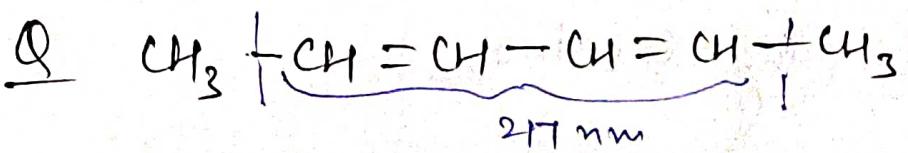
Exo - 1 :- +5 nm

Ring Res. - 3 :- +15 nm

Alkyl sub. 2 :- +50 nm

278 nm

283 nm



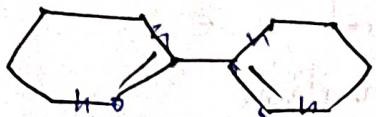
Butadiene system

$$\text{B.V.} = 217 \text{ nm}$$

$$2\Delta \text{Alkyl} = +10 \text{ nm}$$

$$227 \text{ nm}$$

Q



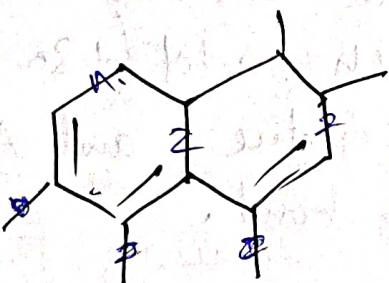
Hetero annular

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

$$4 \text{ ring Residu} = +20 \text{ nm}$$

$$235 \text{ nm}$$

Q



Homo annular

$$\text{B.V.} = 253 \text{ nm}$$

$$1 \text{ D.B. Ext. D.B.} = +30 \text{ nm}$$

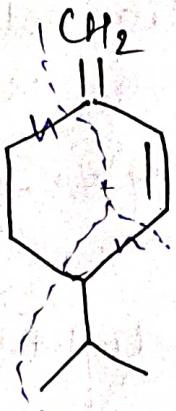
$$1 \text{ exp.} = +5 \text{ nm}$$

$$3 \text{ ring Residu} = +15 \text{ nm}$$

$$3 \text{ Alkyl sub.} = +15 \text{ nm}$$

$$318 \text{ nm}$$

Q



### Butadiene Systems

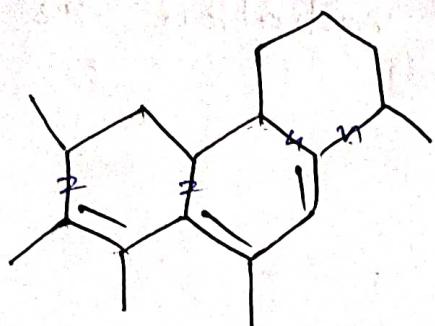
$$B.V. = 217 \text{ nm}$$

$$1\text{EXO} = +5$$

$$2\text{R.R.} = +10$$

$$\underline{\underline{230 \text{ nm}}}$$

Q



### Homo Annular

$$B.V. = 253 \text{ nm}$$

$$2\text{EXO} = +10 \text{ nm}$$

$$4\text{R.R.} = +20 \text{ nm}$$

$$3\text{Alkyl} = +15 \text{ nm}$$

$$\underline{\underline{298 \text{ nm}}}$$

### Lambert - Beer's Law

Acc. to Lambert's law when a beam of mono chromatic light passes through a homogeneous absorbing medium then the rate of Decrease of Intensity of light w.r.t the thickness of the Absorbing medium is directly proportional to the Intensity of Incident light.

$$-\frac{dI}{dl} \propto I_0$$

$$-\frac{dI}{dl} = K I_0$$

Beer's Modified this law for liq. sol<sup>n</sup> as per Beer's law when a beam of mono chromatic light is passed through a sol<sup>n</sup> of Absorbing substance then the decrease in Intensity of radiation or light w.r.t the thickness is directly proportional to the Intensity of Incident radiation as well as conc<sup>n</sup>. of sol<sup>n</sup>.

$$\frac{-dI_t}{dl} \propto I_0 \cdot c$$

$$\frac{-dI_t}{dl} = k I_0 c$$

### Combined Lambert & Beer's law :-

This law states that when a beam of the mono chromatic light is passed through a homogeneous sol<sup>n</sup> then the rate of decrease of Intensity of light or Absorbance is directly proportional to the prod. of conc<sup>n</sup> and its path length.

Therefore

$$A \propto l \cdot c$$

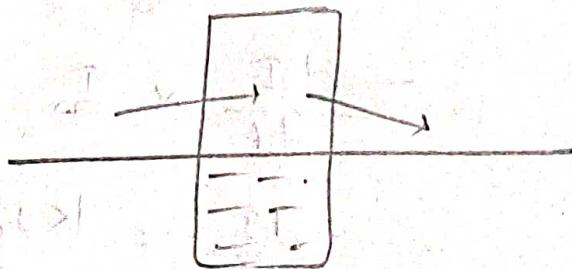
$$A = \epsilon l c = \log \frac{I_0}{I_t}$$

$l$  = Path length

$c$  = concentration

$\epsilon$  = molar absorptivity coeff.

$$= -\log \frac{I_t}{I_0} \rightarrow \text{Transmittance}$$



Let  $I_0$  and  $I_t$  be the Incident light and transmitted light respectively then ~~absorption~~ absorbance can also be written as:-

$$\text{Transmittance} = \frac{I_t}{I_0}$$

Q A  $80\text{l}^m$  of thickness 3cm transmit 30% of the Incident light calculate conc' of  $80\text{l}^m$  if ~~the~~  $\epsilon = 4000 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$

$$A = \log \frac{I_0}{I_t} = \log \frac{100}{30}$$

$$A = 0.522$$

$$A = \epsilon LC$$

$$C = \frac{0.522}{4000 \times 3}$$

$$C = 4.35 \times 10^{-5} \text{ mol/dm}^3$$

Q The percentage Transmittance of light for an eq.  $80\text{l}^m$  for of any unknown comp. is 20%. If the conc' of  $80\text{l}^m$  is  $4 \times 10^{-5} \text{ mol/L}$  and path length is 2cm calculate the ( $\epsilon$ ) Molar Absorbtivity coeff

$$A = \log \frac{I_0}{I_t} = \log \frac{100}{20} = 0.522 - 0.69$$

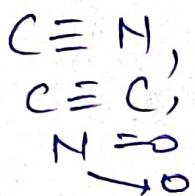
$$A = \epsilon LC$$

$$\epsilon = \frac{0.522 - 0.69}{2 \times 4 \times 10^{-5}} = 8737.5$$

## Chromophores

Chromophores are colour imparting groups. It can be defined as any isolated covalently bonded group that shows an absorption of light in the near U.V. or visible region.

Eg:- Nitro group responsible for imparting yellow colour to all the comp.



## Auxochromes :-

Auxochromes are colour intensifying groups.

They may be defined as any such group which do not itself acts as a chromophores but whose presence in the comp. shift the absorption from the violet to red end of the visible spectrum.

Eg:- OH group, NH<sub>2</sub> group, -OR' group

## -Types of electronic Transition in U.V. Visible

UV Visible spectroscopy is commonly known as Electronic spectroscopy because it involves the promotion of  $e^-$ 's from the ground state Energy to the next higher  $\sigma$  state energy level.

Following type of Electronic Transition are observed in UV. Visible spectroscopy.

### (i) $\sigma - \sigma^*$ for Transition

This type of electronic Transition takes place in saturated hydrocarbon molecule without having any lone pair of  $e^-$ . Since it requires the highest amt of energy, Hence these transition takes place in the Far U.V. region. ( $1250\text{ A}^\circ - 1350\text{ A}^\circ$ )

e.g:- Methane, Ethane

### (ii) $n - \sigma^*$ Transition

This type of electronic Transition involves the promotion of non bonding  $e^-$  to the higher ( $\sigma$ ) anti bonding orbitals. This type of Transition generally takes place in Saturated Hydrocarbon Compounds with atleast one hetero atom having a lone pair of  $e^-$

e.g:-  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{C}_2\text{H}_5\text{OH}$

# Types of Absorption shift in UV visible spectrum

↓  
Wavelength shift ( $\lambda_{max}$ )

↓  
Intensity shift ( $E_{max}$ )

↓  
Bathochromic  
shift

↓  
Hypsochromic  
shift

↓  
Hyper-  
chromic  
shift

↓  
Hypo-  
chromic  
shift

## Bathochromic shift

When the value of  $\lambda_{max}$  of a compound shift towards longer wavelength. This may be due to addition of chromophores, Auxochrome, presence of conjugation, Solvent (PH) and its polarity.

## Hypsochromic

If the value of  $\lambda_{max}$  of any compound shift towards shorter wavelength. This is due to removal of chromophores, Auxochrome, conjugation or change in (PH) or polarity of solvent.

Range of  $n - \pi^*$  Transition ( $1700 \text{ \AA}^\circ - 1800 \text{ \AA}^\circ$ )

(3)  $n - \pi^*$  Transition :-

This type of electronic Transition Takes Place in unsaturated compounds containing Double or Triple bonds.

e.g.- ~~Alkene~~ Alkene, Alkyne, Ago compounds etc

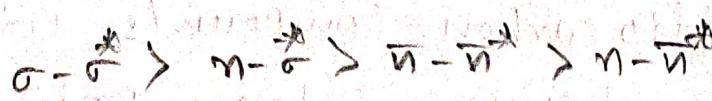
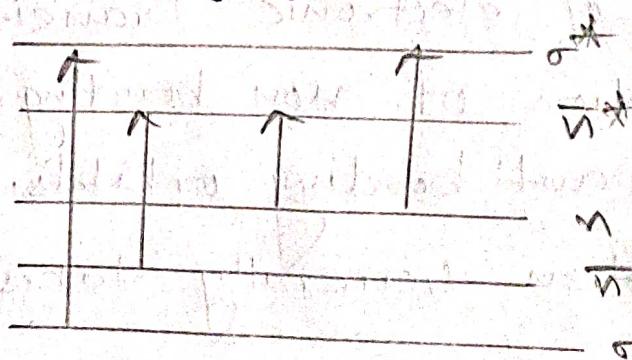
Since its requires comparatively less energy Hence, These Transition takes place in visible region.

(4)  $n - \pi^*$  Transition :-

It involves the promotion of non-bonding  $e^-$  to the higher  $\pi$  antibonding orbital.

This takes place in those unsaturated compounds containing an hetero atom with a lone or unpaired  $e^-$ .

e.g.- ~~CH<sub>3</sub>CHO~~, carbonyl groups, Acetone ( $2970 \text{ \AA}^\circ$ )



## Hyperchromic shift :-

When the value of  $E_{max}$  (Intensity max) of a compound shift towards higher end such a change in the value of  $E_{max}$  is called Hyper chromic shift.

## Hypochromic shift

When the value of  $E_{max}$  shift towards of lower end such a change is called Hypochromic shift.

