

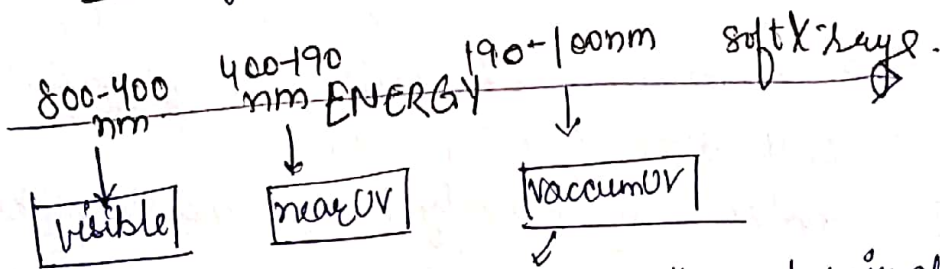
# Ultraviolet (UV) &

## Visible Spectroscopy

- \* Are used to measure multiple bonds or aromatic conjugation with the molecule.
- ⇒ \* Are electronic spectroscopy - i.e. involves the measurement when absorption of  $E$  occurs which should be the proper / required electromagnetic radiation. An  $e^-$  is promoted from HOMO to LUMO.
- ⇒ As conjugation inc, HOMO-LUMO Energy gap dec. and position of  $\pi-\pi^*$  absorption shifts to longer wavelength (lower energy)
- ⇒ Simple aldehydes & ketones don't have  $\pi-\pi^*$  absorption in visible UV region.

### Introduction:

- ⇒ Requires Electromagnetic Radiation of High Energy.
- ⇒ UV region - 400-200nm.  
Visible region:- 800-400nm.



- ⇒ vacuum because the mol of air absorbs radiation in this region, & thus this region is accessible only with special vacuum assembly.
- ⇒ The amt of absorption depends on wavelength of radiation and the structure of the compound.

⇒ Absorption of radiation is due to the subtraction of energy from the radiation beam when  $e^-$  in orbitals of lower energy excited into orbitals of higher energy.

⇒ UV is also called electronic spectroscopy, since this is an electron excitation.

⇒ In UV spectrum wavelength of an absorption maximum, i.e.  $\lambda_{max}$  and strength of absorption i.e. molar absorptivity or extinction coefficient  $E_{max}$  -

By Lambert-Beer Law

$$\log\left(\frac{I_0}{I}\right) = \epsilon \cdot l \cdot c$$

$$\boxed{\epsilon = \frac{A}{cl}}$$

where,  $I_0$  = intensity of incident light (or light intensity passing through a reference cell)

$I$  = light transmitted through the sample solution

$$\log\left(\frac{I_0}{I}\right) = \text{optical density (OD)}$$

or absorbance (A) of solution

$c$  = concentration of solute ( $\text{mol dm}^{-3}$ )

$l$  = path length of sample in (cm)

$\epsilon$  = molar absorptivity (extinction coefficient)

$E_{1cm}^{1\%}$  = Absorption [ $\log_{10}(I_0/I)$ ] of a 1 percent solution in a cell with a 1 cm path length.

↑ This is used in place of  $\epsilon$  when mol wt of compd is not known or when a mixt is being examined.

⇒  $\epsilon$  = constant for an organic compound at given wavelength is reported as  $E_{max}$  - molar absorptivity at an absorption maximum.

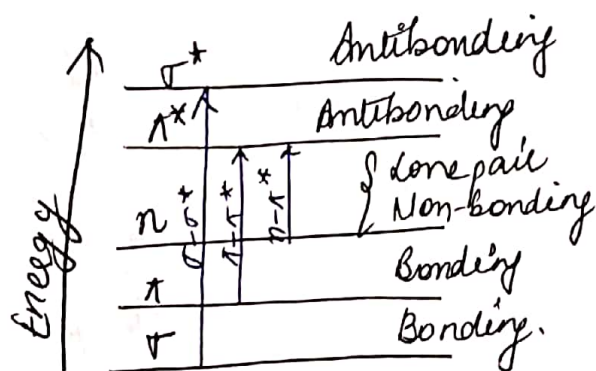
~~Ultraviolet~~

$\Rightarrow \epsilon \text{ units} = 10^{-2} \text{ m}^2 \text{ mol}^{-1}$

$\Rightarrow$  In Infrared spectrum, we use strong (s), medium (m) and weak (w) to define the intensity of different bands. But in UV absorptions the value of  $\epsilon$  is reported.

if  $\epsilon_{\text{max}} = > 10^4$  - strong absorption  
 $< 10^3$  - weak absorption.

### UV Absorption Bands



### Electronic Energy levels

$\Rightarrow$  On absorption of energy by the molecule in UV, charges are produced in electronic energy of mol; since  $e^-$  went to transitions from occupied molecular orbital e.g. a non-bonding or bonding  $\pi$  orbital to next higher energy orbital i.e. an antibonding,  $\pi^*$  or  $\sigma^*$  orbital.

electronic transitions 1)  $\pi \rightarrow \pi^*$

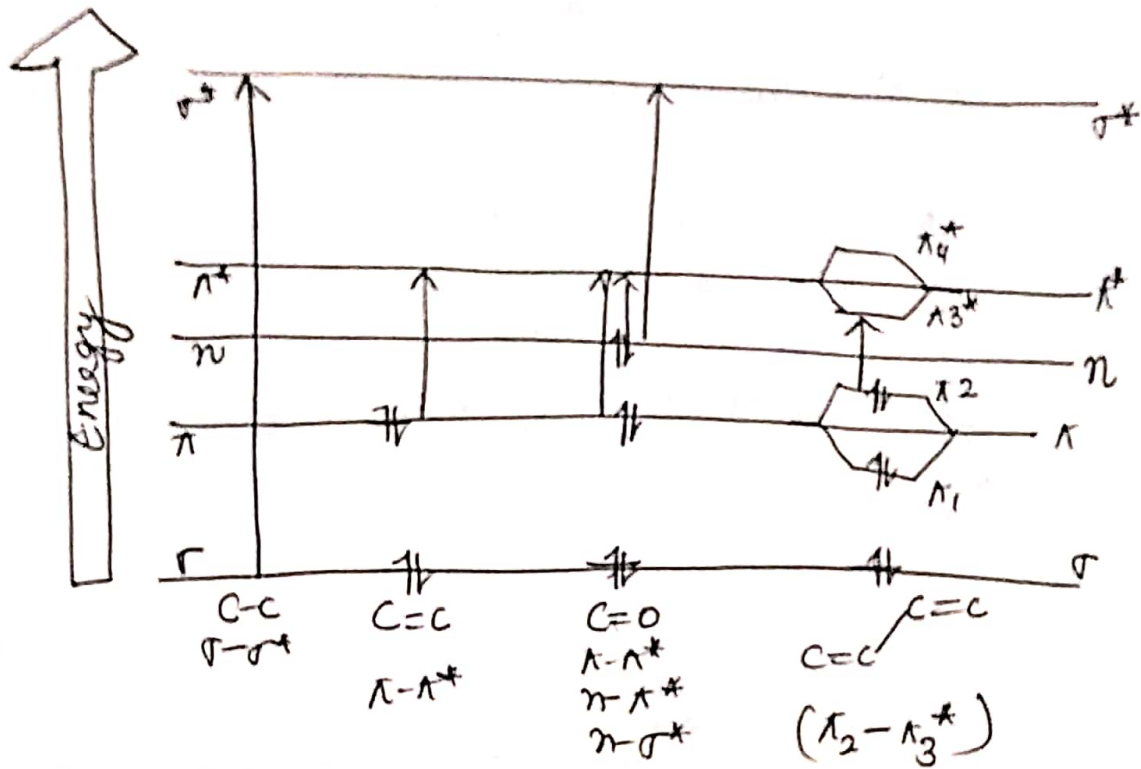
2)  $n \rightarrow \pi^*$

3)  $\sigma \rightarrow \sigma^*$

$$\boxed{\sigma \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*} \rightarrow \epsilon_{\text{gap}}$$

1)  $\sigma \rightarrow \sigma^*$  transition

$\Rightarrow$  alkane gave  $\sigma \rightarrow \sigma^*$  transition  
 $\sigma$  bonds are strong so this is high energy process  
 & hence require short wavelength  
 i.e. high UV light  $\approx 150 \text{ nm}$



2)  $n \rightarrow \sigma^*$  transition:

$\Rightarrow$  this involves saturated compounds with one hetero atom with unshared pair of  $e^-$  ( $n$  electrons)

i.e. saturated halides  
 alcohols, ethers  
 aldehyde, ketones  
 amides

$\Rightarrow$  these transitions require less energy than  $\sigma \rightarrow \sigma^*$   
in saturated alkyl halide as size of halogen  $\uparrow$ , the energy reqd from transition  $\downarrow$

OR  
if electronegativity of halogen  $\uparrow$ ,  $E_{\text{reqd}}$  will be  $\uparrow$

since  $E_{\text{at } n} - \text{then if } E_{\text{Reqd}} \downarrow$

Imp  $\Rightarrow$   $\text{CH}_3\text{Cl}$  v/s  $\text{CH}_3\text{I}$

or  
 $\text{Cl}$  v/s  $\text{I}$

$\Rightarrow$  the electronegativity of  $\text{Cl}$  is higher than  $\text{I}$   
therefore,  $\text{CH}_3\text{Cl}$  require more Energy to excite its  $e^-$   
than  $\text{CH}_3\text{I}$ .

$\Rightarrow$  Also  $n$ -electrons on  $\text{I}$  atom are loosely bound. So  
transition is more probable than  $\text{CH}_3\text{Cl}$ .

Imp  $n \rightarrow \sigma^*$  are sensitive to H-bonding.  
or  
 $n \rightarrow \sigma^*$  are dependable to H-bonding.

$\Rightarrow$  H-bonding brings about remarkable downward  
frequency shifts.

Stronger the H-bonding, absorption shift  $\uparrow$  towards  
larger wavelength.

1) intermolecular - broad bands

2) intramolecular - sharp bands -

$\Rightarrow$  Such association occurs due to presence of non-  
bonding  $e^-$  on the hetero atom and thus this  
transition requires Energy.

