4) when absorbing material gets coagulated.

5) when solute & solvent form complexes through some sort of association.

6) when diff. forms of the absorbing molecules are in equilibrium as keto-enol tautomers.

UV-VIS Spectroscopy

Electronic spectrum

When any molecule absorbs UV or visible radiation, its electrons gets promoted from lower energy level (G.S.) to higher energy state (E.S.), then electronic spectrum is obtained.

The study of this spectra is called UV-VIS spectroscopy.

→ 95% alcohol, H_2O, hexane etc are used as solvent.

An org. compound is dissolved in a solvent that does not absorb the radiations in 200-800 nm range of electromagnetic radiation (UV-VIS range)

Source of light → Hydrogen-deuterium discharge lamp & tungsten filament lamp.

(used to obtain visible spectrum)

→ This technique is not useful below 200 nm b'coz oxygen absorbs strongly at 200 nm & below.

→ Region below 200 nm is c/a Vacuum UV region.

→ Low λ region can be extended upto 150 nm by flushing

→ Glass cells, used in visible region

→ Silica cells/ Quartz cells in UV region.

Solvent = methanol

Solution in cell

↓

passed. Monochromatic beam of equal intensity

↓

Intensity of respective transmitted beams are then compared over the whole λ range of instrument.

↓

Now absorbance/ Transmittance can be measured.

λ where absorbance is max is called λ_{max} i.e. λ of max. absorption of light radiation. This is characteristic property of compound.

λ_{max} value changes slightly with change in solvent or with ↑ or ↓se in conjugation.

Selection Rule :-

① Transitions which involve a change in spin quantum no. of an electron during transition and is not allowed i.e. singlet - triplet transitions are forbidden.

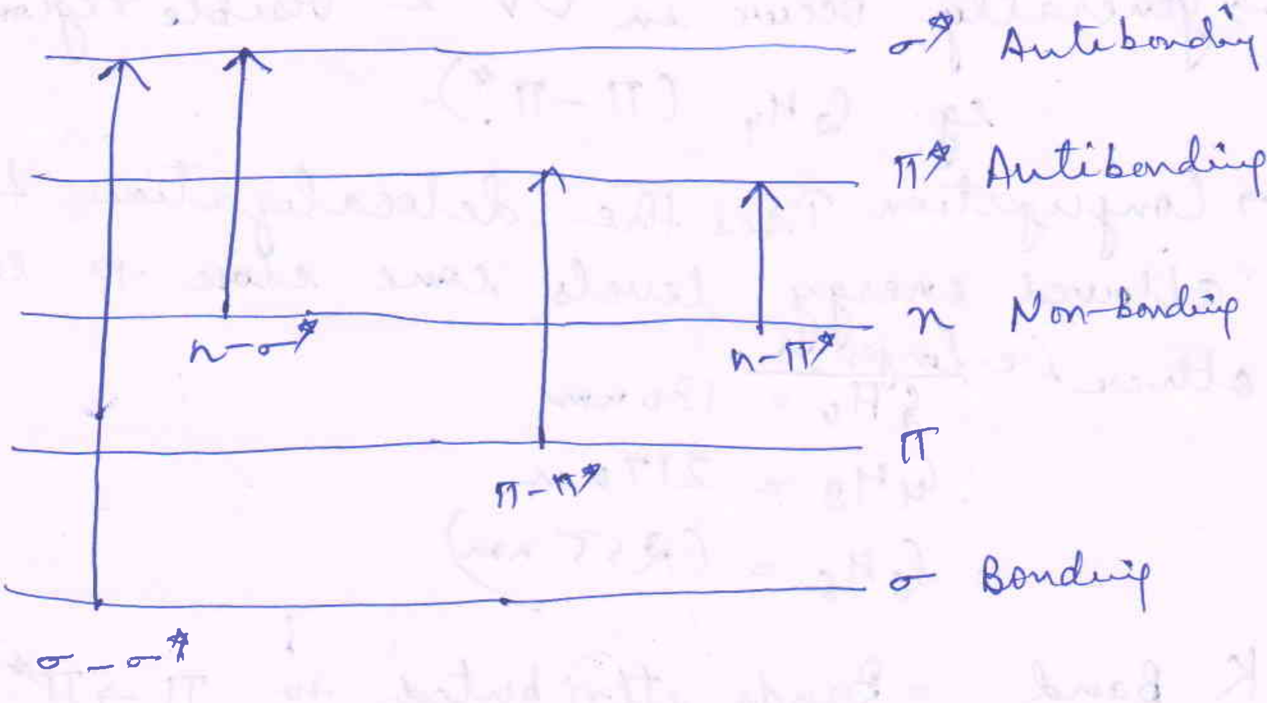
② Transitions b/n orbitals of diff. symmetry are not

Electronic Absorption Bands:-

→ Electrons in an atom reside in the atomic orbitals, & e⁻'s in a molecule reside in the molecular orbitals.

→ Acc. to MOT, when a molecule is formed, e⁻ participating in the formation of bond remain in bonding M.O.

→ Bonding orbitals (σ, π)
Antibonding orbitals (σ*, π*)
Non-bonding orbitals (some e⁻ are not involved in formation of any bond)



σ – σ* transition = (σ bond) No lone pair.
High energy required
eg. Saturated hydrocarbon
CH_4 = λ_{max} = 125 nm

n – σ* transition :- (180 – 200 nm)

Sat. compounds containing heteroatoms (O, N, S, X)

→ n – σ* energy less than to σ → σ*

eg. CH_3Cl (173 nm)
CH_3OH (184 nm)
CH_3NH_2 (215 nm)

π – π* transition :- unsaturated compds.

Less energy.

→ generally occur in UV & visible region.

eg. C_2H_4 (π – π*)

→ Conjugation ↑ses the delocalization & allowed energy levels come close to each other i.e. longer λ.

C_2H_4 = 180 nm
C_4H_8 = 217 nm
C_6H_6 = (255 nm)

K Band = Bands attributed to π → π* transition. Such bands arise in compounds like diene, polyenes, enones at longer λ & ↑ed intensity.

B band :- generated by aromatic or heteroaromatic compounds due to $\pi-\pi^*$ transition

→ This band originates from being excited when mol. vibrates. The symmetry of aromatic ring is destroyed, when molecules enters in excited state while vibrating. formed at longer λ & is of low intensity.

eg. C_6H_6

K band	B band
λmax (nm)	λmax (nm)
204 (ϵ_{max} = 7400)	255 (ϵ_{max} = 204)

$n-\pi^*$ Transition :-

→ by unsaturated compounds in which a heteroatom containing unshared pair of e^- (eg C=O, NO_2 gp)

$n-\pi^*$ transitions of single chromophoric groups ($>C=O$, NO_2) are forbidden and corresponding bands (weak) are characterized by low intensity, generally less than 100. These bands are called R bands.

Sat. Ketone (Acetone) exhibits lowest energy forbidden transition around λmax = 280 nm.

* $n-\pi^*$ transition bands disappear in acidic solution eg. $n\rightarrow\pi^*$ transition in pyridine disappear in acidic solution, why?

b'coz formation of bond b'n acidic proton & lone pair of e^- on N atom

$$C_5H_5-\ddot{N} + H^+ \rightarrow \underline{C_5H_5-\overset{+}{N}H}$$

Chromophore :-

→ Any isolated covalently bonded unsaturated gp that shows a characteristic absorption band in UV or visible region & provides colour to the compound.

→ Compound containing a chromophore is called chromogen.

eg: $>C=C<$, $-C\equiv C-$, $>C=O$, $>C=S$, $-C\equiv N$, $-N=O$, $-N=N$, $-\overset{\overset{O}{\uparrow}}{N}=O$.

Colour of a molecule is due to one or more such chromophoric groups, which are all unsaturated in nature.

Auxochrome :-

Colour enhancing gp, which does not itself acts as a chromophore but when attached to a chromophore, it bring about a shift of absorption bands towards red end of spectra (longer λ).

$-\ddot{O}H$, $-\ddot{O}R$, $-\ddot{N}H_2$, $-\ddot{N}HR$, $-\ddot{N}R_2$, $-\ddot{S}H$, $-\ddot{S}R$
$-\ddot{Cl}:$, $-\ddot{Br}:$, $-\ddot{I}:$

→ Absorption bands usually becomes intense (ϵ_{max} ↑ses) & shifts to longer λ (towards visible region) due to +nce of auxochrome.

→ eg. Benzene λmax = 255 nm (ϵ_{max} = 203)
Aniline λmax = 280 nm (ϵ_{max} = 1430)


= λmax = 268 nm


λmax = 381 nm.

Shift of Absorption peaks :-

Bathochromic
Hypsochromic
Hyperchromic
Hypochromic

Bathochromic shift :-

Shift of absorption band (λmax) to a longer λ due to +nce of an auxochrome (-OH, $-CH_3$, $-NH_2$) or by change of solvent is c/a bathochromic

eg: C_6H_6 → absorbs at 254 nm.
$C_6H_5-CH_3$ → " " 261 nm.
Conjugation of = bonds also cause bathochromic shift,

UV spectrum of ethanol in acetone absorbs at 272 nm but in hexane, it absorbs at 279 nm.

Hypsochromic Shift → Shift of absorption band (λ_{max}) to a shorter λ due to Substitution with e^- withdrawing gps like NO_2, etc or solvent is c/a Hypsochromic shift. or blue shift.

eg → $C_6H_5NH_2$ absorbs at 230 nm in neutral solvent while it absorbs at 203 nm in acidic medium, b'coz → aniline gets protonated in acidic medium & lone pair is no longer present & conjugation removed & thus, blue shift occurs.

Hyperchromic shift:-

→ ↑se in intensity (ϵ_{max}) of a band, then effect is c/a hyperchromic shift.

→ ↑se in intensity of absorption band is due to ↑se in molar extinction cofficient.

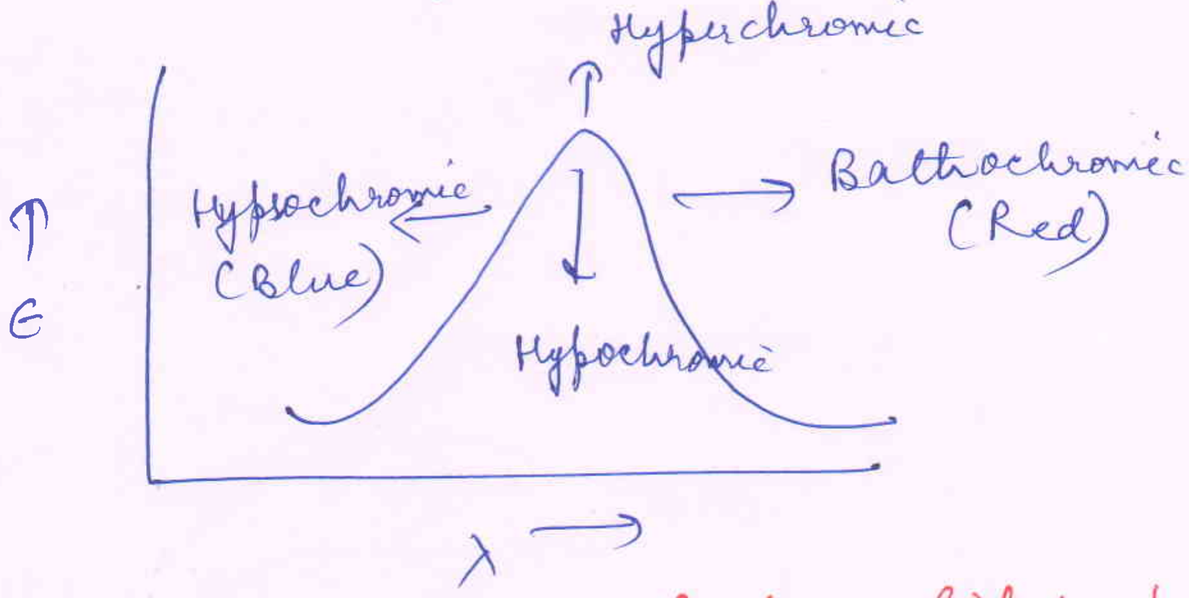
eg. ϵ_{max} $C_6H_6 \rightarrow 7400$
Styrene $\epsilon_{max} \rightarrow 14000$

∴ sub. of vinyl gp ($-CH=CH_2$) in benzene causes hyperchromic shift.

Hypochromic Shift :-

Sub. gp ↓se intensity of absorption band.

eg. ϵ_{max} for B-band of $C_6H_6 = 204$ nm
Chlorobenzene $\epsilon_{max} = 190$ nm.



* Generally, sub. gps that exhibit batho-chromic shift also shows hyperchromic shift + sub. gps that show hypsochromic shift, also show hypochromic effect..