

### 3) $\pi \rightarrow \pi^*$ Transition ( $\kappa$ -band)

→ for compound with unsaturated centres eg. alkenes, aromatics, carbonyl compds etc.

⇒ Requires less energy than  $n \rightarrow \sigma^*$

⇒ In simple alkene, lowest E transition  $\pi \rightarrow \pi^*$  (170-190 nm)  
In saturated ketones →  $\pi \rightarrow \pi^*$  (150 nm)

### 4) $n \rightarrow \pi^*$ Transition ( $R$ -band)

⇒ an  $e^-$  of unshared  $l^p$  pair on hetero-atom is excited to  $\pi^*$  antibonding orbital.

⇒ least E required for this (longer wavelength)

⇒ In satd aliphatic ketone  $n \rightarrow \pi^*$  - 280 nm

this  $n \rightarrow \pi^*$  is forbidden due to symmetry consideration, thus low intensity of band, although longer wavelength

### 5) Conjugated Systems and Transition Energies

⇒ In dienes,  $\pi$  orbitals of alkene combine to give  $\pi_1$  &  $\pi_2$  the 2 bonding and 2 antibonding  $\pi_3^*$  &  $\pi_4^*$ . Now  $\pi_2 \rightarrow \pi_3^*$  have low E gap than  $\pi \rightarrow \pi^*$  of simple alkene. So bathochromic shift.

butadiene →  $\lambda_{max} = 217 \text{ nm}$

ethylene →  $\lambda_{max} = 171 \text{ nm}$

⇒ Conjugated ketones i.e.  $\alpha, \beta$ -unsaturated ketone shows  $n \rightarrow \pi^*$  &  $\pi \rightarrow \pi^*$  of low E, higher  $\lambda$ .

### different Bands :-

a) K-band →  $\pi \rightarrow \pi^*$  ( $E_{max} > 10,000$ )

b) R-Band →  $n \rightarrow \pi^*$  ( $E_{max} < 100$ ) for Carbonyl & Nitro it is forbidden.

⇒ Kband is intense & at longer wavelength, due to less E the  $n \rightarrow \pi^*$  (presence of heteroatom) R-band undergoes a red shift with little change in intensity.

c) B-Bands → these are characteristic of aromatic and heteroaromatic compounds.

B-band of benzene - 256 nm.

d) E-Band → also characteristic of aromatic systems.

Chromophores → It is a covalently unsaturated group responsible for electronic absorption

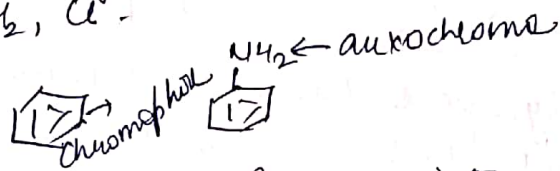
e.g. C=C, C=O & NO<sub>2</sub>.

⇒ simple compds containing chromophoric grps are benzene, ethene, acetone.

Auxochromes : It is a saturated group containing unshared electrons which when are attached to chromophore changes both intensity as well as wavelength

e.g. -OH, NH<sub>2</sub>, Cl-

for example



In aniline B-band is more intense and at longer wavelength as compared to Benzene.

⇒  $\lambda_{max}$  to longer wavelength (lower E) ⇒ Red shift or Bathochromic

⇒  $\lambda_{max}$  to short wavelength (high E) ⇒ Blue shift or Hypsochromic

⇒ Increased conjugation ↑ the intensity  
so - Hyperchromism.

⇒ A decrease in intensity of  $\lambda_{max}$  = hypochromism.

Imp

- 1)  $E_{max} > 10^4 \rightarrow$  allowed transitions  
generally arise due to  $\pi \rightarrow \pi^*$   
e.g. conjugated diene system.
- 2)  $E_{max} = 10-100 \rightarrow$  forbidden transition  
arise due to  $n \rightarrow \pi^*$  in carbonyl compds
- 3) Symmetrical molecules (e.g. benzene) have more restrictions on their transitions than comparatively less symmetrical molecules.

### Effect of Extension of Conjugation:-

longer the conjugation,  $E$  gap will less b/w LUMO & HOMO  
if  $E$  less then  $\lambda$  will be giving Red / Bathochromic shift.

$\lambda_{max}$  is in order :-

tetraenes > trienes > dienes

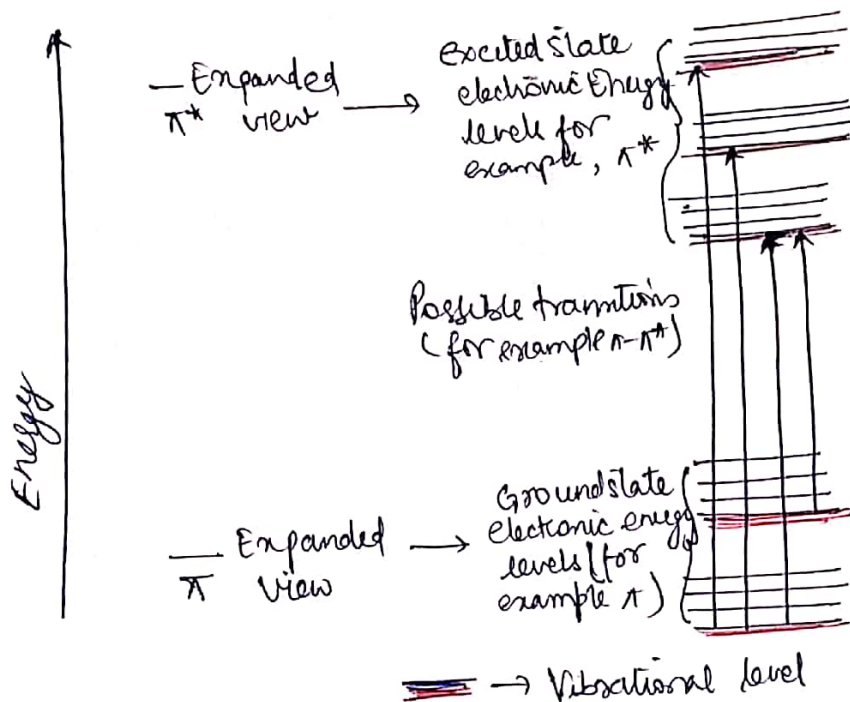
for example lycopene have red colour due to 11 conjugated bonds i.e.  $\lambda_{max}$  reach to visible region

- 1) From UV distinction b/w conjugated and non-conjugated compounds can occur.
- 2) detection of a chromophore in an unknown compound by comparison of its spectra with that of a known compound.

Imp Absorption bands in UV spectrum are very broad when compared to IR spectrum.

$\Rightarrow$  Because energy put into the sample is sufficient to allow a large no of diff electronic transitions to occur b/w several diff allowed vibrational & rotational  $E$  levels of the molecule.

$\Rightarrow$  Each transition is quantized, however,  $\Delta E$  values are very close, so that complete resolution in the sol<sup>n</sup> phase is not possible. Thus a broad band is displayed which consists of all these overlapped transitions.



- ⇒ With ultraviolet absorptions a large no of possibilities exists within each electronic state and the individual absorption bands normally become very broad.
- ⇒ The  $E$  transition is a change that will actually be from a vibration level in the electronic ground state to one of several vibrational levels with the excited state.