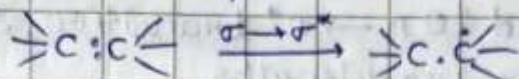


a)  $\sigma \rightarrow \sigma^*$  transitions:

- Shown by saturated hydrocarbons, like methane, propane, etc... Absorption occurs near 150 nm.



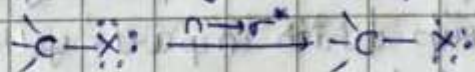
- Excitation of  $\sigma$  bond  $e^-$  to  $\sigma^*$  (antibonding) level occurs with net retention of  $e^-$  spin  $\rightarrow$  excited singlet state, which may in turn, gets converted to excited triplet state.

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

- Occurs in saturated compounds containing one hetero atom with unshared pair of  $e^-$  ( $ne$ ), eg: saturated halides, alcohols, ethers, aldehydes, ketones, amines etc...

- Requires less energy than  $\sigma \rightarrow \sigma^*$  transition.

- In <sup>case of</sup> saturated alkyl halides, the energy required for such transition  $\downarrow$  with  $\uparrow$  in size of halogen atom. (or  $\downarrow$  in electronegativity of atom)



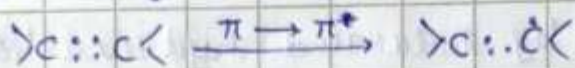
- Similarly, amines absorb at higher wavelengths as compared to alcohols.
- $n \rightarrow \sigma^*$  transitions are very sensitive to H-bonding. H-bonding shifts the UV absorption to shorter wavelengths.

c)  $\pi \rightarrow \pi^*$  transition:

- Occurs in unsaturated centres of molecule i.e., in compounds containing double or triple bonds and also in aromatics. eg: alkenes, alkynes, carbonyl



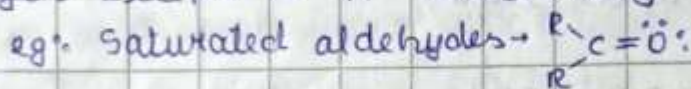
compounds, cyanides, azo compounds etc...



- This transition requires still lesser energy as compared to  $n \rightarrow \sigma^*$  transition,  $\therefore$  absorption occurs at longer wavelengths.

d)  $n \rightarrow \pi^*$  transition:

- In this type,  $e^-$  of unshared  $e^-$  pair on hetero atom gets excited to  $\pi^*$  antibonding orbital



- Requires least amount of energy out of all transitions and hence occurs at longer wavelengths.

\* **Chromophore:**

- All these compounds which absorb light of  $\lambda$  b/w 400-800 nm appear coloured to human eye
- Originally, chromophore was considered any system which is responsible for imparting colour to compounds  
eg. Nitro group which imparts yellow colour to nitro compounds

CHROMOPHORE is defined as any <sup>isolated</sup> covalently bonded group that shows a characteristic absorption in the UV or visible region."

- ethylenic, acetylenic, carbonyls, acids, esters, nitrile group, etc...

Types of chromophores-

- a) chromophores in which the group contain  $\pi$  etc

and they undergo  $\pi \rightarrow \pi^*$  transition.

eg: ethylenes, acetylenes, etc...

- b) Chromophores which contain both  $\pi$  electrons and  $n$  (non bonding) electrons, and undergo two types of transitions i.e.  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$ , eg: carbonyls, nitriles, azo compounds, nitro ~~gto~~ compounds, etc

Note: In compounds of type  $\text{>C=C<}$  and  $\text{>C-H}$  absorption occurs around 150 m $\mu$  as a result of  $\sigma \rightarrow \sigma^*$  transition and in compounds containing  $\text{-O-}$ ,  $\text{-S-}$ ,  $\text{>N}$  atoms at 190 m $\mu$  due to  $n \rightarrow \sigma^*$  transition.

### \* Auxochrome:

- An auxochrome can be defined as any group which does not itself act as a chromophore but whose presence brings about a shift of the absorption band towards the red end of the spectrum (longer wavelength).
- It increases the intensity of colour, 'colour enhancing group'.
- Examples of auxochromes -OH, -OR, -NH<sub>2</sub>, -NHR, -NR<sub>2</sub>, -SH, etc...

Mechanism- All auxochromic groups contain non-bonding electrons. due to this, there is extension of conjugation of the chromophore by sharing the non-bonding electrons.

