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UV-visible spectra. Phy. chem.

Designation of Bands

UV absorption bands may be designated by using electronic transitions or the letter designation.

K-band: The band due to $\pi \rightarrow \pi^*$ transition in a compd. with conjugated π system is usually intense ($E_{max} = 10,000$) and is frequently ~~referred~~ referred to as ~~K-band~~ the K-band. (German: Konjugierte)

Ex Butadiene, mesityl oxide.

R-Band (German: Radikal) :- $n \rightarrow \pi^*$

The absorption shift to lower λ (blue shift) with increase in polarity of the solvent.

B-band :- The position as well as well as intensity of the B-band is not shifted by increasing the polarity of the solvent. But in hetrocyclic aromatic compounds, a marked hyperchromic shift (increase in ϵ_{max}) is observed by increasing the polarity of the solvent. B-bands are characteristic of aromatic and hetroaromatic compds.

← Benzenoid band $\pi \rightarrow \pi^*$ aromatic and hetroaromatic molecules.

~~A~~ E band :- i.e., ethylenic bands are characteristic of aromatic systems like B-bonds

Chromophores and Auxochromes

Chromophores :-

A chromophore is a covalently unsaturated group responsible for electronic absorption. e.g., C=C, C=O and NO_2.

or

It is defined as any isolated covalently bonded group that shows a characteristic absorption in the UV or the visible region.

(Ex compds. containing chromophoric groups are ethene, ethyne, benzene, acetone)

Ex Some of the important chromophores are ethylinic, acetylenic, carbonyls, acids, esters, nitro group etc.

There are two types of chromophores

(a) ~~compd~~ Chromophores in which the group contains π electrons and they undergo $\pi \rightarrow \pi^*$ transition

Ex ethene, acetylene, benzene etc.

(b) chromophore which contains both
π electrons and n (non bonding) electrons
Such chromophores undergo two types
of transitions i.e., $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$
Ex carbonyl, nitriles, azo compds,
nitro compds.

(chromophore = any conjugated system which is responsible for imparting colour to the compound)

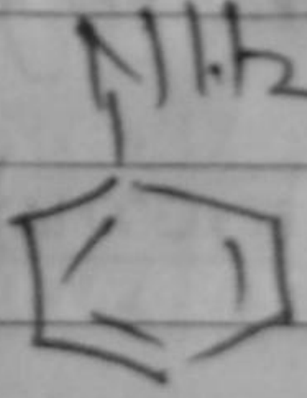
[There are no set rules for the identification
of chromophore] following points may helpful
* Spectrum consisting a band near 350 nm may
contain two or three conjugated unit.
* Absorption bands near 270-350 nm with
very low intensity, ε_{max} 10-100 are due to
$n \rightarrow \pi^*$ transitions of the carbonyl group
* Simple conjugated chromophores such as
diene or α, β-unsaturated ketones have
high ε_{max} value i.e., from 10,000 to 20,000
* The absorption b/w ε_{max} 10,000 to 20,000 shows
an aromatic system.

Auxochrome :- An auxochrome represents a saturated group containing unshared electrons which when attached to a chromophore changes both intensity as well as the wavelength of the absorption maximum. e.g., -OH, NH_2, Cl, etc.

(An auxochrome can be defined as any group which does not itself act as a chromophore but whose presence bring about a shift of the absorption band towards the red end of the spectrum).

Ex effect of NH_2 gr. on λmax and ϵmax:
comparision of B-band benzene and aniline

Benzene



$\lambda max = 255$ nm. $\lambda max = 280$ nm

$\epsilon max = 203$ $\epsilon max = 1430$

Hence $-NH_2$ is an auxochrome