

UV –Visible Spectroscopy

- It involves the measurement of absorption of light in the UV region(10-200(far UV)-200-400nm(near UV) and visible region(400-800nm)by the compound under investigation.
- It is also known as **electronic spectroscopy** because it occurs due to transition between electronic energy level within the molecule.

Principle

When ever UV or visible radiation is passed through the solution of an organic compound ,it is either absorbed or transmitted depending upon its wavelength and the molecular structure of the organic compound.

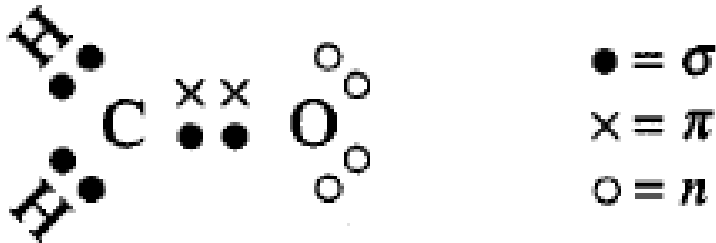
As a result of absorption of energy ,an electron gets excited from ground state to some higher energy state and when it come back to lower energy state ,it will emit the radiation of the same wave length ,which initially absorbs.

Types of electrons

Type of electrons participated in transitions are

π electrons involved in double and triple bond

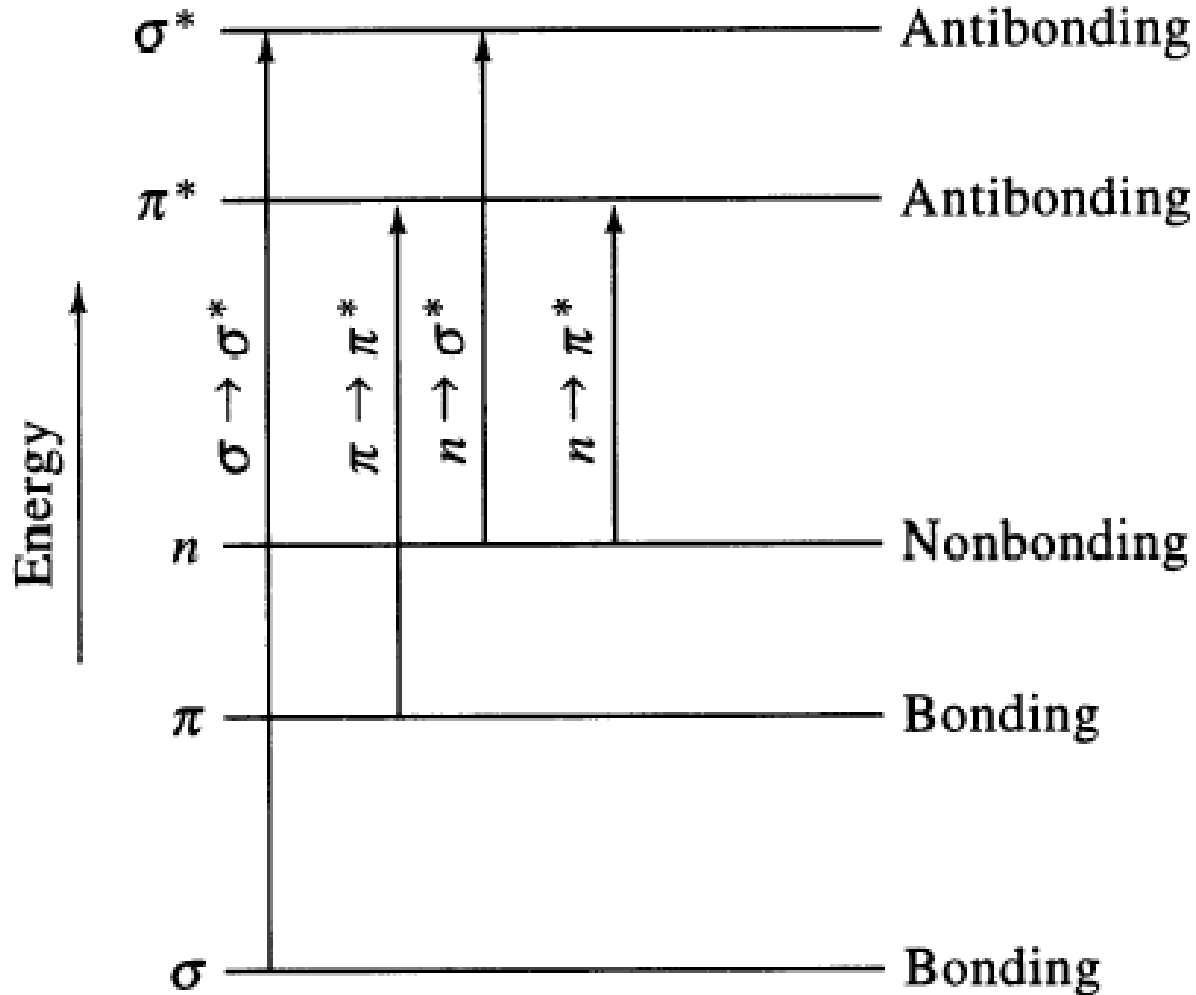
σ electrons C-C, C-H etc. amount of energy is higher than provided by near UV radiation



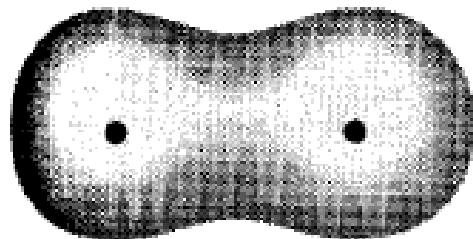
Compound containing σ bond do not absorb in near UV region, that is the reason liquid paraffins used as a solvent in UV spectroscopy.

n electrons These are unshared electrons and not involved in the bonding between atoms. These electrons can be excited by UV radiations. Therefore compounds containing N, O, S, and halogens or unsaturated hydrocarbons may absorb UV radiations.

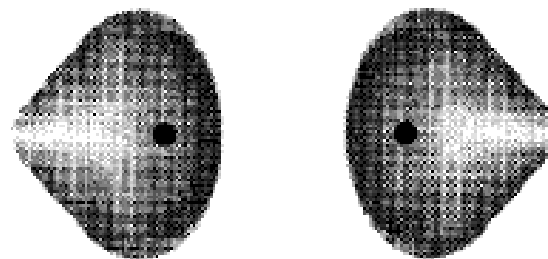
Electron transitions



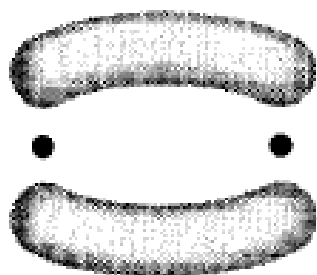
Sigma and Pi orbitals



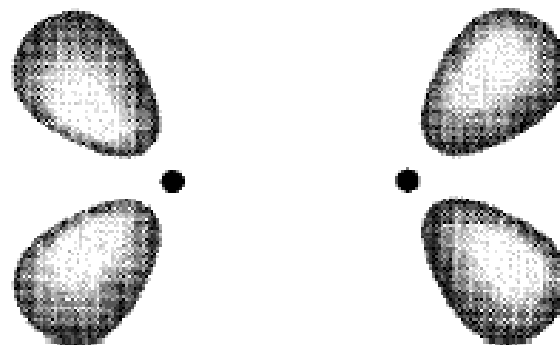
(a) σ orbital



(c) σ^* orbital



(b) π orbital



(d) π^* orbital

σ - σ^* transitions

σ - σ^* transitions-Electron move from σ to σ^* .

1. Energy required is very high ,so it takes place towards shorter wave length side.
2. These transitions takes place in saturated hydrocarbons, which do not posses lone pair of electrons.
3. Absorption occur at far UV region.
4. Example-Methane shows band at 121.9-125nm
Propane at 135 nm
5. Commercial spectrophotometers are unable to record this range.

n- σ^* Transitions

1. This transition occurs in saturated organic compounds having lone pairs of electrons (in heteroatoms eg. O, N, halogens, etc)
2. Energy required is less than **σ - σ^* transitions**
Absorption band appears at 180-200 nm (longer wavelength region)
3. Lower the E.N. of heteroatoms, higher will be the wavelength for absorption.

CH₃Cl-173nm

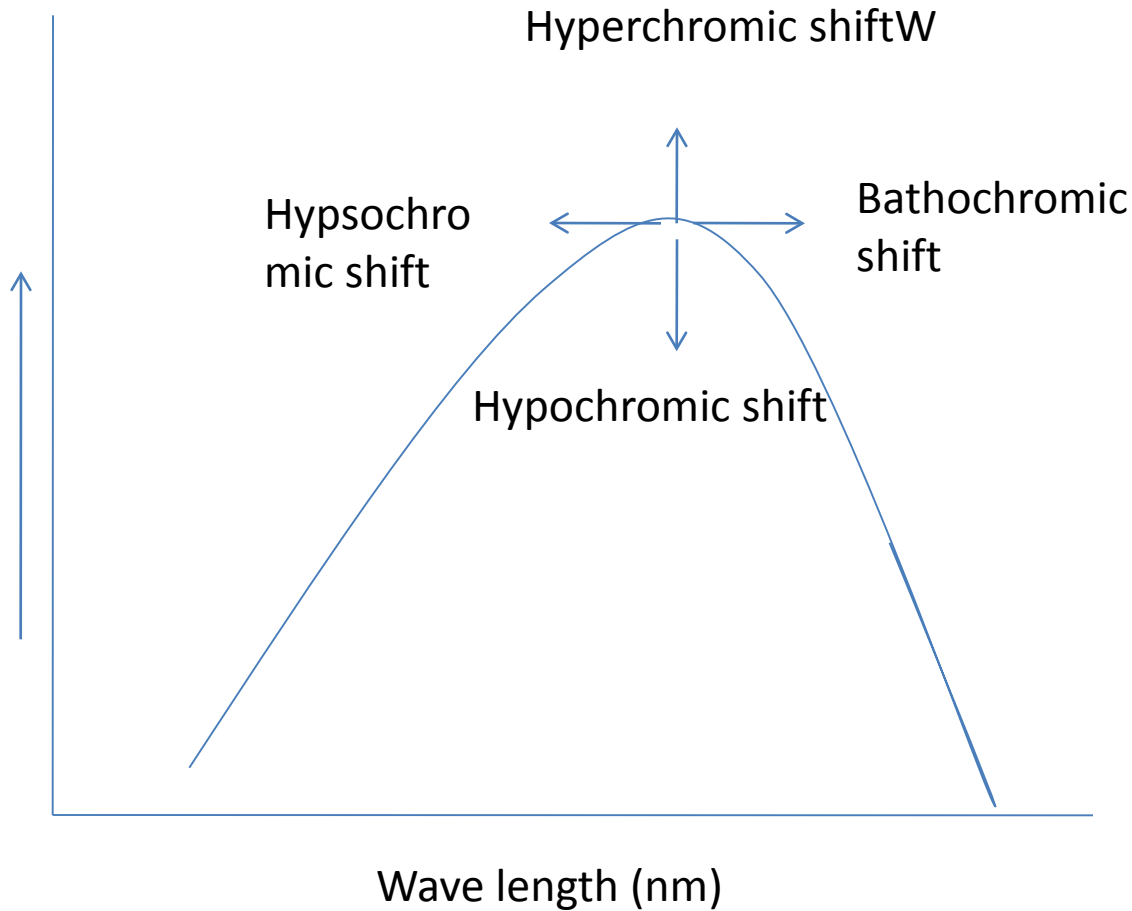
CH₃I-258nm

$\pi - \pi^*$ Transition

1. This transition takes place in the molecules having **π electron system**.
2. This transition takes place within the framework of **selection rules**.
3. These rules are based upon symmetry concept and determine whether the transition is allowed or forbidden.
4. Ethylene-Two bands-174nm, and 200 nm(forbidden)

5. Intensity of absorption is independent of solvent due to nonpolar nature of double bond.
6. If an alkyl group is substituted then absorption maxima shift towards longer wavelength side. This effect is called **bathochromic shift or red shift**.

Absorption and intensity shift



Selections Rules

1. Transitions which involve the change in the spin quantum no. of an electron during the transitions state ,do not occur.In other words direct singlet triplet transitions are forbidden.
2. Transitions between orbitals of different symmetry usually do not occur.

Allowed or forbidden Transitions

Allowed Transition-Transition having ϵ_{\max} value between 10^4 - 10^6 are called allowed transitions.

These obey the given selection rules.

Example- $\pi - \pi^*$ Transition in 1,3 butadiene shows strong absorption at 217 nm with ϵ_{\max} value is 20.000.

Forbidden transition-Transitions which violate the selection rules are forbidden transitions.

Example- $n - \pi^*$ Transition

These are having ϵ_{\max} between 10-1000 Kcal/mole.

n - and π^* are in the planes perpendicular to each other. Example-Saturated aldehydes and ketones.

n- π^* Transition

1. Energy required is lesser than **π - π^* Transition.**
2. This transition takes place in compounds containing hetero atoms having lone pair of electrons.
3. The intensity of transitions is low.
4. Saturated aldehydes and ketones having no double or triple bond shows weak bands in the range of 270-300nm.

Example- C=O, C=S, CN etc

solvent effect

The polarity of solvent usually shift the position of absorption band either towards longer or shorter wavelength side ,depending upon type of electronic transitions involved as given below.

(i) **$n \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ Transitions-** If a group is more polar in ground state than in excited state:

If a group is more polar in ground state than in excited state, and dissolved in polar solvent, the electrons in the ground state are more stabilized relative to the excited state due to hydrogen bonding or dipole-dipole interaction with the polar solvent. As a result, the energy difference between the ground state and the excited state increases and hence the absorption shifts towards shorter wavelength (blue colour) or higher energy.

Example-Carbonyl group is more polar in ground state than in excited state.

Example-C=O group

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(ii) If the group is less polar in ground state than in excited state and dissolved in polar solvent –The electrons in the ground state are less stabilized relative to the excited state due to hydrogen bonding or dipole dipole interaction with the polar solvent in excited state. As a result the energy difference between the ground state and the excited state decreases and hence the absorption, shifts towards longer wavelength (red colour) or lower energy. This shift is known as bathochromic shift

Example- C=C

Chromophores

These are colour carrier groups, which are responsible for imparting colour to compound.

Example-Nitro group impart yellow colour to nitro compound.

Types of chromophores

(1) Chromophores which contains π e- and undergoes π - π^* transitions.

Example-Ethylene, Acetylene

(2) Chromophores which contains π and n-. They undergoes π - π^* and n - π^* transitions.

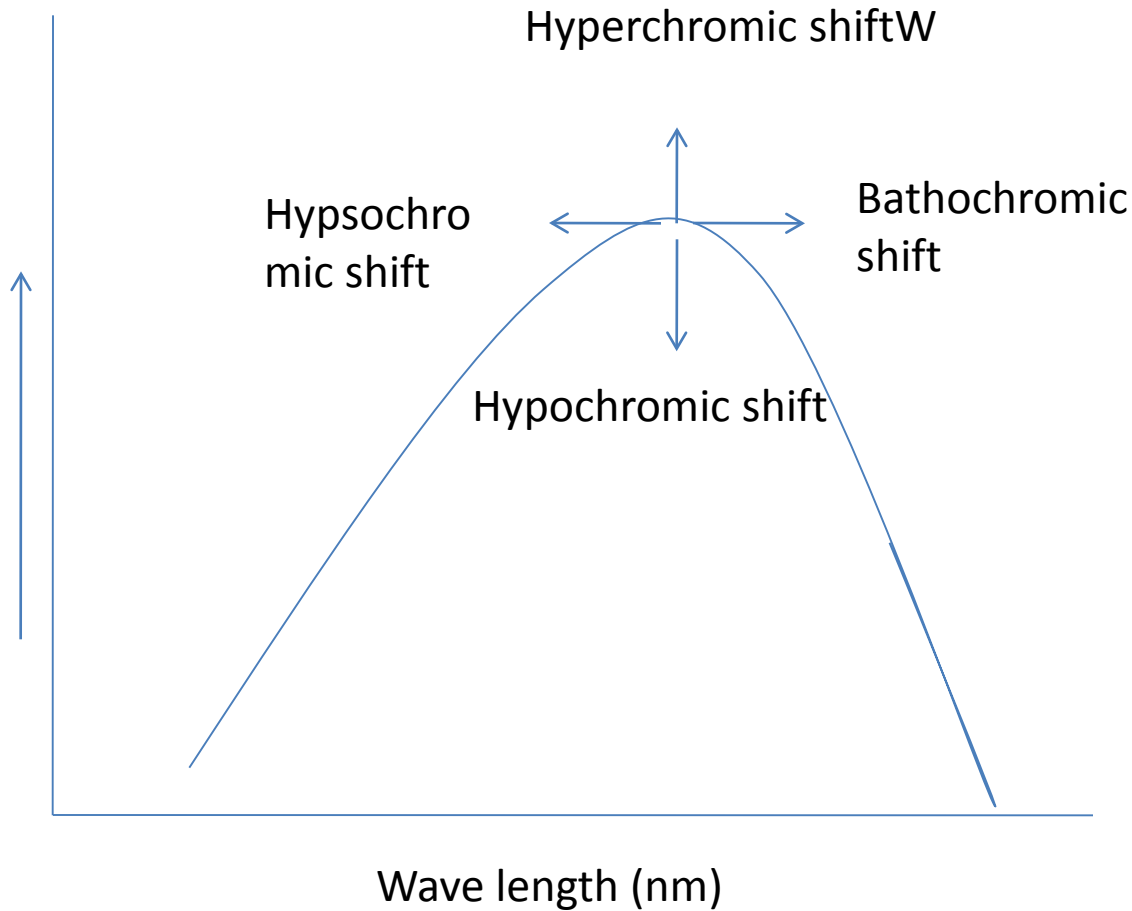
Example-Carbonyles and Nitriles

Auxochromes(Colour enhancing groups)

They have ability to extend conjugation of the chromophores by sharing nonbonding electrons and thus shift the absorption band towards longer wave length side (red end of the spectrum) Auxochromes itself cannot act as a chromophores.

Example—OH, -OR, -NH₂, -SH

Absorption and intensity shift



Absorption and intensity shift

Hypsochromic or Blue shift-

Shift of absorption maxima at shorter wavelength side is called blue shift.

Cause-(1) Due to removal of conjugation

(2) Change in polarity of solvent

Example-Absorption maxima of Aniline shift from 280 m μ to 200m μ in acidic medium, which result in formation of



Here lone pair is no longer present on NH₂ group and hence conjugation is removed, which result in blue shift.

Bathochromic shift or Red shift

Shift of absorption maxima towards longer wave length side is called red shift.

Cause-(1) Presence of auxochromes.

(2) Change of solvent

Examples-Carbonyl compounds shows red shift when polarity of solvent is lowered.

- **Hyperchromic shift**-It is increase in intensity of absorption.

- **Example**- C_6H_6 - ϵ_{max} 204 while $C_6H_5CH_3$ -225

Hypochromic Shift-It leads to decrease in intensity of absorption.

- Example**- C_6H_6 - ϵ_{max} 204 while C_6H_5Cl -190

Charge transfer transitions

Colour may arise due to charge transfer transitions.

Example-Permanganate ion MnO_4^-

(1) Ligand to metal charge transfer Transition-

Example-In Permanganate ion MnO_4^- electrons migrate from orbital of oxygen to orbital of Mn.

(2) Metal to ligand charge transfer Transitions-

Transfer of d orbital electrons to antibonding π e- orbital of aromatic compounds.

Applications

UV-visible spectroscopy has broad applications:

1. Detection of functional group-The presence of any functional group can be detected with the help of this technique.

Example-If a compound does not show λ_{\max} value above 200 nm ,it shows the absence of conjugations.eg $-\text{CHO}$, $=\text{C}=\text{O}$,benzene etc

2. Extent of conjugation: Greater the no. of conjugated double bonds, it will always absorb at higher wave length region. In case of eight or more double bond conjugation, the absorption may occur even in the visible region. Each extent double bond gives the additional of 30nm.

Eg. $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$ λ_{max} value is 217nm

While for $\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2-\text{CH}=\text{CH}_2$ λ_{max} value is 247nm

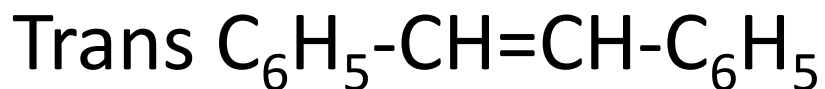
3. Distinction between conjugated and nonconjugated compound.-The conjugated compound absorbs at higher wavelength region as compared to nonconjugated compound.

Eg.- $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$ λ_{max} value is 176nm

$\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ λ_{max} value is 215nm

4. Identifications of geometrical isomers.

The trans isomer absorb e.m. radiations at a longer wave length with longer extinction coefficient than corresponding cis-isomers.



$$\lambda_{\max} \ 290\text{nm} \ \epsilon_{\max} \ 2400$$



$$\lambda_{\max} \ 278\text{nm} \ \epsilon_{\max} \ 9350$$

Application of UV-Visible Spectroscopy

Identification of inorganic and organic species

Widely used method

Magnitude of molar absorptivities

Absorbing species

methods

Absorption Spectrum and λ_{\max} value

1. Application of spectrophotometer is quantitative analysis.
2. The curve shows variation of A or ϵ with wave length for given concentration of solution. And thickness of cell is known as **absorption spectrum** of the compound.
3. It is characteristic property of a compound and no two compounds have same absorption spectrum .
4. The wave length corresponding to maximum absorption is termed as λ_{\max} value ,which is also a characteristic property.
5. Once the absorption spectrum is known, an unknown concentration of such a compound can be determined by measuring absorbance at its λ_{\max}