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Mo Tu We Th Fr Sa Su

3) Electronic spectroscopyORUV - visible spectroscopy

$$\text{frequency } (\nu) = 3 \times 10^{14} \text{ to } 3 \times 10^{16} \text{ sec}^{-1}$$

$\text{Wavelength } (\lambda) = \frac{3 \times 10^8 \text{ m sec}^{-1}}{3 \times 10^{14} \text{ sec}^{-1}}$	$\frac{3 \times 10^8 \text{ m sec}^{-1}}{3 \times 10^{16} \text{ sec}^{-1}}$
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$= 1 \times 10^8 \times 10^{-14}$	$10^8 \times 10^{-16} \text{ m.}$
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$= 10^{-6} \text{ m.}$	10^{-8} m.
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$$\lambda = (1 \mu\text{m.} \text{ --- } 10 \text{ nm.})$$

Energy

$$\text{Wave no. } (\bar{\nu}) = \frac{1}{\lambda}$$

$$= \frac{1}{10^{-6} \text{ m}}$$

$$= 10^6 \text{ m}^{-1}$$

$$= 10^8 \text{ cm}^{-1}$$

$$\text{Energy } E = h\nu$$

$$= 6.626 \times 10^{-34} \text{ J sec} \times 3 \times 10^{14} \text{ sec}^{-1}$$

$$= 1.9878 \times 10^{-20}$$

$$= 1.99 \times 10^{-21} \text{ Joules.}$$

$$= 6.626 \times 10^{-34} \text{ J sec} \times 3 \times 10^{16} \text{ sec}^{-1}$$

$$= 1.99 \times 10^{-19} \text{ Joules.}$$

$$1.99 \times 10^{-21} \text{ Joules.}$$

Introduction:-

When a molecule absorbs UV & visible light, its electrons get excited from ground states to higher energy states.

In the ground state, these electrons are paired. In the higher state, if the spin of electrons are parallel, it is called excited triplet state. & if the spin of electrons are paired, it is called singlet excited state.

The absorption of UV or visible light results in the singlet ground state to excited singlet state transition.

* Electronic spectroscopy involves the promotion of electrons (σ, π, n electrons) from the ground state to the higher energy state. Substance absorbs intensity in the visible range will appear coloured to the human eye.



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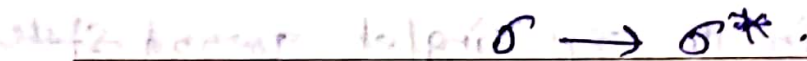
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* Different electronic energy levels.

As to the molecular orbital theory, when a molecule is excited by the absorption of UV or visible light, its electrons are promoted from a bonding to an antibonding orbital.

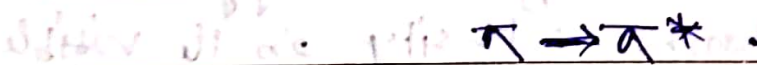
(i) σ to σ^* transition takes place when σ (sigma) electron is promoted to antibonding (σ^*) orbital.

It is denoted by —

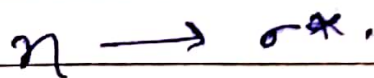


(ii) ~~also~~ π to π^* transition takes place when π (p_z) electron is promoted to antibonding (π^*) orbital.

It is denoted by —



(iii) when a non-bonding electron (n) get promoted to an antibonding (σ^*) orbital, It is denoted by —



(iv) when a non-bonding electron (n) get promoted to an antibonding (π^*) orbital, it is denoted



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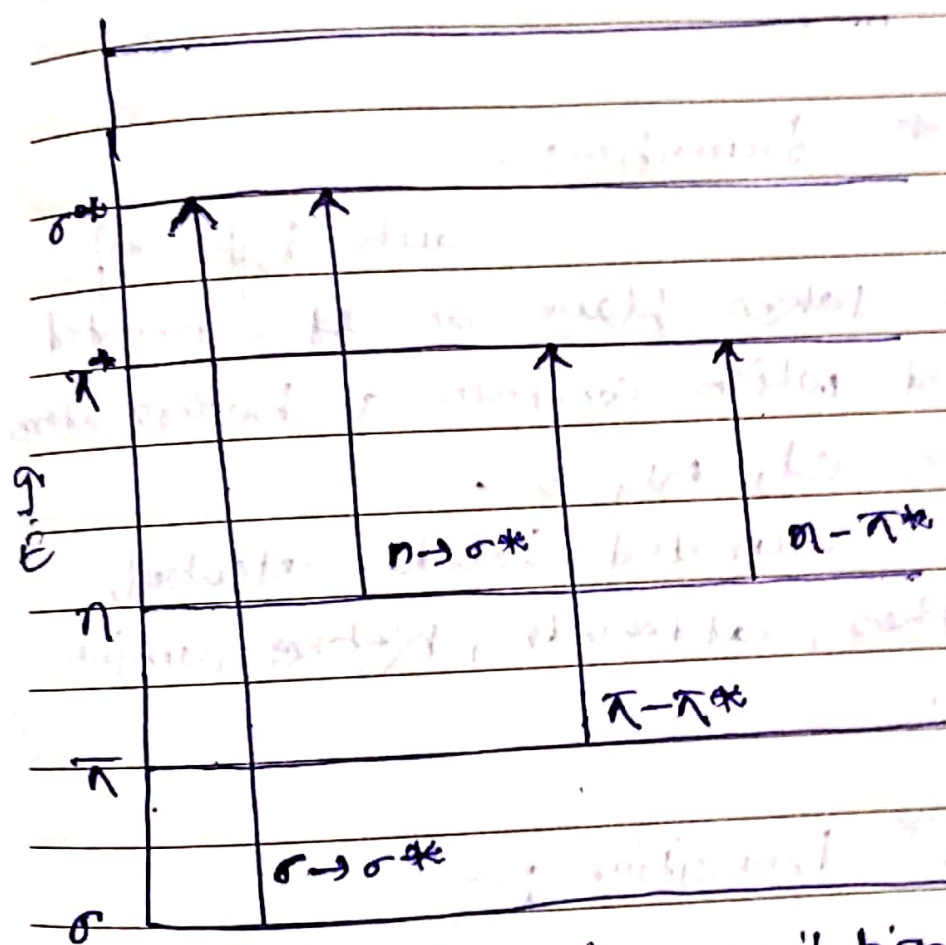
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by —
 $n \rightarrow \pi^*$

The energy required for various transitions obey the following order

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$



electronic excitation energy \rightarrow



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① $\sigma \rightarrow \sigma^*$ transition :-

It is a high energy process as σ -bonds are generally strong bonds.

Saturated hydrocarbons like methane, propane etc show such type of transition.

② $n \rightarrow \sigma^*$ transition :-

Such type of transition takes place in saturated compound which contains a hetero atom such as Cl, N, O.

eg \rightarrow Saturated halide, alcohol, ether, aldehyde, ketone, amine etc.

③ $\pi \rightarrow \pi^*$ transition :-

Such type of transition occurs in the unsaturated hydrocarbon contains double bond, triple bond and also in aromatic.

eg \rightarrow Alkene, Alkynes, carbonyl compound, cyanide, etc

④ $n \rightarrow \pi^*$ transition :-

Such type of transition occurs in the hetero atom gets excited to π^* antibonding orbital.

Saturated aldehyde, saturated ketones show both types of transitions -

(a) low energy, $n \rightarrow \pi^*$

(b) High energy, $\pi \rightarrow \pi^*$.

selection Rule -

① The transitions between s to p-orbital and p-p orbitals are allowed transitions. ($\Delta l = \pm 1$)

② The transition which involves a change in the spin quantum no. of an electron during the transition do not occur. Thus singlet-triplet transitions are forbidden.

③ The transition between orbitals of different symmetry do not occur
eg $n \rightarrow \pi^*$ transitions are forbidden

④ The transitions from s to s orbital and from p to p orbital are forbidden.
† ($\Delta l = 0$).