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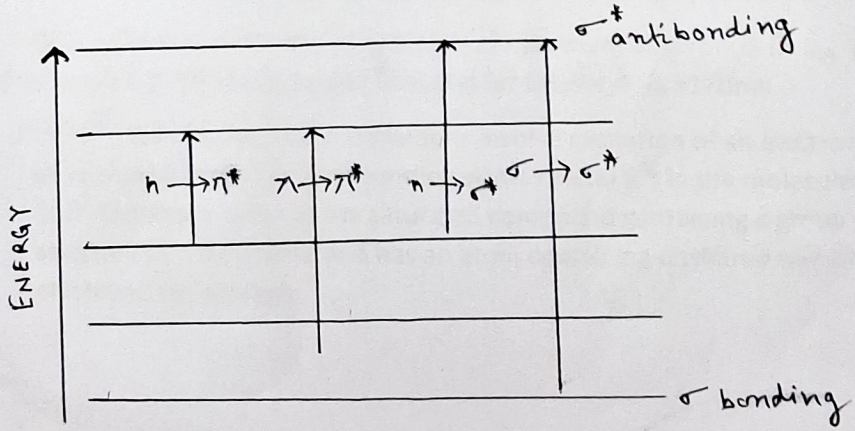
ELECTRONIC SPECTRA OF TRANSITION METAL COMPLEXES (CONTINUED):

Type of electronic transition:

When a beam of light falls on a molecule, absorption of energy (photon) takes place causing rotational, vibrational and electronic transitions in the molecule. Electronic transitions involve the change of valence electron from the ground state to excited state. Since the molecule of a substance contains different type of valency electrons, different amount of energy is absorbed causing different type of electronic transitions. In normal state electrons are present in bonding orbitals. These electrons are promoted to anti-bonding orbitals after absorption of energy. Anti-bonding orbitals are indicated by putting asterisk (*). Few orbitals do not take part in bond formation. These are known as non-bonding orbitals and denoted by (n).



Electronic transition and energy level of a molecule.

The energy absorbed in the U V region may bring about the following electronic transitions:

Electronic Spectra of Transition Metal Complexes

(i) Sigma bonding electron to sigma antibonding orbital ($\sigma \rightarrow \sigma^*$)

(ii) Pi bonding electron to pi anti-bonding orbital ($\pi \rightarrow \pi^*$)

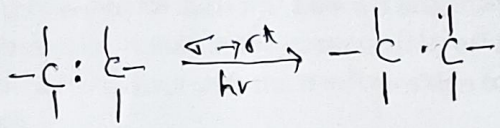
(iii) Non-bonding electron to sigma anti- bonding orbital ($n \rightarrow \sigma^*$)

(iv) Non-bonding electron to Pi anti-bonding orbital ($n \rightarrow \pi^*$)

Since a molecule sigma electron are more tightly bonded than the Pi

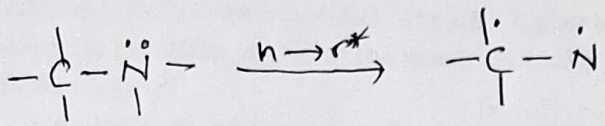
$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

(i) $\sigma \rightarrow \sigma^*$ Transitions: These transitions involve excitation of an electron of a single (σ) bond to a higher anti-bonding orbital (σ^*). The energy required for such transitions is so high that the absorption occurs in vacuum region of the spectrum and falls outside side the range generally available in U.V spectrophotometers. Saturated hydrocarbons do not show absorption in U-V region of spectrum. However they show absorption in vacuum.



The presence of a group containing non-bonding electron such as --NH_2, --OH etc., shifts the wavelength of maximum absorption (λ_{max}) to a higher value e.g. CH_4 has λ_{max} =125nm and for $CH_3\ddot{N}H_2$ λ_{max}=170nm.

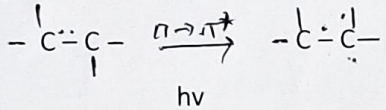
(ii) $n \rightarrow \sigma^*$ Transitions: These transitions involve excitation of an electron of unshared pair of an anti-bonding sigma orbital (σ^*) in the molecule. Such Transition occur in the saturated compound containing a group attached by single bond and has an atom containing unshared pair of electrons, for example



These transitions require less energy than transitions. Thus, the molecule having non-bonding electrons absorb in the common U.V region.

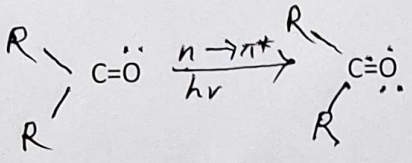
$CH_3—\ddot{N}H_2$, λ_{max}=215 nm
$CH_3—OH$, λ_{max}=183 nm
$(CH_3)_3N$, λ_{max}=227 nm

(iii) $\pi \rightarrow \pi^*$ Transitions : These involves excitation of an electron of bonding π orbital to a higher energy anti-bonding Pi molecular orbital (π^*).Such transitions are observed in unsaturated compouns.



The energy required for such transitions is less than $\pi \rightarrow \pi^*$ transitions and the absorption occurs in the common U.V region. Polar solvents in conjugated compound shift the $\pi \rightarrow \pi^*$ transition towards longer wavelength.

(iv) $n \rightarrow \pi^*$ Transitions: These transitions involve bonds excitation of one of the non-bonding (n) electrons of an atom to a higher energy anti-bonding pi molecular orbital (π^*). Such transitions are characteristics of compounds containing multiple bonds involving hetero atoms such as C = O, C≡N etc. These are lowest energy transitions and so absorption occurs at higher wavelength.



Conjugation shift the absorption to such a higher wavelength that it extend in the visible region of the spectrum and the compound appears coloured

A molecule containing σ, π and n electrons may undergo all types of possible transitions giving rise to number of absorption bands.