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B.Sc VI - Chemistry

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Electronic Spectra of Transition Metal Complexes (42)

Generally two important experimental parameters are measured in various branches of spectroscopy.

- (i) Energy of absorbed or emitted radiation by the system.
- (ii) Intensity of spectral lines

Electromagnetic spectrum are mainly of two types.

- (i) Emission spectrum
- (ii) Absorption spectrum

Thus a spectrum in which any wavelength of various wavelengths of white light being absorbed is called absorption spectrum. These are of three types, electronic energy, vibrational and rotational energy.

Internal energy of each molecule is the sum of all types of energy found in it

$$E_{\text{internal}} = E_{\text{ele}} + E_{\text{vib.}} + E_{\text{rot.}}$$

	Wavelength	Energy	Kcal
Electronic (UV)	200 - 350 nm	143-82	143-82
(Visible)	350 - 800 nm	82-36	82-36
Vibrational (IR)	2.5 - 15 μm	14.3-2.8	14.3-2.8
Rotational (Microwave)	1 cm	10^{-4}	10^{-4}

Electronic Spectra =

Electron spectra of transition metal ions and complexes are obtained in visible and UV regions.

Transition of electron from one energy level to another energy level involves large energy. Bandwidths are generally found of the order of $1000 - 3000 \text{ cm}^{-1}$.

Compounds of transition elements are found to be colored due to absorption of light of definite wavelength in visible region. Extent or intensity of absorbed light on passing light of a definite wavelength through a solution may be -

$$A = \log \frac{I_0}{I}$$

where A = absorbance, I_0 = intensity of incident light and I = intensity of light transmitted.

Amount of energy absorbed depends on nature of substance. Every compound gives a specific spectrum. In UV spectrum molecular extinction coefficient is used in place of intensity of absorption

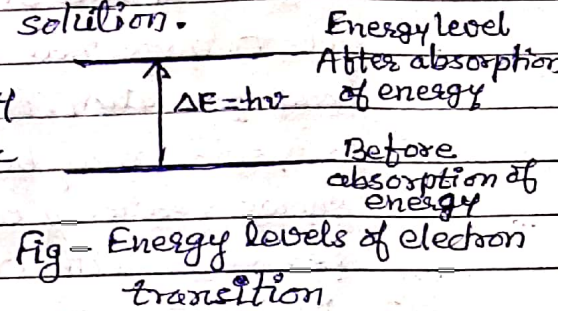
$$\epsilon = \frac{A}{cl}$$

where ϵ = molecular extinction coefficient.
 c = concentration of the substance and l = length of the tube used to place solution.

Excitation of an electron by absorbing energy from lower energy to higher energy level is called electron

transition. Each electron

transition gives one band in absorption ~~spectrum~~ spectrum of the substance.



Electronic Transition in Complexes -

In metal complexes some important electron transition are given as below.

(1) d-d transition or Ligand field transition -

This transition is possible in near IR, visible or UV region in complexes. These regions have range from 10000 to 3000 cm^{-1} , or 1000 to 333 nm. Some d-d transition are beyond this range. Experimentally it is not possible to get frequency less than 10000 cm^{-1} .

Though frequency more than 40000 cm^{-1} is available easily but such transition are coupled by charge transfer and inter ligands transition. In this way d-d transition are limited to visible region spectrum.

These transition are possible only in metal ions i.e. transition of electrons occurs between energy levels of metal ion. These transitions may be explained by CFT and to some extent by LFT. According to MOT this transition occurs when electron is excited from t_{2g} energy level to e_g^* energy level.

(2) Ligand to Metal Charge transfer transition —

Excitation of electron from molecular orbital of ligand to molecular orbital of metal atom is called ligand to metal charge transfer transition. Molecular orbital of ligand is σ or π orbital of M-L bond of ligand initially i.e. bonding orbital which is σ or π orbital between metal and ligand is associated with ligand in the starting. It has low energy. Metal orbital gets transformed to antibonding or non bonding after bond formation. It has comparatively high energy. These transition may be only explained by MOT. This transition shows reducing capacity of a ligand to reduce metal i.e. ease with which a ligand can reduce a metal.

(3) Metal to ligand Charge transfer transition —

Metal to ligand charge transfer transition is the excitation of electron from non bonding or antibonding orbital to antibonding orbital. Non bonding or antibonding orbitals which have low energy level ligand initially. Thus this transition is opposite to ligand to metal charge transfer transition in one way. Energy of this transition shows capacity of metal to reduce ligand. Lower oxidation states of metal ion show such transitions in UV region. These transitions are not possible in visible region many times. For example, position of band gets changed on substituting F^- , Cl^- , Br^- or I^- in place of X in complex ion

(4) Intra ligand transition — Intra ligand transition is the excitation of an electron from orbital of one ligand to orbital of another ligand. This transition of electron needs high energy, hence these transitions are found in UV region. Though intensity of bands obtained in metal to ligand charge transfer is equal to intra ligand transition even when both these are different. It is because band of its spectra is not affected by other ligands. They depend on metal to ligand bond strength to some extent.