Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science (T. Y. B. Sc.)

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Unit: 2 - Spectra and Magnetic Properties

Module Name: Effect of Crystal Field Splitting on Properties of Octahedral Complexes: Spectral

Module No: 15

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Notes

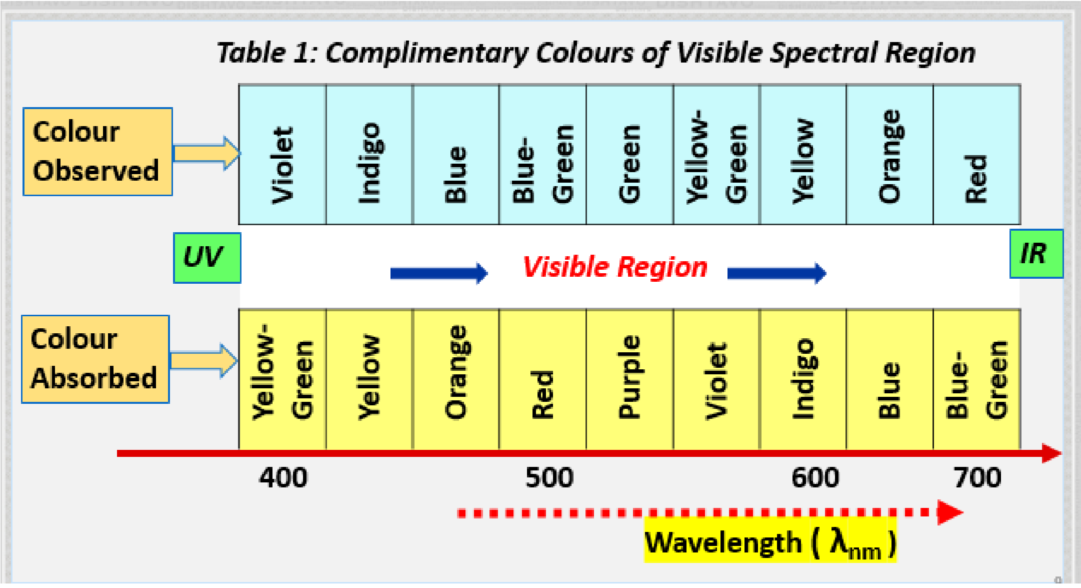
Effect of Crystal Field Splitting on Spectral Properties of Octahedral Complexes:

The spectral property of complexes explains why different complexes show different colours. The concept of spectral property is based upon *Crystal Field Splitting(CFS)* and the *Magnitude of CFS(Δo)* in an Octahedral Complex.

Colour and Spectra of Complexes:

When whole white light is absorbed by the complex, it appears black. When whole white light is transmitted by the complex, it appears white. But if a complex absorbs some light from the visible region (of the electromagnetic radiation) and transmits the remaining light, then the complex appears coloured.

The colour of the complex then depends upon the wavelength (λ_{max}) at which it absorbs the visible light and at which wavelength the transmission takes place. Any substance that absorbs light in visible region (λ = 400nm to 800 nm) of electromagnetic spectrum will be coloured. The colour OBSERVED is the complimentary colour of the visible light ABSORBED. (Table 1)



Examples:

1) Hexa ammine Copper(II) complex $[Cu(NH_3)_6]^{2+}$ ion is blue because it absorbs yellow light in the visible region (λ = 470nm)

2) The tetrahedral complex of the type $[CoCl_4]^{2-}$ requires less energy for the transition of the electron. Therefore it absorbs red light and appears blue.

3) The solution containing $[Ti(H_2O)_6]^{3+}$ absorbs yellow–green light and appears violet.

Principles involved in Colour of Complexes

For a substance to show colour, there should be presence of unpaired electron. Electronic Transitions occur when this unpaired electron within a molecule, absorbs light in the visible region of the spectrum; And undergoes excitation from lower energy level to higher energy level and this is based upon Crystal Field Splitting.

<u>Crystal Field Splitting (CFS)</u>

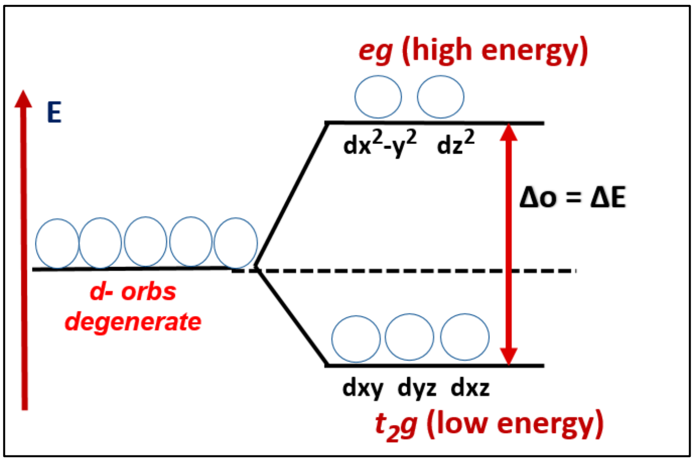
In an octahedral complex, the energy levels are created by splitting of *d orbitals* of the central metal atom by the ligand.

The *d* orbitals are split into two sets t_2g and *eg*

t_2g is the Lower energy orbitals

***eg* is the Higher energy orbitals**

This is called as Crystal Field Splitting (CFS). A representation of Crystal Field diagram is shown below.



Electronic transitions from lower energy *d*–orbitals*(t_2g)* to higher energy *d-orbitals (eg) are* called as d-d transitions. The energy gap between the *t_2g* and *eg* orbitals (Δo) equals the energy of a photon and is given by the equation;

$$\Delta o = E = h\nu \quad \text{and} \quad (\nu = c/\lambda)$$

$$E = hc/\lambda$$

E = amount of energy required for transition

Δo = Magnitude of CFS

h = Photon of light

ν = Frequency (*cm^{-1}*)

λ = Wavelength (*nm*)

c = speed of light (*cm/sec*)

From Planks equation, Because the energy of a photon of light is inversely proportional to its wavelength, the colour of the complex depends on the magnitude of Δo, which then depends upon the type of ligand in an octahedral complex.

Type of Ligands

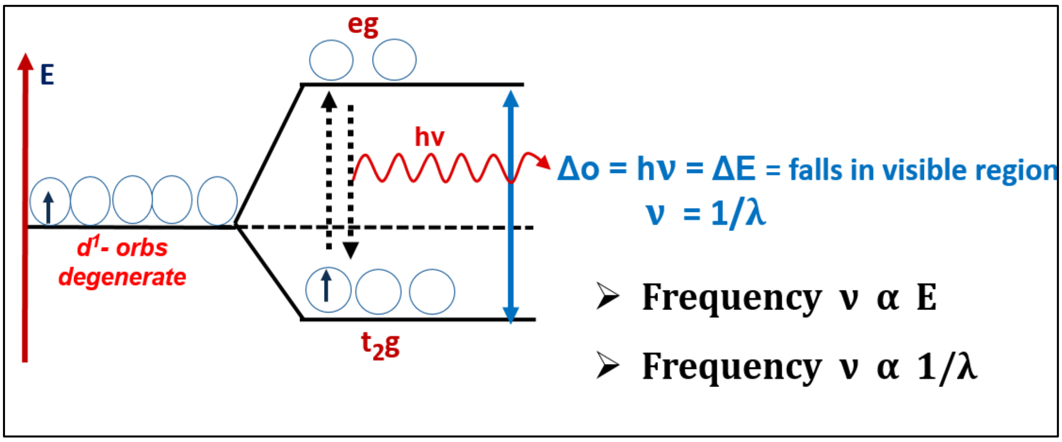
- **For a Strong Field Ligand**, ***Δo = maximum*** and the electron requires high energy for its excitation. Thus it will absorb at a higher energy (*shorter wavelength λ*) and will show Low intensity colour ***such as***

Yellow, Orange or Red; as these complexes will absorb high energy violet or blue light.

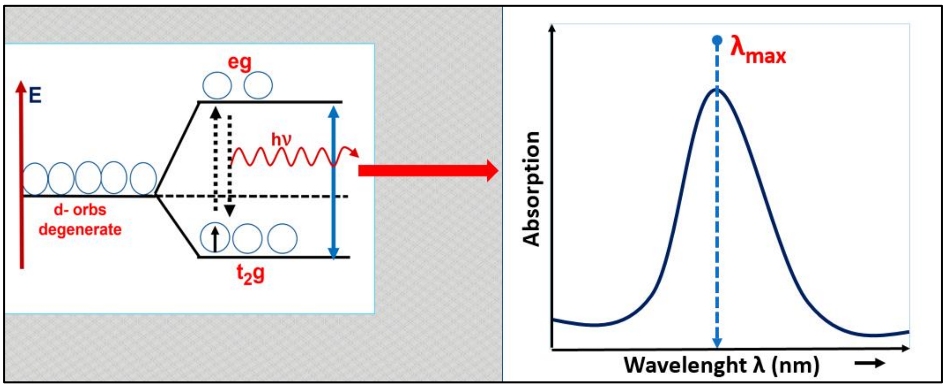
- For a Weak Field Ligand, *Δo = minimum* and the electron requires less energy for its excitation. Thus it will absorb at a low energy (*longer wavelength λ*) and will show high intensity colour s*uch as* Blue, Green or Violet; as these complexes will absorb low energy yellow, orange or red light.
- Depending upon their field strength, the ligands are arranged in the order of their increasing splitting power. This arrangement of ligands is called as Spectrochemical Series given as

  I^- < Br^- < S^{2-} < SCN^- < Cl^- < ONO^- < F^- < OH^- < H_2O < NCS^- < NH_3 < en < dipy < phen < NO_2^- < CN^- < CO

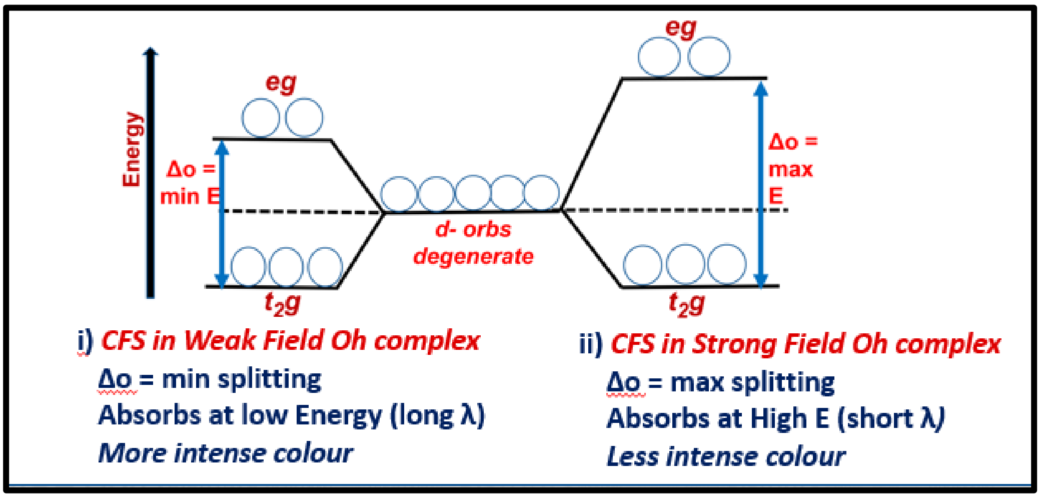
<u>CFS diagram</u> showing transition of an unpaired electron from t_2g orbitals to *eg* orbitals in an Octahedral Complex



The spectrum of a coloured solution is recorded and analysed using a **Spectrophotometer**. The spectra shows a peak with *λmax in the visible range* which is characteristic of that coloured complex.



CFS diagrams showing d-d transitions in Weak Field and Strong Field Octahedral complexes



***<u>Example 1</u>*.**

Aqueous solution of Co(II) i.e. Octahedral $[Co(H_2O)_6]^{2+}$ is Pink. In $[Co(H_2O)_6]^{2+}$ complex, H_2O is WFL and Δo = min . Therefore complex absorbs at lower energy (λmax=512 nm) and shows PINK colour

<u>Example 2</u>.

Aqueous solution of Ni(II) *ie*. Oh $[Ni(H_2O)_6]^{2+}$ is GREEN. In octahedral $[Ni(H_2O)_6]^{2+}$ complex, H_2O is WFL and Δo = min . Therefore complex absorbs at lower energy (λmax=720 nm) and shows GREEN colour

***Example 3*.**

Aqueous solution of Ni(II) *ie*. Oh $[Ni(NH_3)_6]^{2+}$ is BLUE. In octahedral $[Ni(NH_3)_6]^{2+}$ complex, NH_3 is SFL and Δo = max. Therefore complex absorbs at (λmax=570 nm) and shows BLUE colour

***Example 4*.**

Aqueous solution of Ti(III) *ie*. Oh $[Ti(H_2O)_6]^{3+}$ is PURPLE. In octahedral $[Ti(H_2O)_6]^{3+}$ complex, H_2O is WFL and Δo = min. Therefore complex absorbs at lower energy and shows a strong absorption at λmax=490 nm and appears PURPLE in colour

Hence Crystal Field Splitting can explain *Electronic Spectra* of complexes which can further provide valuable information on bonding and structure of complexes.