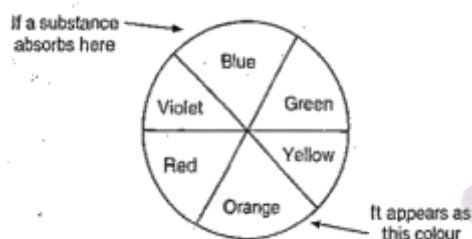


Study Notes on Color Spectra

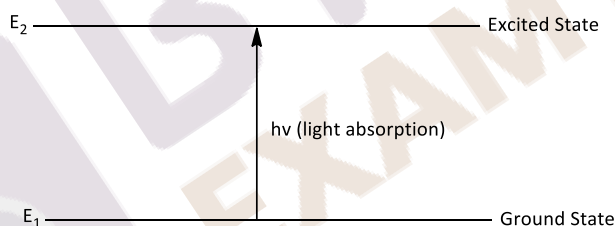


Color Spectra

The electromagnetic spectrum consists of photons of different wavelengths that have both wave and particle character. These create visible light in the EM spectrum (small portion). If a compound absorbs light (photon) of one Color, (say orange), then it reflects (or transmits) light of blue Color. Each specific wavelength corresponds to a different color and in case of white light, all wavelengths are present. There are many transition metal complexes that show a variety of colors that depend on both the nature of metal and ligand. For example, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is purple, $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ is pink, $[\text{Ni}(\text{en})_3]^{2+}$ is violet.



Any compound shows color due to the electronic transition from ground to the excited state. The striking colors that are shown by the transition-metal complexes is due to the excitation of an electron from lower energy d-orbital to higher one. For this transition, energy must be equal to the difference in energy between the two d-orbitals that depend on the value of Δ . In complexes, the electronic transitions take place from t_{2g} to e_g or e_g to t_{2g} orbitals in octahedral or tetrahedral complexes and such types of transitions are called d-d transitions.



If the electromagnetic radiation absorbed by a compound lies in the UV or IR region, then the transmitted (or reflected) light will lie in the UV or IR region and the compound will appear colorless.

The energy of separation between two states is given by:

$$\Delta E = E_2 - E_1 = hv = \frac{hc}{\lambda} = hc\bar{\nu} \quad \left(\because \bar{\nu} = \frac{1}{\lambda} \right)$$

Where, ΔE = energy

h = Planck constant = 6.63×10^{-34} J.s

c = velocity of light = 10^{10} cm s^{-1}

λ = wavelength of light absorbed (cm)

ν = frequency of light absorbed (s^{-1})

$\bar{\nu}$ = wave number (cm^{-1}) = $\frac{1}{\lambda}$

For some complexes, the Δ value is very small due to which these absorb light radiations in the infrared region and as a result, appear colorless because infrared radiations are colorless.

Similarly, for complexes that have large Δ value, (large energy difference between ground state and excited state), these absorb light radiations in the UV region and appear colorless.

The magnitude of Δ can be measured with the wavelength which is getting absorbed. It will become clear by taking one example. It has been observed that the color of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion is purple. In this complex ion, the electron occupies the orbital of the lowest energy i.e., any one of the degenerate t_{2g} orbitals. The purple color of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ion is due to absorption of blue-green light and transition of electrons of the t_{2g} orbitals to one of the degenerate e_g orbitals. Along with this, the absorption spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ shows that the d-d transition occurs with a single broad peak with a maximum absorption at 20300 cm^{-1} (wavelength of 498 nm) which corresponds to 243 kJ mol^{-1} energy.

Since $1 \text{ kJ mol}^{-1} = 83.7 \text{ cm}^{-1}$

$$\text{Thus, } \Delta_o \text{ for } [\text{Ti}(\text{H}_2\text{O})_6]^{3+} = \frac{20300}{83.7} \approx 242.53 \text{ kJ mol}^{-1}.$$

Among all the d configurations, d^1 is the simplest one because energy of absorbed light is equal to the magnitude of Δ_o . For other d^n electronic configurations, the electron-electron interactions must be considered, and more calculations are involved in the determination of Δ_o value. As M-L bonds are not rigid in transition-metal complexes, electronic transitions and vibrations occur simultaneously when light is absorbed. This phenomenon is known as vibronic transitions. Due to vibrations of ligands, change in energy of d-electrons takes place. When a ligand moves towards the transition metal, the value of Δ_o increases and when it moves away from the transition metal, energy of d-electrons increases. The two additional factors which are responsible for broad bands are spin-orbit coupling and Jahn-Teller distortion. It has been observed that sharp peaks are shown by complexes where Δ_o does not change or energy of ground state and excited state changes equally and these are generally observed for high spin Mn^{2+} complexes.

In case of lanthanide complexes, sharp bands are observed. As f-orbitals are buried due to which there occurs no interaction between f-orbitals and ligands. Any vibration of ligands or change in nature of ligands does not change the energy of f-electrons due to which magnitude of Δ_o will remain unaffected.

SELECTION RULES:

Intensities of Absorption Bands of Complexes: In case of octahedral complexes, when transitions take place from t_{2g} to e_g , this is known as d-d transition. When the centre of symmetry is present, then the intensities of absorption bands are low. For complexes without centre of symmetry, such as tetrahedral complexes and octahedral cis complexes of the type MA_4B_2 , strong absorption bands are observed. There are certain rules to describe the variation in the relative intensities of absorption bands.

(1). Laporte's Selection Rule: This rule is applied to molecules that are centrosymmetric. It states that transitions that take place between states of the same symmetry are forbidden. For example, d-d transitions are forbidden because d-orbitals are gerade, that is they have a centre of symmetry with respect to wave function. It can also be explained in terms of the value of azimuthal quantum number.

For $\Delta L = \pm 1$, transitions are Laporte allowed, and absorbance may be high. If $\Delta L = 0$, the transitions are Laporte forbidden and therefore, absorbance is low.

Relaxation in Laporte's Selection Rule: The d-d transitions are Laporte forbidden but still have lower absorbance in the range of $10-50 \text{ L mol}^{-1} \text{ cm}^{-1}$ because there is slight relaxation in the Laporte's selection rule. Octahedral complexes can vibrate unsymmetrically when a UV light incident falls. This results in loss of symmetry temporarily. Also, there is a very small mixing of p-d orbitals due to which d-d transitions are not purely Laporte forbidden but there is slight relaxation in Laporte's rule, Therefore, the octahedral complexes show Color of low intensity. In case of tetrahedral complexes, due to the absence of a centre of symmetry, p-d mixing becomes more pronounced because of formation of seven molecular orbitals from atomic d (gerade) and p (ungerade) orbitals. Therefore, these complexes absorb more strongly than octahedral complexes. Hence, tetrahedral complexes give more intense color as compared to octahedral complexes.

(2): Spin Selection Rule: As spin is directional in nature, it is said to have odd parity. Transitions in which direction of spin changes are forbidden. States having the same total spin quantum number are generally spin allowed.

i.e., $\Delta S \neq 0$, spin forbidden

Relaxation in Spin Selection Rule: There are some complexes in which spin orbit coupling can take place which will relax the spin selection rule. Due to this, transitions can be observed from ground state of one spin multiplicity to excited state of different spin multiplicity. These spin forbidden transitions are very weak as compared to spin allowed transitions. In case of lighter atoms, the strength of spin orbit coupling is lower as compared to heavier ones. An increase in atomic number will increase the intensity of such bands. For first series transition metal complexes, spin-orbit coupling is weak and, therefore, the absorption bands are weak and for 4d and 5d, this coupling is strong which gives rise to strong absorption bands. Also, a Laporte forbidden d-d transition is more intense than a spin forbidden transition.

Charge Transfer Spectra:

It is defined as the peak which arises from the transitions in which transfer of an electron from an atom or group to another one takes place. Unlike d-d transitions, charge transfer transitions are Laporte, and spin allowed i.e.,

$$\Delta l = \pm 1 \quad \text{and} \quad \Delta S = 0$$

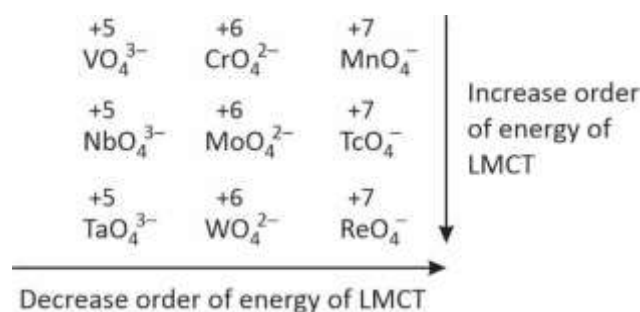
Thus, charge transfer transitions give rise to more intense (strong) absorptions. These are of four types:

(1). Ligand to Metal Charge Transfer (LMCT): This takes place when electrons get transferred from a molecular orbital having ligand like character to those having metal like character. The conditions for this transfer are:

- There should be lone pairs of electrons on ligands having relatively high energy such as O^{2-} , Br^- , Cl^- or Se .
- Metal should be in a low oxidation state and must have low lying empty orbitals.

Energy required to transfer an electron from ligand to metal depends upon the lowest unoccupied molecular orbital (LUMO) of the metal cation and the highest occupied molecular orbital (HOMO) of the ligand.

The size of metal cation increases on moving from 3d to 4d to 5d series due to which energies of LUMO (i.e., vacant d-orbitals) centred on metal cation increases and, therefore, energy required to transfer of an electron from HOMO of oxide ion to LUMO of metal cation in tetra oxo-anions increases on moving down the group.



In the case of 4d and 5d, tetra oxo-anions are colorless due to the large energy difference between the 2p of oxide ion and 4d, 5d orbitals. This transfer requires a very high amount of energy which lies in the UV-region.

(2). Metal to Ligand Charge Transfer (MLCT): This takes place when electrons get transferred from a molecular orbital having metal like character to those having ligand like character. The conditions for this transfer are:

- The oxidation state of metal should be low and should have filled d orbitals.
- Ligands have empty π -antibonding orbitals.

This transfer takes place in case of ligands having π^* orbitals such as CO, CN⁻, SCN⁻, pyridine, bipyridine, NO, etc. In case of an octahedral complex, when t_{2g} and e_g^* orbitals (both belong to metal) are occupied, two MLCT bands $\pi^* \leftarrow e_g^*$ are observed. (π^* is the vacant orbital of the ligand). If either t_{2g} or e_g^* orbitals are occupied, then only one charge transfer band $\pi^* \leftarrow t_{2g}$ or $\pi^* \leftarrow e_g^*$ is observed. The compounds and their Colors arising from MLCT are shown below:

Compound	Color
K ₄ [Fe(CN) ₆]	Yellow
K ₃ [Fe(CN) ₆]	Red
[Fe(Phen) ₃] ³⁺	Blue
[Fe(acac) ₃]	Red

(3). Intervallence Transitions (or Metal to Metal Charge Transfer Transitions): In this, excitation followed by transfer of an electron from a low oxidation state cation to a neighbouring cation having higher oxidation state takes place.

(4). Intra Ligand Charge Transfer: There are some ligands which behave as a chromophore which is responsible for the color. There are four electronic transitions $\sigma - \sigma^*$, π^* , $n - \pi^*$ or $n - \sigma^*$ within a chromophore. When such a ligand is coordinated with a metal ion/atom, energy of absorption changes.

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