

Coordination Chemistry: Theories of Metal Complexes Molecular Orbital Theory (MOT)

(Chemistry-DSE-1002D: **Inorganic and Physical Chemistry**,
Section-I)

BY

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Objectives

1. Introduction
2. Salient features of MOT of octahedral complexes with sigma bonding such as $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{CoF}_6]^{3-}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$
3. Merits and demerits of MOT.

Limitations of CFT

1. CFT gives total emphasis on ionic bonding. Even partial covalent bonding is not considered.
2. CFT considers only metal d-orbitals. Other metal orbitals, s- and p-orbitals not considered.
3. CFT does not consider ligand orbitals. Therefore their interaction with metal orbitals is not explained by CFT.
4. Pi bonding not considered by CFT.
5. CFT fails to explain charge transfer spectra.
6. Nephelauxetic effect (Cloud expansion effect) is not explained by CFT.
7. CFT fails to explain the relative strength of ligands. For e.g. Though H_2O is neutral ligand, it is stronger ligand than negatively charged OH^- .

Molecular Orbital Theory (MOT)

MOT was proposed by Hund, Mulliken and Huckel in 1930

This theory consider metal-ligand bonding as purely ionic, purely covalent or any intermediate case.

According to this theory atomic orbitals combine to form molecular orbitals. To form molecular orbitals, atomic orbitals must have

- i. Same symmetry
- ii. Similar or comparable energy
- iii. Appreciable overlap (i.e. extent of overlap should be large)

Symmetry classes of Atomic Orbitals (Group Theoretical symbols)

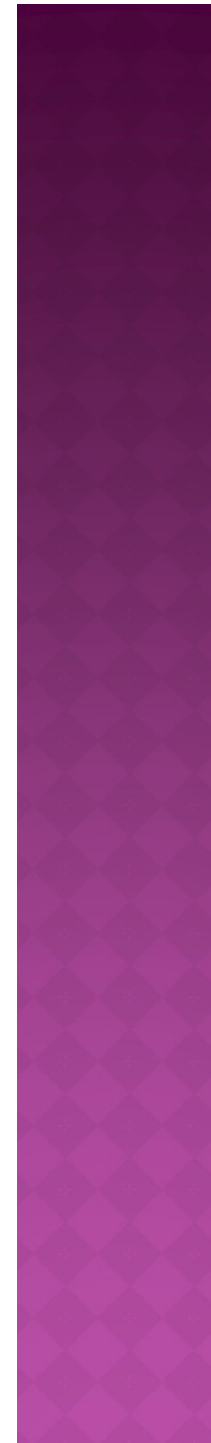
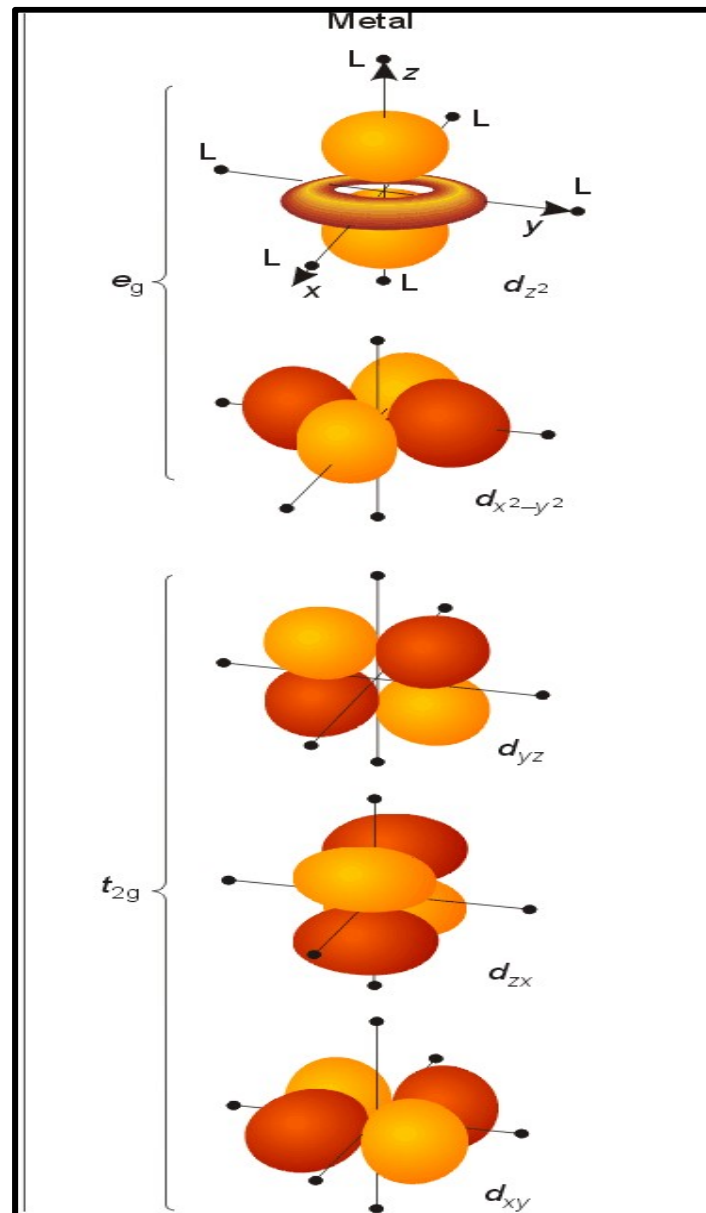
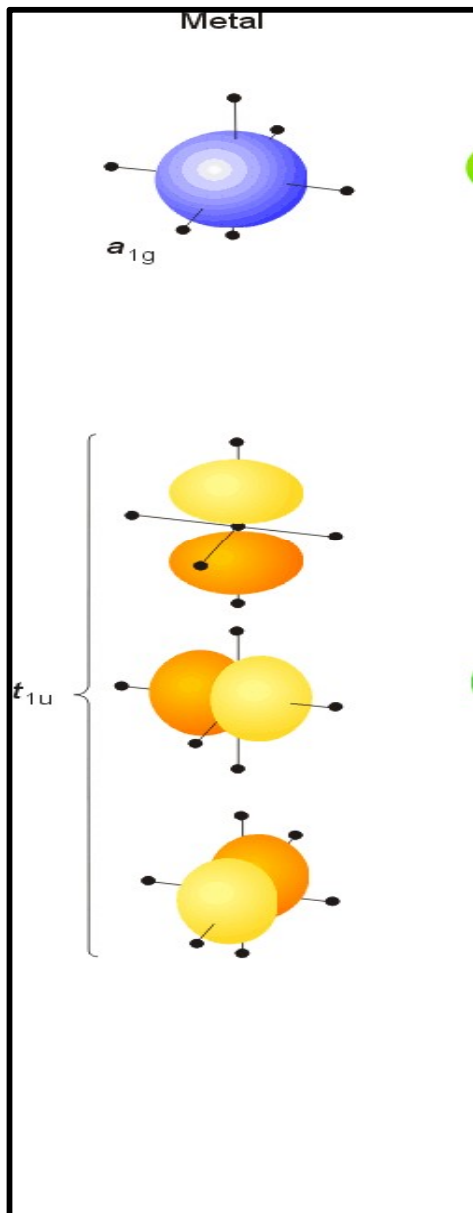
Sr. No.	Metal orbitals	Symmetry symbols of metal orbitals
1	s	a_{1g}
2	P_x, P_y, P_z	t_{1u}
3	$d_{x^2-y^2}, d_z^2$	e_g
4	D_{xy}, d_{yz}, d_{xz}	t_{2g}

a = absency of degeneracy i.e. singly degenerate

e = doubly degenerate

t = triply degenerate

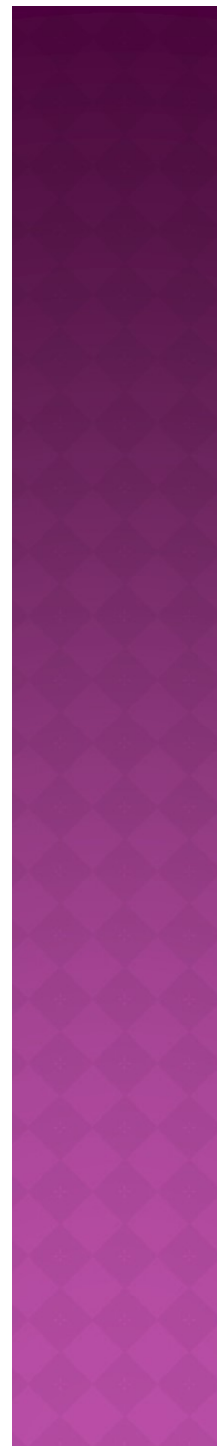
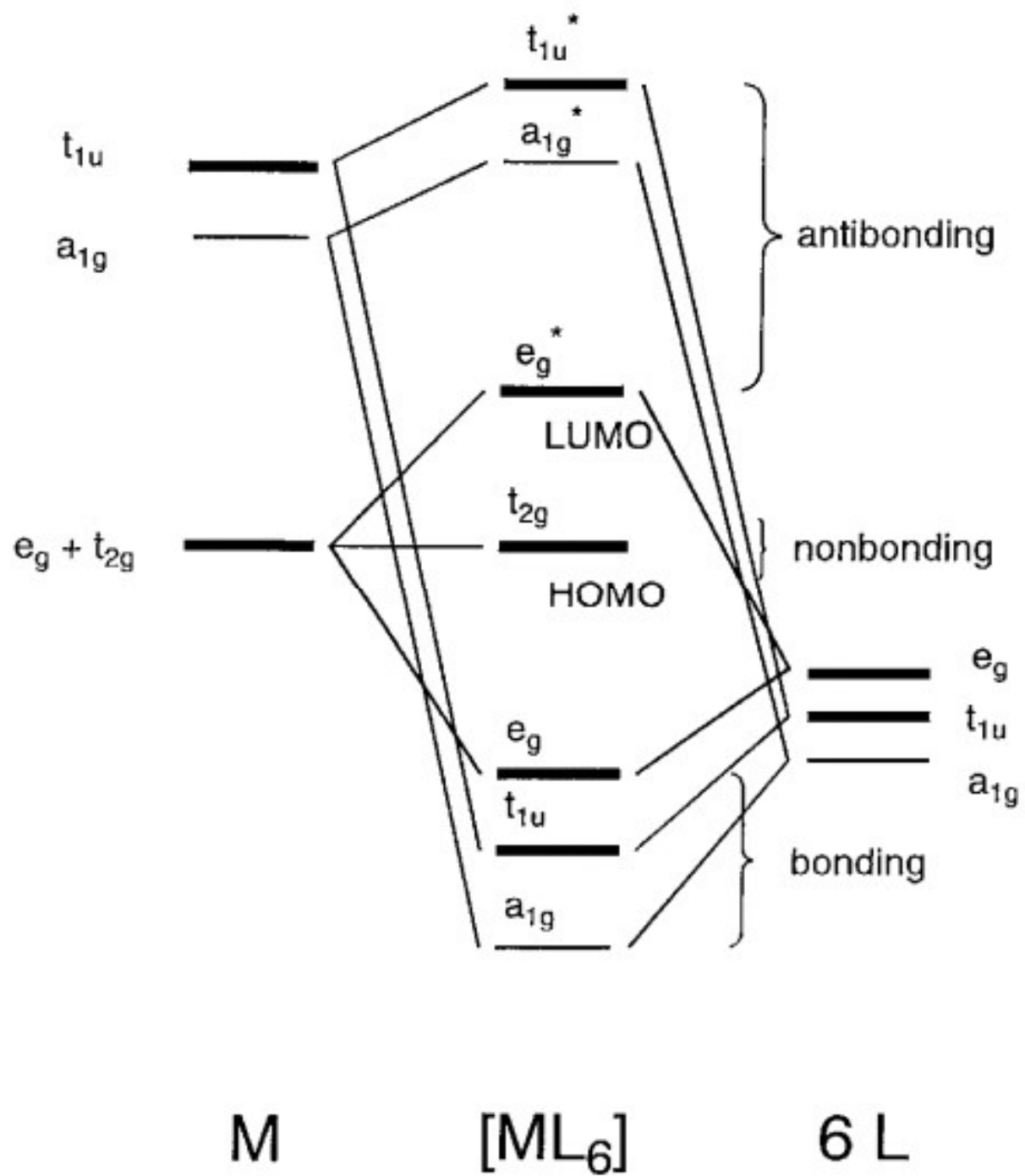
u = ungerade (non-centrosymmetric) i.e. uneven
g = gerade (centrosymmetric) i.e. even



7.3 Group Theoretical Symbols

The $d_{x^2-y^2}$ and d_z^2 orbitals are collectively denoted as e_g and the d_{xy} , d_{yz} and d_{xz} orbitals are collectively denoted as t_{2g} . The symbol 't' means there are three degenerate orbitals (d_{xy} , d_{yz} , d_{xz}) and the symbol 'e' means there are two degenerate orbitals ($d_{x^2-y^2}$, d_z^2) (that are equal in energy i.e. they are degenerate). The symbol 'g' stands for gerade (German, even). The orbital is said to be gerade if it is centrosymmetric i.e. it has the same sign of the wave function at the same distance in opposite direction from the centre of symmetry. The symbol 'u' stands for ungerade (German, uneven). The orbital is said to be ungerade if it changes the sign of the wave function at the same distance in opposite direction from the centre of symmetry. The 's' and 'd' orbitals are 'g' i.e. gerade and 'p' and 'f' orbitals are 'u' i.e. ungerade. The e_g orbitals are doubly degenerate while t_{2g} orbitals are triply degenerate.

In addition to these symbols, sometimes the subscripts 1 and 2 are also used. The subscripts 1 and 2 mean respectively that the orbital or orbitals do not change sign on rotation about the Cartesian axes and that they do not change sign on rotation about axes diagonal to the Cartesian axes. Thus the metal 's' and 'p' orbitals are designated a_{1g} and t_{1u} . The symbol 'a' denotes a singly degenerate orbital.



Assumptions of MOT

1. Central metal ion makes available 9 orbitals for bonding
Six orbitals s , p_x , p_y , p_z , $d_{x^2-y^2}$ and d_{z^2} orbitals for sigma bonding.
Three orbitals d_{xy} , d_{yz} and d_{xz} orbitals for pi bonding
2. Each ligand must have at least one sigma bonding orbital.
3. Six sigma ligand orbitals are combined to form a set of six ligand group orbitals LGOs.
Each of these having matching symmetries is constructed so as to have effective overlap with metal orbitals as shown in figure
4. Each metal orbital linearly combines with its matching symmetry ligand orbital LGOs to form corresponding bonding MOs and antibonding MOs.
5. If the ligand possesses pi orbital along with sigma orbitals, then pi orbitals also combine to form symmetry orbitals which should be further able to overlap effectively with the matching metal ion pi orbitals and form bonding and antibonding MOs

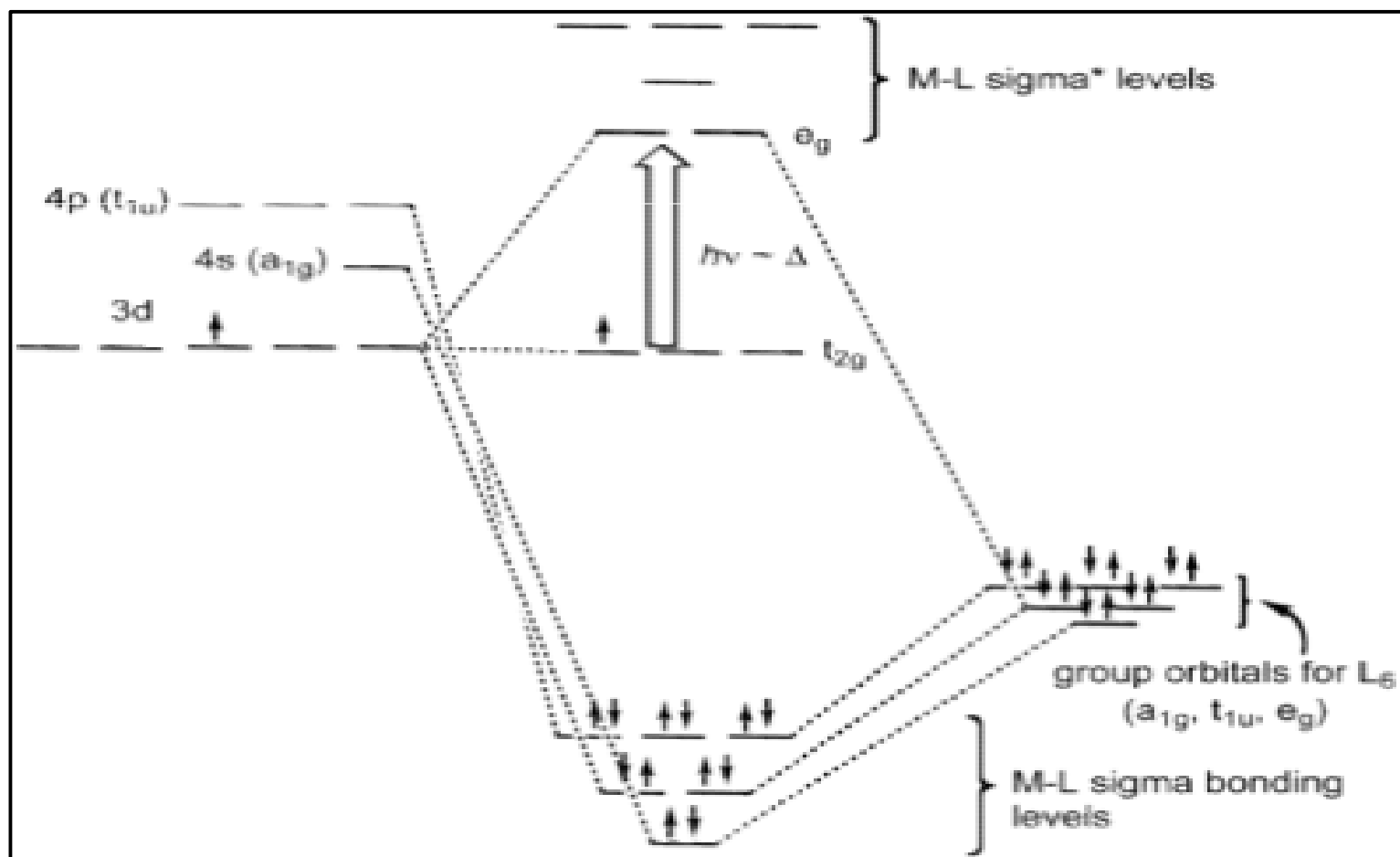
MOT of Octahedral complex with sigma bonding

Formation of octahedral complex $[\text{TiH}_2\text{O})_6]^{3+}$

Ti (Z=22) $[\text{Ar}] 4s^2, 3d^2$

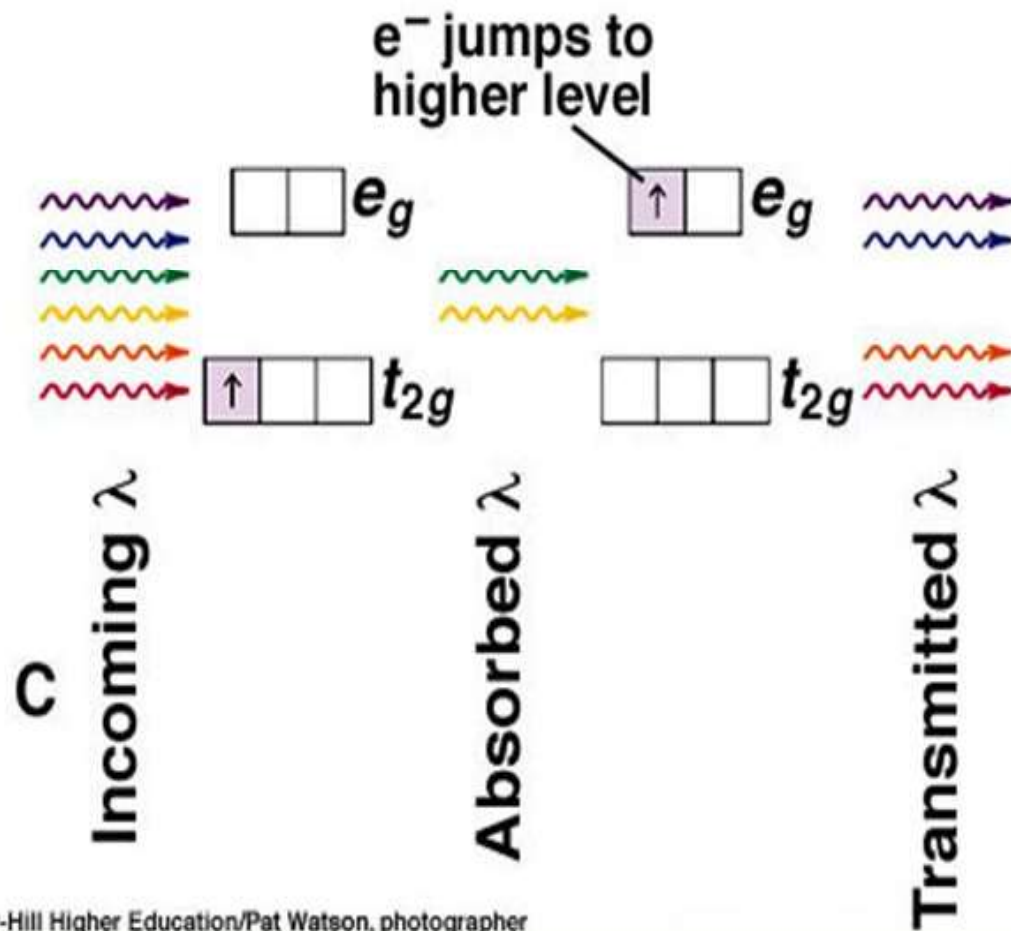
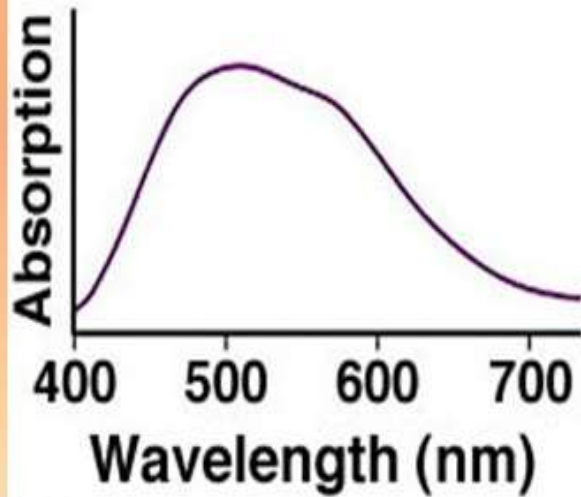
Central metal ion $\text{Ti}^{3+} = [\text{Ar}] 4s^0, 3d^1$

Ligand = six H_2O molecules



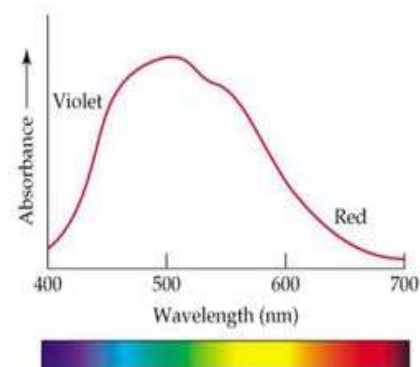
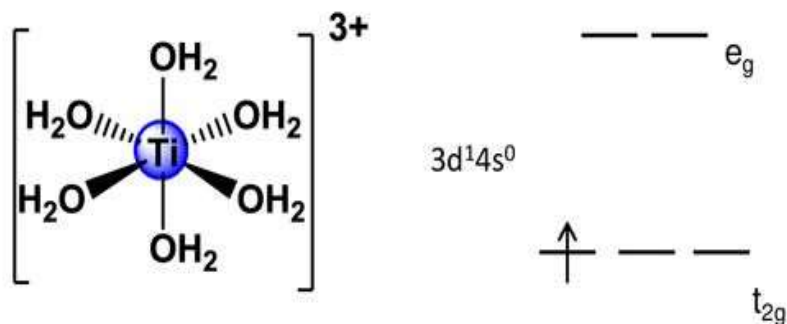
The Color of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$

A



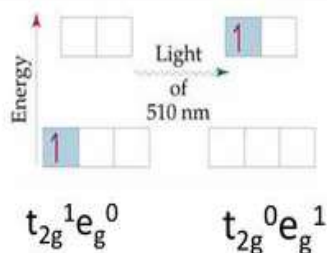
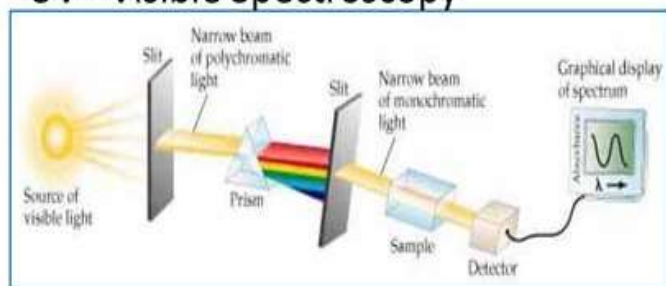
Significance of Δ_o and its physical measurement

Electronic spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



$$494 \text{ nm} = 20,300 \text{ cm}^{-1}$$

UV-Visible Spectroscopy



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

$$[\text{Ti}(\text{H}_2\text{O})_6]^{3+} \quad \Delta_o = 20,300 \text{ cm}^{-1} = 243 \text{ kJ/mol}$$

Since an electron in the t_{2g} set is stabilized by $-0.4 \Delta_o$ $243 \times -0.4 = -97 \text{ kJ/mol}$

The complex is stabilized to the extent of 97 kJ/mol compared to a hypothetical spherical field due to the splitting of the d orbitals; This extra stabilization of the complex is called **crystal field stabilization energy (CFSE)**

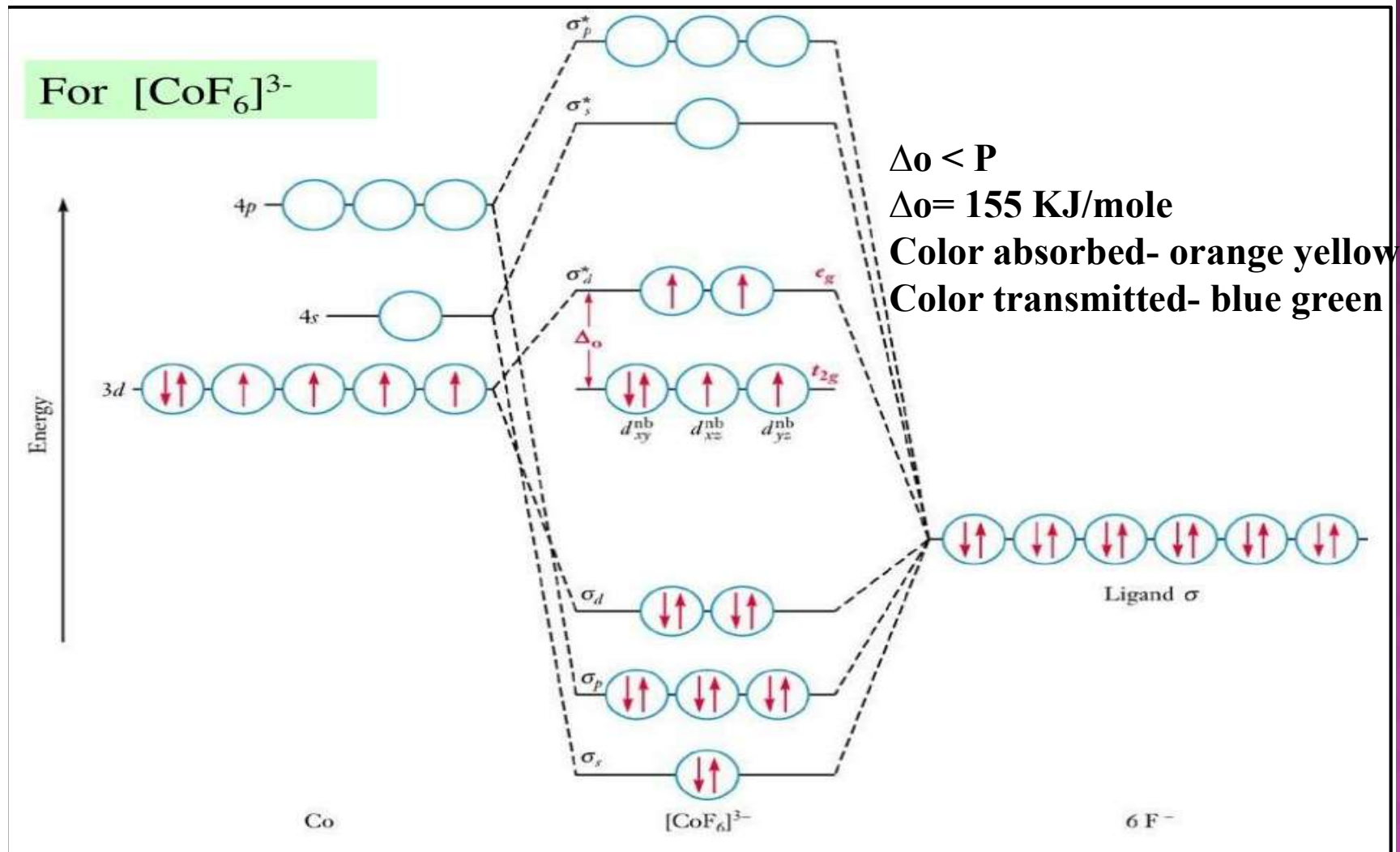
Because the sample absorbs most strongly around the green region of the visible spectrum, it appears purple.

Formation of octahedral complex $[\text{CoF}_6]^{3-}$

Co (Z=27) $[\text{Ar}] 4s^2, 3d^7$

Central metal ion $\text{Co}^{3+} = [\text{Ar}] 4s^0, 3d^6$

Ligand = six F^-



Total number of electrons = 6 from Co^{3+} and 12 from six F^- ligands

Complex is paramagnetic due to presence of 4 unpaired electrons

Table 7.7 : Colours of transmitted light with wave number of absorbed light

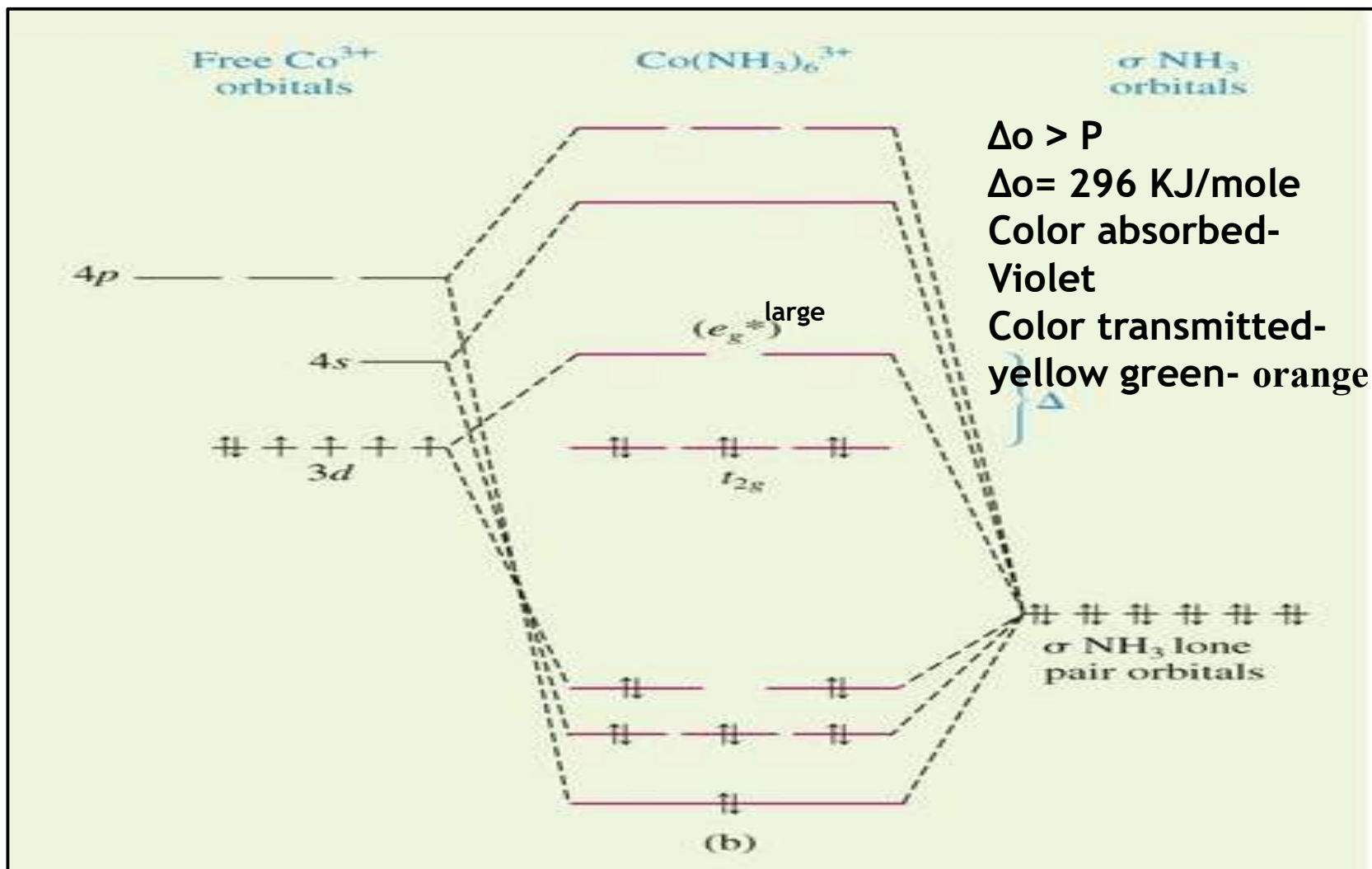
Wave Number of absorbed light cm^{-1}	Colour of absorbed light	Colour of transmitted light
25000 – 22990	Violet	Yellow - Green
22990 – 20830	Blue	Yellow
20830 – 20410	Green - Blue	Orange
20410 – 20000	Blue - Green	Red
20000 – 17800	Green	Purple
17800 – 17240	Yellow - Green	Violet
17240 – 16810	Yellow	Blue
16810 – 16530	Orange	Green - Blue
16530 – 13330	Red	Blue - Green

Formation of octahedral complex $[\text{Co}(\text{NH}_3)_6]^{3+}$

Co (Z=27) $[\text{Ar}] 4s^2, 3d^7$

Central metal ion $\text{Co}^{3+} = [\text{Ar}] 4s^0, 3d^6$

Ligand = six NH_3 molecules



Merits of MOT

1. It is complete theory.
2. It has considered every possible interaction between metal orbitals and ligand orbitals.
3. Pi bonding is explained.
4. Charge transfer spectra explained satisfactorily.
5. Nephelauxetic effect (Cloud expansion effect) is explained.
6. Magnetic properties are explained very well.

Limitations of Molecular Orbital Model

1. MO diagrams are complex.
2. MO diagrams are difficult for molecules with more than two atoms.
3. No prediction of geometry

