

CH 101

Lecture 6

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Intensity of absorbance (height of the peak) depends on

1. Energy of incident photon
2. Concentration
3. Path Length
4. ϵ , extinction coefficient (molar absorptivity)

For d-d transitions $\epsilon = 5 - 100 \text{ M}^{-1}\text{Cm}^{-1}$

Why So low??

Selection Rules for Electronic Spectra of Transition Metal Complexes.

The Selection Rules governing transitions between electronic energy levels of transition metal complexes are:

$\Delta S = 0$ The Spin Rule

$\Delta l = \pm 1$ The Orbital Rule (Laporte)

The first rule says that allowed transitions must involve the promotion of electrons without a change in their spin.

Selection Rules for Electronic Spectra of Transition Metal Complexes.

- **Laporte Selection Rule:** In a molecule having center of symmetry, transitions between states of the same **parity** (symmetry with respect to a **center of inversion**) are forbidden.
- For example, transitions between states that arise from d orbitals are forbidden ($g \rightarrow g$ transitions; d orbitals are symmetric to inversion), but transitions between states arising from d and p orbitals are allowed ($g \rightarrow u$ transitions; p orbitals are anti-symmetric to inversion). **Therefore, all d-d transitions in octahedral complexes are Laporte-forbidden.**
- Laporte-allowed transitions involve **$\Delta l = \pm 1$.**

Selection Rules for Electronic Spectra of Transition Metal Complexes.

■ Some transitions are not allowed does not mean that such a transition will never occur, but that it is less likely and that the **intensity (molar absorption coefficient)** of such an absorption band is very low.

Relaxation of the Rules can occur through:

- a) Spin-Orbit coupling - this gives rise to weak spin forbidden bands
- b) Vibronic coupling - an octahedral complex may have allowed vibrations where the molecule is asymmetric. Absorption of light at that moment is then possible.
- c) π -acceptor and π -donor ligands can mix with the d-orbitals so transitions are no longer purely d-d.

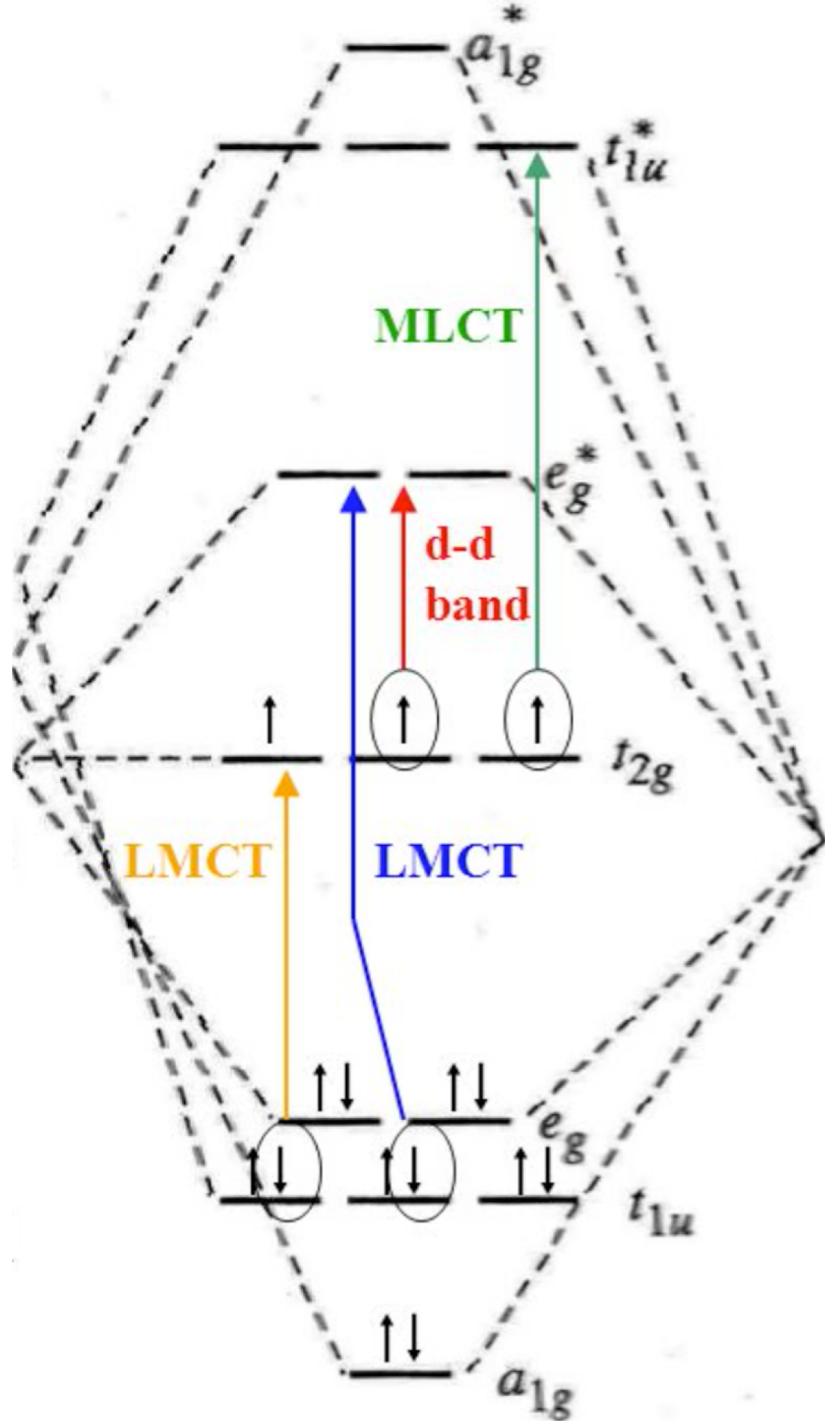
Spin-Orbit Coupling.

The electron is spinning on its axis thereby generating “Spin Magnetic Moment”

Simultaneous rotation of electrons about nucleus generates “Orbital Magnetic Moment”

Interaction of nucleus and electrons slightly perturb the “Orbital Magnetic Moment”. As total angular momentum must be conserved, this slight change must be exactly compensated by a slight change in “Spin Magnetic Moment”

Spin-orbit coupling results in “mixing of wavefunctions” such that t_{2g} and e_g are no longer 100% pure in nature. The rigorously forbidden $g \rightarrow g$ *“are a bit less forbidden” the extent of which depends on the magnitude of mixing.*



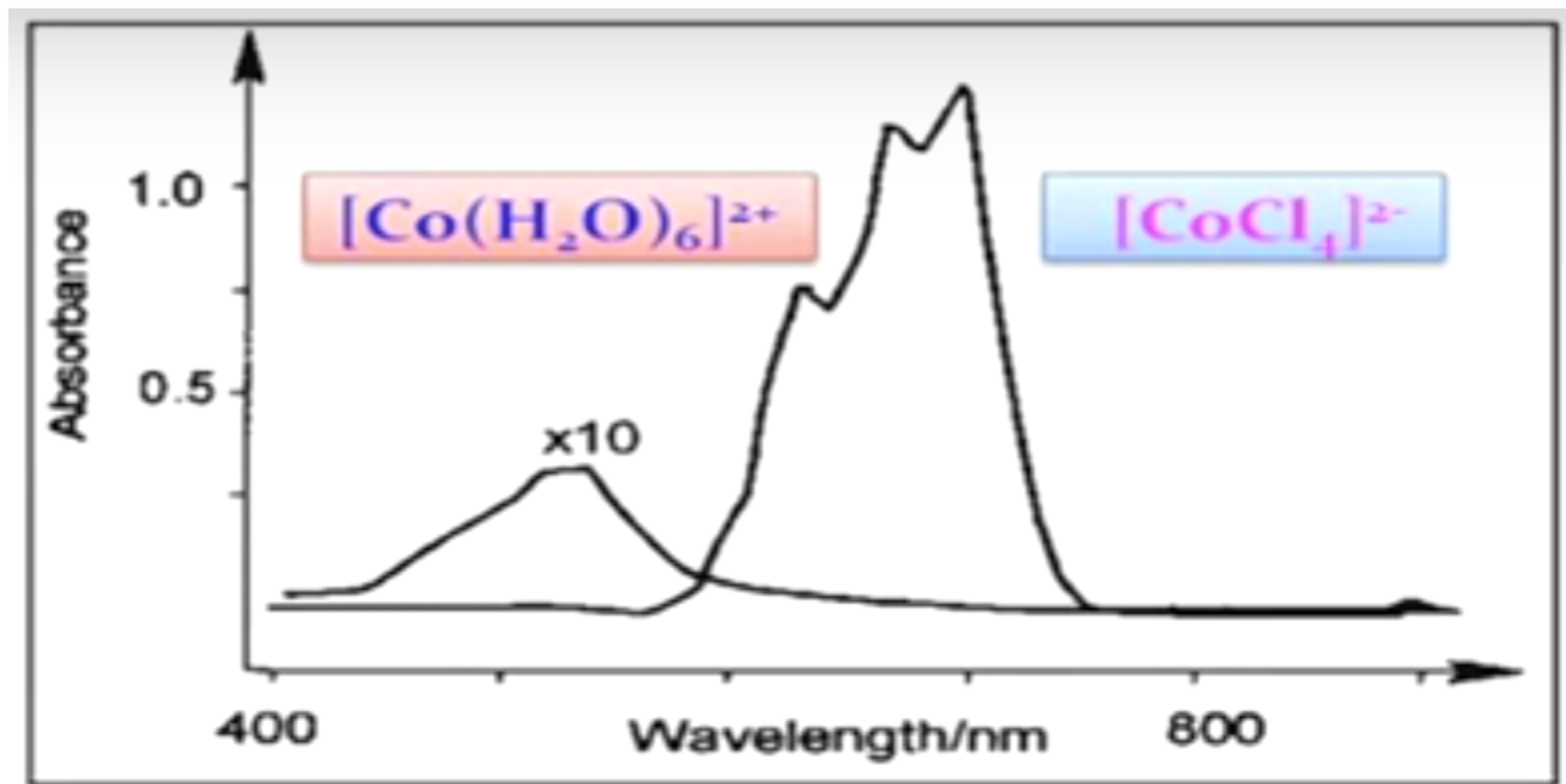
For d-d transitions
 $\epsilon = 5 - 100 \text{ M}^{-1}\text{Cm}^{-1}$

For L-MCT and M-LCT
 $\epsilon = 500 - 10000 \text{ M}^{-1}\text{Cm}^{-1}$

Trend in molar extinction coefficient

$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	<	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	<	$[\text{NiCl}_4]^{2-}$	<	$[\text{MnO}_4]^-$
Spin & Laporte Forbidden $g \rightarrow g$		Spin Allowed Laporte Forbidden $g \rightarrow g$		Spin Allowed Laporte Forbidden No g or u term		Spin Allowed Laporte Allowed $u \rightarrow g$

Comparison between T_d and O_h complexes



Tetrahedral complexes will have absorptions at longer wavelengths and higher ϵ