Electronic Spectra - Ultraviolet and Visible Spectroscopy - Metal to Ligand and Ligand to Metal Charge Transfer Bands

Prepared by Dr. Manash Jyoti Deka

In the field of inorganic chemistry, color is commonly associated with d–d transitions. If this is the case, why is it that some transition metal complexes show intense color in solution, but possess no d electrons? In transition metal complexes a change in electron distribution between the metal and a ligand gives rise to charge transfer (CT) bands when performing Ultraviolet-visible spectroscopy experiments. For complete understanding, a brief introduction to electron transfer reactions and Marcus-Hush theory is necessary.

Outer Sphere Charge Transfer Reactions

Electron transfer reactions(charge transfer) fall into two categories:

- **Inner- sphere mechanisms**– electron transfer occurs via a covalently bound bridging ligand.
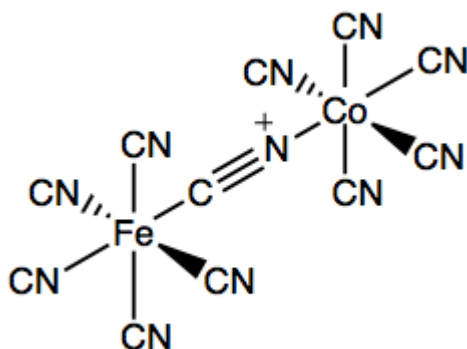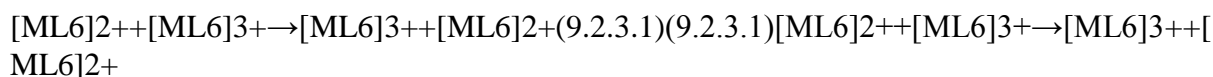

Figure 9.2.3.19.2.3.1: Intermediate formed in the reaction between $[Fe(CN)_6]^{3-}$ and $[Co(CN)_5]^{3-}$

- **Outer -sphere mechanisms**– electron transfer occurs without a covalent linkage forming between reactants

$[ML6]2++[ML6]3+\rightarrow[ML6]3++[ML6]2+(9.2.3.1)(9.2.3.1)[ML6]2++[ML6]3+\rightarrow[ML6]3++[ML6]2+$

Here, we focus on outer sphere mechanisms.

In a self-exchange reaction the reactant and product side of a reaction are the same. No chemical reaction takes place and only an electron transfer is witnessed. This reductant-oxidant pair involved in the charge transfer is called the precursor complex. The **Franck-Condon approximation** states that a molecular electronic transition occurs much faster than a molecular vibration.
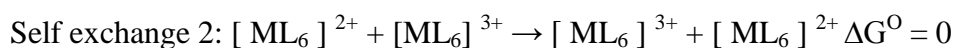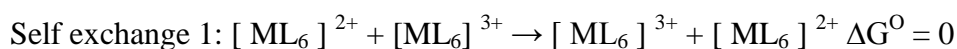
Let's look at an example:

[ML6]2++[ML6]3+→[ML6]3++[ML6]2+(9.2.3.2)(9.2.3.2)[ML6]2++[ML6]3+→[ML6]3++[ML6]2+
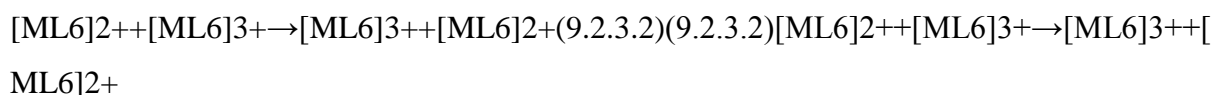
This process has a Franck-Condon restriction: Electron transfer can only take place when the M–L bond distances in the ML(II) and ML(III) states are the same. This means that vibrationally excited states with equal bonds lengths must be formed in order to allow electron transfer to occur. This would mean that the $[ML_6]^{2+}$ bonds must be compressed and $[ML_6]^{3+}$ bonds must be elongated in order for the reaction to occur.

Self exchange rate constants vary, because the activation energy required to reach the vibrational states varies according to the system. The greater the changes in bond length required to reach the precursor complex, the slower the rate of charge transfer.

A Brief Introduction to Marcus-Hush Theory

Marcus-Hush theory relates kinetic and thermodynamic data for two self-exchange reactions with data for the cross-reaction between the two self-exchange partners. This theory determines whether an outer sphere mechanism has taken place. This theory is illustrated in the following reactions

Self exchange 1: $[ML_6]^{2+} + [ML_6]^{3+} \rightarrow [ML_6]^{3+} + [ML_6]^{2+}$ $\Delta G^O = 0$

Self exchange 2: $[ML_6]^{2+} + [ML_6]^{3+} \rightarrow [ML_6]^{3+} + [ML_6]^{2+}$ $\Delta G^O = 0$

Cross Reaction: $[ML_6]^{2+} + [ML_6]^{3+} \rightarrow [ML_6]^{3+} + [ML_6]^{2+}$

The Gibbs free energy of activation $\Delta G^{\ddagger}$ is represented by the following equation:

$$\Delta G^{\ddagger} = \Delta_w G^{\ddagger} + \Delta_o G^{\ddagger} + \Delta_s G^{\ddagger} + RT\ln(k'T/hZ) \quad (9.2.3.3) \quad (9.2.3.3) \quad \Delta G^{\ddagger} = \Delta_w G^{\ddagger} + \Delta_o G^{\ddagger} + \Delta_s G^{\ddagger} + RT\ln(k'T/hZ)$$

- T = temperature in K
- R = molar gas constant
- k' = Boltzman constant
- h = Plancks constant
- Z = effective frequency collision in solution ~ 10^{11} dm^3 mol^{-1} s^{-1}
- $\Delta_w G^{\ddagger}$ = the energy associated with bringing the reactants together, includes the work done to counter any repulsion
- $\Delta_0 G^{\ddagger}$ = energy associated with bond distance changes
- $\Delta_s \Delta G^{\ddagger}$ = energy associated with the rearrangements taking place in the solvent spheres
- ln (k'T / hZ) = accounts for the energy lost in the formation of the encounter complex

The rate constant for the self-exchange is calculated using the following reaction

$$k = \kappa Z e^{-\Delta G^{\ddagger}/RT} \quad (9.2.3.4)$$

where κ is the transmission coefficient ~1

The Marcus-Hush equation is given by the following expression

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2} \quad (9.2.3.5)$$

where:

$$\log f_{12} = \frac{(\log K_{12})^2}{4\log\left(\frac{k_{11}k_{22}}{Z^2}\right)} \quad (9.2.3.6)$$

- Z is the collision frequency
- k_{11} and $\Delta G^{\ddagger}_{11}$ correspond to self exchange 1
- k_{22} and $\Delta G^{\ddagger}_{22}$ correspond to self exchange 2
- k_{12} and $\Delta G^{\ddagger}_{12}$ correspond to the cross-reaction
- K_{12} = cross reaction equilibrium constant
- ΔG^{O}_{12} = standard Gibbs free energy of the reaction

The following equation is an approximate from of the Marcus-Hush equation:

$$\log k_{12} \approx 0.5\log k_{11} + 0.5\log\log \quad (9.2.3.7)$$

since $f \approx 1$ and $\log f \approx 0$.

How is the Marcus-Hush equation used to determine if an outer sphere mechanism is taking place?

- values of k_{11}, k_{22}, K_{12}, and k_{12} are obtained experimentally
- k_{11} and k_{22} are theoretically values
- K_{12} is obtained from Ecell

If an outer sphere mechanism is taking place the calculated values of k_{12} will match or agree with the experimental values. If these values do not agree, this would indicate that another mechanism is taking place.

The Laporte Selection Rule and Weak d–d Transitions

d- d transitions are forbidden by the Laporte selection rule.

- Laporte Selection Rule: $\Delta l = \pm 1$

- Laporte allowed transitions: a change in parity occurs i.e. $s \rightarrow p$ and $p \rightarrow d$.

- Laporte forbidden transitions: the parity remains unchanged i.e. p → p and d → d.

d-d transitions result in weak absorption bands and most d-block metal complexes display low intensity colors in solution (exceptions d^0 and d^{10} complexes). The low intensity colors indicate that there is a low probability of a d-d transition occurring.

Ultraviolet-visible (UV/Vis) spectroscopy is the study of the transitions involved in the rearrangements of valence electrons. In the field of inorganic chemistry, UV/Vis is usually associated with d – d transitions and colored transition metal complexes. The color of the transition metal complex solution is dependent on: the metal, the metal oxidation state, and the number of metal d-electrons. For example iron(II) complexes are green and iron(III) complexes are orange/brown.

Charge Transfer Bands

If color is dependent on d-d transitions, why is it that some transition metal complexes are intensely colored in solution but possess no d electrons?

Figure 1: Fullerene oxides are intensely colored in solution, but possess no d electrons.

Solutions from left to right: C_{60}, $C_{60}O$, $C_{60}O$, and $C_{60}O_2$. Fullerenes, nanometer-sized closed cage molecules, are comprised entirely of carbons arranged in hexagons and pentagons. Fullerene oxides, with the formula $C_{60}O_n$, have epoxide groups directly attached to the fullerene cage.

In transition metal complexes a change in electron distribution between the metal and a ligand give rise to charge transfer (CT) bands.[1] CT absorptions in the UV/Vis region are intense (ε values of 50,000 L mole^{-1} cm^{-1} or greater) and selection rule allowed. The intensity of the color is due to the fact that there is a high probability of these transitions taking place. Selection rule forbidden d-d transitions result in weak absorptions. For example octahedral complexes give ε values of 20 L mol^{-1} cm^{-1} or less.[2] A charge transfer transition can be regarded as an internal oxidation-reduction process. [2]

Ligand to Metal and Metal to Ligand Charge Transfer Bands

Ligands possess σ, σ*, π, π*, and nonbonding (n) molecular orbitals. If the ligand molecular orbitals are full, charge transfer may occur from the ligand molecular orbitals to the empty or partially filled metal d-orbitals. The absorptions that arise from this process are called ligand-to-metal charge-transfer bands (LMCT) (Figure 2). LMCT transitions result in intense bands. Forbidden d-d transitions may also take place giving rise to weak absorptions. Ligand to metal charge transfer results in the reduction of the metal.
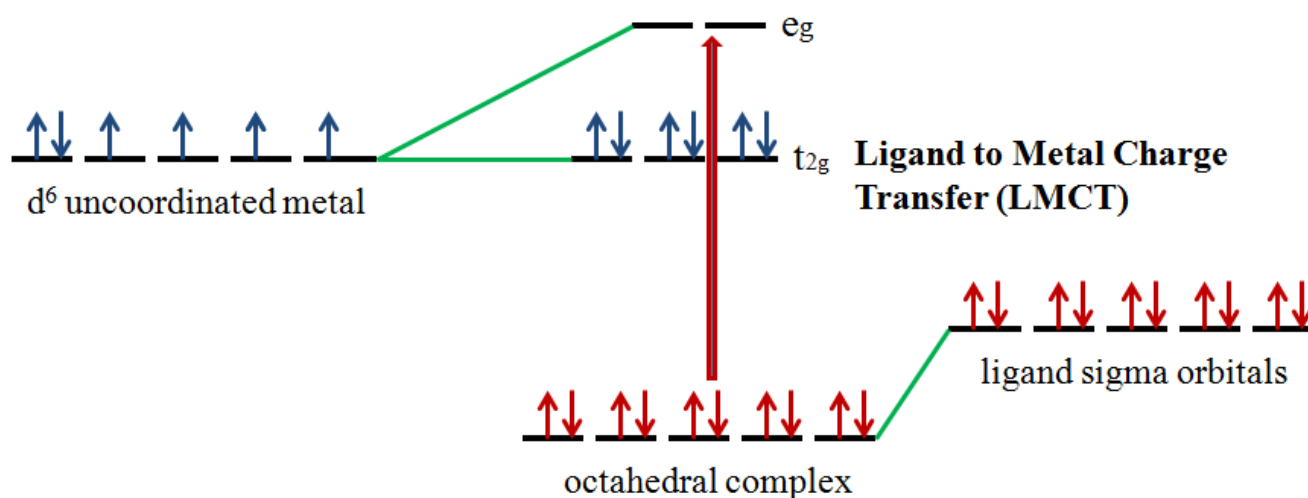

Figure 2 Ligand to Metal Charge Transfer (LMCT) involving an octahedral d6 complex.

If the metal is in a low oxidation state (electron rich) and the ligand possesses low-lying empty orbitals (e.g., CO or CN^-) then a metal-to-ligand charge transfer (MLCT) transition may occur. LMCT transitions are common for coordination compounds having π-acceptor ligands. Upon the absorption of light, electrons in the metal orbitals are excited to the ligand π* orbitals. Figure 3 illustrates the metal to ligand charge transfer in a d^5 octahedral complex. MLCT transitions result in intense bands. Forbidden d − d transitions may also occur. This transition results in the oxidation of the metal.
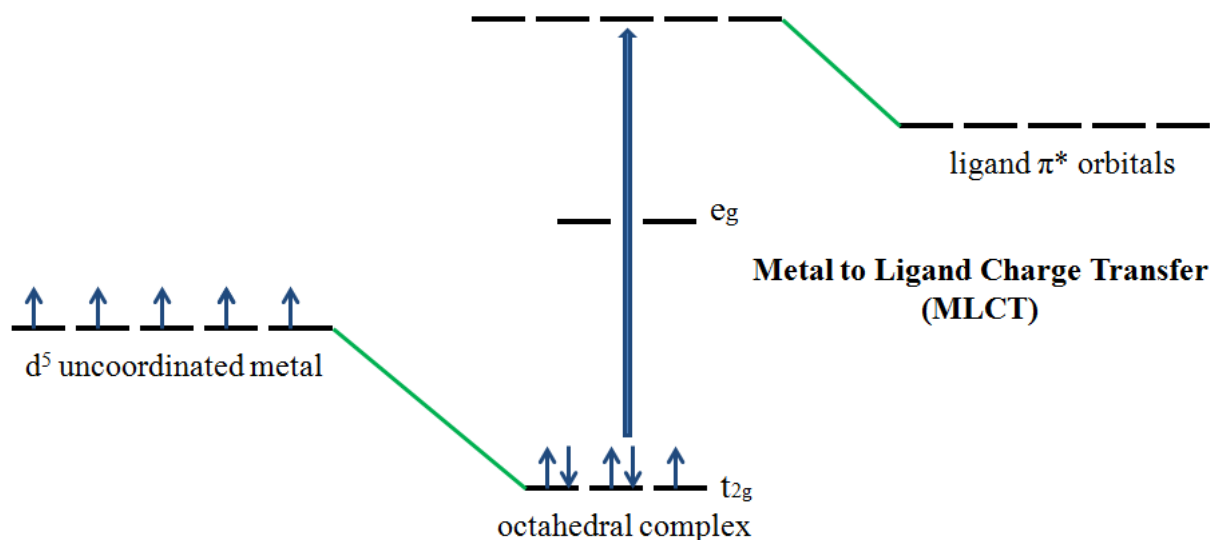
Figure 3. Metal to Ligand Charge Transfer (MLCT) involving an octahedral d5 complex.

Effect of Solvent Polarity on CT Spectra

(This effect only occurs if the species being studied is an ion pair)

The position of the CT band is reported as a transition energy and depends on the solvating ability of the solvent. A shift to lower wavelength (higher frequency) is observed when the solvent has high solvating ability.

Polar solvent molecules align their dipole moments maximally or perpendicularly with the ground state or excited state dipoles. If the ground state or excited state is polar an interaction will occur that will lower the energy of the ground state or excited state by solvation. The effect of solvent polarity on CT spectra is illustrated in the following example.

How to Identify Charge Transfer Bands

CT absorptions are selection rule allowed and result in intense (ε values of 50,000 L mole^{-1} cm^{-1} or greater) bands in the UV/Vis region.[2] Selection rule forbidden d-d transitions result in weak absorptions. For example octahedral complexes give ε values of 20 L mol^{-1} cm^{-1} or less.[2] CT bands are easily identified because they:

- Are very intense, i.e. have a large extinction coefficient
- Are normally broad
- Display very strong absorptions that go above the absorption scale (dilute solutions must be used)

You are preparing a sample for a UV/Vis experiment and you decide to use a polar solvent. Is a shift in wavelength observed when:

- **a) Both the ground state and the excited state are neutral**
- When both the ground state and the excited state are neutral a shift in wavelength is not observed. No change occurs. Like dissolves like and a polar solvent won't be able to align its dipole with a neutral ground and excited state.
- **b) The excited state is polar, but the ground state is neutral**
- If the excited state is polar, but the ground state is neutral the solvent will only interact with the excited state. It will align its dipole with the excited state and lower its energy by solvation. This interaction will lower the energy of the polar excited state. (increase wavelength, decrease frequency, decrease energy)

b)

Polar excited state

Polar
Solvent
Addition

Higher energy

Polar excited state

Lower energy

Neutral ground state   **Neutral ground state**
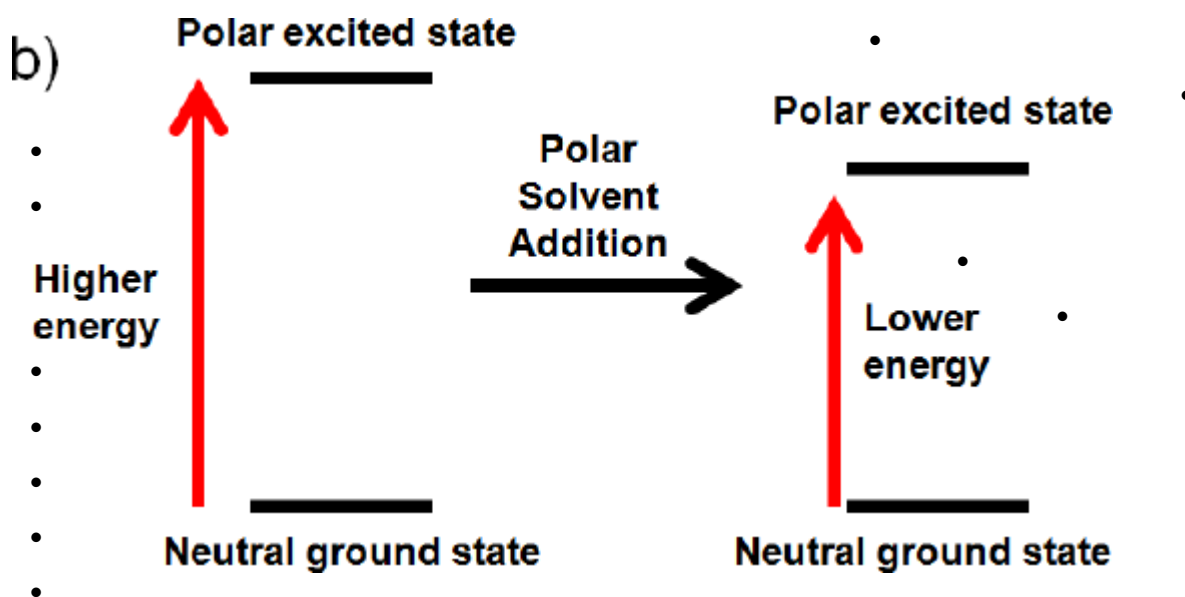
- **c) The ground state and excited state is polar**
- If the ground state is polar the polar solvent will align its dipole moment with the ground state. Maximum interaction will occur and the energy of the ground state will be lowered. (increased wavelength, lower frequency, and lower energy) The dipole moment of the excited state would be perpendicular to the dipole moment of the ground state, since the polar solvent dipole moment is aligned with the ground state. This interaction will raise the energy of the polar excited state. (decrease wavelength, increase frequency, increase energy)

c)

Polar excited state

Polar excited state

Lower energy

Polar Solvent Addition →

Higher energy

Polar ground state
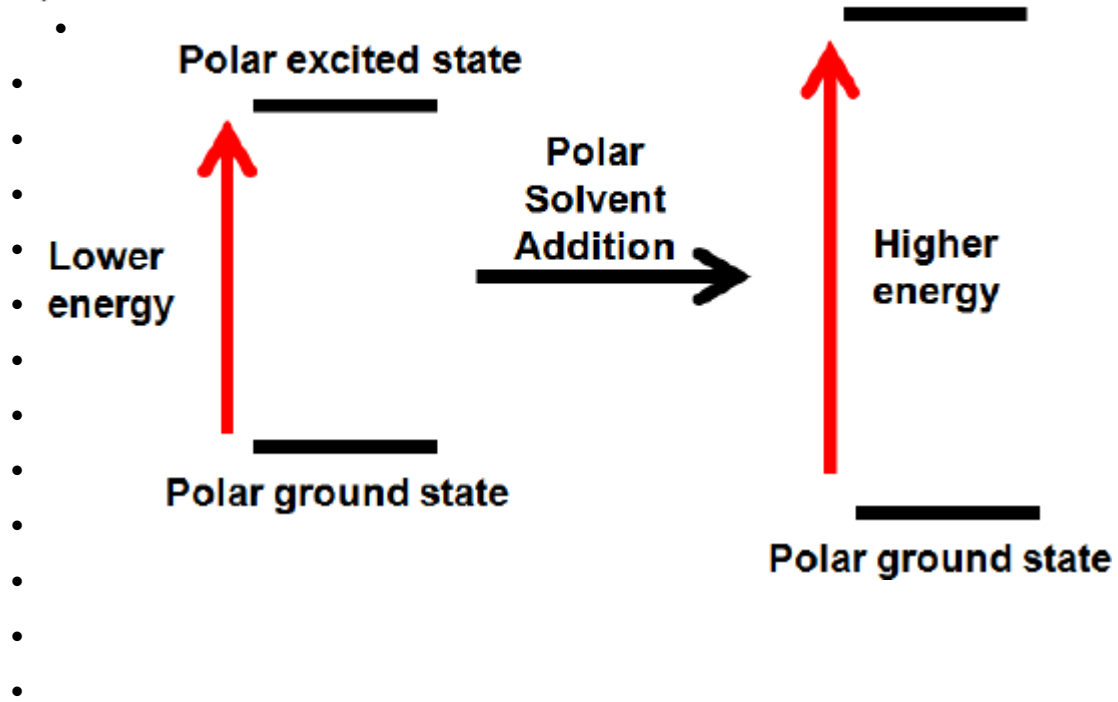
Polar ground state

- **d) The ground state is polar and the excited state is neutral**
- If the ground state is polar the polar solvent will align its dipole moment with the ground state. Maximum interaction will occur and the energy of the ground state will be lowered. (increased wavelength, lower frequency, and lower energy). If the excited state is neutral no change in energy will occur. Like dissolves like and a polar solvent won't be able to align its dipole with a neutral excited state. Overall you would expect an increase in energy (Illustrated below), because the ground state is lower in energy (decrease wavelength, increase frequency, increase energy).[4]

d)

Neutral excited state

Neutral excited state

Lower energy

Polar Solvent Addition →

Higher energy

Polar ground state

Polar ground state