

## 2.16: Charge Transfer Bands

**Charge transfer** (CT) transitions are important these days because they represent an interaction between light and energy in which an electron can be moved from one part of a molecule to another. Such processes are potentially important in solar energy conversion schemes, optical devices storage etc.

### 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? In transition metal complexes a change in electron distribution between the metal and a ligand give rise to charge transfer (CT) bands.<sup>1</sup> CT absorptions in the UV/Vis region are intense ( $\epsilon$  values of 50,000 L mole<sup>-1</sup> cm<sup>-1</sup> 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  $\epsilon$  values of 20 L mol<sup>-1</sup> cm<sup>-1</sup> or less.<sup>2</sup> A charge transfer transition can be regarded as an internal oxidation-reduction process.<sup>2</sup>

### Ligand to Metal and Metal to Ligand Charge Transfer Bands

Ligands possess  $\sigma$ ,  $\sigma^*$ ,  $\pi$ ,  $\pi^*$ , 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 2.16.1).<sup>2</sup> LMCT transitions result in intense bands. Ligand to metal charge transfer results in the reduction of the metal.

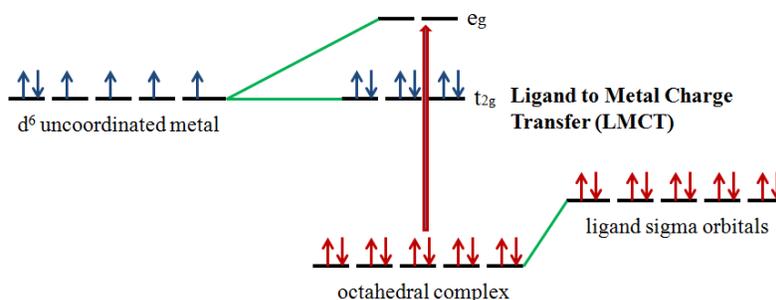


Figure 2.16.1: Ligand to Metal Charge Transfer (LMCT) involving an octahedral  $d^6$  complex.

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  $\pi$ -acceptor ligands. Upon the absorption of light, electrons in the metal orbitals are excited to the ligand  $\pi^*$  orbitals.<sup>2</sup> Figure 2.16.2 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.

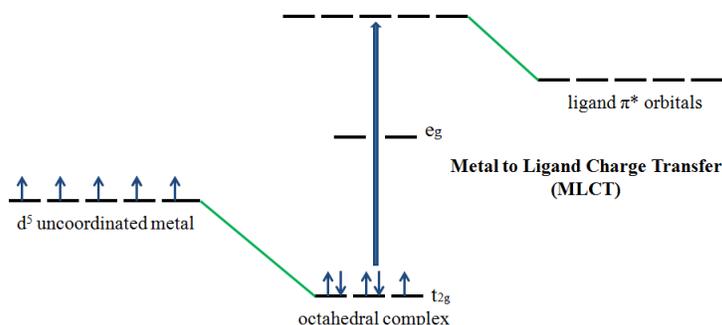


Figure 2.16.2. Metal to Ligand Charge Transfer (MLCT) involving an octahedral  $d^5$  complex.

### Effect of Solvent Polarity on CT Spectra

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.

### ✓ Example 2.16.1

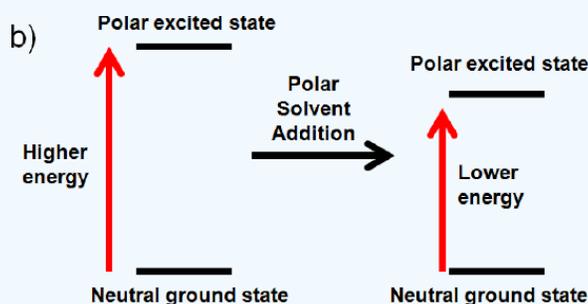
You are preparing a sample for a UV/Vis experiment and you decide to use a polar solvent. Is a shift in wavelength observed when:

#### 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.

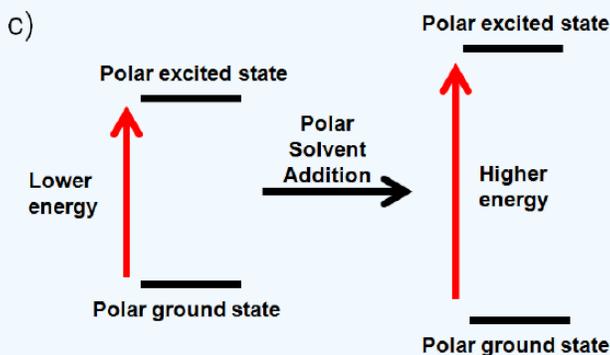
#### The excited state is polar, but the ground state is neutral

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)



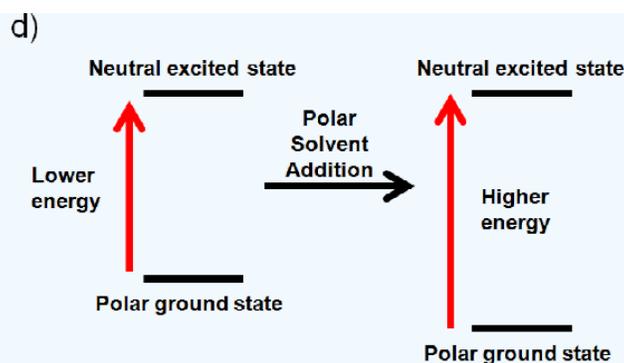
#### The ground state and excited state is polar

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)



#### 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).<sup>4</sup>



## How to Identify Charge Transfer Bands

CT absorptions are selection rule allowed and result in intense ( $\epsilon$  values of  $50,000 \text{ L mole}^{-1} \text{ cm}^{-1}$  or greater) bands in the UV/Vis region.<sup>2</sup> Selection rule forbidden d-d transitions result in weak absorptions. For example octahedral complexes give  $\epsilon$  values of  $20 \text{ L mol}^{-1} \text{ cm}^{-1}$  or less.<sup>2</sup> 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)

### ✓ Example 2.16.2: Ligand to Metal Charge Transfer

$\text{KMnO}_4$  dissolved in water gives intense CT Bands. The one LMCT band in the visible is observed around 530 nm.

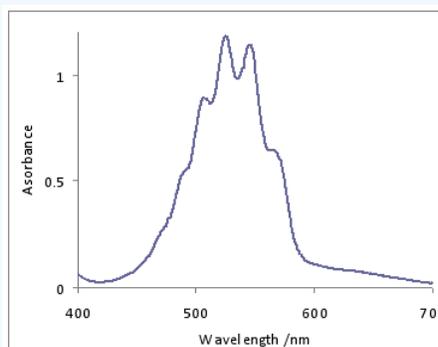


Figure 2.16.5: Absorption spectrum of an aqueous solution of potassium permanganate, showing a vibronic progression. (CC BY-SA 3; [Petersans](#) via [Wikipedia](#))

The band at 528 nm gives rise to the deep purple color of the solution. An electron from a “oxygen lone pair” character orbital is transferred to a low lying Mn orbital.<sup>1</sup>

### ✓ Example 2.16.3: Metal to Ligand Charge Transfer

Tris(bipyridine)ruthenium(II) dichloride ( $\text{[Ru(bpy)}_3\text{Cl}_2\text{]^{2+}}$ ) is a coordination compound that exhibits a CT band is observed (Figure 2.16.6)

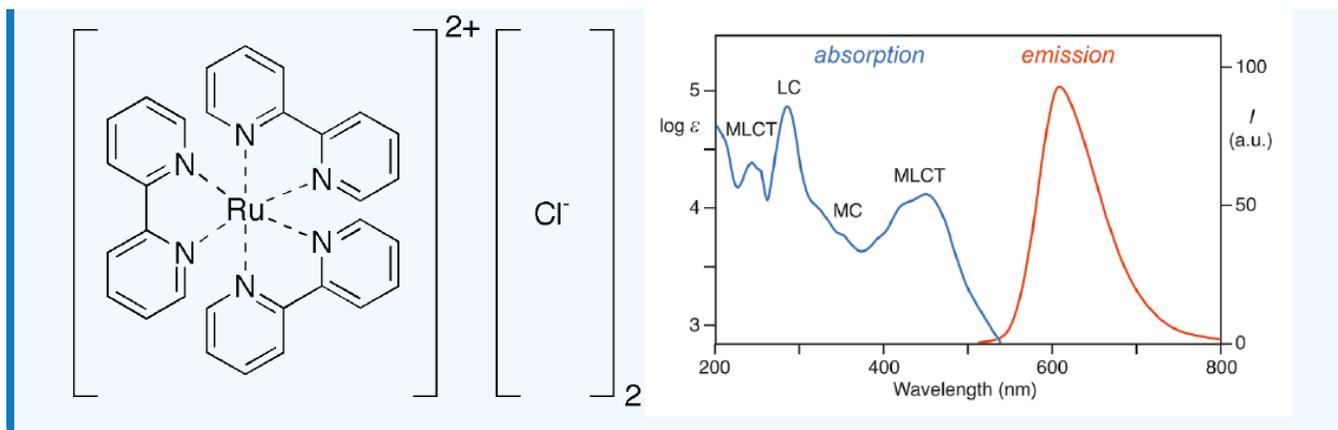


Figure 2.16.6: a) Structure of [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>, b) CT band observed in its V/Vis spectrum. (CC BY-SA 4.0; Albris via Wikipedia)

A d electron from the ruthenium atom is excited to a bipyridine anti-bonding orbital. The very broad absorption band is due to the excitation of the electron to various vibrationally excited states of the π\* electronic state.<sup>6</sup>

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