

# Electronic Spectroscopy

## Selection rules and molar absorptivity:

- There are two **selection rules** which govern the relative intensities of electronic absorption bands:

Spin Selection Rule – Transitions between different spin multiplicities are forbidden. For example, transitions between  $^4A_2$  and  $^4T_1$  states are spin-allowed, but between  $^4A_2$  and  $^2A_2$  are spin-forbidden.

Laporte (Parity) Selection Rule – Transitions between states of the same parity (symmetry with respect to inversion) are forbidden. For example, transitions between d-orbitals are forbidden (these are  $g \rightarrow g$  transitions) but transitions between d and p orbitals are allowed ( $g \rightarrow u$ ).

- These rules would seem to rule out many of the electronic transitions for metal complexes. However, many transition metal complexes are famous for their bright colours; a consequence of various mechanisms by which the above rules can be relaxed. The most important **relaxation mechanisms** are:

Vibronic Coupling (molecular vibrations) temporarily changes molecular symmetry, and can result in temporary loss of the centre of symmetry in an octahedral complex. This provides a way to *relax the Laporte selection rule*. As a consequence, d-d transitions often have extinction coefficients ( $\epsilon$ ) of 10 to 100  $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  which is responsible for the bright colours of many transition metal complexes.

# Electronic Spectroscopy

Tetrahedral Complexes absorb more strongly than octahedral complexes. Metal-ligand  $\sigma$ -bonding in transition metal complexes of  $T_d$  symmetry, and the lack of a centre of symmetry makes transitions between d-orbitals more allowed (*relaxation of the Laporte selection rule*). As a result, extinction coefficients  $\sim \epsilon = 500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  are common. As a qualitative example,  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  is *pale green* while  $[\text{Ni}(\text{PPh}_3)_4]^{2+}$  is *deep blue*.

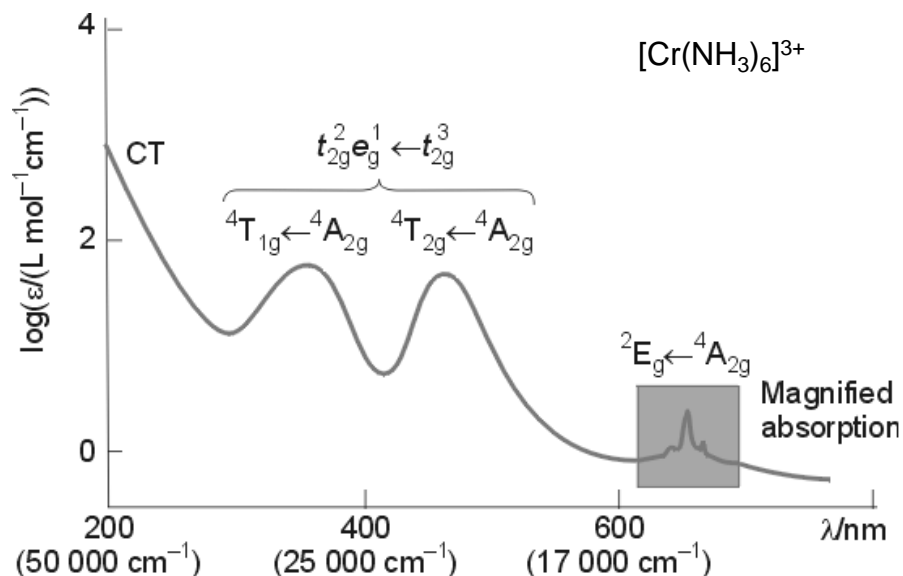
Spin-Orbit Coupling can provide a mechanism for *relaxation of the spin selection rule*. Such absorption bands for first-row transition metal complexes are generally weak, with typical extinction coefficients  $\sim \epsilon = 1 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . For example, octahedral  $\text{Mn}^{2+}$  complexes ( $d^5$ ) cannot undergo any spin-allowed transitions from the  ${}^6A_1$  ground state, so are extremely pale coloured. By contrast, Spin-Orbit coupling can be more important for 2<sup>nd</sup> and 3<sup>rd</sup> row transition metal complexes.

The molar absorptivity ( $\epsilon$ , extinction coefficient) is a good indicator of the type of electronic transition:

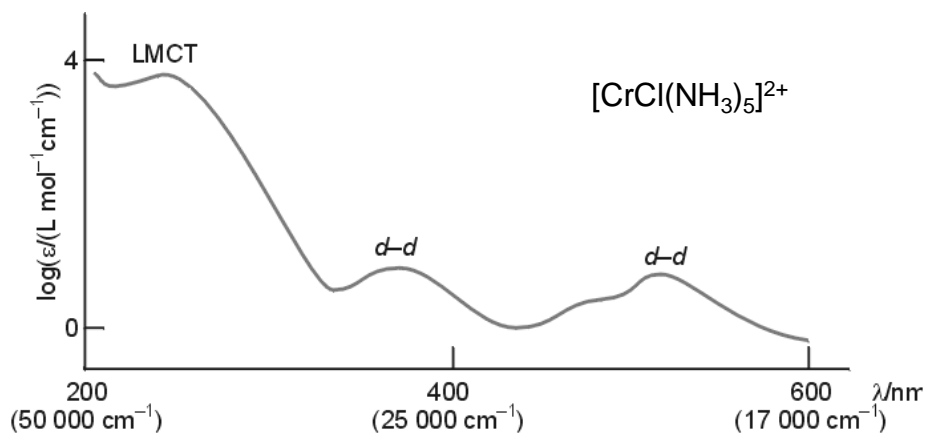
Type of transition	$\epsilon$ ( $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )	Example
Spin-forbidden	< 1	$\text{Mn}^{2+}$ (aq)
d-d Laporte-forbidden	10-100	Most 3d $O_h$ complexes
d-d noncentrosymmetric system	$\sim 500$	$T_d$ complexes
$\pi-\pi^*$ transitions, symmetry allowed	$\sim 10,000$	Organic chromophores

# Charge Transfer Absorptions

- $[\text{Cr}(\text{NH}_3)_6]^{3+}$ : There is an intense absorption in the UV region of the spectrum.



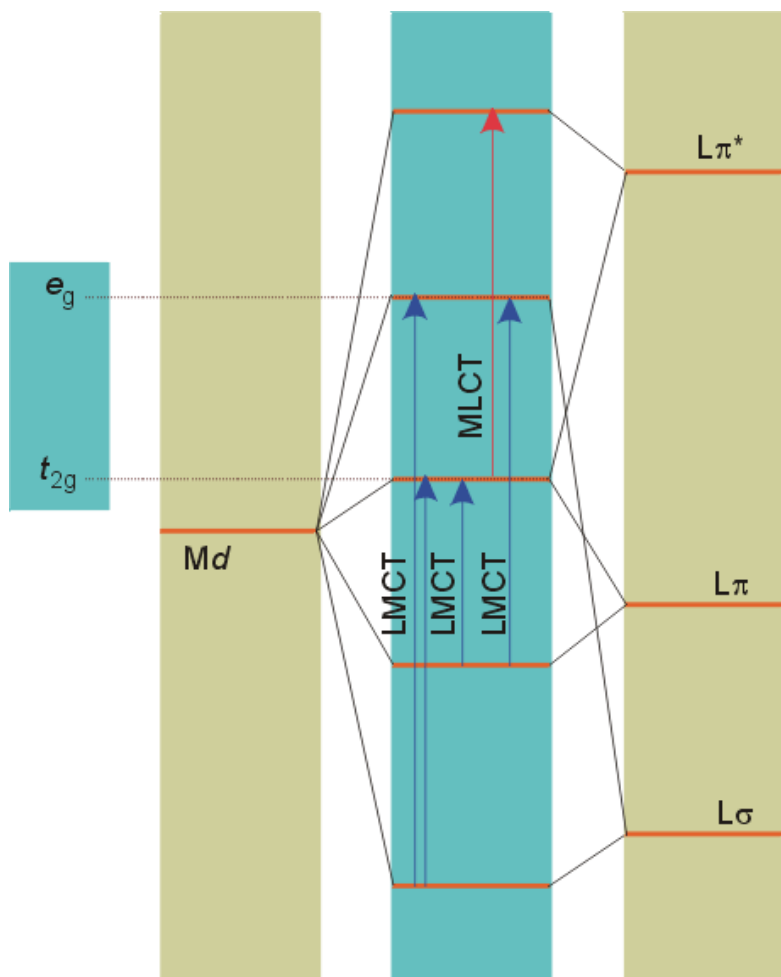
- This type of intense absorption ( $\epsilon \sim 10^4 \text{ dm}^3 \text{ cm}^{-1} \text{ mol}^{-1}$ ) can be seen more clearly in  $[\text{CrCl}(\text{NH}_3)_5]^{2+}$ :



- Note: The lowest energy  $d \leftarrow d$  transition in  $[\text{CrCl}(\text{NH}_3)_5]^{2+}$  is significantly lower in energy than that of  $[\text{Cr}(\text{NH}_3)_6]^{3+}$  due to a smaller  $\Delta_o$  ( $\text{Cl}^-$  is lower in the spectrochemical series than  $\text{NH}_3$ ).
- Note: For  $[\text{CrCl}(\text{NH}_3)_5]^{2+}$ , there are shoulders on the  $d \leftarrow d$  transitions due to reduced symmetry ( $C_{4v}$  instead of  $O_h$ ).

# Charge Transfer Absorptions

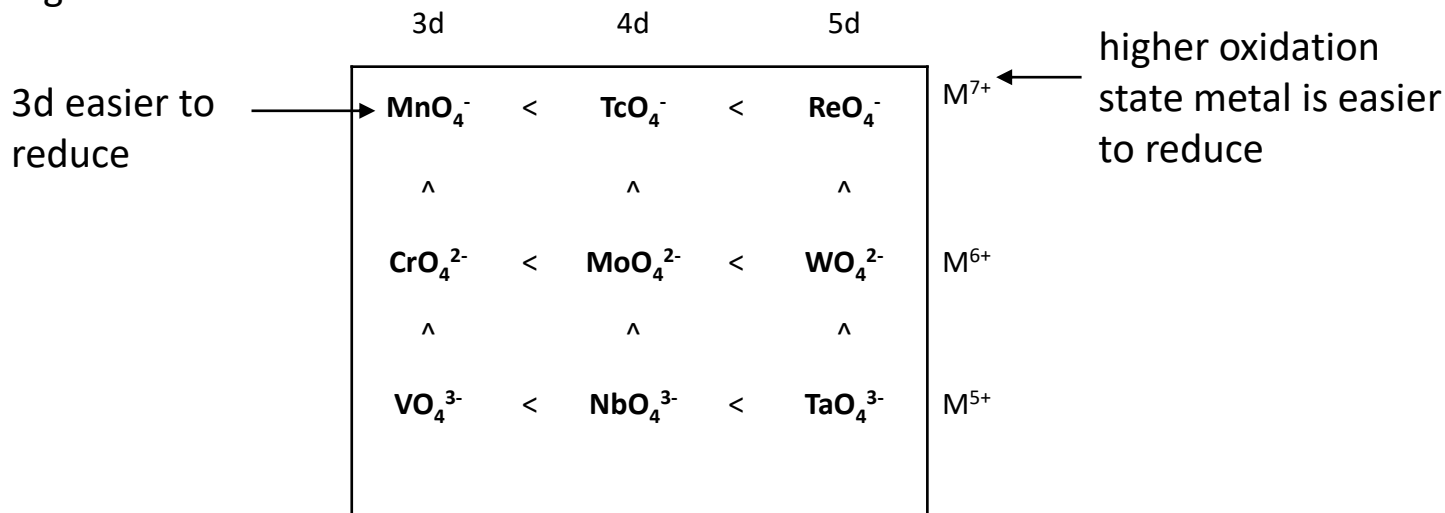
- Both peaks are examples of **LMCT** (Ligand to Metal Charge Transfer), which involves the transfer of electrons from molecular orbitals that are primarily ligand based to orbitals that are primarily metal based.



- LMCT = Transfer of electrons from filled ligand based orbitals to the  $e_g$  and  $t_{2g}$  metal based orbitals.
- MLCT = Transfer of electrons from the  $e_g$  and  $t_{2g}$  metal based orbitals to low lying  $\pi^*$  orbitals on the ligands.

# Charge Transfer Absorptions

- Other examples of complexes with prominent LMCT absorptions are shown below (relative energies of the LMCT absorptions are also shown using < and >). These are all  $d^0$  complexes, so cannot undergo  $d \leftarrow d$  transitions:



- In complexes with ligands that have low-lying, empty  $\pi^*$ -orbitals, MLCT (Metal to Ligand Charge Transfer) can occur. This is often found for diimine type ligands (*e.g.* bipyridine, phenanthroline), as well as a variety of other soft ligands, such as  $S_2C_2R_2^{x-}$ ,  $S_2CNR_2^-$ , CO,  $CN^-$  and  $SCN^-$ .
- Examples of molecules that exhibit strong MLCT bands:
  - $[M(bipy)_3]^{2+}$  (M = Fe or Ru)
  - $[W(CO)_4(phen)]$  and  $[Fe(CO)_3(bipy)]$
  - $[Cr(CO)_6]$  exhibits both LMCT and MLCT absorptions.
- Both MLCT and LMCT result in a dramatic redistribution of electron density between the metal and the ligands (hence, the name “charge transfer”). This redistribution of electron density generates differences in the solvation for the ground state and excited state molecules. Thus, the energy of *charge transfer bands* is highly dependent on solvent (SOLVATOCHROMISM).