
Transitions absorption spectra:

❖ d-d Transitions spectra

From these two molecular orbital energy diagrams for transition metals, we see that the pi donor ligands lie lower in energy than the pi acceptor ligands. According to the spectrochemical series, one can determine whether a ligand will behave as a pi accepting or pi donating. When the ligand is more pi donating, its own orbitals are lower in energy than the t_{2g} metal orbitals forcing the frontier orbitals to involve an antibonding pi* (for t_{2g}) and an antibonding sigma* (for eg). This is in contrast to the pi accepting ligands which involve a bonding pi (t_{2g}) and

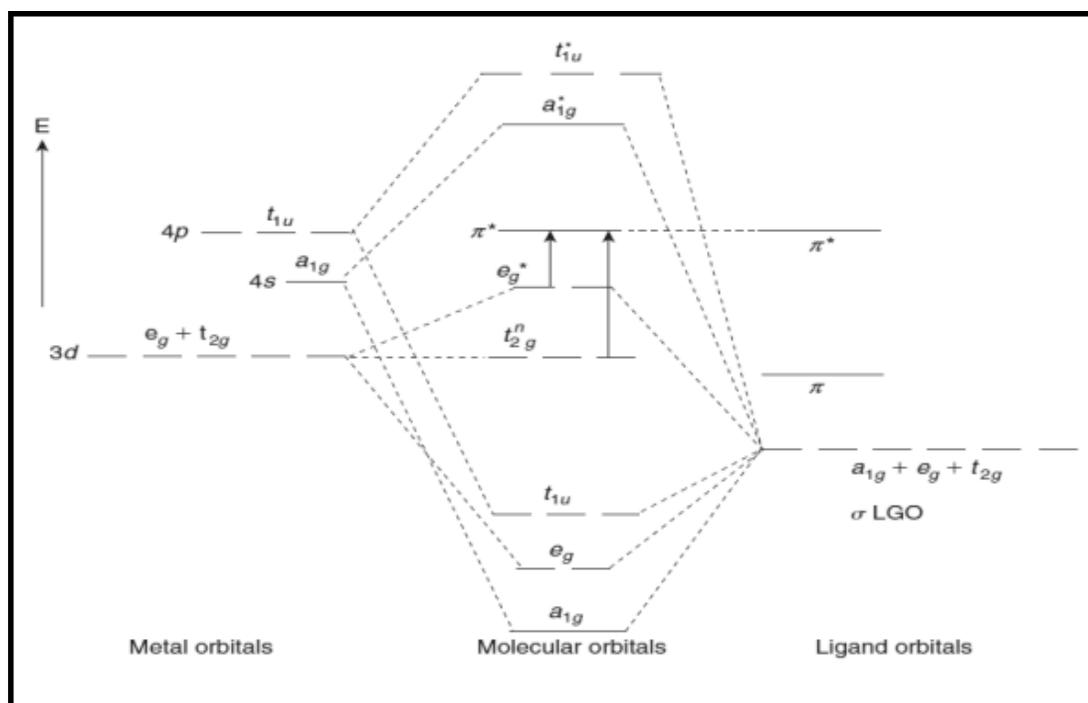
an antibonding sigma* (eg). Because of this, the d-d transition (denoted above by delta) for the pi acceptor ligand complex is larger than the pi donor ligand. In the spectra, we would see the d-d transitions of pi acceptor ligands to be of a higher frequency than the pi donor ligands. In general though, these transitions appear as weakly intense on the spectrum because they are Laporte forbidden. Due to vibronic coupling; however, they are weakly allowed and because of their relatively low energy of transition, they can emit visible light upon relaxation which is why many transition metal complexes are brightly colored. The molar extinction coefficients for these transitions are around 100.

❖ Charge Transfer (CT) Transitions

Electronic transitions that occur between spectroscopic states for the metal ion in the ligand field. However, these are not the only transitions for which absorptions occur. Ligands are bonded to metal ions by donating electron pairs to orbitals that are essentially metal orbitals in terms of their character. Transition metals also have nonbonding eg or t_{2g} orbitals (assuming an octahedral complex) arising from the d orbitals that may be partially filled, and the ligands may have empty nonbonding or anti bonding orbitals that can accept electron density from the metal. For example, both CO and CN _ have empty π^* orbitals that can be

involved in this type of interaction. Movement of electron density from metal orbitals to ligand orbitals and vice versa is known as *charge transfer*. The absorption bands that accompany such shifts in electron density are known as *charge transfer bands*.

Charge transfer (CT) bands are usually observed in the ultraviolet region of the spectrum, although in some cases they appear in the visible region. Consequently, they frequently overlap or mask transitions of the *d - d* type. Charge transfer bands are of the spin-allowed type, so they have high intensity. If the metal is in a low oxidation state and easily oxidized, the charge transfer is more likely to be of the metal-to-ligand type, indicated as $M \rightarrow L$. A case of this type occurs in $\text{Cr}(\text{CO})_6$ where it is easy to move electron density from the metal atom (which is in the 0 oxidation state), especially because the CO ligands have donated six pairs of electrons to the Cr. The empty orbitals on the CO ligands are π^* orbitals. In this

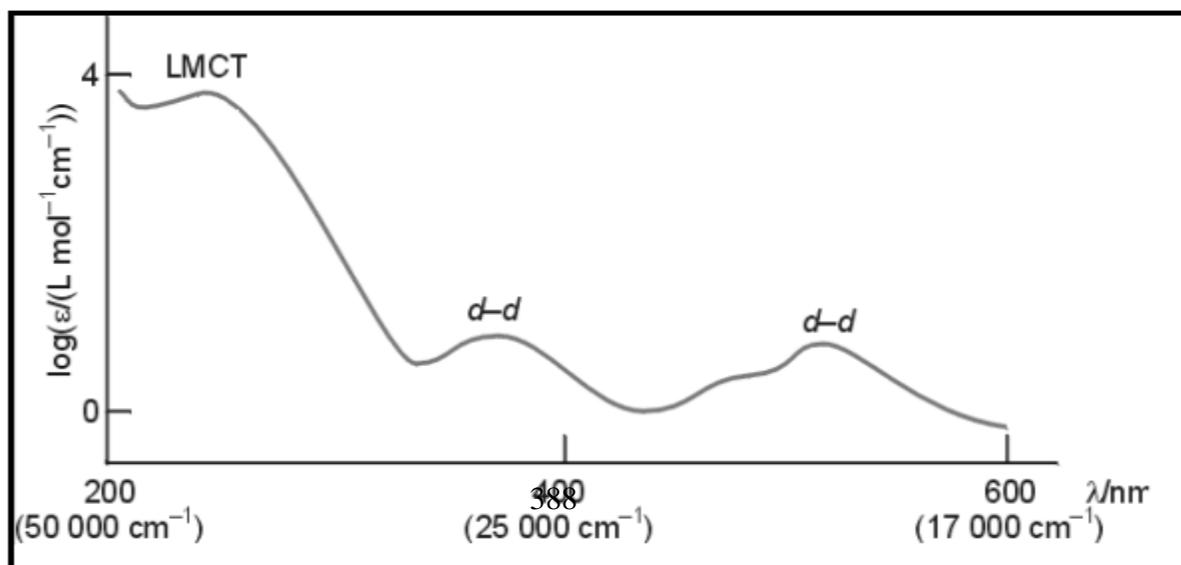


case, the electrons are in nonbonding t_{2g} orbitals on the metal so the transition is designated as $t_{2g} \rightarrow \pi^*$. In other cases, electrons in the e_g^* orbitals are excited to the empty π^* orbitals on the ligands. Below Figure shows these cases on a modified molecular orbital diagram for an octahedral complex. Although CO is a ligand that has π^* acceptor orbitals, other ligands of this type include NO, CN^- , olefins, and pyridine.

The intense purple colour of MnO_4^- is due to a charge transfer band that occurs at approximately $18,000 \text{ cm}^{-1}$ and results from a transfer of charge from oxygen to the Mn^{7-} . In this case, the transfer is indicated as $\text{L} \rightarrow \text{M}$, and it results from electron density being shifted from filled p orbitals on oxygen atoms to empty orbitals in the e set on Mn. As a general rule, the charge transfer will be $\text{M} \rightarrow \text{L}$ if the metal is easily oxidized, whereas the transfer will be $\text{L} \rightarrow \text{M}$ if the metal is easily reduced. Therefore, it is not surprising that Cr 0 in $\text{Cr}(\text{CO})_6$ would have electron density shifted *from the metal to the ligands* and Mn^{7-} would have electron density shifted *from the ligands to the metal*. The ease with which electron density can be shifted from the ligands to the metal is related in a general way to how difficult it is to ionize or polarize the ligands. We have not yet addressed the important topic of absorption by the ligands in complexes. For many types of complexes, this type of spectral study (usually infrared spectroscopy) yields useful information regarding the structure and details of the bonding in the complexes. This topic will be discussed later in connection with several types of complexes containing specific ligands (e.g., CO , CN^- , NO^- and olefins).

(A) LMCT Transitions

Charge transfer (CT) transitions involve the movement of a charge from one atom to another during the electronic transition. In $d-d$ transitions, the electron goes from one metalcation based molecular orbital to another metal-cation based MO; the electron stays practically on the same atom. If an electron resides in an MO that is primarily located on the ligand and gets excited to an MO that is metal-cation

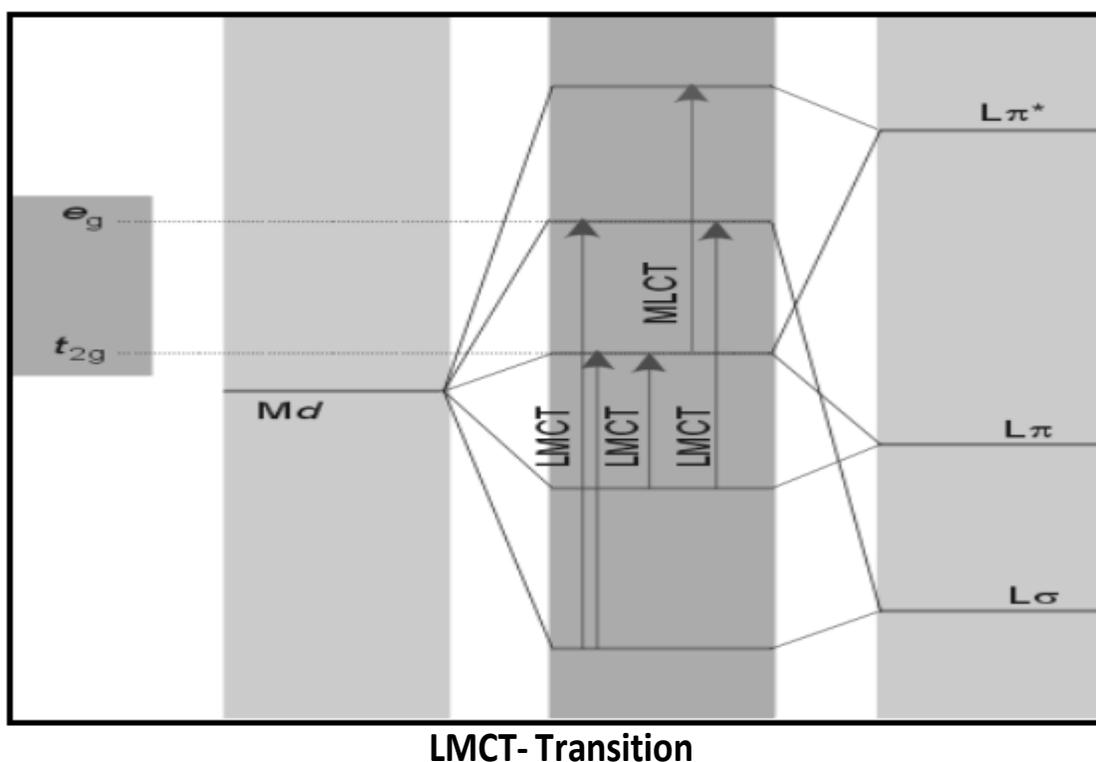


based, we talk about a ligand to metal charge transfer transition. In the figure on the left-hand side, LMCT transitions are depicted for an octahedral

complex that start from a bonding ligand MO and end in one of the d orbital sets, t_{2g} or e_g . Such transitions are usually very intense and give rise to a deep coloration. An example for a LMCT band is found in the absorption spectrum of $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$:

An electron in the MO, that represents the lone pair on chlorine can be excited into a metal-based molecular orbital. As you can see in the spectrum, the LMCT band is much stronger than the d-d bands. The permanganate ion, MnO_4^- , is intensely coloured.

The reason for this coloration cannot be attributed to d-d transitions, since manganese does not have any d-electrons left. The purple colour is a result of a LMCT transition in which the oxygen lone-pair electron is promoted into a low-lying e metal orbital.



(B) MLCT Transitions

If the CT band in an electronic spectrum is associated with an excitation of an electron from a d orbital (metal-centred) to an ligand-centred MO (in most cases and antibonding MO), we refer to such a band as an metal to ligand charge transfer (MLCT) band. For such MLCT band in the visible region, we require low-lying empty ligand orbitals. Empty π^* orbitals are usually the only antibonding orbitals that lie low enough in energy to produce an absorption band in the visible part of the electromagnetic spectrum. An example for such a complex is $[\text{Ru}(\text{bipy})_3]^{2+}$.

