Charge Transfer Transitions

1. Ligand to Metal (LMCT)
2. Metal to Ligand (MLCT)
3. Metal to Metal (Intervalence, IT)
4. Intra-Ligand

- Ligand to metal charge transfer in an octahedral complex

Four general types of CT transitions

\[ \pi \rightarrow \pi^* (t_{2g}) \quad v_1 \]
\[ \pi \rightarrow \sigma^* (e_g) \quad v_2 \]
\[ \sigma \rightarrow \pi^* (t_{2g}) \quad v_3 \]
\[ \sigma \rightarrow \sigma^* (e_g) \quad v_4 \]
Examples: \([\text{OsX}_6]^{2-}\)

\[
\begin{array}{ccc}
X = \text{Cl} & v_1 & 24 - 30,000 \text{ cm}^{-1} & v_2 & 47,000 \text{ cm}^{-1} \\
X = \text{Br} & 17 - 25,000 & & 36 - 41,000 \\
X = \text{I} & 12 - 19,000 & & 27 - 36,000 \\
\end{array}
\]

Note:
- \(v_1\) and \(v_2\) each consist of several (overlapping) transitions because there are six ligands and different inter-electronic repulsions in the various excited states.
- \(v_1\) bands are narrower than \(v_2\)'s because excited state is less anti-bonding.
- Energies for corresponding transitions decrease in the order Cl > Br > I.
Parameterization of CT energies – **Optical Electronegativities**

\[ E_{L\rightarrow M} = x(X) - x(M) + q(\Delta x(M)) + 4D/3 \quad (Jørgensen) \]

where
- \( x(X) \) and \( x(M) \) are the optical electronegativities of ligand and metal;
- \( \Delta x(M) \) is the difference in optical electronegativity for \( M^{n+} \) and \( M^{(n-1)+} \);
- \( D \) is a spin-pairing energy parameter (~7B) for d-electrons;
- \( q \) is the number of d-electrons.

A simpler version of this equation is

\[ v'_{CT} = 30,000[x(X) - x(M)] \text{ cm}^{-1} \]

where \( v'_{CT} = v_{obs} - f(D) \)

and \( f(D) = [\langle S(S+1) \rangle - S(S+1)] \)

\( \langle S(S+1) \rangle \) is the average value of \( S(S+1) \) for the configuration \( \ell^q \)

\[ \langle S(S + 1) \rangle = \frac{q(q + 2)}{4} - \frac{(2 \ell + 2)q(q + 1)}{2(4 \ell + 1)} \]

\( f(D) \) ranges from -20/3 to +2 for different \( d^n \) configurations.
Some typical values for $x(X)$ and $x(M)$

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<table>
<thead>
<tr>
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<tbody>
<tr>
<td>$F^-$</td>
<td>3.9</td>
<td>$Cr^{3+}$</td>
</tr>
<tr>
<td>$Cl^-$</td>
<td>3.0</td>
<td>$Pt^{4+}$</td>
</tr>
<tr>
<td>$Br^-$</td>
<td>2.8</td>
<td>$Fe^{3+}$ (low spin)</td>
</tr>
<tr>
<td>$I^-$</td>
<td>2.5</td>
<td>$Fe^{3+}$ (tetrahedral)</td>
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Example: $PtCl_6^{2-}$

$f(D) = 0$, because $Pt^{4+}$ is $t_{2g}^6$ and electron is transferred from the ligand to an empty metal orbital ($e_g$).

Thus $v_{obs} = v'_{CT} = 30,000(3.0 - 2.6) = 12,000$ cm$^{-1}$ (~800 nm)

- MLCT can be handled in a similar manner to LMCT

Examples involve metals in low oxidation states and ligands with empty $\pi^*$ orbitals, such as pyridines, phenanthrolines.

$[Co(C_5H_5NO)_{6}]^{2+}$  
$t_{2g} \rightarrow \pi^* 25450$ cm$^{-1}$

$[Cu(1,10$-phenanthroline$)]^+$  
$e_g \rightarrow \pi^* 23000$ cm$^{-1}$
• Intervalance (metal to metal) Charge Transfer

Classification of mixed valence compounds

Class I Element in two recognizably different oxidation states. Little or no electronic communication. Spectra are superposition of the two components. Example: Pb$_3$O$_4$ has structure containing Pb$^{II}$O$_3$ pyramids and Pb$^{IV}$O$_6$ octahedra. (insulator)

Class II Partial (resonance) interaction between the two valence states A(1) and B(2). The ground state of the system is described by a wave-function

$$\psi = \frac{1}{\sqrt{1 - \alpha^2}} \{ A(1)B(2) + \alpha A(2)B(1) \}$$

Where $\alpha$ is a valence delocalization coefficient, typically <0.05. Example: Fe$_3$O$_4$ has Fe$^{III}$O$_6$ octahedra, Fe$^{III}$O$_4$ tetrahedra and Fe$^{III}$O$_6$ octahedra. (semiconductor)

Class III Complete valence delocalization between the different valence states ($H_2^+$; $\alpha^2 = 0.5$). Infinite class II lattices, e.g. tungsten bronzes Na$_x$WO$_3$ are metallic conductors.
Class II and Class III compounds have spectra with new absorption bands.

Some molecular examples of class II systems

(A) \([(\text{NH}_3)_{5}\text{Ru}^{\text{II}}\text{NC}_4\text{H}_4\text{NRu}^{\text{III}}(\text{NH}_3)_{5}]^{5+}\)

(B) \([(\text{bipy})_2\text{Mn}^{\text{III}}(\text{di-µ-O})\text{Mn}^{\text{IV}}(\text{bipy})_2]^{3+}\)

(C) \([(\text{NC})_{5}\text{Fe}^{\text{II}}\text{CNFe}^{\text{III}}(\text{CN})_{5}]^{6-}\)

spectra show “normal” d-d and CT transitions of each metal valence state plus one or more new intervalence CT (IT) bands, often in the near IR.

For (a) IT band at 9700 cm\(^{-1}\)
for (b) at 12,000 cm\(^{-1}\) and for (c) at 7700 cm\(^{-1}\)
Simple perturbation theory can be applied to the two-center case when $\alpha$ is small. This leads to the potential energy diagram shown and to a simple relationship between the energy of the IT transition (optical electron transfer) and the activation energy of a thermal electron transfer.

$$E_{th} = \frac{E_{op}}{4} - J + \frac{J^2}{E_{op}}$$

$J$ can be estimated from the IT band parameters

$$J = \sqrt{\frac{(4.2 \times 10^{-4}) \epsilon_{\text{max}} \nu_{1/2} E_{op}}{d^2}}$$

where $\nu_{\frac{1}{2}}$ and $E_{op}$ are in cm$^{-1}$ and $d$ is in Å