Lecture 18

d-Metal Complex Spectra

Suggested reading: Shriver & Atkins, Chapter 20
Ligand Field Theory: $\sigma$ Bonding

- Most of the bonding orbitals are ligand in character
  - The electrons that we regard as provided by the ligands are largely confined to the ligands

- Remaining $n$ electrons provided by the metal enter the non-bonding $t_{2g}$ and antibonding $e_g$ orbitals
Ligand Field Theory: $\pi$ Bonding

If the ligands supply $\pi$ orbitals, the $t_{2g}$ orbitals become bonding or antibonding (as opposed to non-bonding).
**π Donor Ligands**

+ A π donor ligand has filled orbitals of π symmetry around the M-L axis
  - Cl\(^-\), Br\(^-\), OH\(^-\), O\(^2-\)
+ these electrons fill the bonding levels, leaving the electrons from the metal to fill the antibonding states

→ π donors decrease Δ₀
$\pi$ Acceptor Ligands

- A $\pi$ acceptor ligand has empty orbitals of $\pi$ symmetry (vacant antibonding orbitals on the ligand)
  - CO, N$_2$

- Typically higher in energy than the metal d orbitals

$\rightarrow \pi$ acceptors increase $\Delta_0$
Revisiting the Spectrochemical Series

The size of the coordinating atom of ligands increases

The pi-donor character of the ligand increases

\[ \pi \text{ Acceptor} > \text{no } \pi \text{ effects} > \text{weak } \pi \text{ donor} > \pi \text{ donor} \]
Electronic Spectra

Cr$^{3+}$:Al$_2$O$_3$

ZnS

SrAl$_2$O$_4$
Electronic Spectra

Depend on both the ligand-field splitting parameter and electron-electron interactions

\[ \text{Charge transfer band} \]

\[ \text{Spin-forbidden} \]

\[ \text{Spin-allowed, ligand field transition} \]

\[ \text{Magnified absorption} \]

\[ \text{[Cr(NH}_3\text{)}_6\text{]}^{3+} \]
Ligand Field Transitions

• Due to transitions between $t_{2g}$ and $e_g$ states
  • Also called “d-d transitions”
• Energy splitting arises from different microstates of system
Terms of Free Atoms/Ions

**Microstates**: the different ways in which electrons can occupy certain orbitals

**Example**: a few $2p^2$ microstates ($m_{\text{spin}}$):

$(1^+, 1^-) \quad (-1^+, 0^+)$

The energies of the microstates have the same energy only if electron-electron repulsions are negligible.

If we group together the microstates that have the same energy when electron-electron repulsions are taken into account, we obtain the spectroscopically distinguishable energy levels called “**terms**”
Russel-Saunders coupling

For light atoms and the 3d series, the energies of the microstates are determined first by the electron spin (S), then their orbital angular momentum (L).

Total momentum is determined by summing first the spins, then the orbital angular momenta, and then combining both: Russel-Saunders coupling

For heavier atoms, must consider spin-orbit coupling: “jj-coupling”

Clebsch-Gordon Series: \[ L = l_1 + l_2, l_1 + l_2 - 1, \ldots |l_1 - l_2| \]
\[ S = s_1 + s_2, s_1 + s_2 - 1, \ldots |s_1 - s_2| \]

(For more than 2 electrons, combine \( l_3, s_3 \) with values above)
Example: atoms with d\(^2\) configuration (Ti\(^{2+}\))

\[ \text{d}^2 \rightarrow l_1=2, l_2=2, s_1=1/2, s_2=1/2 \]

\[ L = 2+2, \ 2+2-1, \ ... \ |2-2| = 4, 3, 2, 1, 0 \]

\[ S = 1/2+1/2, \ 1/2+1/2-1, \ ... \ |1/2-1/2| = 1, 0 \]

**In general:**
Total orbital angular momentum:
\[ L = 0 \ (S), 1 \ (P), 2 \ (D), 3 \ (F), 4 \ (G) \]

Total Spin
\[ S = 0 \ 1/2 \ 1 \ 3/2 \ 2 \]

Usually reported as 2S+1 (multiplicity)

for d\(^2\): \(^1\!G\) or \(^3\!G\), \(^1\!F\) or \(^3\!F\), etc...
The energies of the terms

1. For a given configuration, the term with the greatest multiplicity lies lowest in energy
   → i.e., the triplet term of a configuration (if one is permitted) will have a lower energy than a singlet term

2. For a term of a given multiplicity, the term with the greatest value of L lies lowest in energy
   → if L is high, the electrons can effectively avoid each other

   Ground term of a d² species: ³F

3. Note: usually little correlation of L with the order of the higher terms

4. Similar terms can be defined for complexes. Won’t cover in this class.
Charge Transfer Bands

- The intense absorption shoulder at high energies

- An electron migrates between orbitals that are predominantly ligand in character and orbitals that are predominantly metal in character
LMCT and MLCT Bands

• LMCT bands occur when the metal is in a high oxidation state and ligands contain non-bonding electrons → acceptor level of metals is low in energy and empty or ligand level is high in energy
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• LMCT bands occur when the metal is in a high oxidation state and ligands contain non-bonding electrons → acceptor level of metals is low in energy and empty or ligand level is high in energy

• MLCT bands occur when the metal is in a low oxidation state and ligands have low-lying acceptor levels
Electronic Spectra

Depend on both the ligand-field splitting parameter and electron-electron interactions

\[ [\text{Cr(NH}_3\text{)}_6]^{3+} \]

Charge transfer band

Spin-forbidden

Spin-allowed, ligand field transition

Magnified absorption

$\log(\varepsilon/(\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}))$

$\lambda/\text{nm}$

(50 000 cm$^{-1}$)  (25 000 cm$^{-1}$)  (17 000 cm$^{-1}$)  (12 500 cm$^{-1}$)
Selection Rules and intensities

• The strength of an electronic transition is determined by the transition dipole moment, linking initial and final wavefunctions with the electric dipole moment “operator” (Fermi’s golden rule)

• Selection rules stem from conservation of momentum

}\begin{center}\begin{tabular}{c}
\textbf{Spin-Allowed} \\
\includegraphics[width=0.4\textwidth]{fluorescence.png} \\
\textbf{Fluorescence} \\
\textbf{Spin-Forbidden} \\
\includegraphics[width=0.4\textwidth]{phosphorescence.png} \\
\textbf{Phosphorescence}
\end{tabular}\end{center}
Intensities of bands in 3d complexes

<table>
<thead>
<tr>
<th>Band type</th>
<th>$c_{\text{max}}/\text{(dm}^3\text{ mol}^{-1}\text{ cm}^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin-forbidden</td>
<td>$&lt; 1$</td>
</tr>
<tr>
<td>Laporte-forbidden</td>
<td>$20 - 100$</td>
</tr>
<tr>
<td>d–d</td>
<td></td>
</tr>
<tr>
<td>Laporte-allowed</td>
<td>c. 250</td>
</tr>
<tr>
<td>d–d</td>
<td></td>
</tr>
<tr>
<td>Symmetry-allowed (e.g. CT)</td>
<td>$1000 - 50 000$</td>
</tr>
</tbody>
</table>

- In a centrosymmetric molecule, the only allowed transitions are those accompanied by a change in parity ($g \rightarrow u$ allowed, but not $g \rightarrow g$ or $u \rightarrow u$)
- Relaxed by departure from perfect symmetry & by asymmetric vibrations
Luminescence and Phosphorescence (in Ruby)

![Diagram showing energy levels and transitions in a ruby crystal, including violet absorption, green absorption, and red emission.](image-url)
Now you’re ‘phenyl’ good!

http://home.icpf.cas.cz/ivonez/jiri/pic.htm