Schedule

- Last Week: Electronic spectroscopy
  Interelectron repulsion, covalency and spin-orbit coupling

- Lecture 4: Re-cap

- Lecture 5: $\pi$-Acceptor Ligands and Biology
  $N_2$, CO, $N_2$ and $O_2$ complexes

- Lecture 6: M-M bonding
  Multiple bonds and metal clusters
Summary of the Last Lecture

Spin selection rule
- The spin cannot change during an electronic transition
- ‘Relaxed’ by spin-orbit coupling for heavy elements

Orbital selection rule
- ‘d-d’ transitions cannot occur
- ‘Relaxed’ by d-p mixing in complexes without centre of inversion (e.g. tetrahedron)

Laporte selection rule
- No ‘d-p’ mixing possible in complexes with a centre of inversion (e.g. octahedron or square planar complex)
- ‘Relaxed’ due to molecular vibrations

Charge transfer transitions
- LMCT, MLCT and IVT – cover up ‘d-d’ if in visible region

Selection Rules and Band Intensity
- The height of the band in the spectrum is called the 'molar extinction coefficient’ – symbol ε:

<table>
<thead>
<tr>
<th>ε (mol⁻¹ cm⁻¹)</th>
<th>type of transition</th>
<th>type of complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>very pale colours</td>
<td>spin forbidden, orbitally forbidden, Laporte forbidden</td>
<td>octahedral d⁵ complexes (e.g. [Mn(H₂O)₆]²⁺)</td>
</tr>
<tr>
<td>10⁻³ - 1</td>
<td>spin forbidden, orbitally forbidden</td>
<td>tetrahedral d⁵ complexes (e.g. [MnCl⁴]²⁻)</td>
</tr>
<tr>
<td>1 - 10</td>
<td>spin allowed, orbitally forbidden</td>
<td>octahedral and square planar complexes</td>
</tr>
<tr>
<td>10 - 10²</td>
<td>spin allowed, orbitally forbidden</td>
<td>tetrahedral complexes</td>
</tr>
<tr>
<td>10 - 10³</td>
<td>spin allowed, orbitally forbidden</td>
<td>tetrahedral complexes</td>
</tr>
<tr>
<td>&gt; 10³</td>
<td>LMCT, MLCT, IVT</td>
<td></td>
</tr>
</tbody>
</table>
Oxidation States of Manganese: +7

- \([\text{MnO}_4\text{]}^-\): the permanganate ion
  - deep purple colour
  - (absorbs green/yellow ~ 18000 cm\(^{-1}\))

- high metal charge (+7) makes it highly oxidizing (and easily reduced)
- O \(\rightarrow\) M charge transfer occurs at relatively low energy (in the visible region)
- LMCT - orbitally allowed and spin allowed so highly intense

Oxidation States of Manganese: VI

- \([\text{MnO}_4\text{]}^{2-}\): the manganate ion

\[
2\text{MnO}_4^{-(aq)} + \text{C}_6\text{H}_{10}(l) + 2\text{OH}^-(aq) \rightarrow 2\text{MnO}_4^{2-(aq)} + \text{C}_6\text{H}_{10}(\text{OH})_2(aq)
\]

- high metal charge (+6) makes it highly oxidizing (and easily reduced)
- O \(\rightarrow\) M charge transfer occurs at relatively low energy (in the visible region but at higher energy than for permanganate)
- LMCT - orbitally allowed and spin allowed so highly intense
- \(d^1\) - ligand-field transition lost under LMCT bands

- deep green colour
  - (absorbs purple ~ 25000 cm\(^{-1}\))
Oxidation States of Manganese: IV and II

- **MnO₂**: manganese dioxide

  \[
  \text{MnO}_4^{2-}(aq) + 3\text{H}^+(aq) + \text{C}_6\text{H}_{10}(l) \rightarrow 2\text{MnO}_2(s) + \text{C}_6\text{H}_{10}((OH)_2(aq)
  \]

- **Mn²⁺(aq)**: manganese ion

  \[
  \text{MnO}_2(s) + 4\text{H}^+(aq) + 2\text{Fe}^{2+}(aq) \rightarrow \text{Mn}^{2+}(aq) + 2\text{Fe}^{3+}(aq) + 2\text{H}_2\text{O}(l)
  \]

  - low metal charge (+2) so O → M charge transfer in ultraviolet
  - high spin d⁵ – all transitions are spin forbidden
  - similar *colour* to permanganate but very different *intensity*

Manganese(II)

- **Mn²⁺ d⁵**: all transitions are spin forbidden:
  - become possible through spin-orbit coupling
  - spin-forbidden transitions are *extremely* weak for 3d metal complexes
  - bands due to spin-forbidden transitions are normally hidden under the spin allowed bands
  - for d⁵, there are no spin-allowed bands allowing spin-forbidden bands to be seen

  ![Ground State Diagram](image)

  - e₉
  - t₂₉

AJB lecture 3
**Manganese(II)**

- Mn$^{2+}$ d$^5$: all transitions are spin forbidden
  - turning a spin over requires energy even if the orbital is not changed
  - called a “spin flip transition”
  - as the orbital occupation does not change, there is very little change in the M-L bond lengths

![Diagram of eg and t$_2g$ orbitals]

**Octahedral and Tetrahedral Cu(II)**

- Cu$^{2+}$
  
  \[
  [\text{Cu(H}_2\text{O)}_6]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \leftrightarrow [\text{CuCl}_4]^{2-}(\text{aq}) + 6\text{H}_2\text{O(l)}
  \]

  - pale blue absorbs $\sim$13000 cm$^{-1}$
  - green absorbs $\sim$10000 cm$^{-1}$

- d$^9$: one d-d transition with frequency = $\Delta_{\text{oct}}$ or $\Delta_{\text{tet}}$
  - $\Delta_{\text{oct}} > \Delta_{\text{tet}}$ (fewer ligands in a tetrahedron)
- Higher intensity for tetrahedral complex
  - d-p mixing possible in tetrahedron
  - d-p mixing only due to vibrations for octahedron

Slide 9/12

Slide 10/12
Octahedral and Tetrahedral Co(II)

- Co$^{2+}$

\[
[\text{Co(H}_2\text{O)}_6]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \leftrightarrow [\text{CoCl}_4]^{2-}(\text{aq}) + 6\text{H}_2\text{O(l)}
\]

- **pale pink** absorbs at 8680, 18400 and 19200 cm$^{-1}$
- **blue** absorbs at 4780, 15700 and 16230 cm$^{-1}$

- d$^7$: three d-d transitions
  
  \[\Delta_{\text{oct}} = v_2 - v_1 = (18400 - 8680) = 9720 \text{ cm}^{-1}\]

- Higher intensity for tetrahedral complex

  - d-p mixing possible in tetrahedron
  - d-p mixing only due to vibrations for octahedron

**Summary**

By now you should be able to

- explain the *number* of bands
- obtain $\Delta_{\text{oct}}$ from spectrum for d$^1$, d$^3$, d$^4$, d$^6$, d$^7$, d$^8$ and d$^9$
- predict relative intensity of spin-allowed vs spin forbidden, octahedral vs tetrahedral and ligand-field vs charge-transfer transitions