**Schedule**

- Last Week: Electronic spectroscopy
  - Interelectron repulsion, covalency and spin-orbit coupling
- Lecture 4: Re-cap
- Lecture 5: π-Acceptor Ligands and Biology
  - N₂, CO, N₂ and O₂ complexes
- Lecture 6: M-M bonding
  - Multiple bonds and metal clusters

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**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

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**Selection Rules and Band Intensity**

- The height of the band in the spectrum is called the 'molar extinction coefficient' – symbol $\varepsilon$:

<table>
<thead>
<tr>
<th>$\varepsilon$ (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></td>
<td></td>
</tr>
<tr>
<td>10⁻³ - 1</td>
<td>spin forbidden</td>
<td>octahedral d⁶ complexes (e.g. [Mn(H₂O)₆]²⁺)</td>
</tr>
<tr>
<td></td>
<td>orbitally forbidden, Laporte forbidden</td>
<td></td>
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<tr>
<td>1 – 10</td>
<td>spin forbidden</td>
<td>tetrahedral d⁶ complexes (e.g. [MnCl₄]²⁻)</td>
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<tr>
<td></td>
<td>orbitally forbidden, Laporte forbidden</td>
<td></td>
</tr>
<tr>
<td>10 – 10²</td>
<td>spin allowed, orbitally forbidden</td>
<td>octahedral and square planar complexes</td>
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<tr>
<td></td>
<td>Laporte forbidden</td>
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<tr>
<td>10 – 10³</td>
<td>spin allowed, orbitally forbidden</td>
<td>tetrahedral complexes</td>
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<tr>
<td>&gt; 10³</td>
<td>LMCT, MLCT, IVT</td>
<td></td>
</tr>
</tbody>
</table>
Oxidation States of Manganese: +7

• [MnO_4]^-: the permanganate ion

  - deep purple colour (absorbs green/yellow ~ 18000 cm^-1)

  - high metal charge (+7) makes it highly oxidizing (and easily reduced)
  - O → 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

• [MnO_4]^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 → 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

• MnO_2: manganese dioxide

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

• Mn^{2+}(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 d^5 - all transitions are spin forbidden
  - similar colour to permanganate but very different intensity

Manganese(II)

• Mn^{2+} d^5: 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 d^5, there are no spin-allowed bands allowing spin-forbidden bands to be seen

  \[ e_g \]
  \[ t_{2g} \]

  ground state

5000 10000 15000 20000 25000 30000 35000 cm^-1
**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

**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

**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
  - $\Delta_{\text{oct}} = \nu_2 - \nu_1 = (18400 - 8680) = 9720$ 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