COMMONWEALTH OF AUSTRALIA

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Schedule

- **Lecture 1:** Electronic absorption spectroscopy
  Jahn-Teller effect and the spectra of $d^1$, $d^4$, $d^6$ and $d^9$ ions

- **Lecture 2:** Interpreting electronic spectra
  Interelectron repulsion and the nephelauxetic effect

- **Lecture 3:** Interpreting electronic spectra
  Selection rules and charge transfer transitions
Summary of Last Lecture

d-d spectroscopy
• For $d^2$, $d^3$, $d^7$ and $d^8$, the effect of repulsion between the d-electrons must be considered through the Racah parameter $B$
• Three transitions are predicted in their ligand-field spectra

Band Shapes
• Exciting $d$-electrons usually increases the bond length
• This leads to broad bands

Today’s lecture
• Selection rules
Energies of $d$-$d$ Transitions

**Octahedral $d^1$, $d^4$, $d^6$ and $d^9$:**
1 band energy $= \Delta_{\text{oct}}$

**Octahedral $d^2$:**
3 bands
$\Delta_{\text{oct}}$ and B from calculation

**Octahedral $d^7$:**
3 bands
$\Delta_{\text{oct}} = v_2 - v_1$ B from calculation

**Octahedral $d^3$ and $d^8$:**
3 bands
$v_1 = \Delta_{\text{oct}}$ B from calculation
Features of an Electronic Spectrum

- The **frequency, wavelength** or **energy** of a transition relates to the energy required to excite an electron:
  - depends on \( \Delta_{\text{oct}} \) and B for ligand-field spectra
  - decides **colour of molecule**

- The **width** of a band relates to the vibrational excitation that accompanies the electronic transition:
  - narrow bands: excited state has similar geometry to the ground state
  - broad bands: excited state has different geometry to the ground state

- The **height** or **area** of a band relates to the number of photons absorbed
  - depends on concentration and path length
  - transition probability
  - decides **intensity or depth of colour**

Ni\(^{2+}\), \(d^8\):

\[
\begin{align*}
8500 \text{ cm}^{-1} & \quad 13800 \text{ cm}^{-1} \\
\downarrow & \quad \downarrow \\
25300 \text{ cm}^{-1}
\end{align*}
\]
Transition Probability

- When light is shined on a sample, some of the light may be absorbed and some may pass straight through
  - the proportion that is absorbed depends on the ‘transition probability’

- To be absorbed, the light must interact with the molecule:
  - the oscillating electric field in the light must interact with an oscillating electric field in the molecule

- During the transition, there must be a change in the dipole moment of the molecule:
  - if there is a large change, the light / molecule interaction is strong and many photons are absorbed:
    large area or intense bands $\rightarrow$ intense colour
  - if there is a small change, the light / molecule interaction is weak and few photons are absorbed:
    low area or weak bands $\rightarrow$ weak colour
  - If there is no change, there is no interaction and no photons are absorbed
Selection Rules

- During the transition, there must be a change in the dipole moment of the molecule:
  - if there is a large change, the light / molecule interaction is strong and many photons are absorbed:
    large area or intense bands $\rightarrow$ intense colour
  - if there is a small change, the light / molecule interaction is weak and few photons are absorbed:
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  - If there is no change, there is no interaction and no photons are absorbed

Selection rules tell us which transitions give no change in dipole moment and hence which will have zero intensity
Selection Rules - IR

- During the transition, there must be a change in the dipole moment of the molecule.
- Octahedral ML\textsubscript{6} complexes undergo 3 types of M-L stretching vibration:

\[
[\text{Co(CN)}\textsubscript{6}]^3^-
\]

- There is one band in the M-L stretching region of the IR spectrum.
Selection Rules – Spin Selection Rule

The spin cannot change during an electronic transition

- **Ground state**: $d^4$ (spin configuration)
- **1st excited state**: $t_{2g}$ (spin configuration)
- **2nd excited state**: $t_{2g}$ (spin configuration)

Only one spin allowed transition
Selection Rules – Spin Selection Rule

The spin cannot change during an electronic transition

$d^5$

$e_g$

$\uparrow \uparrow$

$\downarrow \downarrow$

$t_{2g}$

ground state

NO spin allowed transitions for high spin $d^5$
Selection Rules – Orbital Selection Rule

- A photon has 1 unit of angular momentum
- When a photon is absorbed or emitted, this momentum must be conserved

$$\Delta l = \pm 1 \text{ or:}$$

- ‘s ↔ p’, ‘p ↔ d’, ‘d ↔ f’ etc allowed ($$\Delta l = \pm 1$$)
- ‘s ↔ d’, ‘p ↔ f’ etc forbidden ($$\Delta l = \pm 2$$)
- ‘s ↔ s’, ‘p ↔ p’, ‘d ↔ d’, ‘f ↔ f’ etc forbidden ($$\Delta l = 0$$)

...so why do we see ‘d-d’ bands?
‘Relaxing’ The Orbital Selection Rule

- The selection rules are **exact** and cannot be circumnavigated
- It is our **model** which is too simple:
  - the ligand-field transitions described in Lectures 2 and 3 are in molecules not atoms
  - labelling the orbitals as ‘d’ (atomic orbitals) is **incorrect** if there is any covalency

Through covalent overlap with the ligands, the metal ‘d’ and ‘p’ orbitals are mixed
‘Relaxing’ the Orbital Selection Rule

Through covalent overlap with the ligands, the metal 'd' and 'p' orbitals are mixed

- As the molecular orbitals are actually mixtures of $d$ and $p$-orbitals, they are actually allowed as $\Delta l = \pm 1$
- **But**, if covalency is small, mixing is small and transitions have **low intensity**

In tetrahedral complexes, the ‘$d$-$d$’ transitions become allowed through covalency but the ‘$d$-$d$’ bands are still weak as covalency is small
Laporte Selection Rule

- This way of ‘relaxing’ the orbital selection rule is not available in octahedral complexes

A metal p-orbital overlaps with ligand orbitals

A metal d-orbital cannot overlap with the same ligand orbitals

In general, no mixing of the ‘d’ and ‘p’ orbitals is possible if the molecule has a centre of inversion (Laporte rule)
‘Relaxing’ the Laporte Selection Rule

• Again our model is deficient:
  - molecules are not rigid but are always vibrating

During this vibration, centre of inversion is temporarily lost:

\[ d-p \] mixing can occur

• Vibrational amplitude is small so deviation and mixing is small:
  - octahedral complexes have lower intensity bands than tetrahedral complexes
  - the intensity of the bands increases with temperature as amplitude increases
‘Relaxing’ the Spin Selection Rule

- Again our model from lectures 1 and 2 is deficient:
  - electrons can have magnetism due to the spin and orbital motions
  - this coupling allows the spin forbidden transitions to occur

spin-orbit coupling: the interaction between spin and orbital magnetism

- $\text{Mn}^{2+} \ d^5$: all transitions are spin forbidden

spin-orbit coupling gets stronger as elements get heavier and so spin forbidden transitions get more important
Charge Transfer Transitions

- As well as ‘d-d’ transitions, the electronic spectra of transition metal complexes may 3 others types of electronic transition:
  - Ligand to metal charge transfer (LMCT)
  - Metal to ligand charge transfer (MLCT)
  - Intervalence transitions (IVT)

- All complexes show LMCT transitions, some show MLCT, a few show IVT
Ligand to Metal Charge Transfer

- These involve excitation of an electron from a ligand-based orbital into a d-orbital

![Diagram of LMCT process](image)

- This is always possible but LMCT transitions are usually in the ultraviolet.
- They occur in the visible or near-ultraviolet if
  - metal is easily reduced (for example metal in high oxidation state)
  - ligand is easily oxidized

If they occur in the visible or near-ultraviolet, they are much more intense than ‘d-d’ bands and the latter will not be seen.
Ligand to Metal Charge Transfer

- They occur in the visible or near-ultraviolet if
  - metal is easily **reduced** (for example metal in high oxidation state)

<table>
<thead>
<tr>
<th></th>
<th>TiO₂</th>
<th>VO₄³⁻</th>
<th>CrO₄²⁻</th>
<th>MnO₄⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Ti⁴⁺</td>
<td>V⁵⁺</td>
<td>Cr⁶⁺</td>
<td>Mn⁷⁺</td>
</tr>
<tr>
<td></td>
<td>white</td>
<td>white</td>
<td>yellow</td>
<td>purple</td>
</tr>
<tr>
<td></td>
<td>in far UV</td>
<td>~39500 cm⁻¹</td>
<td>~22200 cm⁻¹</td>
<td>~19000 cm⁻¹</td>
</tr>
</tbody>
</table>

more easily reduced
Metal to Ligand Charge Transfer

- They occur in the visible or near-ultraviolet if
  - metal is easily oxidized and ligand has low lying empty orbitals
  
\[
\begin{align*}
M &= \text{Fe}^{2+}, \text{Ru}^{2+}, \text{Os}^{2+} \\
\text{Sunlight} &\text{excites electron from } M^{2+} (t_{2g})^6 \text{ into empty ligand } \pi^* \text{ orbital} \\
\text{method of capturing and storing solar energy}
\end{align*}
\]
**Intervalence Transitions**

- Complexes containing metals in two oxidation states can be coloured due to excitation of an electron from one metal to another.

  "Prussian blue" contains $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$

- Colour arises from excitation of an electron from $\text{Fe}^{2+}$ to $\text{Fe}^{3+}$
### 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>( 10^{-3} - 1 )</td>
<td>spin forbidden, orbitally forbidden, Laporte forbidden</td>
<td>octahedral d(^5) complexes (e.g. ([\text{Mn}(\text{H}_2\text{O})_6]^{2+}))</td>
</tr>
<tr>
<td>( 1 - 10 )</td>
<td>spin forbidden, orbitally forbidden</td>
<td>tetrahedral d(^5) complexes (e.g. ([\text{MnCl}_4]^{2-}))</td>
</tr>
<tr>
<td>( 10 - 10^2 )</td>
<td>spin allowed, orbitally forbidden, Laporte forbidden</td>
<td>octahedral and square planar complexes</td>
</tr>
<tr>
<td>( 10 - 10^3 )</td>
<td>spin allowed, orbitally forbidden</td>
<td>tetrahedral complexes</td>
</tr>
<tr>
<td>( &gt; 10^3 )</td>
<td>LMCT, MLCT, IVT</td>
<td></td>
</tr>
</tbody>
</table>

**very pale colours**

**intense colours**
Summary

By now, you should be able to....

• Explain that the spin cannot change during an electronic transition
• Explain that pure ‘d-d’ transitions cannot occur
• Explain that d-p mixing in complexes without centre of inversion (e.g. tetrahedron) ‘relaxes’ this rule
• Explain that ‘d-p’ mixing for complexes with a centre of inversion (e.g. octahedron or square planar) can only occur due to molecular vibrations
• Explain that origin of LMCT, MLCT and IVT transitions
• Predict the relative intensities of spin, Laporte and orbitally forbidden transitions
Practice

1. Solutions if \([\text{Cr(H}_2\text{O)}_6]^{3+}\) ions are pale green but the chromate ion \([\text{CrO}_4]^{2-}\) is an intense yellow. Characterize the origins of the transitions and explain their relative intensities.

2. Common glass used for windows and many bottles is green because of \(\text{Fe}^{2+}\). It is decolourized by addition of \(\text{MnO}_2\) to form \(\text{Fe}^{3+}\) and \(\text{Mn}^{2+}\). Why is the glass decolourized?

3. \([\text{Co(NH}_3)_4\text{Cl}_2]^+\) exists in two isomeric forms.
   
   (i) Draw the structures of these isomers
   
   (ii) Predict which isomer will give rise to the more intense 'd-d' bands