Electronic Spectroscopy of Transition Metal Ions

• colour is one of the distinguishing features of TM complexes (except \textit{d}^0 and \textit{d}^{10} of course!)

• visible and long UV light absorption causes electronic transitions from a filled or partially filled \textit{d} orbital to a higher energy empty orbital (usually \textit{d})

\[ \Delta E = h \nu = \frac{hc}{\lambda} \]

• complexes are often pale in colour but there are some notable exceptions:

<table>
<thead>
<tr>
<th>\textit{d}→\textit{d} transitions</th>
<th>Charge transfer (CT) transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>weak ((\varepsilon &lt; 100\text{ L mol}^{-1}\text{ cm}^{-1}))</td>
<td>strong ((\varepsilon &gt; 10,000\text{ L mol}^{-1}\text{ cm}^{-1}))</td>
</tr>
<tr>
<td>[Cr(H₂O)₆]²⁺ \textit{d}⁴ sky blue</td>
<td>MnO₄⁻ \textit{d}⁰ intense purple</td>
</tr>
<tr>
<td>[Mn(H₂O)₆]²⁺ \textit{d}⁵ pale pink</td>
<td>[CoCl₄]²⁻ \textit{d}⁷ deep blue</td>
</tr>
<tr>
<td>[Co(H₂O)₆]²⁺ [Cl⁻]₂ \textit{d}⁷ pink</td>
<td></td>
</tr>
<tr>
<td>CoCl₂ (s) \textit{d}⁷ blue</td>
<td></td>
</tr>
</tbody>
</table>

**Beer’s Law**: \(A = \varepsilon cl\)

(A = absorbance; \(\varepsilon\) = molar extinction coefficient or molar absorptivity; \(c\) = molar concentration; \(l\) = pathlength of light through the solution in cm)

• \(\varepsilon\) ranges from 0-100 (pale colours) to >100,000 (intense colours) due to selection rules (\textit{dealt with later})

• bands are broad due to \textit{vibronic coupling}: electronic transitions occur on a timescale much shorter than vibrations. Oscillating ligands = different transition energies
Electronic spectroscopy in multi d electron ions

- in order to understand the spectroscopy of d ions with more than one d electron we must take the effect of $e^- - e^-$ repulsion into account (we have ignored this so far)

- each $e^-$ has spin and orbital angular but it is the interaction of the **TOTAL RESULTANT spin and angular momentum** with light that is important

- we can treat the total spin and angular momentum separately OR we can combine them to form a new quantum number $J$ and then come up with a total $J$...which is best to use depends on where we are in the periodic table:

Lighter d metal ions: S and L total separately (**Russell-Saunders** coupling – dealt with in this course)

Heaviest d and f metal ions: need to define $J$ states (**jj coupling**)
The energy levels derived from a \(d^2\) ion in an Oh field:

\[
\begin{align*}
\text{Term symbols: } & \text{ energy differs by total } S \text{ and } L \text{ for a ‘term’} \\
& (2S+1)_{L_J}
\end{align*}
\]

where \(S = \text{total spin multiplicity, } L = \text{total orbital angular momentum and } J\) is combined TOTAL angular momentum (spin and orbital combined which can range from \(L+S\) to \(L-S\))

\(\text{eg. } ^3F \text{ has } S = 1 \text{ and } L = 3\)

With most TM ions, the spin-orbit coupling is small due to electron delocalization onto the ligands so the energy differences between the possible \(J\) states are negligible but the possibilities would be \(J = 4, 3 \text{ or } 2\) giving rise to \(^3F_4, ^3F_3\) and \(^3F_2\) states.
Russell-Saunders coupling scheme for a $d^2$ ion

- each $e^-$ in a d orbital has $l = 2$ ($m_l = 2,1,0,-1,-2$) and $s = \frac{1}{2}$ ($m_s = +1/2, -1/2$)

- combine these into $S$ and $L$ which represent the TOTAL spin and orbital angular momentum

- there are many different arrangements of electrons in d orbitals so this gives rise to many possible states (Russell-Saunders ‘terms’) that represent different energies for the system as a whole

  eg. $d^2$ ion

  1$^\text{st}$ electron: any of the 5 d-orbitals and spin up or down gives rise to 10 possibilities

  2$^\text{nd}$ electron: can go in any d orbital but only spin paired in the one already occupied = 9 possibilities

- therefore there are 90 ways to do this but since $e^-$ are indistinguishable, there are actually only 45 unique arrangements (called ‘microstates’ of the system)

- but L and S are quantized so an $S = 1$ state has $M_S = 1,0,-1$ and an $L = 2$ state has $M_L = 2,1,0,-1,-2$ thus we need to group these microstates together into the terms with unique L and S that give rise to them
Figure 7.1 Microstates and Russell-Saunders terms for a $d^n$ transition metal ion.
So the RS terms arising for a $d^2$ ion are: $^1G, ^3F, ^1D, ^3P$ and $^1S$ but... which one is lowest in energy (the ground term)?

Hund’s rules take care of this:

a) lowest energy term has the largest spin multiplicity

b) if two terms share the same multiplicity, the largest $L$ value is lowest in energy

So that means $^3F$ is lowest for a $d^2$ ion (Hund’s rules only apply to the ground term NOT the order overall)

Here are the complete lists of RS terms for each d electron count:

**d count**  RS Terms (ground term listed last in bold)

$d^1$, $d^9$  $^2D$

$d^2$, $d^8$  $^1S, ^1D, ^1G, ^3P, ^3F$

$d^3$, $d^7$  $^2D, ^2P, ^2D, ^2F, ^2G, ^2H, ^4P, ^4F$

$d^4$, $d^6$  $^1S, ^1D, ^1G, ^1S, ^1D, ^1F, ^1G, ^1I, ^3P, ^3F, ^3P, ^3D, ^3F, ^3G, ^3H, ^5D$

$d^5$  $^2D, ^2P, ^2D, ^2F, ^2G, ^2H, ^2S, ^2D, ^2F, ^2G, ^2I, ^4P, ^4D, ^4F, ^4G, ^6S$

- Since an electron in an empty shell behaves in the same way as an ‘electron hole’ in a filled shell, the $d^1$ and $d^9$ ions have the same set of terms and similarly for the other pairs listed.
Okay, so what happens when we consider crystal field effects?

RS terms $^{2S+1}L$ split exactly the same way in a crystal field as do orbitals with the same value of $l$:

<table>
<thead>
<tr>
<th>Free ion term</th>
<th># of states (ML)</th>
<th>Oh crystal field terms</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1</td>
<td>$A_{1g}$</td>
</tr>
<tr>
<td>P</td>
<td>3</td>
<td>$T_{1g}$</td>
</tr>
<tr>
<td>D</td>
<td>5</td>
<td>$T_{2g}$, $E_g$</td>
</tr>
<tr>
<td>F</td>
<td>7</td>
<td>$T_{1g}$, $T_{2g}$, $A_{2g}$</td>
</tr>
<tr>
<td>G</td>
<td>9</td>
<td>$A_{1g}$, $E_g$, $T_{1g}$, $T_{2g}$</td>
</tr>
</tbody>
</table>

so the $^3F$ ground term for a $d^2$ ion gives rise to:

$^3T_{1g}$, $^3T_{2g}$ and $^3A_{2g}$ states in an Oh crystal field

Simplest case: $d^l$ ion (like Ti$^{3+}$)

$s = \frac{1}{2}$ ($m_s = +1/2, -1/2$); $l = 2$ ($m_l = 2, 1, 0, -1, -2$)

therefore: $S = \frac{1}{2}$ and $L = 2$ which gives only one RS term: $^2D$

which in an Oh crystal field splits just like a simple d orbital into:

$^2E_g$ and $^2T_{2g}$ and the transition observed by spectroscopy is from $^2T_{2g}$ to $^2E_g$