Electronic Spectroscopy

• Colours of complexes come from movement of electrons (electronic transitions) from the ground state to an excited state.
• There is typically only one ground state, which obeys Aufbau, Pauli Principle and Hund’s Rules.
• Several possible excited states exist for a d-electron configuration.
• Need a new nomenclature for describing the specific electronic configurations (microstate).
• Movement between states is quantized into specific energies (known as absorption bands). Some of these transitions are more probable than others (allowed vs. forbidden) and are defined by selection rules.
• The bands are determined by the interactions (coupling) of electrons and the orbitals (known as Russell-Saunders or LS coupling).

\[
\begin{align*}
\text{s orbital} & : l = 0 \quad m_l = 0 \\
\text{p orbital} & : l = 1 \quad m_l = -1, 0, +1 \\
\text{d orbital} & : l = 2 \quad m_l = -2, -1, 0, +1, +2
\end{align*}
\]
Consider a $p^2$ electron configuration

- Two electrons in the 2p orbital can be paired or unpaired. Hund says unpaired is lower in E, so that must mean the GS has 2 upe. Having the electrons paired is a possible excited state (ES*).

- So, how many ways can we put 2 upes into three p orbitals ($2p_x$, $2p_y$, $2p_z$)?

- The p-orbitals have $n = 2$, $l = 1$, $m_l = -1, 0, +1$

- $l$ is the orbital angular momentum q.n., which has three possible solutions (three-fold degerate), $m_l$ is the magnetic q.n., and $s$ is the spin q.n. ($s$ is like $m_s$, only where $m_s = +\frac{1}{2}$, or $-\frac{1}{2}$, $s$ is just $\frac{1}{2}$ for an electron)

- Capitalized labels $L$, $M_L$, $M_S$ and $S$ are the quantum numbers for all the electrons in an electron configuration (aka the microstate), which are just the sums of the individual electron q.n.s

- L is special. Just like $l = 0, 1, 2, 3, 4$ gives us s, p, d, f, g, orbitals, respectively, $L = 0, 1, 2, 3, 4$, gives us S, P, D, F, G terms, respectively. These are called ATOMIC TERM SYMBOLS and don’t refer to any orbital, but only to the number of different orbital arrangements the electron configuration may have in an atom.
Atomic/Free Ion Term Symbols

• Just like there is one s orbital, three p orbitals, five d orbitals and seven f orbitals (in general 2l + 1), the atomic term symbols represent the orbital degeneracy of the total electron configurations (2L +1):
• S terms singly degenerate, P terms are triply degenerate
• D terms are five-fold degenerate, F terms are seven-fold degenerate, etc.
• The orbital degeneracy is multiplied by the spin degeneracy (2S +1) where S is the total number of unpaired spins:
• Upe = 0 1 2 3 4 5 (each e- s = ½)
• S = 0 ½ 1 3/2 2 5/2
• 2S+1 1 2 3 4 5 6

Giving a spin... singlet doublet triplet quartet quintet sextet

E.g., Atomic term symbol 3P (called “triplet pee”) represents 3 x 3 = 9 microstates
1D “singlet dee” gives 1 x 5 = 5 microstates, 6S “sextet ess” gives 6 x 1 = 6 μstates
How do we determine the orbital degeneracy?

- Determining spin degeneracy is easy: it’s $n + 1$ where $n$ is #upe.
- To determine the orbital contribution, need to consider the different ways to put the electrons into orbitals. Consider the $p^2$ configuration again:

$$\begin{array}{cccc}
\uparrow & \uparrow & M_L & M_S \\
+1 & 0 & 1 & 1 \\
+1 & 0 & 0 & -1 \\
\end{array}$$

$$\begin{array}{cccc}
\uparrow & \uparrow & M_L & M_S \\
+1 & 0 & 2 & 0 \\
+1 & 0 & 0 & -1 \\
\end{array}$$

$$\begin{array}{cccc}
\uparrow & \uparrow & M_L & M_S \\
+1 & 0 & 1 & 1 \\
+1 & 0 & 0 & -1 \\
\end{array}$$

$$\begin{array}{cccc}
\uparrow & \uparrow & M_L & M_S \\
+1 & 0 & 1 & -1 \\
+1 & 0 & 0 & 1 \\
\end{array}$$

$$\begin{array}{cccc}
\uparrow & \uparrow & M_L & M_S \\
+1 & 0 & 1 & -1 \\
+1 & 0 & 0 & 1 \\
\end{array}$$

- 15 different ways! Imagine what happens with d-orbitals or f-orbitals!
Is there an easy way to get the ground state?

• The ground state term symbols are often all we need. Obeying Hund’s rule, we want to **maximize the spin**. Therefore $M_S = 1$ or -1 gives $S = 3$ (it doesn’t matter whether e- are spin “up” or “down”).

• Does it matter which orbital the e- are in? YES! After the max. # of upe are obtained, they must occupy the orbitals which give the highest orbital multiplicity, the highest value of $L$ (remember $M_L = -L \ldots 0 \ldots +L$)

• From the previous table, the max $M_L$ if we have two upe is +/- 1, therefore $L = 1$. Remember, when $L = 1$, we call it a “P term” or “P state”.

• Therefore, the ground state atomic term for a $p^2$ electron configuration is:

  $^3P$ (triplet pee)

  and represents $3 \times 3 = 9$ microstates! The number of microstates is the entropy of a system (Entropy, $S = k_B \ln \Omega$, where $\Omega$ is the # of microstates).

• What about the other 6 microstates? These are for the spin paired arrangements (singlet spin states), of which we have $^1D$ (5 µstates) and $^1S$ (1 µstate). **Practice other electron configurations!**
Ground State Terms for d-Block Compounds

• A trick for determining the number of microstates:
  • \( \frac{\{2(2l+1)\}!}{(x!\{2(2l+1) - x\}!)} \) Where \( x \) is number of electrons.
  • E.g. for \( d^3 \), \( x = 3 \), \( l = 2 \) (a d-orbital, so \( 2l + 1 = 5 \))
  • # microstates = \( \frac{10!}{(3!(10-3)!)} = \frac{10 \times 9 \times 8}{1 \times 2 \times 3} = \frac{720}{6} = 120 \)
• The ground state is going to be a quartet spin (3 up + 1)
• The maximum \( L \) is going to be \( 2 + 1 + 0 = 3 \) (\( L = 3 \) is an F term)
• The Ground State Atomic (Free Ion) Term is given by \( ^4F \) (28 microstates).

• So, these are for atoms in spherical fields. What about octahedra where the d-orbitals split into \( t_{2g} \) and \( e_g \) sets?
• Molecular Term Symbols!
• Just like d-orbitals split into \( t_{2g} \) and \( e_g \), D atomic terms split into \( T_{2g} \) and \( E_g \) molecular terms (three and two microstates, respectively).
• What about others?
Racah Parameters & Molecular Term Symbols

- In multielectron ions, the effects of e⁻-e⁻ repulsion are summarized by the **Racah Parameters**, A, B and C. These are in fact mathematical representations of Hund’s Rules. The energies of the terms are therefore related by:

\[
\begin{align*}
E^{(1S)} &= A + 14B + 7C \\
E^{(1G)} &= A + 4B + 2C \\
E^{(1D)} &= A - 3B + 2C \\
E^{(3P)} &= A + 7B \\
E^{(3F)} &= A - 8B
\end{align*}
\]

- A is common to all, so ignore it to get relative energies.
- C ≈ 4B, so we are left with B, which in an O_h field is related to \( \Delta_0 \).
- B is a mathematical way of weighing out how strong a ligand is in terms of its affect on the splitting in combination with certain electron configurations.
- So, D **atomic terms** split into \( T_{2g} \) and \( E_g \) **molecular terms**. What about others?

<table>
<thead>
<tr>
<th>Atomic Terms</th>
<th>Number of microstates</th>
<th>Molecular 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>
Molecular Terms

• The number of states represented by the individual molecular terms are:
• 1 for an A term (an orbital singlet)
• 2 for an E term (an orbital doublet)
• 3 for a T term (an orbital triplet)
• Because the spins of the molecular terms cannot change from that of the atomic term from which they originate, a \( ^3F \) term \((3 \times 7 = 21\) microstates) becomes \( ^3A_{2g}, ^3T_{1g} \) and \( ^3T_{2g} \) in an octahedral molecule, giving \((3 \times 1) + (3 \times 3) + (3 \times 3) = 21\) microstates

• Is there an easy way of determining these? YES! Correlation Diagrams!
• Most common form of these diagrams is the Tanabe-Sugano Diagram which relates Energy, \( E \), and \( \Delta_0 \) with respect to the Racah parameter, \( B \).
This axis lists the **atomic, or free ion term** symbols for a d$^3$ ion when $\Delta_O = 0$ (no ligands present). The ground state atomic term is at the baseline, with terms representing excited states going up in relative energy.

This axis lists the **molecular term** symbols for a d$^3$ ion when $\Delta_O > 0$. The ground state molecular term is at the baseline, with terms representing excited states going up in relative energy. Notice that as $\Delta_O$ increases, the splitting between most states increases as well. Also, note that molecular terms can only possess the same spin as the atomic term from which they originate. $^4F$ gives $^4A_{2g}$, $^4T_{2g}$ and $^4T_{1g}$ (on the diagram the “g” parity label is removed for clarity).
A Tanabe-Sugano Diagram for a d⁵ ion

- Because ions d⁴ to d⁷ electron configurations have high or low spin configurations, the molecular ground state depends on the strength of the ligand field. Weak ligand fields (small Δ₀) are given to the left of the vertical line while strong ligand fields lie to the right.

- For hs d⁵, the atomic term is ⁶S, which gives a ⁶A molecular state. Once Δ₀ becomes large enough, the ls d⁵ case is favoured, which has a ²T molecular term arising from a ²I atomic state.
Ligand Field Transitions - UV-vis spectrum for a d$^3$ ion

Absorption axis, usually convenient to convert to units of extinction coefficient (molar absorptivity, M$^{-1}$·cm$^{-1}$)

Ratio of energies for the two spin-allowed transitions = $\frac{28500}{21550} = 1.32$

Look at the T-S diagram for d$^3$. Where does this transition ratio occur?
The 1.32:1 ratio occurs at $\Delta_0/B = 32$. This corresponds to an $E/B$ value of 32 for the $^4T_{2g}$ energy level, which had an $E$ of 21550 cm$^{-1}$ from the UV-vis spectrum.

Solve for $B$: $B = 21550 \text{ cm}^{-1}/32 = 673 \text{ cm}^{-1}$

Now use $B$ to measure $\Delta_0$.

$\Delta_0 = 32 \times B = 21550 \text{ cm}^{-1}$

Note, for a $d^3$ ion, $\Delta_0$ is given by the $E$ of the lowest $E$ spin-allowed transition!

Other electron-configurations not as straightforward. Why?

Electron-electron repulsion! Look at the CFS diagram.

You must know how to estimate $B$ and $\Delta_0$ from a UV-vis spectrum and the appropriate T-S Diagram.
Tanabe-Sugano Diagrams for $d^2$ and $d^3$ ions

Available in appendix of S&A
Tanabe-Sugano Diagrams for $d^4$ and $d^5$ ions
Tanabe-Sugano Diagrams for $d^6$, $d^7$ & $d^8$ ions
Typical $O_h$ Ligand Field Transitions for T-metals

Note the value of $\varepsilon$ on the y-axis (esp Mn$^{II}$)

Do the number of bands confirm what is predicted by the TSDs?

For the Fe$^{II}$ and Co$^{II}$ spectra, are the compounds h.s or l.s?
Charge Transfer Bands

• d-d transitions are usually in the vis region (give complexes their colours)
• What about the high energy bands found in the UV (and sometimes vis)?
• These are Charge Transfer (CT) Bands:
• They arise from electrons moving from the populated ligand centred orbitals into empty metal orbitals (Ligand to Metal, or LMCT)
• Or from populated metal centred orbitals into vacant ligand orbitals (usually $\pi^*$ antibonding) giving Metal to Ligand CT, MLCT
Selection Rules

• CT bands are always intense, meaning strong absorptions, \(\therefore\) large extinction coefficients (y-axis of UV-vis spectrum)
• CT bands are \textit{usually} high in energy (x-axis of UV-vis spectrum), but not always (see E-level diagram on previous slide).
• Energy (in cm\(^{-1}\)) is determined by the difference in orbital energies
• Intensity is determined by probability of the event occurring
• Probability is given by the Selection Rules.
  – Spin Selection Rule: Must maintain the \# of upe to be allowed. Robust and hard to “cheat” therefore spin forbidded transitions are not often observed
  – Laporte (Symmetry) Selection Rule: Allowed transitions are those that are accompanied by a change in parity :

\[
g \leftrightarrow u \text{ allowed, } u \leftrightarrow g \text{ allowed but } g \leftrightarrow g \text{ or } u \leftrightarrow u \text{ FORBIDDEN!}
\]

Therefore d-d bands, because they go from \(t_{2g}\) to \(e_g\), are in fact forbidden!
Why do they occur at all? Laporte rule can be “relaxed” by microdistortions.
Relaxation of the Laporte Selection Rule

In $T_d$ complexes, there is no $i$, \( \therefore \) no g or u parity labels. So, the d-d bands in $T_d$ complexes are lower in E, BUT are more intense.

Why do d-d bands occur at all in octahedral complexes?
Not all octahedral complexes are truly $O_h$ symmetry, therefore are actually allowed (lack true $i$)
Even true, homoleptic $O_h$ complexes undergo Static effects: crystal packing, ligand differences (orientation of polyatomic ligands)
Dynamic effects: asymmetrical vibrations destroy inversion centres.

In general, Laporte rule is easier to “break” therefore Laporte “forbidden” transitions are stronger than Spin “forbidden” transitions.

<table>
<thead>
<tr>
<th>Table 19.9</th>
<th>Intensities of spectroscopic bands in $3d$ complexes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band type</td>
<td>$\varepsilon_{\text{max}}$ (dm$^3$ mol$^{-1}$ cm$^{-1}$)</td>
</tr>
<tr>
<td>Spin-forbidden</td>
<td>$&lt; 1$</td>
</tr>
<tr>
<td>Laporte-forbidden $d-d$</td>
<td>20–100</td>
</tr>
<tr>
<td>Laporte-allowed $d-d$</td>
<td>$ca$ 250</td>
</tr>
<tr>
<td>Symmetry-allowed (e.g. CT)</td>
<td>1000–50 000</td>
</tr>
</tbody>
</table>
Examples of LMCT vs. MLCT

- **LMCT:** may occur if ligands have lone pairs of relatively high $E$ (e.g. S, Se or O) or if metal has low lying vacant orbitals (metal in high oxidation state).
  - $\text{MnO}_4^-$ anion is dark purple: $\text{Mn}^\text{VII} (3d^0)$ with $\text{O}^2^-$ ligands = LMCT in visible region (therefore the purple colour!)
  - $\text{ReO}_4^-$ anion is pale: $\text{Re}^\text{VII} (5d^0)$ so v. large $E$ gap! LMCT is in UV region. We can’t see the colour with our eyes b/c it’s too high in $E$.
  - Also, both are $T_d$ so no inversion centres (Laporte rule doesn’t apply!)
  
  - E of LMCT increases down a group b/c empty 3d orbitals are more easily accessible than 4d or 5d from the ligand orbitals (such as 2p in $\text{O}^2^-$)
  
  - Relates to reduction potential! 3d metals are easier to reduce. Therefore, the chemistry of 4d and 5d metals is dominated by their highest possible O.S. Consider Fe triad... only Os can achieve Os$^\text{VIII}$ oxidation state, in Os$\text{O}_4$. 

![Absorbance Graph](image)
Examples of LMCT vs. MLCT

- **MLCT:** Most observed in ligands with low-lying \( \pi^* \) orbitals, especially aromatics (which also show \( n \rightarrow \pi^* \) or \( \pi \rightarrow \pi^* \) UV bands, therefore using benzene as a solvent for UV-vis may be a bad idea)

- Transition is likely if metal is in a low oxidation state (e- rich) and therefore has higher energy metal orbitals (because of lower \( Z_{\text{eff}} \)).
  - The classic: \([\text{Ru(bipy)}_3]^{2+}\) has a long excited state lifetime, and is a useful photochemical reducing agent
  - MLCT can be thought of as oxidation of the metal where it loses electrons into the ligands’ \( \pi^* \) orbitals (can make organic radicals!)

- In complexes like \( \text{Cr(CO)}_6 \), both LM and MLCT are possible but often not easy to distinguish (so we just call it CT)

- Sometimes, strong CT bands overlap with the vis region so may obscure d-d transitions. Careful measurement of \( \varepsilon \) is needed to be sure. Remember, \( \varepsilon \) values above 1000 are probably CT, whereas weaker may be d-d bands.
Cloud Expanding: Nephelauxetic Series

- Some ligands are more capable of delocalizing electron density away from metal orbitals and onto themselves. This results in lower e⁻-e⁻ repulsion at the metal centre.
- Experimentally, this results in the reduction of the Racah parameter, B from its free ion value.
  \[ \beta = \frac{B_{\text{complex}}}{B_{\text{free ion}}} \]
  where \( \beta \) is the nephelauxetic parameter
- We can obtain a “Nephelauxetic Series” of ligands based on their \( \beta \)-value
- Strong delocalization onto the ligands decreases \( B_{\text{complex}} \) vs \( B_{\text{free ion}} \), therefore \( \beta \) is a small value. This gives the following series ranked in order of \( \beta \):
  \[ I^- < Br^- < CN^- < Cl^- < en < NH_3 < H_2O < F^- \]
  I⁻ exhibits a strong nephelauxetic effect (small \( \beta \), large delocalization of e⁻ onto itself)
  F⁻ exhibits a weak nephelauxetic effect (large \( \beta \), little delocalization of e⁻ onto itself)

The position relates to HSAB where the more polarizable a ligand the lower the \( \beta \). Actual effect depends on whether the e⁻ are in the \( e_g \) or \( t_{2g} \) orbital since “cloud expansion is more a property of \( \sigma \)-bonding. There is \( \therefore \) a metal ion effect too:
  Mn(II) < Ni(II) ≈ Co(II) < Mo(II) < Re(IV) < Fe(III) < Ir(III) < Co(III) < Mn(IV)