The Selection Rules governing transitions between electronic energy levels of transition metal complexes are:

1. \( \Delta S = 0 \) The Spin Rule
2. \( \Delta l = +/- 1 \) The Orbital Rule (or \textit{Laporte})

The first rule says that allowed transitions must involve the promotion of electrons without a change in their spin. The second rule says that if the molecule has a center of symmetry, transitions within a given set of p or d orbitals (i.e. those which only involve a redistribution of electrons within a given subshell) are forbidden.

Relaxation of these rules can occur through:

- \textbf{Spin-Orbit coupling}: this gives rise to weak spin forbidden bands
- \textbf{Vibronic coupling}: an octahedral complex may have allowed vibrations where the molecule is asymmetric. Absorption of light at that moment is then possible.
- \textbf{Mixing}: \( \pi \)-acceptor and \( \pi \)-donor ligands can mix with the d-orbitals so transitions are no longer purely d-d.

### Transition Types

1. \textit{Charge transfer}, either ligand to metal or metal to ligand. These are often extremely intense and are generally found in the UV but they may have a tail into the visible.
2. d-d, these can occur in both the UV and visible region but since they are forbidden transitions have small intensities.

#### Expected intensities of electronic transitions

<table>
<thead>
<tr>
<th>Transition type</th>
<th>Example</th>
<th>Typical values of ( \varepsilon /m^2\text{mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin forbidden, Laporte forbidden</td>
<td>([\text{Mn(H}_2\text{O)}_6]^{2+})</td>
<td>0.1</td>
</tr>
<tr>
<td>Spin allowed (octahedral complex), Laporte forbidden</td>
<td>([\text{Ti(H}_2\text{O)}_6]^{3+})</td>
<td>1 - 10</td>
</tr>
<tr>
<td>Spin allowed (tetrahedral complex), Laporte partially allowed by d-p mixing</td>
<td>([\text{CoCl}_4]^{2-})</td>
<td>50 - 150</td>
</tr>
<tr>
<td>Spin allowed, Laporte allowed e.g. charge transfer bands</td>
<td>([\text{TiCl}_6]^{2-}) or ([\text{MnO}_4]^{-})</td>
<td>1,000 - (10^6)</td>
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</tbody>
</table>

### Expected Values

The expected values should be compared to the following rough guide.
• For M^{2+} complexes, expect $\Delta = 7,500 - 12,500 \text{ cm}^{-1}$ or $\lambda = 800 - 1,350 \text{ nm}$.

• For M^{3+} complexes, expect $\Delta = 14,000 - 25,000 \text{ cm}^{-1}$ or $\lambda = 400 - 720 \text{ nm}$.

For a typical spin-allowed, but Laporte (orbitally) forbidden transition in an octahedral complex, expect $\epsilon < 10 \text{ m}^2\text{mol}^{-1}$.

Extinction coefficients for tetrahedral complexes are expected to be around 50-100 times larger than for octahedral complexes. $B$ for first-row transition metal free ions is around 1,000 cm$^{-1}$. Depending on the position of the ligand in the nephelauxetic series, this can be reduced to as low as 60% in the complex.

Contributors

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