Electronic Spectroscopy of Transition Metal Ions
(continued)

What about the spectroscopy!

First some selection rules are found to apply:

1) Spin selection rule: $\Delta S = 0$

   **theory:** transitions can only occur between states of the same spin (and therefore the same spin multiplicity)

   **practice:** spin forbidden transition seldom occur and if they do $\varepsilon < 1 \text{ L mol}^{-1} \text{ cm}^{-1}$ so we can effectively assume that this rule is not violated

2) Laporte (symmetry) selection rule: in centrosymmetric environments, transitions can only occur if there IS a change in parity

   **theory:** this means $g \rightarrow g$ or $u \rightarrow u$ transitions are not allowed in an Oh field since an octahedron has a centre of symmetry which effectively means no $d \rightarrow d$ (or $f \rightarrow f$) transitions are allowed since all $d$ derived orbitals have $g$ parity

   **practice:** molecular vibrations can lower symmetry so this selection rule is ‘partially relaxed’ and $d \rightarrow d$ transitions do occur, albeit with low intensity, eg. $\varepsilon \sim 10 \text{ L mol}^{-1} \text{ cm}^{-1}$
**Other implications:**

- tetrahedra are NOT centrosymmetric so the Laporte rule is relaxed and $\varepsilon$ of 100-1,000 L mol$^{-1}$ cm$^{-1}$ are common

- CT bands are not subject to either selection rule so they are usually very intense with $\varepsilon$ of 10,000-100,000 L mol$^{-1}$ cm$^{-1}$ (eg. MnO$_4^-$)

**Orgel diagrams:** a ‘correlation’ diagram that shows how ligand field strength affects the energy of the crystal field terms. Only terms with the same multiplicity as the GS are shown because only these can be involved in transitions from the GS (spin selection rule)

All of this allows us to predict and understand the number of UV-Vis bands observed for ions with various d counts:

<table>
<thead>
<tr>
<th>e⁻ count</th>
<th>GS term</th>
<th>Oh CF terms</th>
<th>Higher E terms</th>
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<td></td>
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<td>= multiplicity</td>
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[NOTE: SEE FIGURE ON FOLLOWING PAGE]
$e^-$ count  GS term  Oh CF terms  Higher E terms

$= \text{multiplicity}$
A few other points:

- If one ignores the spin multiplicity, it is clear that the Orgel diagrams fall into three related groups shown above: \([d^1,d^4,d^6,d^{10}]; [d^2,d^3,d^7,d^8]\) and \([d^5]\)

- \(\Delta_{\text{oct}}\) can be extracted directly from the spectrum by inspection from frequency of the lone \(d\rightarrow d\) transition in the \([d^1,d^4,d^6,d^{10}]\) case only; in the \([d^2,d^3,d^7,d^8]\) case it can be obtained from a difference in frequencies between the lowest and highest energy \(d\rightarrow d\) transitions. For the \([d^5]\) case it cannot be obtained directly from the spectra.

- It can be shown (but not done here) that the Td and Oh fields essentially cause an inverted set of crystal field states so a general Orgel diagram that reflects this can be constructed:
Charge transfer complexes

**LMCT**: an electron is excited from an orbital that is primarily ligand based to an orbital that is primarily metal based
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requires an acceptor orbital on the ligand that is capable of taking electron density:

metal that is relatively easy to oxidize (high lying metal orbitals):