

1. Know that there are two main selection rules that govern the intensities of electronic transitions between the Ground state (g.s.) and the Excited state (e.s.) in molecules.

(a) **Orbital or Laporte Selection Rule:**

Allowed transitions occur between orbitals of the “g type” and orbitals of the “u type” or vice versa. Transitions between g & g types or u & u types are “Laporte or orbitally forbidden”.

g-gerade means symmetric with respect to a sign change across the orbital and u-ungerade means antisymmetric with respect to a sign change across the orbital

Note: Orbitals are “g” in an Octahedral Molecule but not “g” or “u” in tetrahedral because a tetrahedron does not have an inversion center. The consequences of this is that all d-d transitions in an Octahedron are forbidden and all d-d transitions in a Tetrahedron are allowed.

(b) **Spin Selection Rule:**

The spin multiplicity ($2S+1$) must remain the same between the g.s and the e.s. for the transition to be allowed.

2. The intensities of d-d transitions range from roughly 10^{-2} to $\sim 10^3$ in terms of ϵ (molar absorptivity coefficients) in Beer's Law definition ($A=\epsilon bc$: A = Absorption; ϵ = molar absorptivity; b = path length of cell and c = concentration).

In terms of intensities:

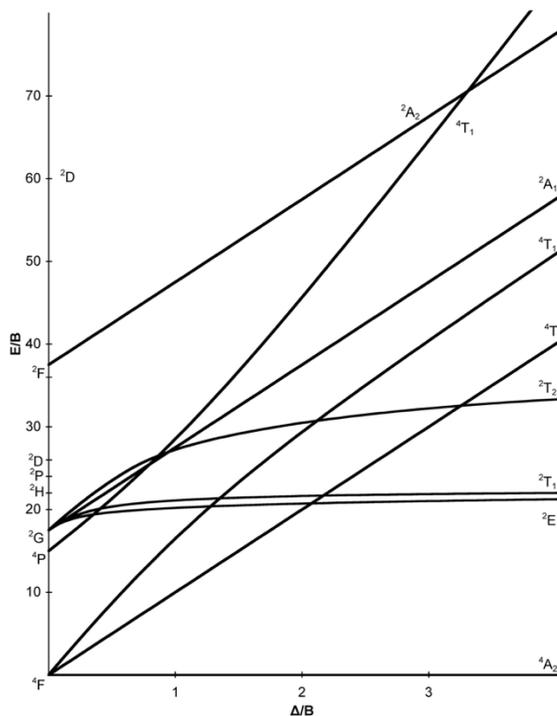
- (a) Spin-forbidden and Laporte-forbidden are the weakest ($\epsilon \sim 10^{-2}$) (see for example H.S. Mn^{2+} complexes).
- (b) Spin-allowed but still Laporte-forbidden (Octahedral complexes are always Laporte-forbidden) are more intense ($\epsilon \sim 10^{-2}$ to 100).
- (c) Spin-allowed and Laporte-allowed (Tetrahedral complexes) are more intense ($\epsilon \sim 100$ -1000).

3. Know how to determine the G.S. of any free ion configuration. (Note: we did this for d electrons but one can also apply it to electrons in any type of orbital. L=0, S; L=1, P; L=2, D; L=3, F; L=4, G; L=5, H etc.

4. Appreciate how the free ion Term Symbols convert into a new labeling scheme for complexes:

In octahedral: S \rightarrow A_{1g} ; P \rightarrow T_{1u} ; D \rightarrow $E_g + T_{2g}$; F \rightarrow $A_{2u} + T_{1u} + T_{2u}$

5. Know that an A state is non-degenerate (only one state), an E state is doubly degenerate (two states) and a T state is triply degenerate (three states)
6. By knowing the Free Ion States and how they translate to States in a Ligand Field, it is possible to construct an Energy Correlation Diagram. The specific diagrams with appropriate energy scaling are called Tanabe-Sugano Diagrams.
7. Know that one can use a Tanabe-Sugano diagram qualitatively or quantitatively. We are using it only as a qualitative tool in this class. The x-axis is roughly the d orbital splitting Δ_0 and the y-axis is the energy axis that shows you the order of the states. In order to predict transitions you must choose the lines above the ground state that have the same spin multiplicity. For example in a d^3 Tanabe-Sugano diagram, the ground state is a 4A_2 state (it is the label on the x axis). The lines above this one that have the same spin multiplicity are 4T_2 , 4T_1 and another 4T_1 . So the three transitions that one can predict that are possible for a d^3 ion are $^4A_2 \rightarrow ^4T_2$, $^4A_2 \rightarrow ^4T_1$ and a different $^4A_2 \rightarrow ^4T_1$.



8. Know that you can observe more transitions than you might predict based solely on the spin selection rule because you can observe spin-forbidden transitions sometimes. Know that, even if you only observe spin-allowed transitions, you can sometimes see more transitions than you would expect → for example, the Ti^{3+} (d^1) molecules. This is due to a lowering of symmetry of the molecule.
9. Know that a lowering of the symmetry of a molecule will lead to more observed transitions (more states!). Know that the Jahn-Teller theorem predicts that non-linear molecules with a degenerate ground state electronic configuration will distort in such a way as to remove (or “lift”) the degeneracy. Know which states in octahedral and tetrahedral are subject to Jahn-Teller distortions. (These are the ones where electrons are distributed unsymmetrically in a degenerate set of orbitals. This leads to more than one choice for how the electrons can be placed in the orbitals). d^1 , d^2 , d^4 (L.S. and H.S.), d^5 (L.S.), d^6 (H.S.), d^7 , and d^9 are all subject to a Jahn-Teller distortion.
10. Know that a Jahn-Teller distortion for an octahedral complex typically leads to shoulders on the main transitions predicted for a purely octahedral molecule from the Tanabe-Sugano diagram.