Topic VIII

Electronic Spectra of Coordination Compounds

VIII.1 Module 40: Electronic Transitions

3/1:
- Suggested reading: Chapter 11.1.
  - Transition metal complexes are known to show rich photophysics and optical properties.
    - For example, $[Ni(NH_3)_6]^{2+}$ has peaks in the infrared, visible, and UV spectra.
  - How electronic transitions occur:
    - Take a solid or aqueous sample and illuminate it with photons of a particular power/intensity P_0 through $l$cm of it.
    - Some will be absorbed and some will pass through. Measure the power P that comes out on the other side.
  - Transmittance $T = P/P_0$.
  - Absorbance $A = -\log T = \log \frac{P_0}{P}$.
  - The Beer-Lambert Law: $A = \varepsilon Cl$, where C is the concentration of the sample in solution, l is the path length (the length through solution), and ε is the molar absorption coefficient.
  - Plotting the wavelength of the impinging photons vs. ε gives us a graph with peaks, where each peak corresponds to an electron transition.
  - Spectral features:
    - Number of transitions.
    - Energy of the transitions.
    - Intensity of the transitions.
    - Shape of the transition.
  - **Transition probability**: The probability of a particular transition taking place.
  - The transition probability depends on:
    - Energy of the transition vs. incident light.
    - Orientation of the molecule/material.
    - Symmetry of the initial and final states.

– Angular momentum (spin).

- The absorption spectra of various hexaaqua complexes of the first-row transition metals give us a zoo of spectra.

- We usually have $\varepsilon < 10$, which means faint colors.

- Types of molecular transitions:

    – Metal Centered (MC): Transitions between the d-orbitals on the metal center.
    – Ligand to Metal Charge Transfer (LMCT): For example, MnO_4^- has $\varepsilon \approx 10\,000$.
    – Metal to Ligand Charge Transfer (MLCT) and Metal to Metal Charge Transfer (MMCT), too.

- The transition probability of one molecule from one state Ψ_1 to another state Ψ_2 is given by $|\vec{M}_{21}|$, the transition dipole moment or transition moment from Ψ_1 to Ψ_2.

    – The transition matrix element $\vec{M}_{21} = \int \Psi_2 \vec{\mu} \Psi_1 \, d\tau$, where $\vec{\mu}$ is the electric dipole moment operator $\vec{\mu} = \sum_n Q_n \vec{x}_n$, where Q_n is charge and $\vec{x}_n$ is the position vector operator.
    – Derived with time-dependent perturbation theory.
    – For an electronic transition to be allowed, the transition moment integral must be nonzero.
    – Note that $\varepsilon \approx \vec{M}_{21}$.

- How the HOMO moves about the molecule depends on the type of incoming light.

    – If $\vec{M}_{21} = 0$, then the transition probability is 0 and the transition from Ψ_1 to Ψ_2 is forbidden or electric-dipole forbidden ($\varepsilon = 0$).
    – If $\vec{M}_{21} \neq 0$, then the transition probability is not 0 and the transition from Ψ_1 to Ψ_2 is not forbidden ($\varepsilon \geq 0$).

        ■ If $\vec{M}_{21} \neq 0$, we do not definitively know that there will be an electron transition or know how intense it will be; we just know that it is not electric-dipole forbidden.

- Calculating $\vec{M}_{21}$:

    – Use the same procedure with $\Gamma_2 \otimes \Gamma_\mu \otimes \Gamma_1$ as in Module 12.
    – If the direct product does not contain the totally symmetric representation, then the transition is forbidden by symmetry arguments.
    – If the direct product does contain the totally symmetric representation, then the transition is allowed by symmetry arguments.

C_{3v}	A_1	A_2	E
A_1	A_1	A_2	E
A_2		A_1	E
E			$A_1 + [A_2] + E$

Table VIII.1: Direct product table for the C_{3v} point group.

- Be aware of direct product tables, such as the above example, which we may readily obtain from Table III.1.

- Example: In a D_{2h} complex, can we excite a d_{z^2} electron to the p_z orbital?

    – From the D_{2h} character table, we have that $\Gamma_1 = A_g$ and $\Gamma_2 = B_{1u}$. We also have that Γ_μ for an x-, y-, and z-basis is B_{3u}, B_{2u}, and B_{1u}, respectively.

– Taking direct products under each basis gives us

$$B_{1u} \otimes B_{3u} \otimes A_g = B_{2g} \quad\quad (x\text{-basis})$$
$$B_{1u} \otimes B_{2u} \otimes A_g = B_{3g} \quad\quad (y\text{-basis})$$
$$B_{1u} \otimes B_{1u} \otimes A_g = A_g \quad\quad (z\text{-basis})$$

– Thus, the x- and y-components are forbidden while the z one is not.

– What this means is that z-plane polarized light will be able to cause the desired electron transition, but x- and y-plane polarized light will not.

- We can use the same procedure to prove that we can never promote an electron from d_{xy} to p_z.

- We can use the same procedure for octahedral complexes, except the calculations of the direct products are just a bit more difficult.

  – For a d^1 complex, we calculate $E_g \otimes T_{1u} \otimes T_{2g}$.

  – For a d^6 complex, we calculate $(T_{2g} \otimes E_g) \otimes T_{1u} \otimes A_{1g} = (T_{1g} + T_{2g}) \otimes T_{1u} \otimes A_{1g}$.

    ■ A low spin d^6 complex has A_{1g} symmetry by taking the direct product of T_{2g} times itself six times.

    ■ The excited state has T_{2g} times itself five times, and then times E_g.

    ■ Basically, we take the direct product of the orbital that each electron occupies.

VIII.2 Module 41: Many Electron States

- Suggested reading: Chapter 11.2.

- For octahedral d^3, we have multiple excited states (six, to be exact).

  – Fortunately, there is an easier way to describe transitions between states (we will talk about this next time).

- A single electron is completely described by the principal quantum number n, its angular momentum ℓ, its magnetic quantum number m_ℓ, and its spin m_s.

- Multielectron states are described by **Russell-Saunders coupling**, *also known as* **LS coupling**, **L-S coupling**.

- For example, consider the d^2 configured V^{3+} ion.

  – There are 45 different possible microstates. Some will have the same energy, some will not.

  – There are five states (denoted by **term symbols**) with distinct energy in total.

- To find the term symbol, we need:

  – L = total orbital angular momentum = $\sum m_\ell$.

  – S = total spin angular momentum = $\sum m_s$.

- Term symbols then are of the form

$$^{2S+1}L_J$$

where $2S+1$ is the spin multiplicity, L is the subshell letter corresponding to the angular momentum quantum number ($0 \mapsto s$, $1 \mapsto p$, $2 \mapsto d$, $3 \mapsto f$, ...), and J is the total angular momentum ($J = L+S, L+S-1, L+S-2, \ldots, |L-S|$, the spin-orbit coupling).

- Some examples:

- ⎯ $\uparrow$ ⎯ ⎯ ⎯ ⎯ : $S = \frac{1}{2}$, so our term symbol will be of the form ^2L_J[1].
      +1/2

- ⎯ $\uparrow$ $\uparrow$ $\uparrow$ $\uparrow$ ⎯ : $S = 1$, so our term symbol will be of the form ^3L_J.
      +1/2   +1/2   −1/2   +1/2

- ⎯ $\uparrow$ $\uparrow$ ⎯ ⎯ ⎯ : $S = 1$ and $L = 3$, so our term symbol will be of the form ^3F_J[2].
      +2   +1   0   −1   −2

- ⎯ $\uparrow$ ⎯ ⎯ ⎯ $\uparrow$: $S = 1$ and $L = 0$, so our term symbol will be of the form ^3S_J[3].
      +2   +1   0   −1   −2

- Spin-orbit coupling is weak for a carbon atom (we can essentially just disregard it).

  - For lanthanides, it becomes very significant.

3/3:
- In term symbols, J is typically a small correction to the energy for light elements.

  - It becomes significant with the lanthanides and actinides.

- We group electrons into terms because each state has a characteristic energy in the absence of external electric and magnetic fields.

  - If we do apply an external magnetic fields, states will split into $2S + 1$ substates.
  - Each term includes multiple microstates, which are atomic states produced by interactions of the atom with a magnetic field.

- Consider the examples from above. The third and fourth examples are very similar but give rise to two different terms. This is because if we have ions with these states, we will observe differing energy levels spectroscopically.

- What if we have one electron in the orbital with $m_\ell = -2$? Then how do we create the term symbol?

  - It is part of one of the microstates of the ^1D term.
  - We fill electrons starting with the lowest energy states, and the lowest energy state has the greatest spin multiplicity (e.g., +2; this is one of Hund's rules).

- Correspondences between d electron configurations and term symbols:

$$d^1 = {}^2D \qquad\qquad d^6 = {}^5D$$
$$d^2 = {}^3F \qquad\qquad d^7 = {}^4F$$
$$d^3 = {}^4F \qquad\qquad d^8 = {}^3F$$
$$d^4 = {}^5D \qquad\qquad d^9 = {}^2D$$
$$d^5 = {}^6S \qquad\qquad d^{10} = {}^1S$$

  - Note that a fully occupied or unoccupied subshell is always ^1S.
  - Now if we take a direct product of a singlet S state with any other state, we will have just that state left over. This implies that we can ignore all fully occupied shells, and the term will be determined entirely by partially filled ones.

- If we want to build the full picture and see all possible states, we need a **microstate table**.

- Microstate table:

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[1]Pronounced "doublet state."
[2]Pronounced "triplet eff state."
[3]Pronounced "triplet ess state."

- – A microstate table contains all possible combinations of m_ℓ and m_s.
  - – Each microstate represents a possible electron configuration.
  - – It includes both ground and excited states.
  - – It must obey the Pauli exclusion principle.
- Example (p^2 electron configuration):
  - – Microstate notation:
    - ■ For each of the n electrons in the configuration, list a special symbol in an n-tuple.
    - ■ The special symbol will be a number (m_ℓ) with either a $+$ or $-$ sign as an exponent (for positive and negative spin, respectively).
  - – There are three ground state configurations.
    - ■ : The microstate is $(1^+, 0^+)$.
    - ■ : The microstate is $(0^+, -1^+)$.
    - ■ : The microstate is $(1^+, -1^+)$.
  - – We will not show all excited state configurations, but we will show a few.
    - ■ : The microstate is $(1^+, 1^-)$.
    - ■ : The microstate is $(0^+, 0^-)$.
    - ■ : The microstate is $(-1^+, -1^-)$.
  - – We can now generate the microstate table.

		M_S	
	-1	0	$+1$
$+2$		1^+1^-	
$+1$	1^-0^-	1^+0^- 1^-0^+	1^+0^+
M_L 0	-1^-1^-	-1^+1^- 0^+0^- -1^-1^+	-1^+1^+
-1	-1^-0^-	-1^+0^- -1^-0^+	-1^+0^+
-2		$-1^+ - 1^-$	

Table VIII.2: Microstate table for a p^2 electron configuration.

- ■ Each column represents a state with a given spin angular momentum.
    - ■ Each row represents the sum of the angular momentum of two electrons.
  - – To analyze the microstate label, rename each microstate with X.
    - ■ Each term consists of multiple microstates of equivalent energies (similar to how we can have multiple degenerate orbitals of a given energy).

- ■ We can lift degeneracy by applying an external electric (**Stark effect**) or magnetic field (**Ziemann effect**).
  - Now each term consists of $(2L + 1)(2S + 1)$ states (this is the **double multiplicity formula**).
  - Group energetically equivalent states:
    - ■ First, focus on the term containing the states with the largest possible L (i.e., those with $+2$). We know that it contains $(2(2) + 1)(2(0) + 1) = 5$ microstates. Choose 5 microstates from the $M_S = 0$ column, one per M_L.
    - ■ Next, focus on the term containing states with the next largest possible L (i.e., those with $+1$ and $M_S = +1$). We know that it contains $(2(1) + 1)(2(1) + 1) = 9$ microstates. Choose 9 microstates, one from each box in the square bounded by $(-1, -1)$ and $(+1, +1)$.
    - ■ The remaining microstate in $M_S = M_L = 0$ forms its own term.
  - Thus, our microstate table can be decomposed into three terms (^1D, ^3P, and ^1S).

- Identifying relative energies with Hund's rules:
  - For a given electron configuration, the term with the greatest spin multiplicity lies lowest in energy (Hund's rule).
  - For a term with a given multiplicity, the greater the value of L, the lower the energy.
  - Note that the rules for predicting the ground state always work, but they may fail in predicting the order of energies for excited states.

- Thus, going back to our example, we have that energetically, $^3P < {}^1D < {}^1S$.

- Example (d^2 electron configuration):
  - In this example, Hund's rules do not provide accurate energy predictions (they would predict $^3F < {}^3P < {}^1G < {}^1D < {}^1S$, but in reality, $^3F < {}^1D < {}^3P < {}^1G < {}^1S$).

- **Electron-hole formalism**: The Russel-Saunders terms for d^n and d^{10-n} configurations are identical for $n = 0, \ldots, 5$.
  - We can rationalize this by thinking of n electrons and $10 - n$ holes (or positrons) as related to $10 - n$ electrons and n holes.

VIII.3   Module 42: Many Electron States and Transitions in Coordination Compounds

- Suggested reading: Chapter 11.3.

- Ligand field dependence (d^1 system):
  - Degenerate symmetric field:
    - ■ Absence of ligand field.
    - ■ Free-ion term.
    - ■ All d-orbitals are energetically equal.
    - ■ If all d orbitals are degenerate, then we can put a single electron in any orbital and we will have a microstate of ^2D.
  - Infinite O_h field:
    - ■ Strong ligand field.
    - ■ Coordination complexes.
    - ■ d-orbitals are not degenerate (d_{z^2, x^2-y^2} have higher energy; $d_{xy,xz,yz}$ have lower energy).
    - ■ In this case, it matters in which d orbital we put the electron.

– Real molecules:

■ We use a correlation diagram or Orgel diagram.

■ If ligand field strength is zero, we have the degenerate symmetric field. If it is at maximum strength, we have two distinct states (t_{2g} and e_g). Anywhere in between, the states are in between in energy, too (as we apply the ligand field, we split the state).

- Ligand field dependence (d^2 system):
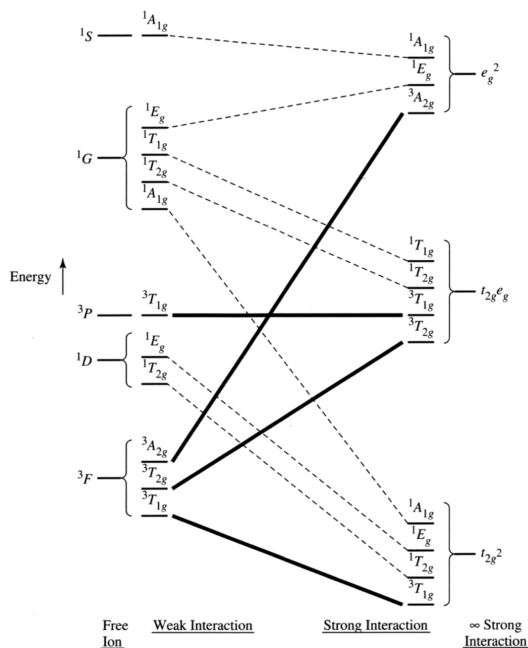
Figure VIII.1: Correlation diagram for a d^2 system.

– Under a weak ligand field, the multielectron states split.

■ From the O_h character table, we can determine how each term transforms similarly to determining how each orbital transforms (however, we may need a character table with cubic, quartic, and beyond functions).

■ For example, S terms transform as A_{1g}, P as T_{1g}, D as $T_{2g} + E_g$, F as $T_{1g} + T_{2g} + A_{2g}$, and G as $A_{1g} + E_g + T_{1g} + T_{2g}$.

– Under an infinitely strong field, we will return to our t_{2g} / e_g formalism with a low energy t_{2g}^2 state, a midlevel $t_{2g}e_g$ state (with one of the d^2 electrons in each level), and a high level e_g^2 state.

■ From the O_h group multiplication table, we can determine how each state splits under strong but finite ligand fields.

■ For example, $E_g \otimes E_g = A_{1g} + E_g + A_{2g}$, so thats why the e_g^2 state coalesces from these three states.

– The bold lines in Figure VIII.1 correspond to triplet states, and the dashed lines to singlet states.

- The direct product of two irreducible representations of dimension 2 or higher is reducible to a sum of symmetric and antisymmetric irreducible representations, so named because their respective symmetry-adapted basis functions are either symmetric or antisymmetric with respect to exchange of the components. It is important to understand these properties when dealing with the electronic states produced by incompletely filled degenerate orbitals.

- The following expressions may be applied to determine the characters (χ) of the symmetric and antisymmetric components of a direct product. The characters of the symmetric irreducible representation(s) (χ^+) are given by

$$\chi^+(R) = \frac{1}{2}\left([\chi(R)]^2 + \chi(R^2)\right)$$

  The characters of the antisymmetric irreducible representation(s) are given by

$$\chi^-(R) = \frac{1}{2}\left([\chi(R)]^2 - \chi(R^2)\right)$$

  In these expressions, $\chi(R)$ is the character under symmetry operation R and $\chi(R^2)$ is the character associated with the operation R^2.

  ■ We do not need to know these formulas since deriving them is outside the scope of this course.

- For example, in the C_{4v} point group, the direct product $E \otimes E = A_1 + A_2 + B_1 + B_2$.

- These results are typically written showing the antisymmetric component in square brackets, i.e., $E \otimes E = A_1 + [A_2] + B_1 + B_2$.

- The electron wave function, which is a product of the orbital and spin wave function components, must be antisymmetric (see Pauli exclusion principle). Therefore, if the orbital component is symmetric, the spin one should be antisymmetric, i.e., singlet state. And vice versa.

- Back to our d^2 example:

  - Symmetric components have electrons with opposite spins; antisymmetric components have electrons with like spin.

    ■ This demonstrates how $T_2 \otimes T_2 = A_1 + E + [T_1] + T_2$ rationalizes the existence of three singlet states and one triplet state under $t_{2g}{}^2$.

- Correlation diagrams are immensely useful, and we can tediously construct them or find them in the textbook. However, we can nicely simplify them into Tanabe-Sugano diagrams:

Correlation Diagram	Tanabe-Sugano Diagram
Number of states.	Number of states.
General sense of field effects.	Field effects.
Only qualitative.	Quantitative.

- Tanabe-Sugano diagrams are designed to intuitively interpret optical spectra and electron transitions in transition metal complexes.

- In a Tanabe-Sugano diagram, we make the lowest line in the corresponding correlation diagram the x-axis/ground state and calculate energies of every state above with respect to the gap between the ground state and the upper state.

- Tanabe-Sugano diagrams show:

  - Relative energies of the states vs. ligand field strength.
  - Electronic states with the same symmetry never cross (**non-crossing rule**).
  - Curvature (^1E and ^1E).
  - Ground state on the x-axis; all other states are excited.
  - Transitions between states.
  - A Tanabe-Sugano diagram is a graph which plots the energy of different spectroscopic terms (on the y-axis) against the strength of the ligand field (on the x-axis). The units used for each are given in terms of the **Racah parameter** B.
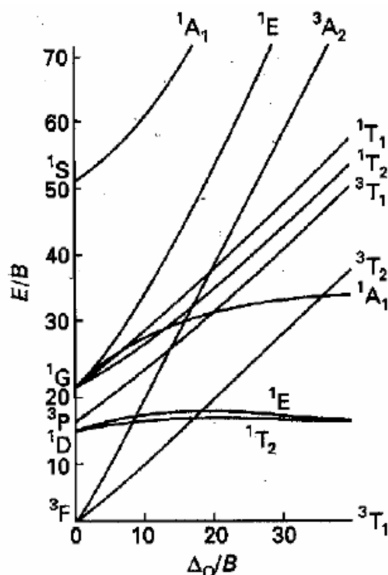
Figure VIII.2: Tanabe-Sugano diagram for a d^2 system.

- – The choice of unit means that the diagram takes account of electron-electron repulsion effects.

- – The lowest energy state is usually placed along the x-axis.

- – The electrostatic repulsion between electrons varies from atom to atom, depending upon the number and spin of the electrons and the orbitals they occupy. The total repulsion can be expressed in terms of three parameters A, B, and C, which are known as the Racah parameters. They are generally obtained empirically from gas-phase spectroscopic studies of atoms.

- • Each particular coordination compound will be a vertical slice through its electron configuration's Tanabe-Sugano diagram.

VIII.4   Module 43: Using Tanabe-Sugano Diagrams

3/5:
- • Suggested reading: Chapter 11.3.

- • Extra Tanabe-Sugano facts:

  - – States of the complex have the same spin multiplicity as the free ion states from which they originate.

  - – States that are the only ones of their type have energies that depend linearly on the crystal field strength, whereas when there are two or more states of identical designation, their lines will in general show curvature. This is because such states interact with one another.

- • Selection rules determine the probability (intensity) of the transition.

- • **Symmetry selection rule**: The initial and final wavefunctions must change in parity. Parity is related to the orbital angular momentum summation over all electrons $\sum m_{l_i}$, which can be even or odd; only even $(g) \leftrightarrow$ odd (u) transitions are allowed. Transitions between the orbitals of the same subshell are forbidden. *Also known as* **Laporte selection rule**, **Parity selection rule**.

  - – For example, $g \rightarrow g$ and $u \rightarrow u$ are forbidden, but $g \rightarrow u$ and $u \rightarrow g$ are allowed.

  - – The weaker of the two selection rules.

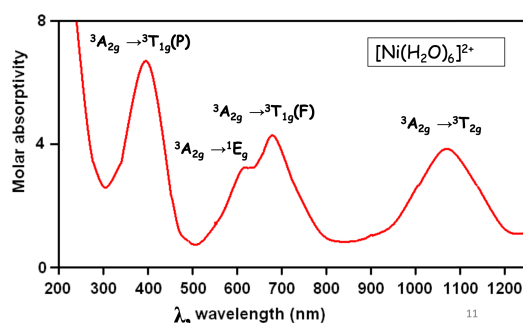 - – This is related back to Fermi's golden rule and $\vec{M}_{21}$.

- For O_h complexes, $\Gamma_{\mu_{xyz}} = T_{1u}$.
- Direct product rules:

$$g \otimes u = u \qquad\qquad g \otimes g = g \qquad\qquad u \otimes u = g$$

- For example, if we try a $g \rightarrow g$ transition in an O_h complex, we would have $\vec{M}_{21} = g \otimes u \otimes g = u$ is unsymmetric to inversion, meaning that there is no totally symmetric representation in $\vec{M}_{21}$.

- Octahedral vs. tetrahedral absorption spectra:

  - A tetrahedron has no center of symmetry, and so orbitals in this point group cannot be gerade. Hence, the d-levels in a tetrahedral complex are e and t_2, with no "g" for gerade. This largely overcomes the Laporte selection rule, making tetrahedral complexes very intense in color.
  - This is why a solution of $[Co(H_2O)_6]^{2+}$ is pale pink, but $[CoCl_4]^{2-}$ is a very intense blue.

- **Spin selection rule**: There must be no change in the spin multiplicity ($\Delta S = 0$) during the transition. i.e., the spin of the electron must not change during the transition.

  - For example, $^1T_1 \rightarrow {}^1T_2$ is allowed, but $^1T_1 \rightarrow {}^3T_1$ and $^3T_1 \rightarrow {}^1A_2$ are forbidden.
  - The stronger of the two selection rules.

- All d-d transitions are symmetry (Laporte) forbidden.

  - Thus, it makes more sense to disregard the complete Tanabe-Sugano diagram and focus on the spin-only one.

- Example: d^8 Tanabe-Sugano Diagram and $[Ni(H_2O)_6]^{2+}$ absorption spectrum.
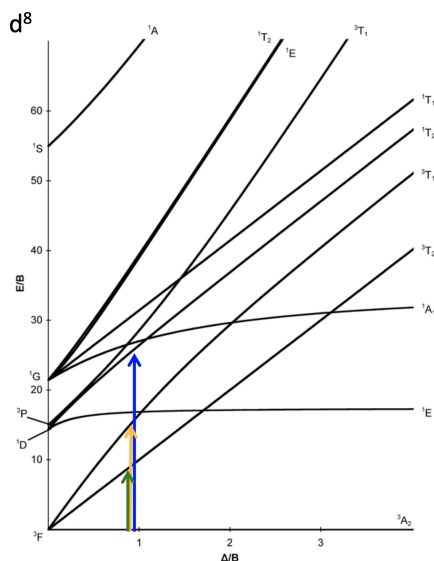
(a) The d^8 Tanabe-Sugano diagram.   (b) The absorption spectrum.

Figure VIII.3: $[Ni(H_2O)_6]^{2+}$: Relating a Tanabe-Sugano diagram and an absorption spectrum.

- The two higher energy peaks involve differences in the magnetic quantum numbers of the d orbitals, and are labeled as $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ to reflect this.
- Note that there is a shoulder near the second band corresponding to a nominally forbidden transition.

- d^1 and d^9 complexes have only one electron transition and, thus, one peak in the absorption spectrum.

  - However, the peak is not symmetric; this is a result of the Jahn-Teller distortion of the excited state.

- Analyzes a ruby's Tanabe-Sugano diagram and spectrum.

- The d^6 Tanabe-Sugano diagram:

  - The curves are not everywhere differentiable, the ground state changes, there is a vertical line, etc.

  - This is because at the line, the complex switches from high-spin to low spin (recall that increasing ligand field strength increases Δ; increasing Δ enough will make it larger than the spin-pairing energy).

- The colors of the electron transitions tell us where the compound falls along the x-axis in the Tanabe-Sugano diagram.

- In the d^5 high-spin configuration, any transition involves spin pairing and does not change parity. Thus, there is a very low probability of transitions occurring.

- In d^n and d^{10-n} complexes, the splitting order in the Tanabe-Sugano diagrams (as we increase ligand field strength) is inverted.

  - For example, in d^2, ^3F splits into (from lowest to highest energy) $^3T_1(F)$, $^3T_2$, and $^3A_2$. In d^8, ^3F splits into (from lowest to highest energy) $^3A_2$, $^3T_2$, and $^3T_1(F)$.

- Other factors that can influence whether or not electrons are promoted:

  - In d^2 complexes, there are three allowed transitions. However, one of them would involve promotion of two electrons from t_{2g} to e_g simultaneously upon the absorption of one photon, and this is highly improbable.

- By comparing the energies of multiple transitions, we can look for a place in the Tanabe-Sugano diagram that would produce such results.

  - For example, if one known transition has 1.5 times the energy of another, we can look for a place where the distance between it and the ground state is 1.5 times that of the other.

- We can also use experimental values to calculate B, the Racah parameter.

  - With the Racah parameter, we can pretty much calculate anything we want.

VIII.5   Module 44: How Can We See "Forbidden" Transitions?

- **Oscillator strength**: A quantity proportional to the integral of ε as measured in the absorption spectrum. *Also known as f.*

  - f relates ε to the matrix element $\vec{M}_{21}$:

  $$\frac{4m_e\pi v}{3e^2\hbar} \cdot |\vec{M}_{21}|^2 = f \propto 4.3 \times 10^{-9} \int \varepsilon \, d\bar{\nu}$$

  - Thus, the probability of light absorption is related to f.
  - Strong absorption occurs when f is around 1.
  - The rate constant k_e^0 for emission is related to ε by

  $$k_e^0 \propto 4.3 \times 10^{-9} \bar{\nu}_0^{-2} \int \varepsilon \, d\bar{\nu} = \bar{\nu}_0^{-2} f$$

■ Good emitters are also good absorbers.

- Allowed transitions:
    - Allowedness is measured by f which can be dissected into

    $$f = (f_e \times f_v \times f_s)f_{\max}$$

    where f_e is related to electronic factors, f_v is related to Franck-Condon factors, and f_s is related to spin-orbit factors.
    - A perfectly allowed transition has $f = 1$.
    - f_s factors:
        ■ A spin-allowed transition has $f_s = 1$.
        ■ For a spin-forbidden transition, f_s depends on spin-orbit coupling.
    - f_e factors: **overlap forbiddenness** and **orbital forbiddenness**.

- **Overlap forbiddenness**: Poor spatial overlap of orbitals involved in electronic transitions.

- **Orbital forbiddenness**: Wavefunctions which overlap in space but cancel because of symmetry.

- Mechanisms that make forbidden electronic transitions allowed: **vibronic coupling**, **spin-orbit coupling**, and **mixing of states**.

- **Vibronic coupling**: Electronic states coupled to vibrational states help overcome the Laporte selection rule.
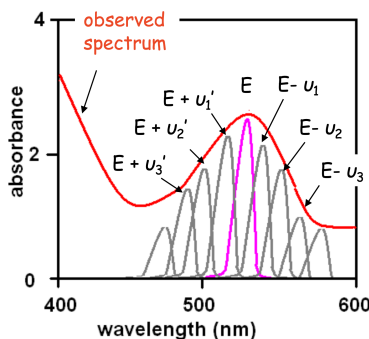

Figure VIII.4: Vibronic coupling.

- For an octahedral complex, there are 15 vibrational normal modes with irreducible representations: $\Gamma_{\text{vibs}} = a_{1g} + e_g + 2t_{1u} + t_{2g} + t_{2u}$.
- Vibrational transitions couple with electronic transition: $\vec{M}_{21} = \int \psi_v^* \psi_e^* \vec{\mu} \psi_e \psi_v \, d\tau$. Indeed, the wavefunction of the complex can be represented by this product (this is called the **Franck-Condon principle**), which will give fully symmetric irreducible representations.
- Essentially, T_{1u} and T_{2u} vibrations can couple with the electronic transition to form the allowed vibronic transition.
- The band one sees in the UV-visible spectrum is the sum of bands due to transitions too coupled electronic (E) and vibrational energy levels (u_1, u_2, u_3, etc.).

- **Spin-orbit coupling**: Spin and orbital angular momenta can interact to make spin forbidden transitions allowed.

    - Allows us to relax spin selection rules and promote an electron from an electron pair *without changing its spin*.

– This is possible in heavy atoms because of their relativistic properties.

- **Mixing of states**: π-acceptor and π-donor ligands can mix with the d-orbitals; transitions are no longer purely d-d.

    – The Tanabe-Sugano diagram assumes pure d-d transitions.

    – However, spin-forbidden transitions can borrow intensity from nearby spin-allowed transitions by mixing of states.

- $\varepsilon_{\max}(\mathrm{M}^{-1}\,\mathrm{cm}^{-1})$ ranges for different transitions:

    – Spin and symmetry forbidden d-d bands: 0.02-1.

    – Spin allowed and symmetry forbidden d-d bands: 1-10.

    – Spin and symmetry allowed CT bands: 10^3-5×10^4.

VIII.6 Module 45: Charge Transfer Transitions

- **Charge-transfer band**: A Laporte- and spin-allowed, very intense absorption peak. *Also known as* **CT band**.

- We can have transitions from metal d orbitals to p orbitals ($t_{2g} \to t_{1u}$).

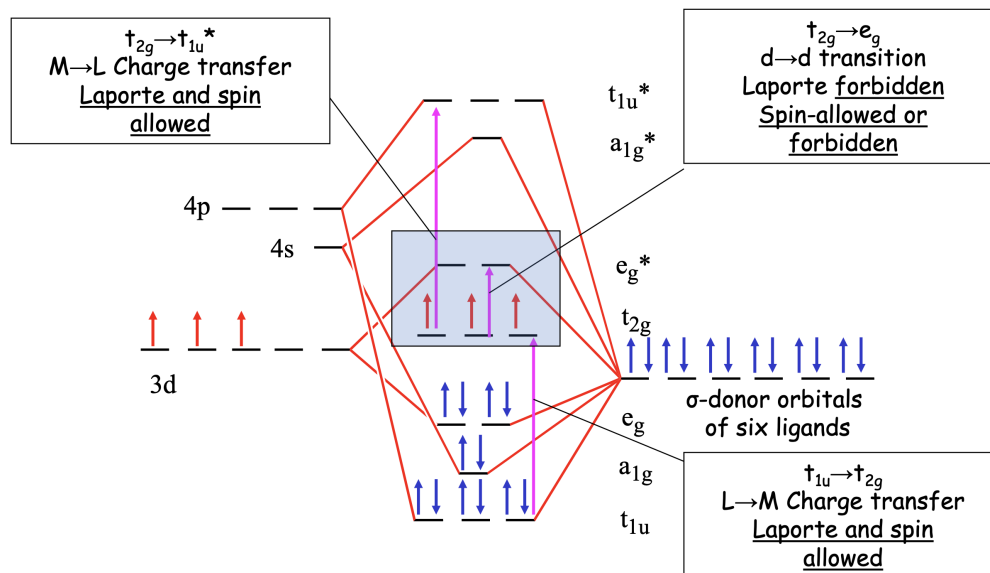Figure VIII.5: Electronic transitions in an octahedral complex.

- There exist $\mathrm{M} \longrightarrow \mathrm{L}$ and $\mathrm{L} \longrightarrow \mathrm{M}$ charge transfer transitions.

VIII.7 Chapter 11: Coordination Chemistry III (Electronic Spectra)

From Miessler et al. (2014).

3/9:   - We will consider the energy levels of d electron configurations, how electrons in such atomic orbitals can interact with each other, and how the electronic absorption spectrum provides a convenient method (via finding Δ_o) for determining the magnitude of the effect of ligands on the metal d orbitals.

- **Complementary colors**: Two colors on opposite sides of the color wheel.

- In an absorption spectrum with one band, the color of the substance will be the complementary color of the wavelength absorbed.

- Beer-Lambert law:

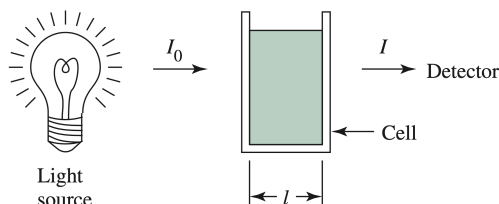$$\log \frac{I_0}{I} = A = \varepsilon l c$$

Figure VIII.6: Absorption of light by solution.

  - Note that ε is the molar absorptivity or **molar extinction coefficient**, measured in units of $\mathrm{L\,mol^{-1}\,cm^{-1}}$.

- Absorbance is a dimensionless quantity.

  - An absorbance of 1.0 corresponds to 90% absorption since

$$1 = \log \frac{I_0}{I}$$
$$10^1 = \frac{I_0}{I}$$
$$I = 0.10 I_0$$

  so 10% of light is transmitted, meaning that 90% is absorbed.

- **Spectrophotometer**: A device that obtains spectra as plots of absorbance versus wavelength.

- Consider a carbon atom, with its p^2 electron configuration.

  - We might expect the p electrons to be degenerate; however, we experimentally observe three major energy levels, one of which splits into three smaller energy levels. Let's find out why.
  - Independently, each of the $2p$ electrons could have any of six possible m_l, m_s combinations since $m_l = +1, 0, -1$ and $m_s = +\frac{1}{2}, -\frac{1}{2}$.
  - However, the electrons are not independent of each other. Indeed, their angular momenta and spin angular moment interact via Russell-Saunders coupling.

    - In oversimplified terms, imagine each electron as a magnet. The magnetic fields interact, producing microstates that can be described by the new quantum numbers M_L and M_S.

  - Note that electrons in filled orbitals do not interact with the p^2 electrons since their net spin and orbital angular momenta are both zero.

- **Microstate**: A set of possible quantum numbers that communicates a unique possible coupling of magnetic fields of the electrons.

- An alternate formulation for the number of microstates is

$$\frac{i!}{j!(i-j)!}$$

where i is the number of m_l, m_s combinations (e.g., six for p^2, as discussed above) and j is the number of electrons.

- Quantum numbers M_L and M_S in turn give quantum numbers L, S, and J.

    - "Quantum numbers L and S describe collections of microstates, whereas M_L and M_S describe the microstates themselves. L and S are the largest possible values of M_L and M_S" (Miessler et al., 2014, p. 408).
    - Just as $m_l = 0, \pm 1, \ldots, \pm l$, we have that $M_L = 0, \pm 1, \ldots, \pm L$. Similarly, like $m_s = +\frac{1}{2}, -\frac{1}{2}$, we have that $M_S = S, S - 1, \ldots, -S$.
    - m_l describes the z-component of the magnetic field due to an electron's orbital motion; M_L describes the z-component of the magnetic field associated with a microstate.
    - m_s describes an electron's magnetic spin; M_S describes the analogous component of the magnetic field produced by electron spin for a microstate.

- "States having spin multiplicities of 1, 2, 3, and 4 are described as singlet, double, triplet, and quartet states" (Miessler et al., 2014, p. 408).

- **Free-ion term**: An atomic state characterized by S and L. *Also known as* **Russell-Saunders terms**.

    - So named because they describe individual atoms and ions, i.e., ones that are free of ligands.

- **Term symbol**: A label corresponding to a free-ion term and consisting of a letter relating to the value of L and a left superscript for the spin multiplicity.

- Note that **term** and **state** are often used interchangeably, but they do technically have different meanings.

- **Term**: The preferred label for the results of Russell-Saunders coupling.

- **State**: The preferred label for the results of spin-orbit coupling, which includes the quantum number J.

- Spin multiplicity is equal to the number possible values of M_S, hence the number of columns in the microstate table.

- Returning to our p^2 carbon atom example:

    - Designate each microstate in Table VIII.2 with an x for the sake of convenience.
    - "To reduce the p^2 microstate table into its terms, all that is necessary is to find the rectangular arrays" (Miessler et al., 2014, p. 410).
    - Notice how the spin multiplicity in each term symbol is the same as the number of columns in each reduced microstate table in Figure VIII.7.
    - The ^3P, ^1D, and ^1S terms have three distinct energies (the three major energy levels observed experimentally).

- **Spin-orbit coupling**: A phenomenon in which the spin and orbital angular momenta (or the magnetic fields associated with them) couple with each other.

- Returning to our p^2 carbon atom example, the ^1D term and ^1S term would only have one J (namely, $2 + 0 = 0$ and $0 + 0 = 0$, respectively). However, the ^3P term subdivides into $^3P_2$, $^3P_1$, and $^3P_0$ since $1 + 1 = 2$, $1 + 1 - 1 = 1$, and $1 + 1 - 2 = 0$.

    - This subdivision explains the experimental observation of three smaller energy levels within one of the major energy levels (see Figure VIII.8).
    - Notice how when we calculate J values, we iterate down from $L + S$ to $|L - S|$. In ^3P for example, $1 + 1 = 2$ and $|1 - 1| = 0$, so the possible J values are 2, 1, and 0.

- **Hund's third rule**: For subshells that are less than half filled, the state having the lowest J value has the lowest energy; for subshells that are more than half filled, the state having the highest J value has the lowest energy. Half-filled subshells have only one possible J value.
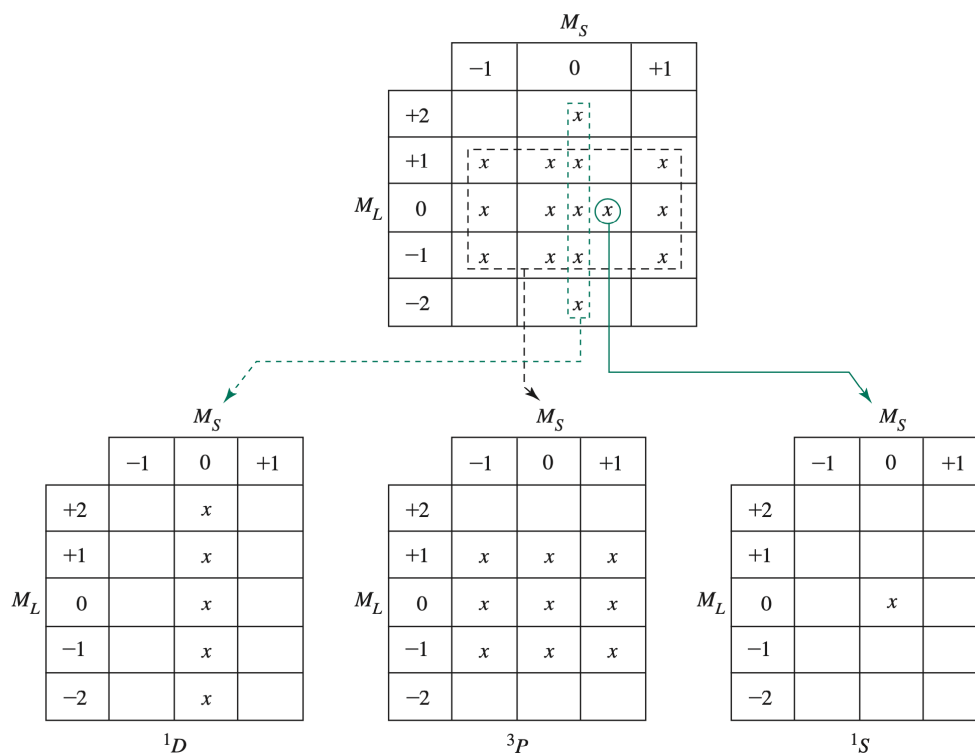
Figure VIII.7: Reduced p^2 microstate table.
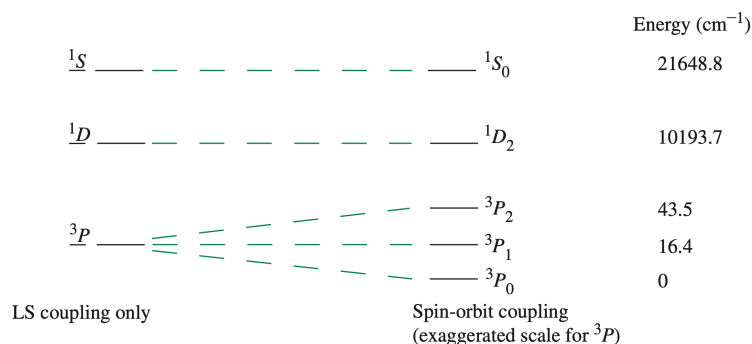
Figure VIII.8: Multielectron energy levels in the p^2 configuration.

- Spin-orbit coupling plays a significant role in heavy metals (atomic number > 40).

- We now connect electron-electron interactions back to absorption spectra.

- Miessler et al. (2014) list free-ion terms for d^n configurations, since they are tedious to determine by hand.

- A method for identifying the lowest-energy term:

  1. Sketch the energy levels, showing the d electrons.

  2. Spin multiplicity of lowest-energy state is the number of unpaired electrons plus 1.

  3. Determine the maximum possible value of M_L (sum of m_l values) for the configuration as shown. This determines the type of free-ion term (e.g., S, P, D).

  4. Combine results of Steps 2 and 3 to get the ground term.

- Example: Applying the above method to d^3 octahedral symmetry.

    - There will be three electrons of parallel spin, one in each of the three degenerate t_{2g} orbitals.
    - $2S + 1 = 3 + 1 = 4$.
    - $2 + 1 + 0 = 3$ (recall that we use Hund's rules to know that it is the $+2, +1, 0$ orbitals filled first); therefore, F.
    - Result: ^4F.