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, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ 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

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

– 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 ($0 \mapsto s,\ 1 \mapsto p,\ 2 \mapsto d,\ 3 \mapsto f,\ \ldots$), 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:

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

- $\underset{+1/2}{\uparrow} \quad \underset{+1/2}{\uparrow} \quad \underset{-1/2}{\uparrow} \quad \underset{+1/2}{\uparrow} \quad \text{—}$: $S = 1$, so our term symbol will be of the form ^3L_J.

- $\underset{+2}{\uparrow} \quad \underset{+1}{\uparrow} \quad \underset{0}{\text{—}} \quad \underset{-1}{\text{—}} \quad \underset{-2}{\text{—}}$: $S = 1$ and $L = 3$, so our term symbol will be of the form $^3F_J{}^{[2]}$.

- $\underset{+2}{\uparrow} \quad \underset{+1}{\text{—}} \quad \underset{0}{\text{—}} \quad \underset{-1}{\text{—}} \quad \underset{-2}{\uparrow}$: $S = 1$ and $L = 0$, so our term symbol will be of the form $^3S_J{}^{[3]}$.

- 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):
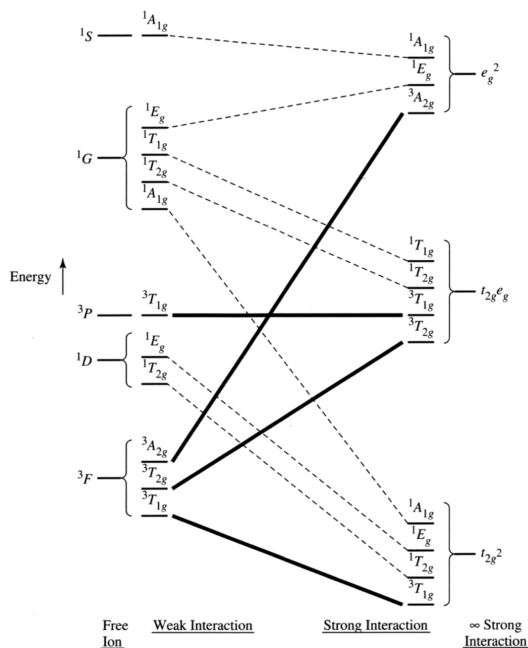
Figure VIII.1: Correlation diagram for a d^2 system.

– 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.
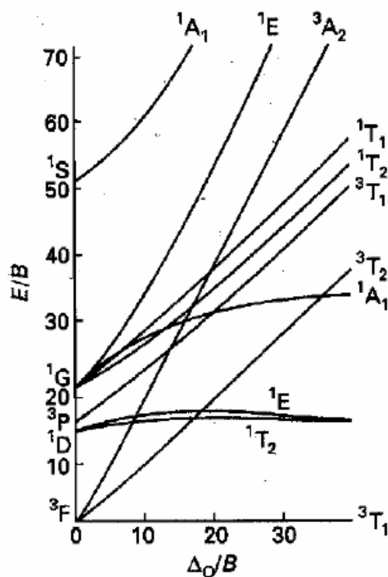
Figure VIII.2: Tanabe-Sugano diagram for a d^2 system.

- – 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.