

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 P_0 through $l\text{cm}$ 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 (how large the cuvette is), 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

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

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

$$B_{1u} \otimes B_{1u} \otimes A_g = A_g \quad (z\text{-basis})$$

- 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 ($J = L + S, L + S - 1, L + S - 2, \dots, |L - S|$, the spin orbit coupling).

- Some examples:

– $\begin{array}{c} \uparrow \\ \text{---} \\ +1/2 \end{array} \text{---} \text{---} \text{---} \text{---} : S = \frac{1}{2}, \text{ so our term symbol will be of the form } {}^2L_J.$

– $\begin{array}{c} \uparrow \\ \text{---} \\ +1/2 \end{array} \begin{array}{c} \uparrow \\ \text{---} \\ +1/2 \end{array} \begin{array}{c} \uparrow \downarrow \\ \text{---} \\ -1/2 \end{array} \begin{array}{c} \uparrow \\ \text{---} \\ +1/2 \end{array} \text{---} : S = 1, \text{ so our term symbol will be of the form } {}^3L_J.$

– $\begin{array}{c} \uparrow \\ \text{---} \\ +2 \end{array} \begin{array}{c} \uparrow \\ \text{---} \\ +1 \end{array} \text{---} \text{---} \begin{array}{c} \uparrow \\ \text{---} \\ 0 \end{array} \begin{array}{c} \uparrow \\ \text{---} \\ -1 \end{array} \begin{array}{c} \uparrow \\ \text{---} \\ -2 \end{array} : S = 1 \text{ and } L = 3, \text{ so our term symbol will be of the form } {}^3F_J.$

– $\begin{array}{c} \uparrow \\ \text{---} \\ +2 \end{array} \text{---} \begin{array}{c} \uparrow \\ \text{---} \\ +1 \end{array} \text{---} \begin{array}{c} \uparrow \\ \text{---} \\ 0 \end{array} \begin{array}{c} \uparrow \\ \text{---} \\ -1 \end{array} \begin{array}{c} \uparrow \\ \text{---} \\ -2 \end{array} : S = 1 \text{ and } L = 0, \text{ so our term symbol will be of the form } {}^3S_J.$

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

– For lanthanides, it becomes very significant.