

# Week 9

## Selection Rules and Exam

### 9.1 Electronic Spectroscopy: Selection Rules

11/28:

- Last in-class assessment on Friday. Same rules and format as last time.
- Review session this Wednesday; submit questions via the GForm. Submit Wuttig questions by the end of the day today. If there are no questions, Wuttig will treat the class as office hours.
- Last time: Electronic spectroscopy. We outlined how to rationalize, assign, and determine  $B$  and  $\Delta_o$  values for experimental electronic transitions for octahedral complexes.
- Today: We will derive the basis for the selection rules.
- **Selection rules:** All of the lines on the TS diagrams inform us of possible transitions. But are they probable?
- When deriving these, something we want to consider is oscillator strength. This is given by

$$\int_0^\infty \varepsilon(\nu) d\nu \propto \langle \Psi_{\text{gs}} | M | \Psi_{\text{es}} \rangle^2$$

- This is the integral under the spectrum of your compound.
- Conclusion: The oscillator strength is directly proportional to the transition moment integral.
- The ground state and excited state have electronic, spin, and vibrational contributions.
- We now dissect  $M$ .
  - By the B-O approximation, we can separate out the total wave function into the electronic contribution and the vibrational contribution because we assume the time-scale of the electronic and vibrational transitions are distinct.

$$\Psi = \Psi_e \Psi_v$$

- Rationale for separating electronic and vibrational motion: Experimental observation of vertical electronic transitions (see Figure 8.4) means that electrons move before the nuclear coordinate can significantly change.

- Thus, we can dissect

$$\hat{M} = \langle \Psi_{\text{esv}} | \Psi_{\text{gsv}} \rangle \langle \Psi_{\text{ese}} | \hat{\mu} | \Psi_{\text{gse}} \rangle \langle \Psi_{\text{ess}} | \Psi_{\text{gss}} \rangle$$

where we write  $v$  for vibrational,  $e$  for electronic, and  $s$  for spin.

- $\hat{\mu}$  is the electronic polarization operator. It transforms as  $xyz$ , meaning that it has  $u$  (ungerade) symmetry as a linear operator, similar to the  $p$ -orbitals.

- We now dissect the components of  $\hat{M}$  further.

- Spin.
  - The spin contribution is nonzero iff  $\Delta s = 0$  (i.e., no change in spin). This justifies the **spin selection rule**.
- **Spin selection rule:** We *must* have the same spin state in the ground and excited states.
- Vibration.
  - Typically, an electronic excitation will produce a vibrationally hot excited state (recall hot bands).
  - Is the hot excited state the result of relaxation after electronic excitation, or will there be a hot excited state?
    - We go to a hot vibrational excited state.
    - For example, in going from  $E = 0$  to  $E = 1$ , we will often go from  $v = 0$  to  $v = 2$  or something (see Figure 8.4 again).
  - This can relax some selection rules and make transitions more probable.
- Electronic.
  - The component is nonzero iff the direct product contains  $a_{1g}$  (i.e., is even over all space).
- Electronic component in the context of *d-d* transitions.
  - For a *d-d* transition,  $\hat{\mu}$  is *u* but the *d* orbitals are *g* (they are symmetric with respect to inversion). Taking the direct product yields *u* symmetry.
 
$$g_{\text{es}} \times u \times g_{\text{gs}} = u$$
  - It follows that the *d-d* transitions are forbidden (this is the **Laporte selection rule**).
  - Even though these transitions are formally Laporte forbidden, coupling with the hot bands in the vibrational state makes these become allowed.
  - Wuttig will not go through all the math.
  - Note: Coupling of  $g_{\text{es}}$  with  $u_{\text{vib}}$  can relax the rule!
- **Laporte selection rule:** *d-d* transitions are allowed iff the overall direct product has gerade symmetry. *Also known as orbital selection rule.*
- Rank the following compounds in terms of oscillation strength.

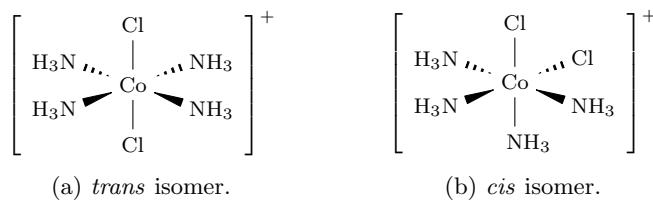


Figure 9.1: Oscillation strength comparison.

- Comparing the compounds: Same *d*-electron count, same ligand composition. Thus perhaps it really is something to do with the ligand field?
- The *trans* isomer is more symmetric than the *cis* isomer ( $D_{4h}$  vs.  $C_{2v}$ ).
- If we have a more symmetric field, we'll have a lower oscillation strength, and vice versa for the less symmetric field. This is because the less symmetric field is more *u*-like, leading to greater vibrational coupling.

- LMCT and MLCT.
- One way to relax the Laporte selection rule is to couple with vibrationally hot excited states. Another way is to have the transition occur from another part of the molecule.
- LMCT transitions.

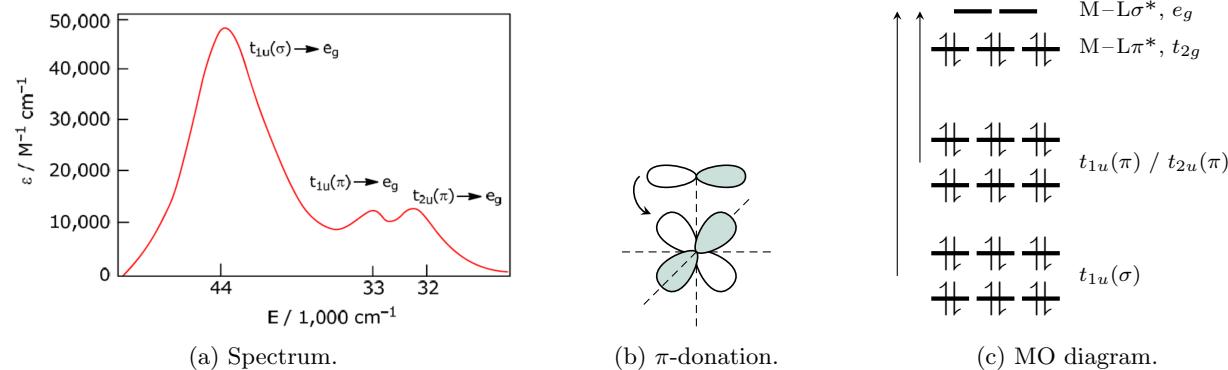


Figure 9.2: LMCT dynamics.

- Figure 9.2a depicts the spectrum for  $[\text{PtBr}_6]^{2-}$ .
- All ligands are  $\pi$ -donating.
- If we think about the MO parentage (ligand  $p$ -orbital and metal  $d$ -orbital), we can have a charge transfer from the ligand to the metal because of the MO diagram (see Figure 9.2b; Wuttig appears to draw it as antibonding?? Reversed  $p$ -orbital sign??).
- All of the orbitals below the frontier  $t_{2g}$   $M-L\pi^*$  set are completely occupied, and what we're observing is the transition from those lower-lying orbitals, up, as illustrated in Figure 9.2c.
  - Notice that the transitions in this MO diagram exactly mirror those in the spectrum in Figure 9.2a.
  - Possible inconsistency??: Figure 9.2a is consistent with Figure 9.2c, but according to Figure 7.3,  $t_{2u}(\pi)$  should be degenerate with  $t_{1g}(\pi)$ , not  $t_{1u}(\pi)$ . Overall actually, the orbitals don't look entirely consistent. What modifications are we making?
- LMCT is Laporte allowed because the ligand  $p$  orbital (ground state) is ungerade and the metal  $d$  orbital (excited state) is gerade. Mathematically,

$$g_{\text{es}} \times u \times u_{\text{gs}} = g$$

- Molar extinction coefficients are *very* high (tens of thousands vs. single-digit  $d$ - $d$  transitions).
- Question: Rank the energy of the LMCT transitions among  $[\text{OsBr}_6]^{2-}$ ,  $[\text{OsCl}_6]^{2-}$ , and  $[\text{OsI}_6]^{2-}$ .
  - Largest electronegativity (chloride) leads to the largest LMCT transition; smallest leads to smallest (iodide).
  - This is because larger electronegativity leads to lower bonding orbitals and thus a higher energy jump up to the frontier orbitals.
- MLCT transitions.
  - Figure 9.3a depicts the spectrum for  $[\text{Cr}(\text{CO})_6]^{3+}$ .
  - All ligands are  $\pi$ -accepting
  - Once again, we get very large extinction coefficients, so we must be relaxing the Laporte selection rule.

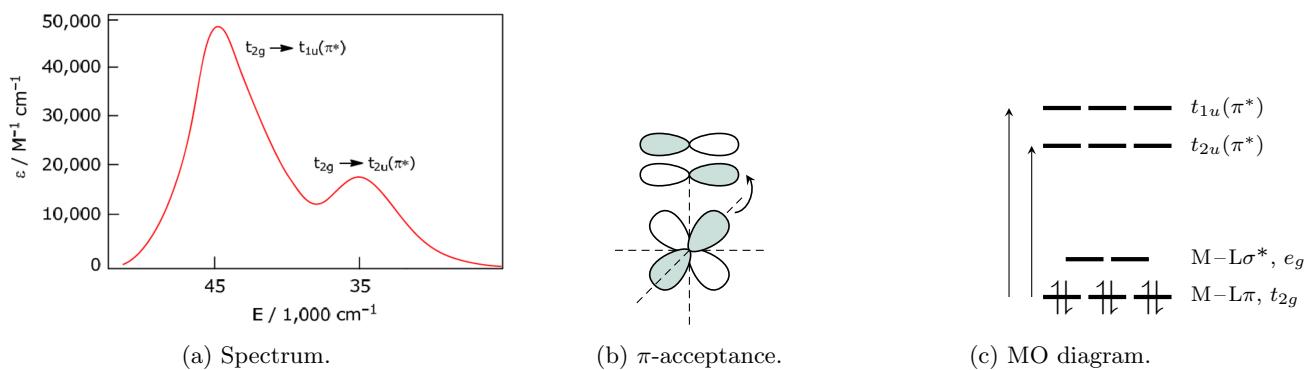


Figure 9.3: MLCT dynamics.

- Laporte allowed due to transitions occurring from gerade ground states to ungerade excited states.
  - We excite electrons from the metal to the ligand in the MO diagram, resulting in two transitions in both the diagram (Figure 9.3c) and the spectrum (Figure 9.3a).
- Technological applications of MLCT.
  - The transitions are so allowed that we get a lot of applications.
- The Grätzel Cell (by Michael Grätzel at EPFL). You can't store energy, but you can take light and generate an electric current.

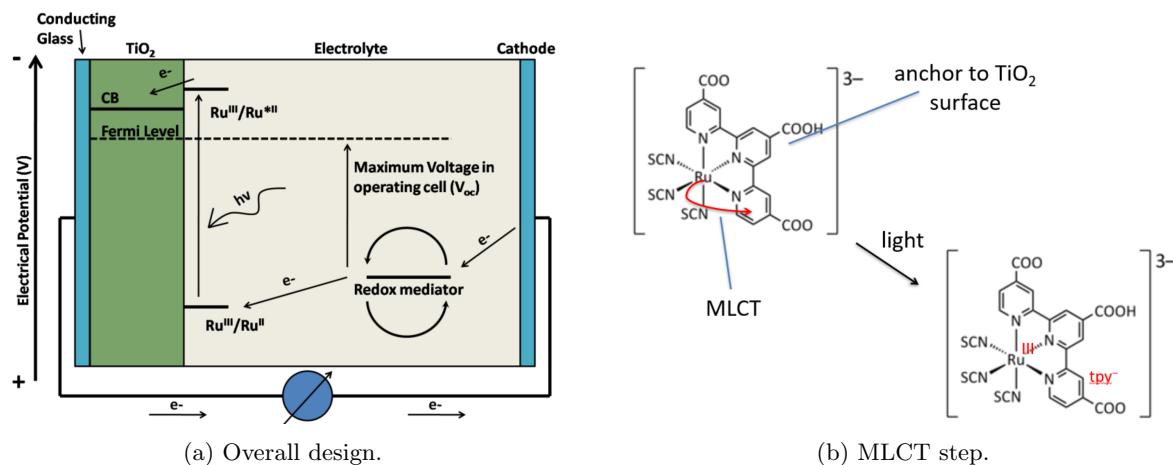


Figure 9.4: Grätzel Cell mechanism.

- A bit like artificial photosynthesis. We can't generate fuel like in a fuel cell, but we can generate current.
- Uses a  $\text{Ru}(\text{SCN})_3\text{L}$  complex. Experimentally, this molecule has a very deep MLCT charge transfer band, allowing it to absorb into the red and IR spectrum (needed for direct sunlight to electricity conversion).
- The compound is anchored onto a  $\text{TiO}_2$  (semiconducting) surface. The band gap is about 3 eV. The **conduction band** (LUMO for an extended solid) is poised at a level such that when you photoexcite  $\text{Ru}^{II}$ , oxidizing via MLCT  $\text{Ru}^{II} \longrightarrow \text{Ru}^{III}$  and reducing the tpy ligand, you get an electron in an orbital (on  $\text{tpy}^-$ ) that is higher than the  $\text{TiO}_2$  conduction band.

- Thus, you can dump the electron into  $\text{TiO}_2$ .
- $\text{TiO}_2$  is connected to a conducting glass (usually fluorine-doped tin oxide) from which you can harvest the electron and use it for electricity.
- An additional redox mediator is used in solution to harvest electrons at a cathode and regenerate  $\text{Ru}^{2+}$ ; this is essential in order to be able to do the same thing again (think salt bridge). The mediator goes from



- The lifetimes aren't that great.
- Selling point is that it is made out of very cheap materials, and is efficient because it makes use of very highly allowed MLCTs.

- Photoredox catalysis.

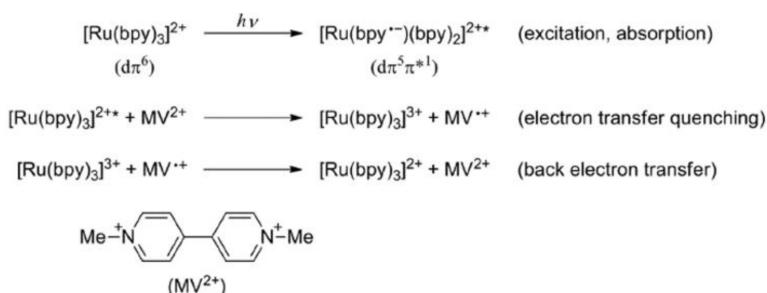
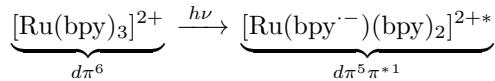
(a)  $[\text{Ru}(\text{bpy})_3]^{2+}$  light absorption.(b) Discovery mechanism: Quenching with  $\text{MV}^{2+}$ .

Figure 9.5: Photoredox catalysis.

- Organic chemists have usurped it for catalysis, but it all came from inorganic chemistry.
- Whitten and Meyer established that  $[\text{Ru}(\text{bpy})_3]^{2+}$  complexes have charge transfer processes, that the excited electron can reduce various organic compounds, and that the hole left behind can be refilled.



- Discovered this by quenching the reaction with methyl viologen ( $\text{MV}^{2+}$ ).
- The seminal papers are the **Meyer papers**.
- We improve photoredox catalysis further by thinking about the relative energy levels between where the  $d$  electrons are coming from and where they're going.
- To this end, people have put in tons of  $\text{CF}_3$  groups to make a more powerful reductant.

- **Meyer papers:** The two papers Bock et al. (1974) and Thompson et al. (2013).

## 9.2 Second Exam Review

11/30:

- Wuttig interpreted everyone's GForm questions as, "we need to go over PSet 4."
- Problem 1 is a descent in symmetry problem.
- First thing to note: You have a Re-Re center with octahedral geometry about each Re atom.
- We want to build the MO diagram to convince ourselves that  $\text{B.O.} = 1$ .

- Descend in symmetry from  $\text{Re}(\text{CO})_6$   $O_h$  to square pyramidal  $\text{Re}(\text{CO})_5$ , which is  $C_{4v}$ . What happens to the orbitals?
  - CO is a  $\pi$ -acceptor.
  - Thus, the  $e_g$  set has M–L $\sigma^*$  parentage, and the  $t_{2g}$  set has M–L $\pi$  parentage.
  - Labeling the orbitals allows you to investigate them individually. In particular,  $d_{z^2}$  decreases in energy and  $d_{x^2-y^2}$  stays the same; get their Mulliken symbols from the  $C_{4v}$  character table. Less  $\pi$ -backbonding gives you a raised  $e$  set ( $d_{xz,yz}$ ) and a conserved  $b_2$   $d_{xy}$ .
- We assume that we are engaging this fragment with itself.
  - Thus, we write the MO hierarchy on both sides of our MO diagram, and then we mix these orbitals similarly to Figure 7.14.
  - Based on the parentage, we can now determine what's  $\sigma$ ,  $\pi$ , and  $\delta$ .
  - We now fill in 14 electrons, corresponding to two neutral  $d^7$  Re atoms.
- Descent in symmetry: Start from a molecule you understand, and then do systematic distortions on it.
- Outside of some Mulliken symbol errors, it looks like I got the question right!
- Can we scale this differently like I did?
  - We can scale this any way we want, as long as we get a bond order of 1 and a splitting ordering of  $\sigma > \pi > \delta$ .
- So antibonding orbitals can be lower in energy than bonding orbitals?
  - Yes.
- Problem 2 asks us to consider a  $d^4$   $O_h$  compound and a  $d^6$   $T_d$  diagram. In sum, it asks us to draw a correlation diagram and walks you through how to do that.
  - 1. Determine the ground state free ion term.
  - We can do so by maximizing spin  $M_S = \sum m_s$  and  $M_L = \sum m_\ell$ .
  - Label a free ion set of 5  $d$ -orbitals with their  $m_\ell$  values and fill in electrons.
    - This gives  $L = 2 + 1 + 0 - 1 = 2$  and  $S = \frac{1}{2} + \frac{1}{2} + \frac{1}{2} + \frac{1}{2} = 2$ , yielding  ${}^5D$  as our free ion term.
    - Doing this for the other case actually also gets us the same answer.
  - 2. What is the splitting of the ground state free ion term in a weak ligand field?
    - We want to determine how  ${}^5D$  splits in a weak (octahedral) field. Take  $L = 2$  and know that the representation can be approximated by the quadratic functions ( $P$  is linear functions,  $S$  is totally symmetric,  $F$  is cubic). Thus, from the  $O_h$  character table, we have  $T_{2g}$  and  $E_g$ . The spin multiplicity of 5 carries over.
    - Very similar to the above, but from the  $T_d$  character table, we get  $T_2$  and  $E$ .
  - We don't know the placement/relative energies of the split terms; we just want to know that it splits.
    - In terms of energy ranking, we just need to be able to find the ground state of the free ion term (i.e., by knowing that it is the lowest in energy according to Hund's rules).
  - 3. The ground state strong-field electron configuration.
    - Strong field means we want to minimize spin multiplicity across the two levels. Our electron configuration for  $d^4$  is  $t_{2g}^4$ . For  $d^6$   $T_d$ , we have  $e^4t_2^2$ .
    - Wuttig says we want to minimize spin multiplicity??

- 4. Split the ground state strong-field electron configuration into strong-field terms.
- We can take the direct product of the electrons in the unpaired set because the interaction between them will split the energetics of the strong field term.
- Take the direct product of  $t_{2g} \times t_{2g}$  and know that the characters are

$O_h$	$E$	$8C_3$	$6C_2$	$6C_4$	$3C_2$	$i$	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$T_{2g}$	3	0	1	-1	-1	3	-1	0	-1	1
$t_{2g} \times t_{2g}$	9	0	1	1	1	9	1	0	1	1

Table 9.1: Representation for the unpaired electrons of an  $O_h$   $d^4$  complex.

- Reduce to

$$\Gamma = A_{1g} + E_g + T_{1g} + T_{2g}$$

- Thus, the strong field  $t_{2g}^4$  can be split into the above states.
- We don't need to put spin multiplicities on the Mulliken symbols because doing so requires additional descent in symmetry analysis beyond we did not do in class.
- $t_{2g}^4$  splits into four terms; are these excited states?
  - These are not excited states per se, it's just that there is finer structure within the strong field electron configuration.
- With these four splittings, we don't necessarily need to fill the electrons into the splitting levels? Do different ones of these levels have varying occupations?
  - Think about these as being electronic energy levels that are useful for TS diagrams, but not for MO diagrams.
- Are the terms we came up with in Problem 2(3) the ground state strong field terms?
  - Yes.
  - This is still related to  $^4F$  and the associated weak field things, but we do this correlation at the very end.
  - We do the correlation using the two axioms (1-to-1 correlation and same spin modes [??]).
- If we have an excited state  $t_{2g} \rightarrow e_g$  transition, could we take the direct product  $t_{2g} \times e_g$ ?
  - Yes.
  - Not intuitive, though, because there are more possibilities.
- Why do we take a two-fold direct product instead of a four-fold direct product for  $t_{2g}^4$ ?
  - We must consider the physical origin of this mathematical calculation; we are determining the ways those two *unpaired* electrons can couple.
  - To reiterate, even though we have more electrons (four), we take the direct product twice to describe the two electrons that are standing alone in the strong field splitting.
  - We assume that all paired electrons cancel.
- Where did we find for the  $T_d$  geometry that the  $e$  orbitals are lower in energy than the  $t_2$  orbitals (inverse of  $O_h$  case)?
  - That comes from crystal field splitting; four ligands on the corners of the tetrahedra shows that the  $e$  orbitals are more effective at overlapping than  $t_2$ , and hence are more raised.

- Same schenanigans on  $t_2 \times t_2$ . We get

$O_h$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$T_2$	3	0	-1	-1	1
$t_2 \times t_2$	9	0	1	1	1

Table 9.2: Representation for the unpaired electrons of a  $T_d$   $d^6$  complex.

- Reduce to

$$\Gamma = A_1 + E + T_1 + T_2$$

- For the reduction, why do we multiply  $t_2 \times t_2$ ?

- Remember the electron hole formalism. 6 – 4 electrons gives 2 holes.
- We will not have to do more than 2 electrons ever in this class. It's beyond the scope, and we can leave that to the physicists. 2 electrons is possible, though.

- 5. Determine if any weak ligand field term to strong-field term exhibit correlation for terms derived for the ground state.
- Draw out the  $x$ -axis for the correlation diagram. Left to right, it reads free ions, weak field, strong field terms, and strong field.
- Make sure to indicate that your solution works analogously for both the  $d^4$  in  $O_h$  case and the  $d^6$  in  $T_d$  case. The only difference between the  $O_h$  and  $T_d$  labels is the presence or absence of  $g$ , so we can indicate this in our single correlation diagram by putting parentheses around each subscript  $g$ .
- But if we wanted to correlate anything, we would need a spin multiplicity of 5 on the strong field terms.
- 6. Indicate why we can use the same energy correlation diagram to describe  $d^4$  in  $O_h$  and  $d^6$  in  $T_d$  ligand field.
- Comes directly from the electron hole formalism.  $T_d$  inverts the energies of the  $E, T_2$  sets; changes the number of electrons and positrons while keeping the environment mostly the same.
- Now to Question 3.
- 1. Ground state term symbol.
- ${}^4F$  is derived much the same way as in problem 2.
- Similar to the above, we get a certain configuration. from which we derive a term symbol, specifically  ${}^4F$  for a  $d^7$  complex. This makes sense since we have a  ${}^4F$  label at the bottom-left corner.
- 2. What are the predicted spectral bands based on selection rules?
- We can get

$$\begin{aligned} {}^4F({}^4T_1) &\rightarrow {}^4T_2 \\ &\rightarrow {}^4A_2 \\ &\rightarrow {}^4T_1({}^4P) \end{aligned}$$

- We got this by reading the lines off of the TS diagram and looking for ones with the same spin (spin selection rule *must* be satisfied, unlike the Laporte selection rule).
- This is purely theoretical; there are no experiments.
- You don't know if you're high-spin or low-spin; you don't know anything. But you should start your transitions with the free ion term ( ${}^4F$  in this case), regardless!

- 3. Calculate the  $\Delta_o$ 's.
- You need to treat the Tanabe-Sugano diagram as a working curve. If it's a working curve, then you can take a ratio of the two energy transitions, namely

$$\frac{v_2}{v_1} = \frac{22,000}{11,300} = 1.95$$

- We do indeed assume that the top two transitions listed above are  $v_1, v_2$ .
- You need to do a sliding scale and figure out where you slide to get the right ratio.
- Note: We're wildly guessing here; there will be huge errors in the numbers we get. Using a system of equations, if applicable, is slightly more elegant.
- Take  $E/B = 17$  for the lower energy. Then we have  $E/B = 28$  for the higher energy by following vertical and horizontal lines on the graph. Since we know the energies, we can calculate the Racah parameter at this point. The two values for the Racah parameter should be the same; if they're not, take the average.
- It turns out that the bipy ligand is not as strong as we think it is.
- Will there be a definition matching question again?
  - There will be some gimme points and some thinking points.