

# 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.

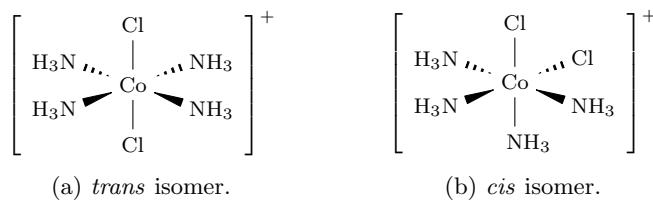


Figure 9.1: Oscillation strength comparison.

- 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.

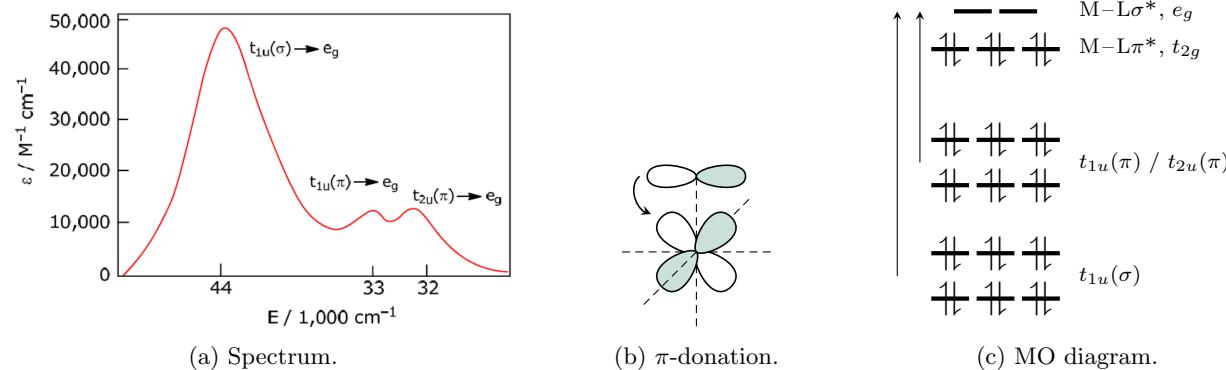


Figure 9.2: LMCT dynamics.

- 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.

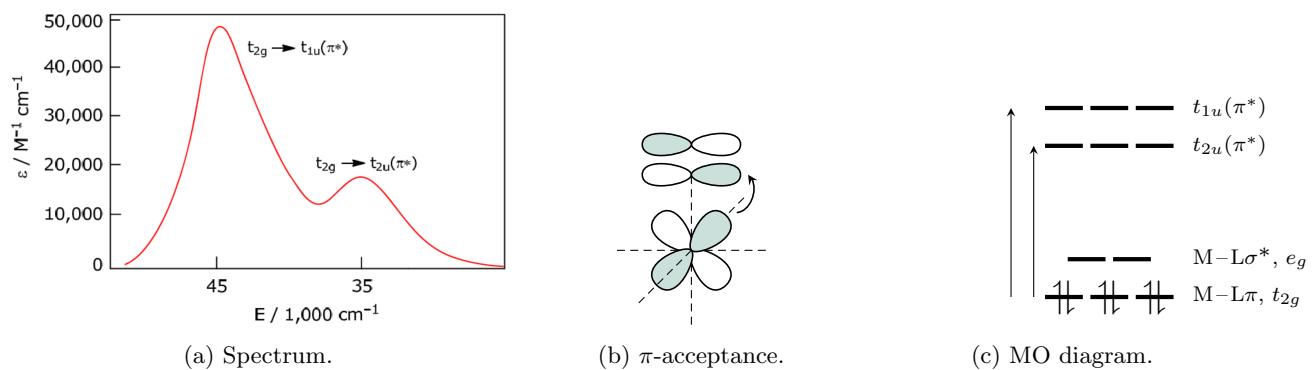


Figure 9.3: MLCT dynamics.

- 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.

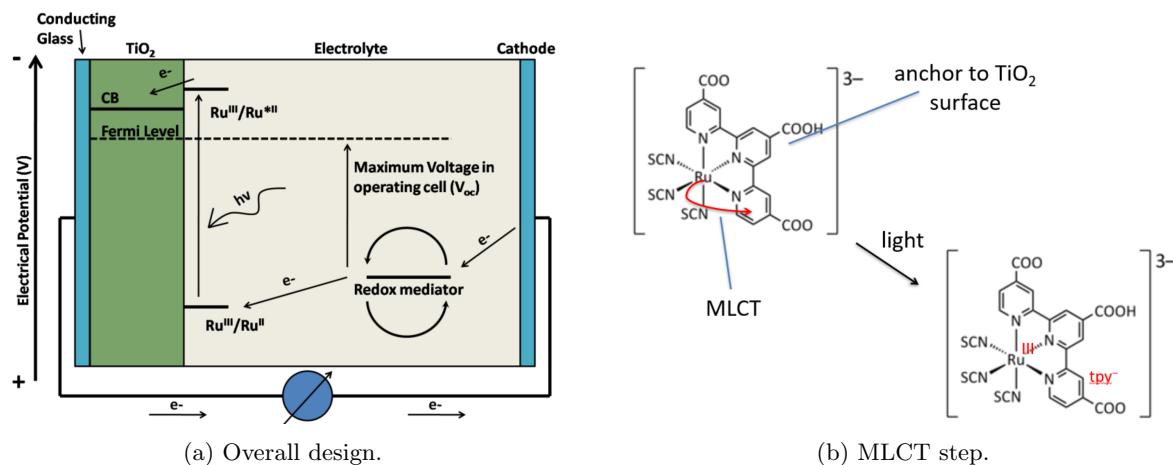


Figure 9.4: Grätzel Cell mechanism.

- 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  $\text{Ru}^{\text{II}}$ , oxidizing via MLCT  $\text{Ru}^{\text{II}} \longrightarrow \text{Ru}^{\text{III}}$  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.

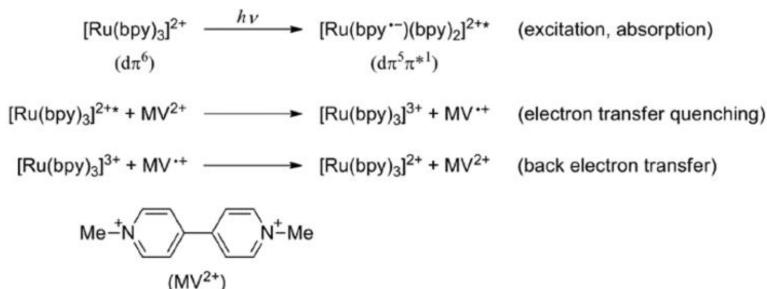
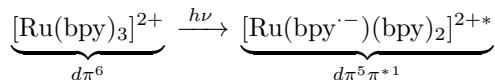
(a)  $[\text{Ru}(\text{bpy})_3]^{2+}$  light absorption.(b) Discovery mechanism: Quenching with  $\text{MV}^{2+}$ .

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).