

## Week 8

# Transition Metal Electronic Structure

## 8.1 Crystal Field Theory and Ligand Field Theory

11/14:

- Questions from the video lectures.
- For descent in symmetry questions, how do we qualitatively describe orbital energy? Do the Mulliken symbols matter?
  - Rationalize based on the molecular orbital parentage.
    - $a_1$  may or may not be more stable than  $a_{1g}$ , for example.
  - We need to visualize the orbitals and see if we're ripping something off from the axial or equatorial positions, for example, because that matters.
  - The labels are just there to make sure that our molecular orbital assignments are correct within the point group. It's mainly a bookkeeping thing. It also helps us create further MOs based on symmetry, though.
  - The Mulliken symbol alone doesn't convey any information about energetics.
- Walsh diagram structure.
  - Curved vs. straight lines is irrelevant; we just need to know whether the energy increases or decreases qualitatively under a procedural change in the molecule.
  - All we need to be able to do is derive the initial and final state and know what maps to what.
- How do you determine straight vs. curved line?
  - No way to do this from first principles; you need a combination of DFT and experiment.
- Comparing orbital energies.
  - If we're deriving from a new set of orbitals (as in the FeBz example), we need SALCs.
  - In an exam setting, though, we won't encounter brand new orbitals.
- We now start in on today's lecture topic.
- **CFT** and **LFT** are frameworks that help us estimate orbital energies.
  - They are quantitative methods for evaluating  $d$ -orbital splitting.
- **Crystal field theory**: A method in which one estimates ligands as point charges (which is not great, but ok) and the metal as a cation  $C$ . *Also known as CFT*.
  - Established by physicists at the same time as the birth of inorganic chemistry, before chemists came on the scene.

- Ligands are structure-less and orbital-less (think like a physicist; no structure, just charge).
- Group theory tells us that a  $d$ -orbital in an  $O_h$  environment has  $t_{2g}$  or  $e_g$  symmetry regardless of how much structure is present.
- Even though the transition metal C is positive, the electrons in the  $d$ -orbitals are negative, so we get the following visualization.
- Visualization: In the free ion, you have five degenerate  $d$ -orbitals. You then first approximate a negatively charged spherical field around the point charge, which causes the  $d$ -orbitals to go-up in energy. Lastly, we split the  $t_{2g}$  and  $e_g$  set in an  $O_h$  field. Essentially, Wuttig redraws Figure VI.11 of Labalme (2022).
- **Crystal field splitting parameter:** The difference in energy between the  $e_g$  and  $t_{2g}$  set. *Denoted by  $\Delta_o$ ,  $10Dq$ . Also known as field strength, field splitting.*
  - $10Dq$  nomenclature will return when we derive Tanabe-Sugano diagrams from scratch.
  - This is a *quantitative* term for the field splitting, different from every other aspect of the course this far (all of which have been qualitative).
  - This is phenomenological parameter that is determined from experiment and cannot be calculated from first principles.
    - The typical experiment is something like UV-Vis spectroscopy.
  - The terms field strength and field splitting are basically synonymous. However, we can also think of “field strength [as] the quantitative number associated with the field splitting.”
- Main takeaway of CFT: The origin of something called field splitting, and the origin of quantitatively understanding  $d$ -orbital energetics.
- We now move on from CFT to LFT.
- **Ligand field theory:** The same as CFT; we just put the bonds back in.
  - It’s not just point charges any more; there are actual bonds created by overlapping the metal  $d$ -orbitals (which we had also previously assumed to exist) with the ligand orbitals (which we are only adding in now).
  - Thus, free  $d$  electrons have adjustable interelectronic repulsion parameters. These are important in free ion terms.
- Field splitting.
  - Origins of ligand field splitting: Molecular symmetry and group theory, as discussed since the beginning of the course.
  - Extent of ligand field splitting: We will talk about this now.
  - Manifestations of ligand field splitting: The colors of TM complexes, reactivity, magnetism, life (bioinorganic chemistry), and many more.
- There are four main things to consider when determining the magnitude of the field strength.
  1.  $\sigma$  and  $\pi$  effects.
    - We talked a bit about this when we derived the  $ML_6$  MO diagrams from scratch with and without  $\pi$  orbitals.
      - Recall the discussion regarding Figures 6.13, 7.3, and 7.5.
    - We want to compare a  $\pi$ -donor, to a  $\sigma$ -only ligand, to a  $\pi$ -acceptor.
      - In every case, the  $e_g$  set will be comprised of  $M-L\sigma^*$  orbitals.
      - However, the  $t_{2g}$  set will decrease in energy from  $M-L\pi^*$  to nb to  $M-L\pi$ , respectively.
      - It follows that  $\Delta_0$  increases as we go from  $\pi$ -donors, to  $\sigma$ -only donors, to  $\pi$ -acceptors.

- People made this observation by looking at a series of homoleptic  $O_h$  complexes, specifically the **spectrochemical series**.

## 2. Oxidation state.

- As oxidation state increases (the metal ion becomes more positive), ligand field splitting increases, too.
- This is because orbital overlap increases as ligands are pulled in and hence the amount of ligand field splitting increases, too.
  - Mathematically, increasing the oxidation state increases the overlap integral  $S$ .
- Alternatively, we can think of this as more electropositive transition metals drawing more electrons toward them.
- Wuttig illustrates this point with example  $\Delta_o$  values for compounds that are alike in every way except for the oxidation state. For instance,

$$\Delta_o(\text{Cr}(\text{H}_2\text{O})_6^{2+}) = 14\,100\text{ cm}^{-1}$$

$$\Delta_o(\text{Cr}(\text{H}_2\text{O})_6^{3+}) = 17\,000\text{ cm}^{-1}$$

## 3. Row of the TM on the periodic table.

- The first row has a lower field strength than the second row, which has a similar field strength to the third row.
- This is because the radial extension of second and third row metals is much higher, leading to better overlap (higher  $S$ ), and thus higher splitting of bonding/anti-bonding orbitals.
- Example: In the following  $d^6$  complexes, we can observe a drastic increase in  $\Delta_o$  between the first- and second-row TM and a smaller increase in  $\Delta_o$  between the second- and third-row TM.

$$\Delta_o(\text{Co}(\text{NH}_3)_6^{3+}) = 22\,870\text{ cm}^{-1}$$

$$\Delta_o(\text{Rh}(\text{NH}_3)_6^{3+}) = 34\,100\text{ cm}^{-1}$$

$$\Delta_o(\text{Ir}(\text{NH}_3)_6^{3+}) = 41\,200\text{ cm}^{-1}$$

## 4. Geometry.

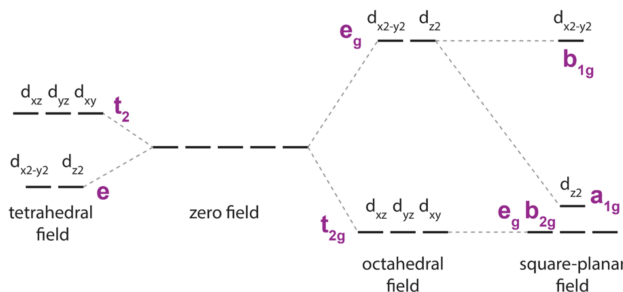


Figure 8.1: Geometry affects field strength.

- The number of ligands around the metal, as well as whether or not certain ligands are on-axis, affects the number of interactions and hence the splitting.
- In a  $T_d$  field for example, there are far fewer on-axis repulsive interactions compared to  $O_h$ .
- **Spectrochemical series:** A measure of the orbital overlap, electronegativity, and VOIE considerations that determine how big the ligand field splitting is.
  - Some ligands engender higher splitting energies than others, and we can measure this via the electronic transitions of (light absorbed/emitted by) homoleptic complexes.

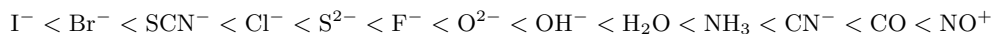


Figure 8.2: The spectrochemical series.

- The spectrochemical series was initially just a qualitative observation; it was later explained by MO theory.
- Example: Rationalize the following energy trends

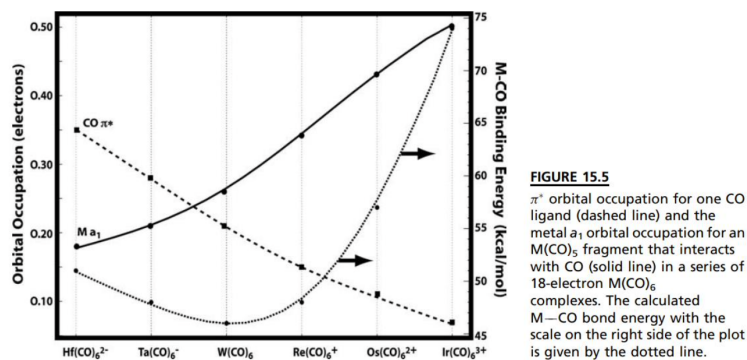


Figure 8.3: Energy trends across a row.

- Trends: The M–CO binding energy increases left to right. The orbital occupation of the  $\text{CO}(\pi^*)$  decreases left to right. Regardless, the orbital occupation of the  $\text{M}(a_1)$  (primarily of  $d_{z^2}$  parentage) increases left to right.
- The analytical procedure is as follows.
- Investigate the ligand: CO is a  $\pi$ -acceptor; thus, the  $d_{z^2}$  orbital is of  $\text{M}-\text{L}\sigma^*$  parentage. Recall from the PES of CO that its LUMO ( $\pi^*$  symmetry) lies higher in energy than the  $d$  atomic orbitals, which are sandwiched between that and the HOMO ( $\sigma$  symmetry).
- Investigate the metal center: All molecules are third-row  $d^6$  transition metals.
- Investigate what changes: The charge (e.g.,  $\text{Ir}^{3+}$  vs.  $\text{Hf}^{2-}$ ) and the electronegativity of the metal center (decreases left to right; does she mean the amount of negative charge?? Seems like she's been using electronegativity and electropositivity potentially wrong a few times??).
- On the left side, the metal  $d$  orbitals are high in energy, so they are close to the high-lying  $\text{CO}(\pi^*)$  orbitals in energy, so they donate a lot of electron density to  $\text{CO}(\pi^*)$ . On the right side, the opposite is true.
- Additionally, there is a smaller gap between  $d_{z^2}$  and  $\text{CO}(\sigma)$  on the right side.
- **Electronic spectroscopy:** Electron absorption spectra are broad — occur much more rapidly than molecular vibrations, i.e., we see a snapshot of the molecule in various rotational vibrational states.
- We're done learning about trends and onto quantifying stuff. To understand how to quantify things better, we need to understand the origins of electronic spectra.
- Thus, we'll discuss some basic properties of UV-Vis spectra in relation to the Franck-Condon principle.
- In the first half of the course, we focused on vibration. Now we're looking at electronic excitations and, in particular, electronic excitation wells.

- Franck-Condon Principle.

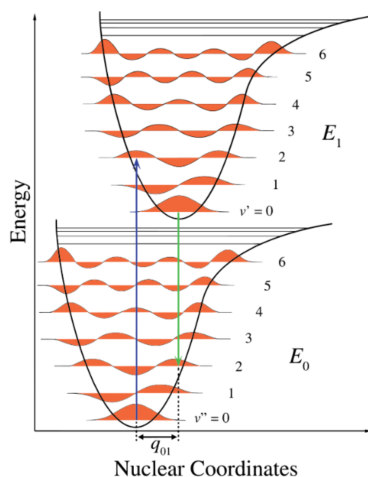


Figure 8.4: Franck-Condon Principle potential wells.

- $E_0$  is our ground electronic state.
- $E_1$  is the first electronic excited state.
- All of the little levels in between are the vibrational energy levels (overtones, etc.) that we discussed in the beginning.
- We now assume that an electronic transition is much faster than a vibrational transition, and hence occurs virtually without a change in nuclear coordinates. We just do a vertical jump from one well to the other, without moving nuclear coordinates along a vibration (“electronic transitions are ‘vertical’ with respect to the nuclear coordinate axis”).
- The Franck-Condon principle arises from the Born-Oppenheimer approximation.
- **Born-Oppenheimer approximation:** We can separate the electronic and vibrational wave functions of a given molecule.
- Terms next time.