Week 8

Mossbauer and EChem

8.1 Mossbauer Spectroscopy

2/21:

- HW will be posted tonight. Due on 3/2.

- Final is still on the same date.

- Mossbauer is pretty short, so we may start on NMR today, too. NMR will be at least 2 lectures.

- Mossbauer was discovered by Rudolf Mossbauer in 1958 when he was 29. He won the Nobel for it in 1961 at age 32.

- Basic principle: Involves the resonant nuclear absorption of a gamma rays.

  - We use these rays to excite spin flips.

- Generating gamma rays: A source nuclei A in an excited state decays, emitting a gamma ray with energy E_γ which will excite our resonant absorption nucleus B and raise it up in energy by E_r.

- Common source nuclei to use.

Common Nuclei	E_γ (keV)	Precursor Nucleus	$T_{1/2}$	Abundance
^{57}Fe	14.4	^{57}Co	267 d	2.2%
^{124}I	26.8	^{125}Te	33 d	0.63%
^{119}Sn	23.9	^{119m}Sn	245 d	8.6%
^{195}Pt	99	^{195}Au	192 d	33.8%
^{61}Ni	67.4	^{61}Co	1.65 h	1.2%

Table 8.1: Typical Mossbauer gamma ray source nuclei.

  - 90% or more of Mossbauer is done with ^{57}Fe.
    - At 14.4 keV, it's a pretty hot but not super hot γ ray.
    - The cobalt precursor nucleus comes from Russia, so a lot of Mossbauer spectroscopists are probably looking at very lean times right now.
  - ^{119}Sn is also pretty common.
    - With respect to the precursor nucleus, 119m means a **metastable** state of tin.

- There are a few synchrotrons in the world that are set up to do Mossbauer as well. Argonne is one of them! Even with a synchrotron source, though, not all nuclei are good; you need a long-ish life time, or your peak is just gonna be way too broad.

- The most common equation in Mossbauer.

$$E_\gamma = E_R + D - R$$

  - R is the recoil energy.
    - ■ Gamma rays are so powerful that when one is emitted, there is literally a shotgun-style recoil of the emitting nucleus.
    - ■ If you lose too much energy to recoil KE, your gamma rays may not match the target source.
    - ■ Thus, you try to hold your atoms very stable, usually by embedding them in a solid lattice.
  - D is the doppler energy.
    - ■ A Doppler shift is relevant to the experimental setup of Mossbauer.
    - ■ Essentially, you literally hook up your emitter to a speaker and vibrate it at a hertz frequency to add or subtract a tiny bit of energy to/from the gamma rays.
    - ■ This setup allows you to get resolution in a very small window around a certain excitation energy of your nucleus.
    - ■ It also leads to the common unit of mm/s.

- **Recoil free fraction**: The fraction of atoms of the source material that are held still enough that R is minimized.

- Mossbauer is one of the only techniques that provides direct information about nuclei.

- Three main factors that influence the energy of a Mossbauer transition (i.e., quantities you can pull out of the data).

  1. Electron density at the nucleus.
    - Usually measured by the **isomer shift** δ (think ppm from NMR).
    - Correlated with oxidation state in theory, but more accurately with bond length.
  2. Electronic symmetry at the metal center.
    - Measured by the quadrupole splitting ΔE_Q.
    - If the charge distribution around the nucleus is totally symmetric, this splitting goes away. But because this is almost never the case, you can get info on SOC, etc.
    - Low spin iron shows up more here because of the anisotropy in the d-orbital splitting diagram (not all orbitals are occupied here, and ring currents may be induced).
      - ■ In general, the electronic symmetry is affected by the d-count or configuration.
    - You can also see enormous quadrupole splitting with very electron dense and short ligands.
  3. Magnetic interactions.
    - In an applied field, the nuclear levels split.

- Typically, the isomer shift spans $\delta = -1$ to $\delta = 3$.

- Where do typical oxidation states of Fe lie along this band?

  - Fe^{IV}: -0.4 to -0.1.
  - Fe^{III}: 0.0 to 0.6.
    - ■ Per quadrupole splitting??
  - Fe^{II}: 0.0 to 1.0.
  - Fe^{I}/Fe^{0}: 1.1 to 2.0.
  - Cautionary note: These numbers hold in general for iron hemes (because all of this was first applied in bioinorganic chemistry), but can vary quite a bit.
  - Like TMS defines the 0 of chemical shift, stainless steel is the standard for the Mossbauer 0.

- What do the spectra look like?

    - It's a percent absorption spectrum plotted against the Doppler shift.

        ■ See Figure 8.1b for an example.

    - An $I = 1/2 \to 3/2$ transition, for instance, induces a single peak.

- Mossbauer spectra of iron compounds.

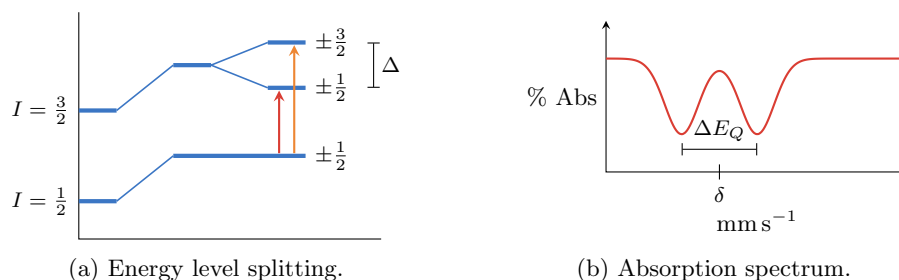

(a) Energy level splitting.   (b) Absorption spectrum.

Figure 8.1: The Mossbauer "vampire fangs" spectrum.

    - Most iron compounds have two transitions, one into each M_I state.

        ■ These are known as the "vampire fangs" (see Figure 8.1b).

    - Recall that $I = 3/2$ is equivalent to $M_I = -3/2, -1/2, 1/2, 3/2$ and $I = 1/2$ is equivalent to $M_I = \pm 1/2$.

    - δ is the center of the quadrupole doublet.

    - ΔE_Q is the splitting between the peaks.

    - The world record for splitting is 6-7 mm/s, for those nitride compounds with massive charge density and very short bonds.

    - Selection rule: $\Delta M_I = 0, \pm 1$.

    - The splitting Δ (see Figure 8.1a) between the upper M_I states is proportional to $e^2 qQ$.

        ■ e is the electric charge.

        ■ q is the electronic field gradient.

        ■ Q is the nuclear quadrupole moment.

- To wrap up, we investigate Mossbauer under applied magnetic fields.

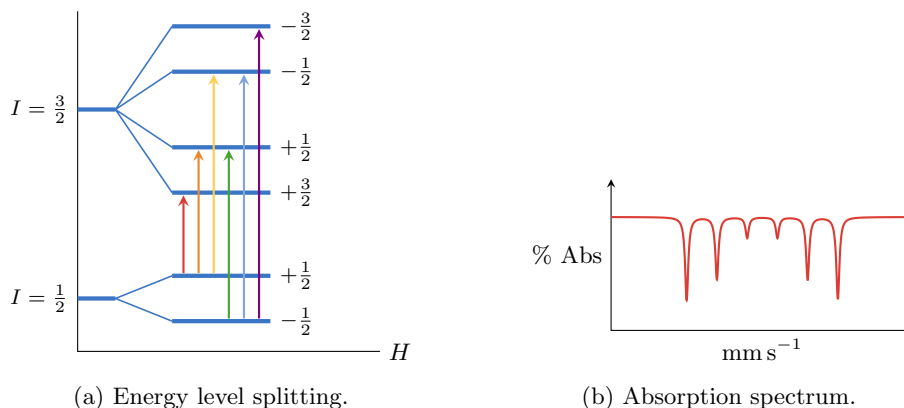(a) Energy level splitting.   (b) Absorption spectrum.

Figure 8.2: Mossbauer spectroscopy under an applied magnetic field.

- Apply H either parallel or perpendicular to the axis of the radiation.
  - All states visible in Figure 8.1a break degeneracy under a magnetic field, yielding Figure 8.2a.
  - We'll assume zero quadrupole splitting for simplicity.
  - We get six total allowed transitions.
    - This is what you see in fact for Fe metal.
    - You can only obtain this splitting at helium temperatures.
  - Takeaway: Huge, clean splitting is obtainable at low temps (low T minimizes recoil).
  - There will be a slight asymmetry due to quadrupole splitting. This allows you to pull out the internal magnetic field of the compound.

- This concludes Mossbauer.

- With the remaining time today, we'll start on electrochemistry.

- Anderson: Professor Wuttig should really be giving this lecture!

- The website "standard operating procedures for cyclic voltammetry," aka, SOP4CV (link) has a lot of good resources.

- Introduction.

  - Enables direct probing of electron transfer events, as well as physical properties such as capacitance and conductivity.
  - Our focus: Solution electrochemistry.
  - Solid state EChem is probably more important, though (think of batteries).

- A typical electrolytic cell.

  - The basis is an an electrolyte solution in some container.
  - There is a **reference electrode**.
  - You then typically apply a voltage across the reference and **working electrode**. The working electrode is where you do your measurement. The electrons flow out of our working electrode and into the **auxiliary electrode**.

- **Reference electrode**: An electrode with a fritted filter at the bottom and some electrolyte like saturated AgCl in there.

  - The potential is extremely well defined, which gives you a good reference.
  - Ag/AgCl is very common. Another one is SCE using Hg/HgCl, but mercury so people try to avoid this.

- Aside: A current hot topic in EChem is organic electrosynthesis. But Anderson has doubts.

  - Constant current electrolysis pumps a lot of electrons into solution, but no one knows into what! There's a lot of black boxes here.
  - A Cornell scientist is working on this.

- Common electrodes materials.

  - Working electrode: Pt, HOPG carbon, glassy carbon (GC), gold, etc. You can also use very specialized, designer electrodes such as nanomaterial-based ones.
  - Auxiliary electrode: Pt wire/mass.

- Aqueous media is common, but nonaqueous solvents include MeCN, THF, DCM, DMF, DMSO; one of Anderson's faves is 1,2-dichlorobenzene (1,2-DCB) since it is very inert.

- The electrolyte added to solution.

    - Aqueous media: You usually throw in Na_3PO_4.
    - Nonpolar media: TBA, PF_6, BAr^F (but expensive).

- **Nernst equation**: The applied potential E_{app} equals

$$E_{app} = E + iR_S = E^\circ + \frac{RT}{nF} \ln \frac{[Ox]}{[Red]}$$

  where F is Faraday's constant and n is the number of electrons you transfer during the process.

    - iR_s is the current times some internal resistance from the system.
    - The Nernst equation is only valid for relatively simple electron transfers. Systems that obey the Nernst equation are referred to as **Nernstian**.

- Intro to CV.

    - You typically scan one way and then scan the other way.
    - The midpoint between the peaks is E°.
    - Peak to peak separation is $57\,\text{mV}$ for $n = 1$, and then it shrinks as n increases.
    - Electrochemists call the shape on a CV diagram a "duck."

8.2   Electrochemistry

2/23:

- Electrochemical data is recorded on current vs. potential axes.

    - The applied potential in volts, both positive and negative, makes up the x-axis.
        - Negative potentials are to the right, and positive ones are to the left.
    - Current makes up the y-axis, with $I_{cathode}$ being positive and I_{anode} being negative.

- We now discuss the electrode surface in solution under an applied potential.

- **Electrochemical double layer**: The complex, multilayered structure that forms near the surface of an electrode under an applied potential.
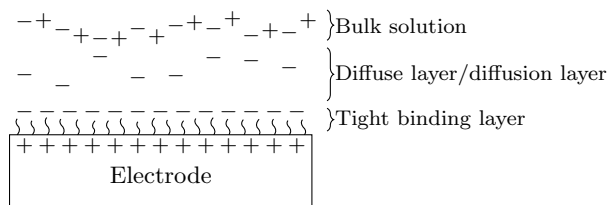

Figure 8.3: Electrochemical double layer.

    - Charge transfer to the analyte occurs through this double layer.

- Cyclic voltammetry.

    - One of the most common experiments in electrochem.
    - You sweep between two potentials linearly, plotting the current that flows vs. the potential applied.
    - The anode oxidizes and the cathode gets reduced during the course of the reaction.

- A *reversible* electrochemical reaction appears at a certain potential as a "duck."
  - Here, the maximum current (I_{P_c}; the peak of the duck) and minimum current (I_{P_a}; the belly of the duck) should have the same magnitude.
- An *irreversible* electrochemical reaction appears at a certain potential as a one-sided hump or dip.
- As stated last time, the peak-to-peak separation should be about $59\,\text{mV}$, but it almost never is.
  - $57\,\text{mV}$ or $59\,\text{mV}$??
  - This is the origin of the following equation (possibly related to the SHE vs. pH one from Labalme [1]?).
  $$E_{P_c} - E_{P_a} = \frac{0.059\,\text{V}}{n}$$
- There is also a scan-rate dependence on peak separation given by
  $$i_P = 2.99 \times 10^{-5} \cdot n(\alpha n)^{1/2} A C_0^* D^{1/2} V^{1/2}$$
  - n is the number of electrons.
  - α is the transfer coefficient.
  - A is the area of the electrode.
  - C_0^* is the concentration.
  - D is the diffusion coefficient.
  - V is the sweep voltage.

- Differential pulse voltammetry.

  - This is another technique that allows better resolution than CV for closely spaced features.
  - More??

- Rotating disk or ring electrodes.

  - Diffusion is difficult to account for in electrochemistry.
  - With rotation, we can eliminate diffusion.
  - We can also add an outside ring around the active electrode to further characterize any compound generated.
  - If the electrode is rotating, the diffusion path of particles in solution is to move toward the center of the working electrode from underneath and then be spun out to the sides.

- Anything else I missed in this lecture??