Week 8

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8.1 Mossbauer Spectroscopy

- 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.

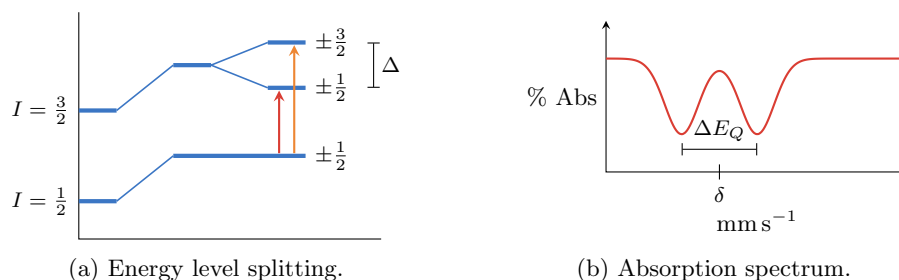(b) Absorption spectrum.

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.

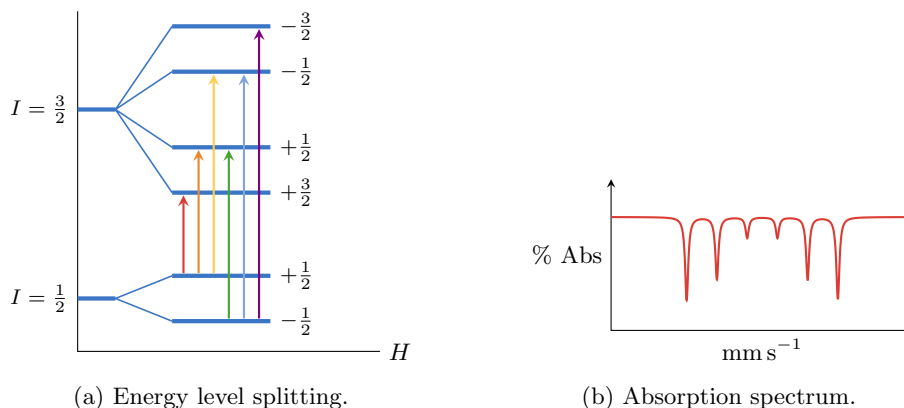- To wrap up, we investigate Mossbauer under applied magnetic fields.

(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

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

  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**.

- You typically scan one way and then scan the other way to

- 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."