

# Week 7

## EPR and XAS

### 7.1 EPR Spectroscopy

- 2/14:
- Today: EPR Spectroscopy.
  - Thursday: XAS and EXAFS (guest lecturer with great experience in the field).
  - As an official policy and a cautionary note, don't use ChatGPT to solve this course's homework.
  - Benefits of EPR.
    - Allows you to look at electronic spin flips.
    - Allows you to look at paramagnetic complexes (the class complementary to those you can observe with NMR).
  - Most of today: Doublets.
  - Electron spin.
    - An electron can be either spin up or spin down.
    - These states are degenerate in the absence of a magnetic field.
    - However, a magnetic field induces a Zeeman<sup>[1]</sup> splitting described as follows.
  - The intrinsic electron spin has a magnetic moment defined as

$$\mu_z = g\beta M_s$$

- $g$  is the gyromagnetic ratio for an *electron* ( $= 2.0023219278$ ; we usually just treat it as 2; can deviate depending on SOC).
- $M_s = \pm 1/2$  is our spin quantum number.
- $\beta = e\hbar/2m_e$  is our Bohr magneton.
- It follows that
$$E = -\vec{\mu} \cdot \vec{H} = -\mu H \cos(\vec{\mu} \cdot \vec{H}) = -\mu_z H = g\beta H M_s = \pm \frac{1}{2} g\beta H$$
  - This Zeeman splitting is pretty easy to visualize (see Figure 6.2a).
  - Thus, the energy to flip an electron is going to be  $g\beta H$ .
  - This is also known as the **resonance condition**.
- Aside: Be familiar with ENDOR spectroscopy, a combination of nuclear and electronic.

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<sup>1</sup>ZAY-mon.

- In an EPR experiment, we apply radiation to stimulate a spin flip.
  - $E = h\nu = g\beta H$ .
  - This energy is in the microwave region.
  - Microwaves are much higher in energy than radio waves, thus are more difficult to handle for technical reasons.
  - Thus, we cannot run complex, pulsed experiments analogous to in NMR; we just run more simple scans.
  - Indeed, herein we *fix* the microwave frequency and vary the magnetic domain.
  - Takeaway: EPR is much cruder than NMR in many ways (for technical reasons).
- The frequency domain  $\nu$  can vary based on the spectrometer from 1-285 GHz.
  - X-band (9.6 GHz) spectrometers are the most common.
  - More rarely, Q-band (35 GHz) and W-band (95 GHz) are used.
  - Milwaukee has an S-band EPR at 2 GHz.
  - High frequencies give you worse splitting (opposite of NMR) but better signal-to-noise.
- **Continuous wave EPR:** EPR experiments run under a fixed frequency domain and variable magnetic domain. *Also known as CW EPR.*
  - All of the setups described above constitute CW EPR.
- We scan across our magnetic field and observe (fairly broad) Gaussian lineshapes. Thus, we usually plot the first derivative.

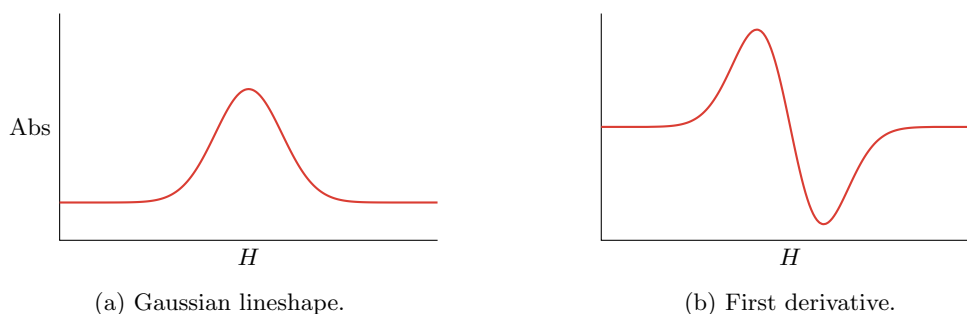


Figure 7.1: EPR spectra are plotted as the first derivative.

- There are two main types of EPR line broadening.
  1. **Secular broadening.** This comes from processes that vary the local magnetic field. Two subclasses.
    - (a) *Dynamic broadening.* A homogeneous broadening obtained by adding a paramagnetic ion to a solution of a free radical. This gives Lorentzian lineshapes.
    - (b) *Static broadening.* This is effectively the same, but induced by frozen solution and hence no longer homogeneous. This gives Gaussian lineshapes.

2. **Lifetime broadening.** This occurs when the excited state lifetime is too short. It mathematically originates from the Heisenberg uncertainty principle. In particular, we have that

$$\begin{aligned}\Delta E \Delta t &= \frac{\hbar}{2\pi} & \Delta h\nu &= \Delta E = g\beta H = g\beta \Delta H \\ \Delta h\nu \Delta t &= \frac{\hbar}{2\pi} & \Delta \nu &= \frac{g\beta}{\hbar} \Delta H \\ \Delta \nu &= \frac{1}{2\pi \Delta t} & \Delta H &= \frac{\hbar}{g\beta} \Delta \nu\end{aligned}$$

so, combining the above two expressions, the FWHM  $\Delta H$  is given by

$$\Delta H = \frac{\hbar}{2\pi} \frac{1}{g\beta \Delta t}$$

Essentially, as  $\Delta t$  gets really small, everything else starts to blow up since its in the denominator in the last term.

- We typically do EPR experiments in a frozen solution.
- Two flavors of EPR we really care about.
- **Spin-lattice relaxation:** The interaction of spin with the surroundings. *Denoted by  $T_1$ . Given by*

$$\Delta H = \frac{\hbar}{g\beta} \frac{1}{2T_1}$$

– In other words, if some spin is oriented away from  $H$ , how much time does it take to “reparallelize?”

- **Spin-spin relaxation.** *Denoted by  $T_2$ . Given by*

$$\Delta H = \frac{\hbar}{g\beta} \frac{1}{T_2}$$

- Combining the two gives the total homogeneous line width  $T_2'$ :

$$\frac{1}{T_2'} = \frac{1}{T_2} + \frac{1}{2T_1}$$

- Result: We need to go to low temperatures for EPR spectroscopy both for the lifetime reason and for technical reasons.
  - We need to go to helium temperatures in many cases.
  - Low spins may be observable at “high” temperatures like 77 K or even room temperature in some cases.
- $g$ -values.
  - The  $g$ -value is sort of like a ppm shift value for the EPR signal.
  - Recall that  $g$  is determined by the resonant frequency  $H_r$  at which we observe the excitation.

$$\begin{aligned}\Delta E &= \Delta E \\ g\beta H_r &= h\nu \\ g &= \frac{h\nu}{\beta H_r}\end{aligned}$$

- Organic radicals almost always exist at  $g = 2$  and are isotropic. Deviation might be 1/10,000. This is because organic compounds are composed of light atoms that just don’t have much SOC.

- For TM's (and lanthanides),  $g$  varies widely. Fortunately, it varies in a way that we can understand with orbitals.
  - Again, we visualize “ring currents.”
  - One that opposes the magnetic field induces  $g < 2$ .
    - Think of a lone electron in a set of 5 degenerate  $d$ -orbitals.
  - If a hole “hops” through and generates a ring current as in  $d^9$   $\text{Cu}^{2+}$ , we have a ring current that reinforces the magnetic field and hence  $g > 2$ .
  - Essentially, there are three scenarios that determine the value of  $g$ .
    - If the  $d$ -orbitals are less than 1/2 filled,  $g < 2$ .
    - If  $>$  half filled,  $g > 2$ .
    - At a perfectly half-filled shell, we should have  $g \approx 2$ .
  - This gives us sign. For magnitude. . .
    - The magnitude of the deviation is related to the magnitude of the SOC.
    - To a first approximation, this will relate to symmetry and the degeneracy of orbitals.
  - Trust the half-filled value, not the hole: When you have  $d^2$  in an octahedral field, for instance, the  $t_{2g}$  set is less than half-filled, so  $g < 2$ ; it's not that you have one hole rotating so  $g > 2$ .
  - It is the possibility of orbital angular momentum coupling with the spin angular momentum that allows  $g$  to change.
- Anisotropy: Thus far, we've only considered the effect of isotropic transitions. But both the magnetic field and spin are tensors with  $x, y, z$ -components.

- An isotropic magnetic field is described by

$$\hat{H}_{\text{iso}} = g\beta\hat{H} \cdot \hat{S}$$

- You spin your samples to try to average this out in solid-state NMR, but it's not perfect so you do need to take axes into account.
- An anisotropic magnetic field is described by

$$\hat{H}_{\text{aniso}} = \beta\hat{H} \cdot \hat{g} \cdot \hat{S} = \beta(H_x, H_y, H_z) \begin{pmatrix} g_x & 0 & 0 \\ 0 & g_y & 0 \\ 0 & 0 & g_z \end{pmatrix} = \beta H_x g_x S_x + \beta H_y g_y S_y + \beta H_z g_z S_z$$

- If a molecule has very high symmetry (e.g.,  $T_d$ ,  $O$ ,  $I_h$ , etc.), then  $g_x = g_y = g_z$ . In this case, we get back to our nice isotropic, one peak picture (Figure 7.1a).
  - Molecular geometry is *related* to  $g$  variations, but they're not the same thing. Don't make the mistake of looking at a highly symmetric molecule and thinking you know what the EPR spectra should be! You have to consider orbitals.
- EPR is often done on frozen solutions (sometimes powders) so that we don't have rapid solution-phase tumbling to average out the  $g$ -values but have everything stuck in some orientation. In particular,  $g$ -values will be inequivalent in frozen solutions!
- Anisotropic spectra.

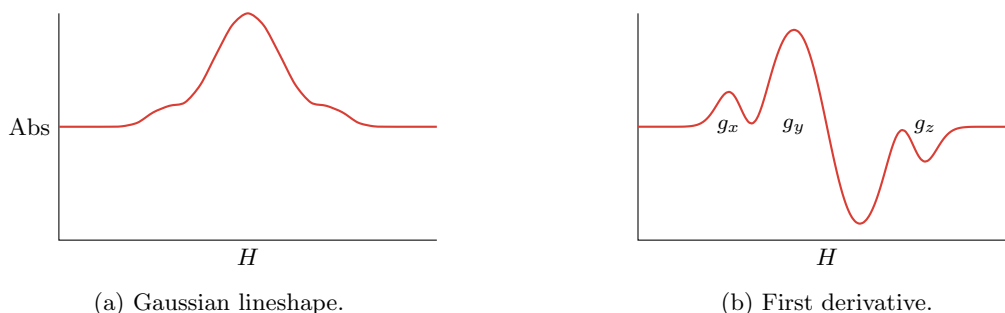


Figure 7.2: Rhombic anisotropic EPR spectra.

- Note that we don't know anything about Cartesian coordinates from the spectrum, so Anderson prefers  $g_1, g_2, g_3$ .
- This is a rhombic spectrum, meaning that  $g_x \neq g_y \neq g_z$ .
- Axial spectra are often referred to as  $g_{\parallel}$  and  $g_{\perp}$ . This corresponds to  $g_x \approx g_y \neq g_z$ .
  - We typically have a small  $g_{\parallel}$  peak downfield of a big  $g_{\perp}$  peak (picture in notes).
  - You see spectra like this for when your molecules have a clear symmetry axis; decreasing the symmetry further will tend to introduce some more rhombicity.
- Anisotropy only occurs via coupling into orbital angular momentum. Thus, it is observed for TMs but typically not for organic radicals.
- We now discuss fine structure for a while.
- Fine structure basics.
  - The electron spin can also interact with nuclear spin in **hyperfine interactions** and **superhyperfine interactions**.
    - These lead to additional signals and structure.
    - Be aware of the differences between hyperfine and superhyperfine, but only hyperfine interactions will be analyzed for the remainder of the time.
  - The quantum-mechanical basis for fine structure involves the following Hamiltonian.

$$\hat{H} = g\beta\vec{H} \cdot \hat{S} + a\hat{I} \cdot \hat{S} = g\beta H \cdot \hat{S}_z + a\hat{I}_z \cdot \hat{S}_z$$

- $\hat{I}$  is the nuclear spin operator.
- $\hat{S}$  is the electron spin operator.
- $z$  is the component along  $H$ .
- $a$  is the hyperfine coupling constant.
- Energies: Found by calculating eigenvalues.

$$E = \pm \frac{1}{2}g\beta H + \frac{a}{4} = \frac{1}{2}g\beta H \pm \frac{a}{4}$$

- **Hyperfine interaction:** An interaction with the direct nucleus which bears the radical.
- **Superhyperfine interaction:** An interaction involving additional coupling to other nuclei via delocalization.
- Hyperfine Zeeman splitting diagram.

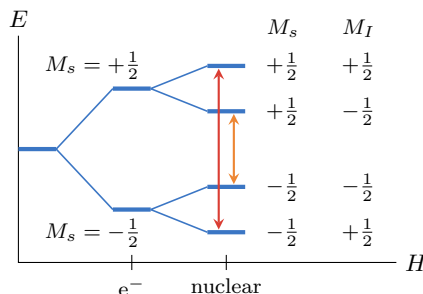


Figure 7.3: Hyperfine splitting.

- We first have our electron splitting.
- Then if we turn on nuclear splitting, that happens next, yielding four distinct states.

- Hyperfine selection rules.
  - Thus far, we have implicitly used  $\Delta M_s = \pm 1$ .
  - We must have  $\Delta M_I = 0$  as well! We can have an electron spin flip, but we can't do a nuclear spin flip at the same time, which may make some intuitive sense as well since the probability that these two unlikely events would happen simultaneously is very low.
  - Thus, we have two allowed transitions in Figure 7.3.
- Hyperfine EPR spectrum.
  - The peak splitting is  $A$ , which is related to the actual hyperfine coupling constant  $a$  as we'll talk about shortly.
  - A lot of the time, you don't see  $y$ -axis labels in EPR spectra because "the first derivative of absorbance" is not a particularly helpful unit.
- A few final notes on hyperfine coupling.
  1. The hyperfine coupling constant  $a$  is field independent.
    - Zeeman splitting is the only thing that is field dependent.
  2.  $a$  is a scalar HF constant and
$$a = g\beta A$$
    - $A$  is measured in Gauss; it is the *experimental* HF constant.
  3.  $a$  can also be anisotropic.
    - Each of the values  $g_x, g_y, g_z$  can have an  $a$ .
    - $a$  can be 0 for some  $g_i$  and not others.
  4.  $M_I$  can have many values.
    - Just like with NMR, a nuclear spin with  $M_I > 1/2$  can give multiline patterns.
    - Examples.
      - $^{14}\text{N}$  has  $M_I > 1/2$ .
      - TMs can go up to  $7/2$  or  $9/2$ , leading to very complicated multiline coupling patterns very quickly.
  5.  $M_I$  sums the contribution from other neighboring nuclei.
    - Multiple nuclei can also give multiline patterns, notably with  $2nI + 1$  lines.
  6. If a spin active nucleus is not 100% abundant, we get a superposition.
    - Cool example:  $\text{Mo}(\text{CN})_8^{3-}$ .
      - This is a  $d^1$   $S = 1/2$  compound.
      - $I = 0$  is 75% abundant, but  $^{97}\text{Mo}$  is 25% abundant with  $I = 5/2$ .
      - Thus, an amount of intensity equivalent to  $1/3$  of the central signal gets divided among 6 smaller neighboring peaks that are all evenly spaced apart (see notes for image).
- We now get move on to higher spin species.
  - This is a further level of complication.
  - However, these species may have more accessible EPR transitions.
  - We usually have larger splitting for higher  $M_s$  values.
- **Kramer's theorem:** Ions with an odd number of electrons will always have as their lowest energy level at least a doublet that will split in an applied magnetic field and give rise to an EPR signal.
- **Kramer's doublet:** The doublet predicted by Kramer's theorem.

- Example: Transitions predicted to be visible for a quartet ( $S = 3/2$ ).

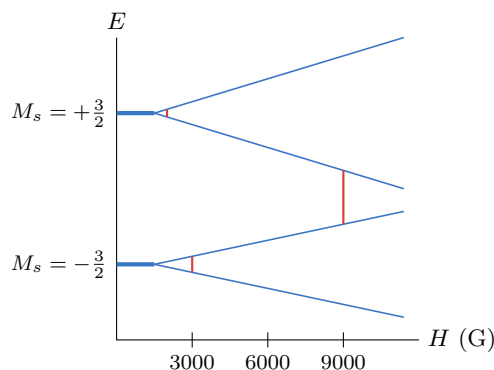


Figure 7.4: Quartet EPR signals.

- Something lower around 2000 G, higher around 3000 G and, if our spectrometer is powerful enough, something around 9000 G.
- Recall  $\Delta M_s = \pm 1$ .
- Example: Transitions predicted to be visible for a triplet ( $S = 1$ ).
  - Triplets are very difficult to see because the lower state takes a long time to drop low enough to see the ground state.
- Treating spin-orbit coupling.
  - We have that  $\vec{\mu} = g\beta\vec{J}$ .
  - It follows that
 
$$g = \frac{J(J+1) \cdot S(S+1) - L(L+1)}{2J(J+1)} + 1$$
  - What people tend to do is look at the spectrum.
- That's it for higher spin species.
- A few practical points on EPR spectroscopy.
  1. Use a microwave cavity, a fixed frequency, and vary the field.
  2. Avoid solvents that strongly absorb microwaves (e.g., water, other polar solvents). This can sometimes be ok if the sample is frozen.
  3. Usually quote  $g$ -values.
    - Do we report values as  $H$  or  $g$ ??
  4. You can double integrate vs. a standard to quantity  $\pm 20\%$ .
- We now move on to advanced EPR techniques.
  - These are analogous to some of the fancy things you can do with NMR.
  - Essentially, they are alternate ways of getting data out of an EPR machine besides straight-up absorption spectra.
- In particular, we will focus on **ENDOR** and **ESEEM** spectroscopy.
- **Electron spin echo envelope modulation** (spectroscopy). *Also known as ESEEM.*
- **Electron nuclear double resonance** (spectroscopy). *Also known as ENDOR.*

- Background.
  - Most EPR spectroscopy compared to NMR is pretty rudimentary.
    - In NMR, every carbon spectrum you take is proton-decoupled (we'll talk about this later).
    - Radiofrequency is really nice to control.
  - However, these are both 2D experiments between EPR and NMR.
    - They allow us to see spin-active nuclei that are close to the paramagnetic center.
    - 2D EPR can give you a ton of information about paramagnetic compounds; the most useful are those that couple electron transitions with nuclear transitions.
  - These are super powerful techniques.
- ENDOR spectroscopy.

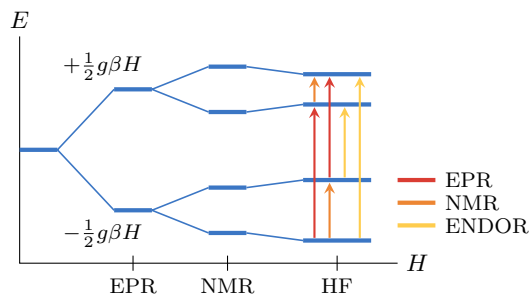


Figure 7.5: ENDOR splitting.

- The quantum-mechanical basis for ENDOR involves the following Hamiltonian.
 
$$\hat{H} = \underbrace{g\beta\hat{H} \cdot \hat{S}}_{\text{EPR}} - \underbrace{g_N\beta_N\hat{H} \cdot \hat{I}}_{\text{NMR}} + \underbrace{ha\hat{I} \cdot \hat{S}}_{\text{HF}}$$
- Three levels of splitting: EPR, NMR, and HF.
  - The last one doesn't actually induce splitting; it's just coupling between the first two that affects energy levels.
- EPR has  $\Delta M_s = \pm 1$ ,  $\Delta M_I = 0$ .
- Here, we turn on semi-forbidden transitions, i.e., those with  $\Delta M_s = \pm 1$  and  $\Delta M_I = \pm 1$ .
- $1 \rightarrow 3$  and  $2 \rightarrow 4$  are EPR allowed.
- $1 \rightarrow 2$  and  $3 \rightarrow 4$  are NMR allowed.
- ENDOR transitions (which we're turning on in this experiment) are  $2 \rightarrow 3$  and  $1 \rightarrow 4$ .
- ENDOR spectra tend to look like a big messy hunk corresponding to the nucleus, and then distinct ones further out which correspond to the NMR transitions.
- Possibly a bit more ENDOR on Thursday.
- We now move on to ESEEM.
  - Do we need to know this??



## 7.2 X-ray Absorption Spectroscopy

- 2/16:
- The pic that Anderson drew wasn't great; you can also find bootleg copies of Drago [1].
  - Patrick (or Pat): Guest lecturer on XAS, which he used a lot in his PhD.
    - He's currently a post-doc in Anderson's group.
    - Studied a lot of high-valent iron complexes.
  - We now begin the lecture.
  - **X-ray absorption spectroscopy**: A range of techniques which are all based on the absorption of X-rays by a nucleus of choice. *Also known as XAS*.

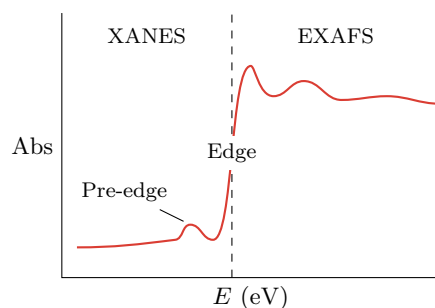


Figure 7.6: An X-ray absorption spectrum.

- In a basic experiment, the absorption of X-rays is directly measured.
- An X-ray with sufficient energy can eject an electron from a core orbital.
  - The ejected electron (**photoelectron**) dissociates at the **edge energy**.
- **Photoelectron**: An electron ejected from a core orbital by an X-ray.
- **Edge energy**: The energy needed to take the photoelectron to the infinite energy level.
- Different edges give different information.
- The *K*- and *L*-edges give the most important information.
  - Pat uses the  $L_{III}$  edge most commonly.
  - It corresponds to a  $2p \rightarrow 3d$  excitation.
- **K-edge**: The excitation of a core  $1s$  electron from an element.
  - The edge that can give you oxidation, symmetry, and structural information based on the photoelectron's environment.
  - The *K*-edge energy roughly correlates with  $Z$ .
  - Serena DeBeer does a lot on *K*-edge spectroscopy.
- **L-edge**: The excitation of a core  $2s$  or  $2p$  electron.
  - The edge that can give you bonding and molecular orbital information.
  - Nothing more on this today; look up Kyle Lancaster's work if you're curious.
- Benefits of XAS.
  - You don't need a crystal.

- Allows you to study transient intermediates, esp. in biochemistry; freeze-quench a reaction and get structural info about active states.
- Better local picture than XRD.
- Sensitive to local geometric structure of an absorber, i.e., ligation, oxidation state, spin state, symmetry.
- Lower X-ray dose needed than in crystallography; more control of photoreduction.
- XAS is *element specific* and can be applied to almost any system — biochemistry, synthetic inorganic chemistry, materials chemistry, etc.
- Can be measured at multiple edges.
- Tolerates less concentrated samples.
- All XAS uses the same fundamental principle, but there are many detection methods to get a lot of information.
  - Beamline scientists love to geek out about this.
  - Transition mode vs. fluorescence mode.
- **Transition mode:** Measure the difference between incident and final intensity.
  - Better for solid samples than frozen solutions, esp. close-packed ones.
- Frozen solutions with an X-ray-transparent window: Collect in fluorescence mode.
- To freeze: Submerge in a liquid nitrogen or isopropanol bath.
- *K*-Edge spectra.
  - Two main regions: XANES (X-ray absorption near edge structure) which includes the pre-edge (symmetry information) and the *K*-edge (oxidation state info).
  - The *K*-edge is the energy at which you actually eject the electron into the continuum.
    - This energy will change with oxidation state: As you probe something that's more oxidized, you know that its electrons will be held more tightly due to decreased repulsions, so the *K*-edge will increase.
  - The pre-edge consists of a  $1s \rightarrow 3d$  transition.
    - While the edge energy is the energy required to eject an electron into the continuum, the pre-edge features correspond to excitation into valence orbitals.
- Pre-edge.
  - In *K*-edge XAS, the pre-edge feature is primarily the  $1s \rightarrow 3d$  transition (electron-dipole forbidden, electric-quadrupole allowed). Thus, as symmetry decreases and we get more coupling, this increases.
  - The pre-edge area is indicative of deviation from centrosymmetry and  $3d/4p$  mixing.
    - High symmetry molecules will give *d-p* mixing/hybridization and thus have more intense pre-edge features.
  - Selection rule:  $\Delta l = \pm 1$ , so technically  $s \rightarrow p$  is allowed and  $s \rightarrow d$  is not.
- Example of XANES:  $\text{Fe}^{\text{V}}$  vs.  $\text{Fe}^{\text{VI}}$ .
  - The pre-edge tends to get over-interpreted.
  - A pure metal foil is often used as a standard; there is some debate about what a pure-metal *K*-edge is, though. Make sure you know what the standard is when you read literature!

- *K*-edge XANES may be the best technique we have to measure oxidation state, even though oxidation state doesn't really exist. Perhaps better for seeing that an electron was removed; much better in a comparative/relative sense than in an absolute sense.
- Pre-edge area is sensitive to the oxidation state.
  - This is because we often lose symmetry as we go to higher oxidation states.
  - Even just shortening the axial ligand in a square pyramidal complex can have a drastic effect.
  - Less symmetry  $\Rightarrow$  greater peak area.
  - You measure the area with any peak-fitting program (e.g., Fit It).
    - There's a paper by Ed Solomon in the 1990s that describes fitting in greater detail; a lot of the best practices are included.
    - You fit with a pseudo-Gaussian that's 50% Gaussian and 50% Voight. Sometimes it's hard to distinguish between two close peaks because there can be substantial overlap.
  - Metal-ligand bonding can turn on more pre-edge area; metal-ligand interactions shouldn't be too important; multiply bonded ligands with shorter oxidation states help more.
- Mossbauer in theory predicts bond lengths. You get a much better correlation with bond states when...
- Case study: Determining  $\Delta$  from the pre-edge region.
  - High-spin  $\text{Fe}^{\text{III}}$  should give two distinct  $1s \rightarrow 3d$  transitions; the splitting between them is  $\Delta$ .
- If you have a metal in different oxidation states, XANES is probably what you want.
  - We use a metal standard because it's somewhat stable and...
  - When you use foil, that's your  $x$ -axis calibration standard.
  - Some compounds don't have a pre-edge.
  - To fit our pre-edge, fit...
- People in the XAS community are usually willing to discuss, share, and argue about their XAS fitting.
  - Parameters varied: Computer program, function or algorithm, procedure.
- Beamline scientists hate giving tutorials on how to do something or how to fix something, but they like looking at data and science.
- A short EXAFS primer.
  - Pat's favorite part.
  - Includes the wavy features after the edge.
  - Mechanism: Ionizing radiation hits an absorber atom, ejecting the  $1s$  electron which leaves the **absorber** atom. Then the surrounding atoms send the waves back, leading to constructive and destructive interference.
  - You can also get multiple scattering (photoelectron may be scattered by more than one atom before returning to the center).
- Equations and quantities relevant to EXAFS.
  - Let  $R_j$  be the distance between the absorber and back scatterer  $j$ .
  - Recall that  $I = I_0 e^{-\mu t}$ , where  $I_0$  is the incident irradiation,  $\mu$  is the linear absorption coefficient, and  $t$  is the thickness.
  - The signal can be modeled with the **EXAFS equation**.
  - We have that  $\chi = (\mu - \mu_s)/\mu_0$ , where  $\mu_s$  is with a smooth background and  $\mu_0$  normalizes for free atoms.

- How we get information from EXAFS: Use the EXAFS equation.

$$\chi(k) = \sum_i \frac{(N_i S_0^2) F_i(k)}{k R_i^2} \cdot \sin(2k R_i + \delta_i(k)) e^{-2\sigma_i^2 k^2} e^{-2R_i/\lambda(k)}$$

- The XAS spectrum is the sum of multiple sines.
- The sine wave overlies the fluorescence decay, which can also be important.
- $\chi(k)$  depends on a number of things, but for a shell made of the same scattering atoms, the variables we control are  $N_i$  — the number of equivalent scatterers.
- $R_i$  is the distance between your absorber and your scatterer.
- $f_j$  is the electron backscattering amplitude of the scatterer.
- It depends on  $Z$ .
- $\sigma_i$  is the root mean square variation in  $R_j$ .
- $\delta_i$  is the scatterer phase shift from the theory or model.
- Together  $\sigma_i$  and  $\delta_i$  make up the **Debye-Waller factor**, which accounts for disorder.
- $k$  is the photoelectron vector.

- It is given by

$$k = \sqrt{\frac{2m_e}{\hbar^2} (E - E_0)}$$

where  $E_0$  is the threshold energy for electron ejection.

- To accurately describe these variables, a lot of information is needed about the system...
- We  $k$ -weight our spectrum to account for differences between heavy and light elements.
- We FT our spectrum to transform it to space data.
- **Debye-Waller factor:** Equivalent to thermal ellipsoids in crystallography. If it's negative, it's fake; if it's too big, it's fake. *Given by*

$$e^{-2\sigma_i^2 k^2}$$

- You get transitions in the edge in some specific compounds.
- Principles to guide data analysis.
  - You can fit anything if you try hard enough. Use your chemical intuition. Does a fit make sense?
  - Error in EXAFS is typically  $\pm 0.02 \text{ \AA}$ , but the shell resolution is usually much larger (equal to  $\pi/(\Delta K)$ ). Don't give things within a shell-resolution of each other!
  - EXAFS is very much a “helper” spectroscopy.
    - XAS should be the last step of any project you perform. Just to fill in the gaps; you need chemical intuition to make sense of your data.
- Information we can get out of our data: A good fit tells us...
  1. The number, type, and distance of scatterers.
    - This can inform on the immediate coordination sphere of a metal center.
    - Heavier atoms scatter more, and shorter distances scatter more.
    - From XAFS, you can get the number of scatterers  $\pm 1$ .
  2. You can pull out angular information if the data is really good and the geometry is right.
    - Pat thinks this is fake, though.
  3. You can do it in solution phase and with amorphous materials.
    - You can also pull out EXAFS data for 6-8  $\text{\AA}$  in certain solids.

- Case study: Oxygen activation at a diiron site.
  - Can't do Mossbauer with iron, so even if it's not giving you approximate...
  - Typically, you want to aim for  $R(\text{\AA}) < 6$ .
  - Both irons will be oxidized...
  - Data can be decomposed with a linear combination analysis.
- Data fitting is not always so easy.
  - Mössbauer...
  - This is the decay of 3.
  - Thermal decay: The things we don't want to see is...
  - Took 11 attempts to fit (that's a lot for Pat).
- Big picture for the diiron system.
  - Getting more and more rigid.
- Not a lot of people use this technique, so a lot of labs publish bad data, but reach out to them if you're confused! They'll usually be willing to work with you.
- Ask for slides!
- Review **XAFS for Everyone!**
- Return to ENDOR spectroscopy.
  - The energy level diagram we want is the one in the picture.
- Experimental considerations.
  - You need a high energy, intense X-ray beam (typically a synchrotron).
    - The closest synchrotron to us is the APS at Argonne.
    - We can also run at the SLAC at Stanford, and there are others elsewhere, too.
  - Data workup is involved and needs to be done carefully.
    - The relevant software suite is called Demeter and published by Bruce Ravel; it is all free.
- A note on the data.
  - After treatment, the data is typically plotted as a Fourier transform.
  - Note: The "distance"  $R$  in an FT plot is often not true distance; true distance is usually  $R$  plus approximately  $0.4 \text{\AA}$ .
- Next Tuesday: Mossbauer.