Week 5

Exam and Molecular Spectroscopy

5.1 Intro to Molecular Spectroscopy

2/2:

- First half of the course: Techniques that apply to materials.
- Second half of the course: Techniques that apply to molecular systems, specifically bioinorganic ones.
- Less structural information now; more **spectroscopy**.
- **Spectroscopy**: The study of the interaction of light with *molecular* systems.
- Today: Intro to spectroscopy (specifically vibrational) and group theory.
- Schedule after today:
  - Magnetism (doesn't really involve radiation, but whatever).
  - EPR, XAS, Mossbauer, elecrochemistry, NMR, and (time-permitting) some examples.
- The final: Tuesday, March 7 at the Registrar time (from 7:30am-9:30am).
  - We will probably start at 8:00am and just have a 1.5 h exam.
- Class will mainly be on the board.
  - If there's something that's completely illegible, please stop him and make him clarify it.
- Spectroscopy is the "eyes of the chemist."
  - It's much more difficult to identify and characterize inorganic compounds vs. organic ones. We also tend to want a lot more information about inorganic systems.
- Flavors of spectroscopy (structure).
  - XRD: Solid-state structure.
    - May have very limited relevance to what's going on in solution.
  - NMR: Solution structure and dynamics.
    - Good for diamagnetic samples.
    - Can work for some paramagnets, but relaxation times keep it from working for many inorganic complexes.
  - EPR: Electron paramagnetic resonance. *Also known as* electron spin resonance (in older papers).
    - Good for paramagnetic samples.
    - Works both in solution and in the solid state.
    - Not good for bulk extended solids; you need isolated spin centers that won't couple.

  - EXAFS/XAS: Extended X-ray Absorption Fine Structure, which is a type of X-ray Absorption Spectroscopy.
    - XAS looks at the *absorption* of X-rays by an atom, not just random scattering and diffraction.
    - Recall from the hands-on class that the first thing you do in XRD data analysis is apply an absorption correction; in XAS, that data is what you want.
    - Works in solution and solid. Allows you to measure bond distances and angles in the first shell.
    - EXAFS can be done on a solution or amorphous, disordered sample. This makes it extremely powerful, esp. relative to XRD.
    - Usually coordination and the first shell. You most commonly excite the K-edge ($1s$) and then look at the electron wave's interactions with nearby nuclei.
    - There is a company that makes a benchtop "Easy EXAFS," and Anderson is trying to get one on campus to help cope with the APS shutdown.

- Dynamics via spectroscopy.
  - Ask, "what is moving?"
  - Moving electrons? Probe with electrochemistry, EPR, optical spectroscopy (not covered much in this course), Mossbauer. We're especially interested in *electron transfer*.
    - Will depend on the time scale of delocalization (this can be quite difficult to tease apart).
    - Electrons may be in stationary, static wavefunction states, but they can also move between locations as both a particle and a wave.
    - Not usually relevant to organic chemistry.
  - Moving nuclei? Probe with NMR, vibrational spectroscopy, kinetics.
    - Anderson would like to get a grad kinetics course.
  - The overall goal here is to obtain a "video" of the molecule.

- The difference between the techniques we've discussed thus far.

- Quick note: It follows from the definition of spectroscopy that XRD if *not* a spectroscopy.
  - This is because spectroscopy necessarily involves absorption of radiation, not diffraction.

- The main difference between different types of spectroscopy is energy regimes!

- Review: A bit of physics.
  - $E = h\nu = hc/\lambda$. Thus,
$$\nu\ (\mathrm{s}^{-1}) = \frac{c\ (\mathrm{cm\,s}^{-1})}{\lambda\ (\mathrm{cm})}$$
  - We can define the wavenumber
$$\nu\ (\mathrm{cm}^{-1}) = \frac{1}{\lambda\ (\mathrm{cm})}$$

- We now look at which energy regimes in the EM spectrum correspond to which types of spectroscopy.
  - $\lambda = 10^{6}\,\mathrm{cm}$: Radio frequency, NMR, nuclear spin flips.
  - $\lambda = 10^{2}\,\mathrm{cm}$: Microwave frequency, EPR, electron spin flip, rotations.
  - $\lambda = 10^{-2}\,\mathrm{cm}$: Infrared frequency, IR and Raman spectroscopy, molecular vibrations.
  - $\lambda = 10^{-4} - 10^{-5}\,\mathrm{cm}$: Visible, electronic transitions, orbital transitions, CD and MCD ([magnetic] circular dichroism, which we will not discuss).
  - $\lambda = 10^{-5} - 10^{-6}\,\mathrm{cm}$: UV photoelectron spectroscopy (PES); won't talk to much about this.
  - $\lambda = 10^{-6} - 10^{-9}\,\mathrm{cm}$: X-rays, XRD and XAS.

  - $\lambda = 10^{-10}\,\text{cm}$: Gamma rays, Mossbauer (allows you to get very small peaks using very high energy radiation).
  - Beyond gamma rays is electron beams.

- Now we have a bunch of different types of spectroscopy. The next logical question is, "what dynamic processes can be probed with each spectroscopy?"
  - To answer this question, we must consider the *timescales* on which dynamic processes occur.
  - Specifically, in order to relate processes to regions of the EM spectrum, we need to know the timescales as a function of the energies involved.

- Recall that
$$\frac{1}{t} = \nu = \frac{c}{\lambda}$$
  - t is the maximum time resolution.
  - $\nu = 1/t$ follows from the Heisenberg uncertainty principle.
  - The above equation implies that
$$t = \frac{\lambda}{c}$$

- Example: For UV radiation at 300 nm, we have
$$t = \frac{3 \times 10^{-7}\,\text{m}}{3 \times 10^{8}\,\text{m}\,\text{s}^{-1}} = 10^{-15}\,\text{s} = 1\,\text{fs}$$
  - The period of a molecular vibration is on this order, so that's why UV/Vis is pretty good at resolving molecular vibrations.

- Time resolution ranges.
  - Electron diffraction: $10^{-20}\,\text{s}$.
  - Neutron diffraction: $10^{-18}\,\text{s}$.
  - XRD: $10^{-18}\,\text{s}$.
  - UV: $10^{-15}\,\text{s}$ (per the above).
  - Vis: $10^{-14}\,\text{s}$.
  - IR/Raman: $10^{-13}\,\text{s}$.
  - EPR: 10^{-4}-$10^{-8}\,\text{s}$.
  - NMR: 10^{-1}-$10^{-9}\,\text{s}$.
  - Mossbauer: $10^{-7}\,\text{s}$.
  - Molecular beams: $10^{-6}\,\text{s}$.
  - Experimental isomer separation: $10^{2}\,\text{s}$.
  - For kinetics, about the fastest we can do is stop flow at 10^{-3}-$10^{-5}\,\text{s}$.

- A few misc. notes on time resolution follow.

- We cannot use XRD to resolve a molecular vibration (which happens much more slowly), or at least not easily.
  - This is because an XRD experiment collects many frames over 30-60 seconds and we average over all nuclear configurations that occur during that time.
  - It is this molecular vibration that makes our diffractograms not perfectly spherical but more ellipsoidal.
  - An individual X-ray pulse could resolve vibrations.

- Similarly, Mossbauer is relatively low time resolution even with gamma rays due to experimental limitations.
  - Units are $\mathrm{mm\,s^{-1}}$.
- You need to think about what's going on physically in this course!
- Tangent on Lawrence Berkeley Laboratory (LBL) and determining the mechanism of water oxidation (which is only done by one natural system, chlorophyll photosystem II).
  - They use the FEL to get very good time resolution, growing thousands of crystals on a conveyor belt, dropping them in front of the laser, collecting one frame, and moving onto the next crystal. The random distribution of orientations (as opposed to rotating the goniometer) in the falling crystal leads to really good data.
- An example of where time resolution matters: Studying the Creutz-Taube ion.

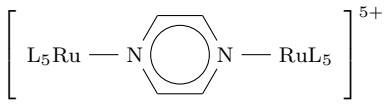

Figure 5.1: The Creutz-Taube ion.

  - History.
    - Henry Taube was a Nobel laureate and a physical inorganic chemist.
      - ➢ He did most of his work at Stanford and then UChicago lured him away and he's now proudly displayed on our website.
      - ➢ Anderson: This is a repeating pattern at UChicago.
    - Carol Creutz was his grad student (very brilliant). Anderson went to grad school with her nephew, who's now a professor in his own right.
  - The ligand is most typically NH_3.
  - A pertinent question: What is the oxidation state of Ru? Is it a fractional 2.5 oxidation state, or do we have one Ru^{II} and one Ru^{III}?
    - Where time resolution comes in: The answer to the above question depends on which technique you use.
    - With good enough time resolution, the electron hopping rate is on the order of $3 \times 10^8\,\mathrm{s^{-1}}$, so the lifetime $1/\nu$ is on the order of $3.3 \times 10^{-7}\,\mathrm{s}$. Look for an IVCT (inter-valence charge transfer).
    - Visible and IR are the best techniques to use here. 1000-1600 nm is what you want to analyze these types of things.
  - Misc. note: Be aware when you're doing UV/Vis! Make sure there's not something extra at the far end of the spectrum that might actually be important.
- Anderson is going to put all of his notes up on Canvas; make sure that we follow up if he forgets!
- Moving on: Vibrational spectroscopy now.
- IR is super boring and doesn't always tell you anything, but there are reasons to appreciate it.
  - Super fast time resolution.
  - Completely insensitive to the electronic structure of what you're looking at.
    - E.g., diamagnetic, paramagnetic, semiconductor, etc.
  - All that matters is the symmetry of the thing you're probing and certain selection rules.

- Very brief overview of group theory, character tables, and how they relate to spectroscopy.
  - Example: Water modes.
  - We can find nice GIFs of water vibrating by Googling "water vibration modes" (link).
  - Three modes: Symmetric stretch, asymmetric stretch, bending.
    - Called A_1, B_2, A_1.
  - A_1, B_1, B_2 are IR active via the character table (dipole must change, so x, y, z is important).
  - A_1 is Raman active via the character table (polarization must change, so x^2, y^2, z^2 is important).
  - An IR-active stretch must not be centrosymmetric.
  - Prussian blues contain M−C≡N−M motifs; because the C≡N moieties are always polar, we get IR. If it's M−N≡N−M instead, IR is forbidden, though we'll still get Raman of course because *something* is changing in the molecules.
  - With Raman, you can see just about everything.
- IR has a pretty simple setup; Raman is much more complicated.

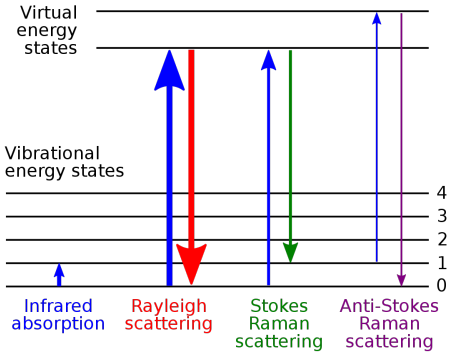

Figure 5.2: Raman spectroscopic mechanics.

  - IR: Pump an electron up one vibrational mode. Sometimes multiple via overtones.
  - Raman: Take your molecule, shoot a laser at the sample, and see what light scatters. You're least interested in **Rayleigh scattering**. What you care about is different changes (**Stokes** and **Anti-Stokes Raman scattering**). Note that the latter will be far less intense than the former due to the differences in populations between the $v = 0, 1$ states. We resolve vibrational energy levels by looking at differences between input and output frequency.
    - Indeed, in words: Rayleigh scattering is the most intense, Stokes is ok, and Anti-Stokes is poor.
  - Populations are proportional to the sizes of the arrows in Figure 5.2.
  - Raman is good for materials, not for molecules.
    - Great for MoS_2, but for molecules, you need huge fluxes which tend to fry your sample.
  - Anderson is not a huge fan of Raman spectroscopy.
  - How Raman actually works: Your photon doesn't so much get absorbed as it scatters off of the electron cloud by coupling with the polarization wavefunction.
  - Rayleigh is elastic; Raman is inelastic scattering.
  - Conjugated macrocycles (e.g., heme groups) are great, but most aren't. Worth trying in the lab, but don't get your hopes up.
  - Resonance is when you have a specific optical bond being much more intense.

- To finish off our brief treatment of vibrational spectroscopy, we'll discuss isotope effects.
  - Many times we want to test whether an observed vibration corresponds to specific atoms. To do this, we want to do an isotopic substitution.
  - This can change the energy of a vibration by an amount that can be predicted by the simple harmonic oscillator approximation.
- Example: Consider $^{16}O_2$ vs. $^{18}O_2$.
  - In Raman spectroscopy, we have $\nu_{00} = 749\,\mathrm{cm}^{-1}$ and $\nu_{00} = 708\,\mathrm{cm}^{-1}$, respectively.
  - Recall that $\nu = k\sqrt{F/\mu}$, where

$$\frac{1}{\mu} = \frac{1}{^{16}\mathrm{O}} + \frac{1}{^{16}\mathrm{O}} = \frac{^{16}\mathrm{O} + ^{16}\mathrm{O}}{^{16}\mathrm{O}\,^{16}\mathrm{O}}$$

  - Thus,

$$\mu_{16} = 8 \qquad\qquad \mu_{18} = 9$$

  - It follows that

$$\frac{\nu_{18}}{\nu_{16}} = \frac{\sqrt{^{16}\mathrm{O}_2}}{\sqrt{^{18}\mathrm{O}_2}}$$
$$\nu_{18} = \frac{\sqrt{8}}{\sqrt{9}} \cdot 749$$
$$\nu_{18} \approx 706\,\mathrm{cm}^{-1}$$

  - We'll get to practice this on the HW.
- The HW will be due 1-2 weeks before the final.
- Further examples.
  1. Test if chlorophyll photosystem II is actively producing oxygen.
     - Air has regular ($^{16}O_2$) oxygen, so we set the photosystem up with $^{18}OH_2$ and use IR to hopefully detect $^{18}O_2$ being generated.
  2. Test if a metal complex has a M≡N bond.
     - Synthesize your complex with both ^{14}N and ^{15}N.
     - Know that M≡^{14}N is approximately $1000\,\mathrm{cm}^{-1}$ and use the above to calculate that M≡^{15}N is about $920\,\mathrm{cm}^{-1}$.
     - Take spectra of both complexes and then subtract the two to obtain a difference spectrum. If nitrogen is being incorporated, your difference spectrum should be flat except for two peaks (one positive and one negative) at $1000\,\mathrm{cm}^{-1}$ and $920\,\mathrm{cm}^{-1}$.
- Last example from Anderson's written notes.
- **Nuclear resonance vibrational spectroscopy**: A type of vibrational spectroscopy that uses a synchrotron to induce a nuclear excitation. *Also known as* **NRVS**.
  - This excitation can then couple to vibrations of the excited nucleus.
  - Particularly relevant for Fe, the most common nucleon to study with NRVS.
  - Related to Mossbauer spectroscopy.