

CHEM 26700 (Experimental Physical Chemistry) Notes

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Week 1

Thinking Spectroscopically

1.1 Experimental Physical Chemistry: An Introduction

1/3:

- Questions:
 - Is “Introduction to Nanotechnology by Lindsay” the same as “Introduction to Nanoscience by Stuart M. Lindsay?”
 - They’ll check on this.
 - Access to Panopto recordings?
 - I have access now.
 - Recordings of class content?
 - Yes, if they can get the AV working.
- Intro by Hannah Lant (instructional professor to manage lab meetings). Tokmakoff handles lectures/non-in-lab stuff.
- Goals of the course.
 - Demonstrate and interrogate principles from your theory courses, e.g., from QMech/Thermo.
 - Learn practical techniques to characterize chemical and physical properties of molecules and nanomaterials, and the related spectroscopic techniques.
 - Analysis of data (in-class and in-lab).
 - What have you learned, and how can you communicate your findings to a scientific audience.
- Everything helps everything else; it’s cyclical from experimental theory, to collecting data, to data analysis, to communication, and back to more theory.
- Lectures will be more like workshops/recitations. There are recordings for content.
- Rest of today: Logistics and individual experiments.
- Canvas page.
 - Syllabus.
 - Most info on the Modules page.
 - Fitting exercises will be in in-class meetings in the day to come.
 - Experiments.
 - Video lectures on Panopto.
- Watch the 15-min Lecture 1 before class on Thursday!

- 6/9 weeks in lab. Complete a total of 6 experiments.
 - Core experiments for weeks 2, 4-6 (UV/Vis, FT-IR, NMR, GC-MS).
 - Full lab report on one of these; short lab report on the other ones.
 - Choose your experiments for weeks 7-8.
 - Highlight content in nanomaterials and kinetics.
 - Week 7 requires a full lab report on that experiment.
 - Week 8 requires a group presentation on your experiment.
 - Survey to determine what you do before Friday of Week 2!
- Grading breakdown.
 - Prelab quizzes: 15% (2.5% per quiz).
 - About 5 questions.
 - Must get 80% or above to attend lab.
 - 2 attempts.
 - Focus on safety, but also thinking critically about the theory for the lab.
 - Short reports: 40% (10% per report).
 - How to do info — in the lab manual.
 - ACS citation style.
 - There will be rubrics posted on Canvas (grading is not subject to the whims of our TAs).
 - Full reports: 30% (15% per report).
 - Group oral presentation: 15%.
 - Attend a few other presentations and give ours during finals week.
- A full schedule of assignments and labs is available in the syllabus.
- See announcement for which lab cohort I'm supposed to be in!
- What the experiments are and what their purposes are (nontechnical because we haven't done the theory yet).
- Weeks 2, 4-6.
 - UV/Vis to get a vibronic spectrum of iodine (to get electronic/vibrational data on I_2).
 - FT-IR: Rovibrational information on HCl.
 - NMR: $C_5H_{11}OH$.
 - GC-MS: Separation science and MS. Analyze gasoline, which is a complex mixture of organic molecules.
- Week 7 (+ info on who should choose these; think about it next week after first lab).
 - Fluor: Fluorescence spectra of analytes, including pyrene.
 - Both spectroscopy and kinetics. If you're really interested in physical chemistry and kinetics, do this. Uses custom built stuff in the labs.
 - QDots: Cadmium and Selenium nanocrystals.
 - Applications of particle-in-a-box ideas, nanotechnology, synthesis, the prettiest one.
 - EChem: Developed by Anna Wuttig.
 - More training in CV. Look at a number of different electrodes, and assay their activity in the hydrogen-evolution reaction. Applications in renewable energy.
 - Will run both weeks 7-8.

- Includes some interaction with Wuttig.
- AFM: Atomic force microscopy.
 - Imaging a number of different materials, e.g., the grooves on a DVD. Great for anyone interested in nanoscience.
- Week 8:
 - Photo: Alternate addition this week.
 - Photodissociation of CO from that hemoglobin structure and then some kinetics.
- The PChem lab suite: Enter Jones laboratory and turn left. We'll go elsewhere for special instrumentation. Lant's office is next door.
- NMR and GC-MS in Searle 340 instrumentation center. Usually meet our TA in the PChem lab suite and then travel.
- Attendance.
 - You are required to attend all six lab sessions and record your own data (often in groups).
 - Excused absences include university travel, family emergencies, and illness; please be in touch with Prof. Lant as soon as possible to reschedule your lab.
 - Unexcused absences may be able to reschedule at a 20% penalty if availability allows (this is an overenrolled class).
- Safety.
 - General lab safety policies from Gen Chem and OChem still apply.
 - Bring your own goggles.
 - Acknowledge you've reviewed the policies on Canvas in the first lab quiz.
 - Safety tour of the lab space on your first lab day by your TA.
 - Lab aprons will be provided.
 - Specific safety concerns will be communicated in lab manuals and pre-lab quizzes.
- We're all coming in with diverse scientific experiences. Fill out a survey on Canvas > Assignments > surveys or at tinyurl.com/pchemlabsurvey!
- No formal lecture on Thursday in this room! There will be a series of about 7 video lectures over the first two weeks that cover what we need to know for our first core experiments (watch these!). Workshops during this period, too. E.g., if they find from the surveys that we don't have experience with fitting data very well, we'll work through that. There is an exercise for this on Canvas?? (Data Fitting Exercises.pdf explains it.)
- Tokmakoff puts a big emphasis on communication :)
 - “Any professional science is communicated; otherwise, it’s just a hobby.”
 - Should be nicely formatted with good figures, etc.
- My lab group: Thursday A.
- Schedule.
 - UV/Vis: 1/12.
 - FT-IR: 1/26.
 - NMR: 2/2.
 - GC-MS: 2/9.

1.2 Lecture 1: Principles of Spectroscopy

- **Spectroscopy:** Studying the properties of matter (e.g., molecules and materials) through its interaction with different frequency components of the electromagnetic spectrum. *Etymology spectron* from Latin “ghost” or “spirit.”
 - More on the etymology: An apt description because you never see the molecule itself; you see a representation/image/apparition of it.
- Each type of spectroscopy gives a different picture (the *spectrum*).

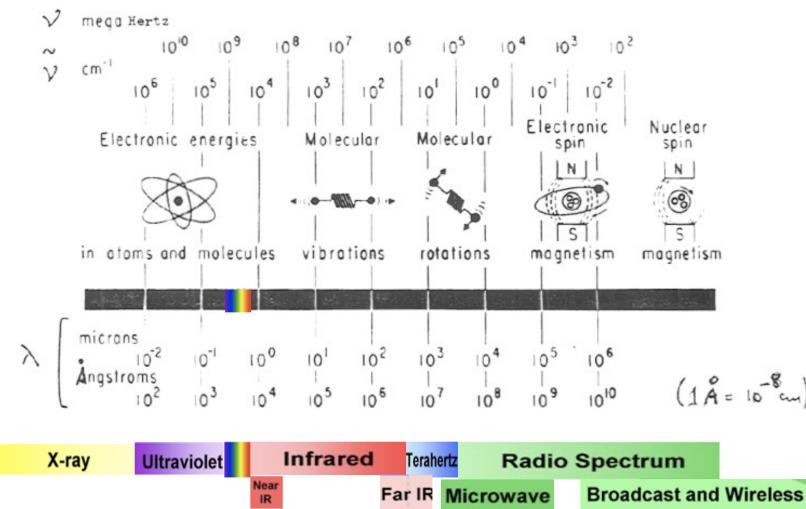


Figure 1.1: Types of light used by different forms of spectroscopy.

- UV/Vis: Electronic absorption (esp. valence electrons).
- Infrared: Vibrations.
- Microwave: Rotations and crystal lattice vibration.
- Radio: NMR.
- Goals.
 - Understand how light interacts with matter and how you can use this to quantitatively understand your sample (e.g., molecular structure, dynamics, reactivity).
 - Understand spectroscopy the way you understand other common tools of measurement (like a ruler).
 - See that spectroscopy is a set of tools that you can put together in different ways to solve the chemical problems that are of interest to you.
- A spectrum measures...
 - The interaction of light with a sample influences the sample and the light.
 - Two universal steps: Excitation and detection.
 - Light passes through the sample and then gets characterized on its way out (e.g., absorption, emission, scattering, reflection, dispersion, rotation). We can also characterize a change in the sample (e.g., photothermal, photoelectron and ionization, photochemistry).
 - In most cases, we characterize how a sample modifies the incident light.
- Two common measurements.

- **Absorption:** The attenuation of a light field passing through a sample.
 - Photodetectors measure intensity, which is related to the square of the electric field.
- **Emission:** Excitation induces light emission from the sample, typically of a different frequency.
- **Fluorescence:** Emission from singlet states.
- **Phosphorescence:** Emission from triplet states.
- **Raman scattering:** Light taken up shifts the frequency.
- The basics of an absorption spectrum.

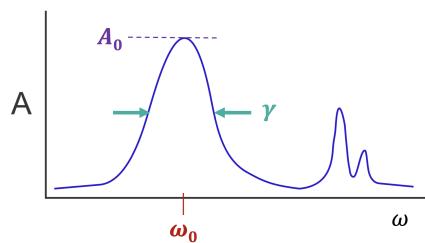


Figure 1.2: Features of an absorption spectrum.

- x -axis: Characterizes the input light in terms of frequency (frequency, angular frequency, or wavenumber), wavelength, or energy.
- y -axis: How the intensity of the light was attenuated at a particular frequency. Look at transmission ($T = I/I_0$) or absorbance ($A = -\log T = \epsilon(\nu)CL$, where ϵ is the extinction coefficient [unit $\text{L mol}^{-1} \text{cm}^{-1}$], C is the concentration [unit M], and L is the sample pathlength [unit cm]).
- Features: Resonance frequency ω_0 , peak height A_0 or peak area, linewidth γ (different frequencies absorbed; gives information on dynamical processes), lineshape (actual functional form of the peak).
- How do you measure absorption spectra?
 - Measure the change of intensity of light at different frequencies as it passes through a sample.
 - Two types of spectrometers: Dispersive (common for visible spectrometers) and Fourier transform (more on this later).
- **Dispersive spectrometer:** A spectrometer that has a dispersive element, that is, one that takes white light and spatially spreads the colors of the rainbow.
 - Could be a reflection grating, prism, etc.
 - Measure the white light without the sample, and then with the sample and see what changes. Calculate the transmission, and then absorbance.
- That was basic definitions and variables.
- This time: We have defined some basic variables for an absorption spectrum.
- Next time: Molecular interactions of light. Analyze this mode: Driven electron on a spring.

1.3 Lecture 2: A Classical Model for Absorption Spectroscopy

1/5:

- Last time: Absorption spectra features.
- Today: Building intuition about how molecules absorb light and what we can learn about them from this.
- Picture absorption of light from a quantum mechanical perspective.
 - Photons with energy that match the energy difference between certain energy levels excite electrons.
 - This is true, but it doesn't tell us much about the molecule itself. Thus, let's gain insight from a classical model of absorption.
- Why is there light absorption?
 - Classically, light interacts with *charges*.
 - Molecules are composed of charged particles (e.g., electrons and protons).
 - An electromagnetic field E exerts a force F on these charges q via

$$F = qE$$

- A classical model of absorption: Start with $F = ma$.
 - How do we describe light? As an oscillating electromagnetic field.
 - How do we describe matter? As a harmonic oscillator.
 - How do we describe the interaction? An oscillating EM field drives the harmonic oscillator.
- Review of electromagnetic radiation.
 - EM radiation: A traveling wave in the EM field that oscillates in time and space orthogonal to the direction of motion in both of the (orthogonal) E and B fields.
 - These waves have a characteristic periodicity λ called the **wavelength** that is inversely proportional to the **wavevector** k via

$$\lambda = \frac{2\pi}{k}$$

- The electric field vector $\hat{\varepsilon}$ — also known as the polarization of the light field — is orthogonal to the direction of propagation.
- Since speed is fixed, the spacial periodicity is linked to time. Hence, the period $\tau = 2\pi/\omega = 1/\nu$.
- Important equation: The variables in this equation are the most important ones we'll deal with in one form or another during this class.

$$\bar{E}(\bar{r}, t) = \hat{\varepsilon} E_0 \cos(\omega t - \bar{k} \cdot \bar{r})$$

- $\bar{\varepsilon}$ is the polarization vector.
- The electric field amplitude E_0 is our main observable, and we primarily deal with it through the intensity $I = \frac{1}{2}\varepsilon_0|E_0|^2$.
- ω is the frequency in radians per second. In class, we'll typically use $\nu = \omega/2\pi$, though.
- \bar{k} is the wavevector.
- For our model, we'll drop several of the variables to yield

$$E(t) = E_0 \cos(\omega t)$$

- We drop all vector quantities (i.e., $\hat{\varepsilon}, \bar{k}$) to simplify the math.
- We can drop the wavevector because all of the particles that the light will interact with are spatially localized in a much smaller area than the wavelength. Thus, the spatial variation of the field can be neglected.

- **Wavevector:** A vector that defines the direction in which the light travels at the speed of light. *Denoted by \mathbf{k} .*
- Molecules consist of bound charges.
 - Why is it reasonable to treat a charged particle in a molecule as a harmonic oscillator? Because electrons and nuclei in molecules have well defined equilibria and thus feel a restoring force when a field pushes them away from equilibrium.
 - Example: For nuclei, bond length is a balance between attractive and repulsive forces (think Lennard-Jones potential).
 - Example: For electrons, orbitals represent a distribution that can be distorted.
 - Example: For nuclear and electronic spins, a magnetic field aligns spins with the field and a secondary radio-frequency field tries to flip them.
- Relating bound charge variables to harmonic oscillator variables.
 - We approximate the very bottom of the Lennard-Jones potential well as a parabola. This is justified by the Taylor series expansion of the potential at the minimum.
 - The curvature at the bottom is the force constant in a harmonic potential.

$$F_{\text{res}} = -\frac{\partial V}{\partial x} = -kQ$$

- Note that Q is the displacement from equilibrium.
- Assembling the classical model.
 - Derive an equation of motion for the charged particle of mass m : Use $F = ma$.
 - Inputs:
 - Light: $E(t) = E_0 \cos(\omega t)$.
 - Matter: $F_{\text{res}} = -kQ$.
 - Interaction: $F_{\text{ext}} = qE(t) = qE_0 \cos(\omega t)$.
 - Expanding Newton's second law with the inputs, we obtain

$$m \frac{\partial^2 Q}{\partial t^2} = F_{\text{res}} + F_{\text{ext}}$$

- To rationalize the final harmonic oscillator result, let's slowly add in different contributions to the force instead of starting all at once.
 - We'll do this in three steps: No external force, damping, and damping plus external driving force.
- Harmonic oscillator with no external force.
 - The equation of motion is
 - $$m \frac{\partial^2 Q}{\partial t^2} + kQ = 0$$
 - The solution is
 - $$Q(t) = A \sin(\omega_0 t) + B \cos(\omega_0 t)$$
 - where $\omega_0 = \sqrt{k/m}$ is the **harmonic frequency** of the oscillator.
 - The exact nature of the solution will depend on initial conditions.
 - If we hold the particle away from equilibrium and release it at $t = 0$, we'll need cosine.
 - If we kick it away from equilibrium at $t = 0$, we'll need sine.
 - For now, we'll consider only the sine solutions (i.e., take $B = 0$).

- Harmonic oscillator with damping.

- The equation of motion is

$$m \frac{\partial^2 Q}{\partial t^2} = F_{\text{res}} + F_{\text{damp}} = -kQ - b \frac{\partial Q}{\partial t}$$

- This harmonic oscillator doesn't just oscillate periodically forever, but dissipates its energy at a characteristic rate b .
 - Two reasons to include damping.

- It simplifies the math a bit.
 - It tells us how irreversible relaxation processes influence spectra (we'll measure this in our NMR experiment). Think about it as a correction for physical reality: No harmonic oscillator is a perpetual motion machine, i.e., they all lose energy to friction, heat, or something else.
 - The solution is

$$Q(t) = Ae^{-\gamma t} \sin(\Omega_0 t)$$

with **reduced frequency** and **damping constant**

$$\Omega_0 = \sqrt{\omega_0^2 - \gamma^2} \quad \gamma = \frac{b}{2m}$$

respectively.

- In our scenario, we'll imagine that damping is weak, i.e., that $\omega_0 \gg \gamma$ so that $\Omega_0 \approx \omega_0$.

- Harmonic oscillator with the external driving force.

- The equation of motion is

$$\begin{aligned} m \frac{\partial^2 Q}{\partial t^2} &= F_{\text{res}} + F_{\text{damp}} + F_{\text{ext}} \\ &= -kQ - b \frac{\partial Q}{\partial t} + F_{\text{ext}} \\ \frac{\partial^2 Q}{\partial t^2} + 2\gamma \frac{\partial Q}{\partial t} + \omega_0^2 Q &= \frac{F_0}{m} \cos \omega t \end{aligned}$$

- Note that we have defined $F_0 = qE_0$ to be the maximum force that the field exerts on the oscillator, where we recall that E_0 is the maximum magnitude (amplitude) of the electromagnetic field.

- Solution: We get a driven particle that oscillates as a sine but with a different phase. Mathematically,

$$Q(t) = A \sin(\omega t + \beta)$$

where

$$A = \frac{F_0}{2m\omega_0} \frac{1}{\sqrt{(\omega_0 - \omega)^2 + \gamma^2}} \quad \tan \beta = \frac{\omega_0^2 - \omega^2}{2\gamma\omega}$$

- Observations:

- When we're **on resonance**, we get the largest displacement of the particle by the field. This is the most efficient point at which we can drive the charged particle to move. This is evident from the denominator of A (i.e., A is maximized when $\omega_0 - \omega = 0$).
 - The particle oscillates at the driving frequency ω , not ω_0 .
 - The particle oscillates 90° out of phase with the external force field when on resonance.

- **On resonance** (oscillation): An oscillation for which the driving frequency of the external field matches the natural resonance frequency of the harmonic oscillator, i.e., $\omega \approx \omega_0$.

- Now we can actually go and calculate an absorption spectrum.

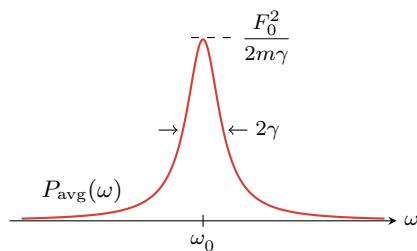


Figure 1.3: Lorentzian lineshape.

- We do this by calculating the power absorbed by the oscillator.
 - We take power = force \times velocity and, as a time-dependent quantity, average it over one cycle.
 - Mathematically, we get
- $$P_{\text{avg}} = \left\langle F(t) \cdot \frac{\partial Q}{\partial t} \right\rangle_{\text{avg}} = \frac{\gamma F_0^2}{2m} \frac{1}{(\omega - \omega_0)^2 + \gamma^2}$$
- Note that the resonance denominator implies that P_{avg} is maximized when the particle is on resonance.
 - The curve $P_{\text{avg}}(\omega)$ is a **Lorentzian lineshape**.
 - The peak is at the resonance frequency ω_0 .
 - The width is twice the damping coefficient when we define the width to be the “full width of the line at half of the maximum height.”
 - The amplitude is related to the square of the maximum magnitude of the driving force, as well as corrections for the mass and the damping coefficient. Alternatively, the area under the curve is $\pi F_0^2 / 4m$.
 - Thus, we have related three important parameters in our model — which is meant to represent molecules — to the spectrum.
 - So how does this model help us study molecules quantitatively?
 - First and foremost, the model provides a dynamic interpretation of spectroscopy.
 - There are experimental observables such as the line width, resonance frequency, and amplitude that are directly related to molecular observables.
 - Most of these results are directly applicable to molecules. These classical analogies work quite well in many cases. Some modifications are needed in more sophisticated cases, though. For example, for multiple particles and charges, we (1) replace the mass with the reduced mass and (2) integrate point charges into the dipole moment.
 - Example of the model helping us: Analysis of the IR spectrum of ethyl acetate.

- Suppose we want to learn a bit more about the C=O bond.
- Observe that $\bar{\nu} \approx 1750 \text{ cm}^{-1}$ and the line width is about 30 cm^{-1} for the C=O absorption.
- Since $\bar{\nu} = \nu c = \omega_0 / 2\pi c$, the vibrational period of the C=O bond is $\tau = 1/\nu = 2\pi/\omega_0 \approx 19 \text{ fs}$.
- k , the curvature of the C=O potential, tells us the bond stiffness (which is closely related to bond strength and bond order) is $k = m_R \omega_0^2$.
- γ tells us the energy dissipation time. Invert the line width (i.e., take $1/\gamma$) to get an effective time scale for the time to dissipate the energy you put into the bond (about 2 ps). Thus, if you kick the bond, it's going to oscillate many times (every 19 fs) before it dissipates half its energy (in 2000 fs).

- In addition to analytical power, the model gives us predictive power.
 - How can we be confident in our vibrational assignment? The model predicts an isotope effect, i.e., that the resonance frequency ω_0 will scale inversely with the reduced mass m_R via

$$\omega_0 = \sqrt{\frac{k}{m_R}}$$
 - Example (comparing two molecules): If we know one molecule's resonance frequency, we can predict another via

$$\frac{\bar{\nu}_1}{\bar{\nu}_2} = \sqrt{\frac{m_{R,2}}{m_{R,1}}}$$
 - Example: $m_R(\text{H}^{35}\text{Cl}) = 0.97$ and $m_R(\text{D}^{35}\text{Cl}) = 1.89$, so if $\bar{\nu}$ for $^1\text{H}^{35}\text{Cl}$ is 2890 cm^{-1} , we predict that $\bar{\nu}$ for $^2\text{H}^{35}\text{Cl}$ is 2070 cm^{-1} , and indeed that is very close to the measured value.
- What, molecularly, gives rise to F_0 ?
 - Molecules are different than the case of a single bound charge because (1) they contain many bound charges (multiple protons and electrons) and (2) they are neutral overall.
 - However, the distribution of these charges in space (the **dipole moment**) can be influenced and changed by the light field.
 - Thus, we want to understand the forces that the electromagnetic field exerts on the dipole moment.
 - The force exerted by the electric field on the dipole can be derived from the potential energy. We know from classical mechanics that the potential energy of a dipole in an electric field is $V = -\bar{\mu} \cdot \vec{E}$ and that $F = -\partial V / \partial Q$, so we must have

$$F = -\frac{\partial V}{\partial Q} = \left(\frac{\partial \bar{\mu}}{\partial Q} \right) \cdot \vec{E}$$

- The final expression implies that in order for the force exerted by the EM field on the molecule to be nonzero, the dipole moment must change with molecular coordinate being driven.
- Example: CO_2 is such a strong absorber of IR radiation even though its nonpolar because it's *bending* mode breaks the symmetry and allows its dipole to change.

- **Dipole moment:** The distribution of the charges in a molecule in space. Denoted by $\mu, \bar{\mu}$. Given by

$$\bar{\mu} = \sum_{i \text{ charges}} q_i \bar{r}_i$$

- This is a vector quantity.
- Light inducing a dipole change.

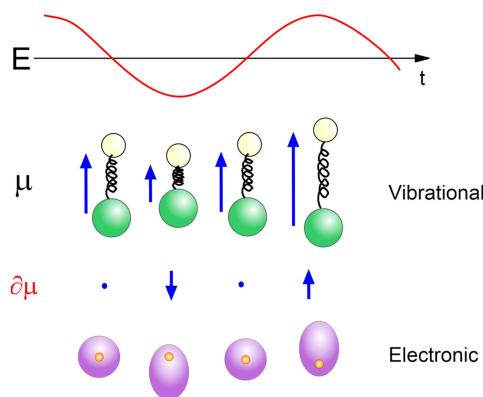


Figure 1.4: Light inducing a dipole change.

- The largest forces on the bond occur at the extrema of the field.
 - A very similar thing happens in electronic spectroscopy. There, though, we don't have a *bond* vibration but assume that the overall *electron cloud* of an atom is polarizable and can oscillate.
 - The interaction depends on alignment.
 - E oscillates along the polarization vector $\hat{\varepsilon}$.
 - The interaction depends on the alignment of the dipole $\bar{\mu}$ with $\hat{\varepsilon}$.
 - The strongest interaction occurs when the dipole moments of the molecules are aligned with the polarization of the electric field, but if they're orthogonal, then they don't interact at all.
 - Thus, we need a dot product, and we take
- $$F_{\text{ext}}(t) = \left| \frac{\partial \bar{\mu}}{\partial Q} \right| \cdot \bar{E}(t) \quad F_0 = \frac{\partial \mu}{\partial Q} E_0 \cos \theta$$
- In a sample of many molecules, we have to average over all of them.
 - Used to investigate...
 - The orientation of bonds in crystals;
 - Rotational motion in liquids or gas.
 - Absorption through rotation of a dipole.



Figure 1.5: Absorption through rotation of a dipole.

- The rotational period has to align with the light period in order for the vibration to be driven.
- This is the origin of rotational spectroscopy.
- Summary.
 - We've developed a classical model for the interaction of a resonant field with charged particles.
 - The observables in an absorption spectrum when classically described are the...
 - Resonance frequency $\omega_0 = \sqrt{k/m}$ where ω_0 is both the natural periodic motion that displaces charges and the spectrum peak position, and k is the quantum mechanical electronic structure holding the molecule together.
 - Line width γ : Irreversible chemical relaxation processes and chemical rate processes.
 - Peak amplitude: A proxy for the **extinction coefficient** ε .

$$\frac{F_0^2}{2m\gamma} = \frac{I}{m\varepsilon_0\gamma} \left| \frac{\partial \bar{\mu}(\omega)}{\partial Q} \right|^2 \langle \cos^2 \theta \rangle$$

Week 2

Interpreting Spectra

2.1 Lecture 3: Time, Frequency, and Fourier Transforms

1/10:

- Frequency- and time-domain spectroscopy.
 - Two ways of extracting the same information.
 1. Absorption spectrum (frequency domain).
 - Vary frequency of driving field or disperse white light after passing through the sample and look at each frequency component.
 - Measure the power absorbed for different frequencies.
 - Tells us the resonance frequency, how strongly the light interacts with the matter, and damping times or relaxation processes.
 2. Pulsed excitation (time domain).
 - Apply a pulsed driving force.
 - Measure resultant periodic oscillation and relaxation.
 - This is the basis for modern NMR and FTIR instruments.
 - Both represent the time-dependent behavior of a molecule.
- A powerful reason to use the time domain is the formal relationship between time and frequency data, the **Fourier transform**.
- **Fourier transform:** A formal relationship between the time domain and the frequency domain.
 - Underlying idea: Any function can be expressed as a sum of sines and cosines, i.e.,
$$F(t) = \sum_{n=1}^{\infty} [a_n \cos(n\bar{\omega}t) + b_n \sin(n\bar{\omega}t)]$$
 - In practice, sample N points over a period T .
 - The values of time at which we sample are $t = n\delta t$ for $n = 1, \dots, m$.
 - Numerical analysis: Expand in harmonics of base frequency, i.e., we let $\bar{\omega} = \pi/T$ be 1/2 cycle of T . The harmonics are $n\bar{\omega}$ for $n = 1$ to N . We thus have as many harmonics as we do data points.
 - Then we plot the expansion coefficients vs. the frequency, and that is the spectrum in the series of expansion coefficients.
 - There's more to it than this, but this is the basic concept.
 - Also, this is only a discrete data set.
- **Fourier analysis:** Determining the coefficients a_n, b_n .

- Fourier transform relations.
 - For continuous functions, we use Fourier transform integrals.
 - Note that although both of the following integrals are sine transforms, there also exist cosine and complex $e^{-i\omega t}$ transforms.
 - Sine and cosine transforms are used for real data; the complex form is more general.
 - To convert to the time domain $S(t)$, we write

$$S(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} \tilde{S}(\omega) \sin \omega t d\omega$$

- To convert to the frequency domain $\tilde{S}(\omega)$, we write

$$\tilde{S}(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} S(t) \sin \omega t dt$$

- Example: Damped harmonic oscillator.

$$S(t) \propto e^{-\gamma t} \sin \omega_0 t \iff \tilde{S}(\omega) \propto \frac{\gamma}{(\omega - \omega_0)^2 + \gamma^2}$$

- Parameters in the time and frequency domains.

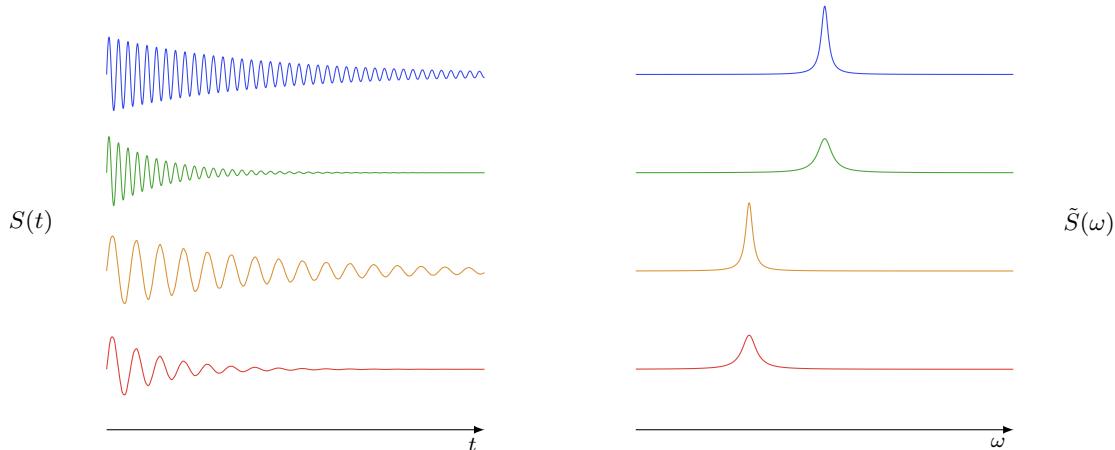


Figure 2.1: Parameters in the time and frequency domains.

Parameter	Time Domain $S(t)$	Frequency Domain $\tilde{S}(\omega)$
Large ω_0	Fast oscillations	High frequency
Small ω_0	Slow oscillations	Low frequency
Large γ	Fast decay	Broad linewidth
Small γ	Slow decay	Narrow linewidth

Table 2.1: Parameters in the time and frequency domains.

- The area under the lines remains constant.
- Notice how the lower-frequency waves (orange and red) have frequency spikes shifted down.
- Broader Lorentzian implies more different types of frequencies are present implies destructive interference takes hold more quickly implies quicker decay.

- F.T. Example: Two resonances.

- Consider a superposition of two oscillating decaying functions

$$C(t) = e^{-\gamma t} \sin(\omega_1 t) + e^{-\gamma t} \sin(\omega_2 t)$$

- This implies two resonances in the spectrum.

- In particular, they manifest as two beat frequencies, one of which is the average frequency, and the other of which is the difference.
 - The average frequency determines the regular vibrations; the difference is the bounding function.

- History of science during the French revolution.

- Lavoisier and Fourier were both strongly influenced by their time (the French revolution).
 - Lavoisier was an elite tax collector, and was sentenced to be executed. When he asked the judge for mercy, the judge said, “the Republic has no need for scientists.”
 - Fourier got into trouble with Robespierre even though he was a revolutionary, but Robespierre’s regime was overthrown a day before his scheduled execution. Thus, we get Fourier transforms!

- Fourier transform infrared spectrometer.

- Michelson Interferometer.
 - Named after UChicago’s first physics chair, also the first American to be awarded the Nobel prize in physics.
 - How it works: Intensity changes with pathlength-induced interference.
 - Incoming monochromatic waves get half reflected, half transmitted, allowing for phase separation.
 - Mathematically,

$$\Delta L = \frac{1}{\bar{\nu}} = \frac{c}{\nu} \quad \Delta t = \frac{\Delta L}{c}$$

- Thus, if our light source is emitting monochromatic light (as it should be), the intensity of the light impinging on the sample changes with the pathlength.
 - In particular, if $\Delta L = n\lambda$, there is no change in intensity, but other forms see destructive interference to varying extents.
 - A Fourier transform then takes the monochromatic wave to a Fourier transform spectrum.
 - The frequency resolution for the spectrometer is given by the scan distance is $\Delta\bar{\nu} = \pi/L_{\text{tot}}$.
 - Frequency resolution given by the scan surface.
 - For higher resolution, you need to scan farther??
 - We use an FTIR lamp (tungsten filament; broad bandwidth).
 - Broad bandwidth is the opposite of monochromatic; thus, it is difficult to obtain repeated peaks, and a Fourier transform yields substantial intensities over a range of frequencies, as expected.
- Measuring an FTIR spectrum.

- Take reference and sample scans (yielding I_0 and I data) with that broadband bulb.
 - Then take an interferogram with and without the sample.
 - Then take an experimental spectrum, which is leveled and calculated from the previous work using $T = I/I_0$ and $A = -\log T$.
 - What is experimental and what is mathematical manipulations here??

- Wrap up.
 - A spectrum originates in the time-dependent behavior of molecules driven by electromagnetic radiation.
 - It is possible to perform experiments as a function of frequency or time.
 - There are practical differences, but they encode the same information.
 - These are related by a Fourier transform.
 - Fourier transform IR spectroscopy uses interferometry to relate changing optical pathlength to optical frequency.
 - More on this??

2.2 Office Hours (Tokmakoff)

- How much do we need to know about data fitting in general? Because I haven't really done data fitting since high school. Also, is what's described in the Excel tutorial enough to get us through this class, or do we need to be able to use the other tools listed in Data Fitting Exercises.pdf, understand the statistics chit-chat, etc.?
 - Just Excel will be enough for this course.
 - Tokmakoff does recommend learning some others though just because they will be useful down the line. He believes he has a video of a former TA explaining Mathematica and he will try to post it.
- Using Solver Constraints for the Fluorescence decay?
 - Yep, that was the right thing to do.
 - Necessary in Excel; in fancier softwares, you get nicer tools for such things.
- Answers to miscellaneous questions in Data Fitting Exercises.pdf?
- Are we measuring taking a spectrum of I_2 in the liquid or gas phase? Are we doing both?
 - Doing both.
 - Electronic spectroscopy will be covered in lecture next week and will not be emphasized in the short lab report; if we choose to write our long lab report on UV-VIS, though, we will be expected to discuss it in more depth.

2.3 Lecture 4: Quantum Principles for Interpreting Molecular Spectra

1/12:

- Today's concepts should be familiar, but reviewing Chapters 5,13 of McQuarrie and Simon [1] would be appropriate at this time.
- Introducing quantum mechanical variables.
 - Classically, light resonantly interacts with the natural periodic motion of bound charges, which induces a change in the dipole moment.
 - Matching the driving force with the particles natural resonance leads to absorption of light.
 - These insights are all correct (and have a quantum analog).
 - As we've seen, a classical description says a lot about spectroscopy. However, it fails to explain many other details, and we'll need quantum mechanics to go any further.
 - Fine structure — as we'll see in our first two experiments — is an example.

- We now seek to describe quantum versions of...
 - Q : The coordinates describing the positions of electrons and nuclei.
 - E : The total energy (kinetic and potential) in the light field and the matter.
 - $\omega - \omega_0$: The resonance condition between the matter and the light.
 - $\partial\mu/\partial Q$: The transition dipole moment; the strength of the light matter interaction, i.e., how much the dipole changes as the particles move.
- Classical vs. quantum coordinates.
 - Classically, there is no restriction on the energy, position, and motion of particles.
 - In quantum mechanics...
 - The state of the system is given by a wavefunction $\Psi(r)$, which is not an observable quantity; the wavefunction only encodes the position.
 - The actual description of particle position and motion is probabilistic, given by $P(r) = |\Psi(r)|^2 dr$.
 - We understand the wavefunction and energy by solving the Schrödinger wave equation $H\psi_i = E_i\psi_i$ to describe discrete states.
 - Each state has a fixed energy (an eigenvalue E_i) and spatial configuration (an eigenstate ψ_i).
 - Unlike classical particles, these waves are extended in space, can have nodes, and can interfere constructively and destructively with each other.
 - The general state of the system $\Psi(r)$ of a system can be formed from a linear combination (or superposition) of its constituent eigenstates:

$$\Psi(r) = \sum_i c_i \psi_i(r)$$

- **Hamiltonian operator:** An operator that describes the total (potential and kinetic) energy of the system.
- Describing states and coordinates: The position and motion of nuclei and electrons.
 - For any particle (either the nucleus or an electron)...
 - The position of the particle is governed by 3 degrees of freedom — (x, y, z) or (r, θ, ϕ) — which are needed to describe the potential and kinetic energy of the particle, as well as any motion and structure.
 - Thus, N_{tot} particles implies $3N_{\text{tot}}$ degrees of freedom.
 - Understanding the energy and behavior of all of these DOFs is a tough problem, so we need strategies.
 - We now explore one such strategy.
 - In a molecule, the positions of these particles is not independent.
 - To analyze the system, let's not work in a laboratory frame but choose a molecular frame of reference.
 - We'll assign internal coordinates, define the origin as the center of mass r_0 , and place the coordinate axes along symmetry axes.
 - Recall that
- How do we separate nuclear and electronic motion?
 - Apply the **Born-Oppenheimer approximation**.

- **Born-Oppenheimer approximation:** Assume that electrons are much lighter (~ 1000 times) than the nuclei, and hence moving far more rapidly, implying that nuclear motion does not meaningfully affect electronic motion on an electronic-motion timescale and electronic motion will essentially instantaneously adapt to changes in nuclear motion on a nuclear-motion timescale.

- Implication: We can solve the electronic Schrödinger equation for a fixed/static nuclear configuration.
 - In particular, we can solve the electronic and nuclear problems separately.
 - It's hard to overstate the importance of this in simplifying our life.
 - Mathematically, if $H\Psi = E\Psi$, we can separate

$$E = E_{\text{elec}} + E_{\text{nuc}} \quad \Psi = \Psi_{\text{elec}}\Psi_{\text{nuc}}$$

- Characterizing molecular structure.



Figure 2.2: Born-Oppenheimer surfaces for H_2 .

- Born-Oppenheimer surfaces characterize bonding.
 - The curves/surfaces represent the possible ways in which electrons can interact and how the energy of the electrons in the system depends on the relative positions of the two hydrogen atoms.
 - The bonding and antibonding behavior of electrons originates from their quantum wavefunction nature since these wavefunctions can constructively and destructively interfere.
 - With respect to H_2 , the bonding and antibonding wavefunctions are, respectively,

$$\Psi^b = c_1(r)\psi_{1s}^{\text{H}1} + c_2(r)\psi_{1s}^{\text{H}2} \quad \Psi^{ab} = c_2(r)\psi_{1s}^{\text{H}1} - c_2(r)\psi_{1s}^{\text{H}2}$$

- Reason for the inversion of c_2, c_1 in the second line??
- Conclusion: The BO approximation not only yields energies but also allows us to visualize the shape/electronic states of the molecule at different separations.
- Electronic states.
 - We can generalize the approach taken above to very complex systems.
 - Examples include the MOs of H_2O , electron distribution of valence electrons in the HOMO and LUMO of chlorophyll a (one of the most important light-absorbing biological molecules) and carotenoids (other biological light-absorbing molecules), carbon nanotubes, and dyes.
 - Wavefunctions describe the electron distribution in different states.
 - The energy between the states is a lot! Circa $20\,000 - 100\,000 \text{ cm}^{-1} = 10 - 50 \text{ kJ/mol}$.

- Having dealt with electronic states, how do we deal with nuclear ones?
 - Nuclear degrees of freedom.



Figure 2.3: Modes of nuclear motion.

- Three types with respect to the center of mass.
 1. Vibration: Displacement of atoms relative to one another / COM fixed.
 2. Rotation: Motion about the COM.
 3. Translation: Motion of the COM.
 - Translation is separated out during the transformation to internal coordinates.
 - Vibration and rotation are separable independent motions.

$$E_{\text{nuc}} = E_{\text{vib}} + E_{\text{rot}}$$

$$\Psi_{\text{nuc}} = \Psi_{\text{vib}} \Psi_{\text{rot}}$$

- As we've discussed (see Figures 1.4-1.5 and the associated discussion), these are the important ones for spectroscopy.

- Nuclear degrees of freedom in molecules.

	Linear	Nonlinear
Vibrational	$3n - 5$	$3n - 6$
Rotational	2	3
Translational	3	3

Table 2.2: Nuclear DOFs in linear and nonlinear molecules.

- For a polyatomic molecule with n atoms, there are $3n$ nuclear degrees of freedom.
 - Linear and nonlinear molecules partition DOFs differently between vibration, rotation, and translation (see Table 2.2).
 - The vibrational DOFs exist as **normal modes**.

• **Normal mode:** An independent vibration that doesn't move the COM.

 - More on this later.

- Vibrations.

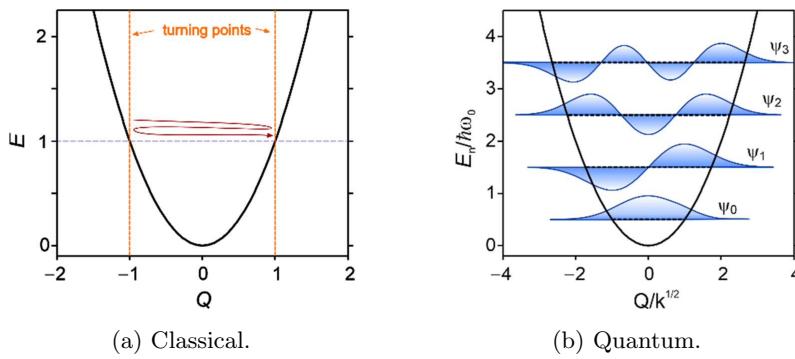


Figure 2.4: Classical vs. quantum picture of vibration.

- Classical treatment.
 - We have a quadratic potential well.
 - Any energy can be put into vibrational motion.
 - More energy means a higher displacement.
 - Motion is periodic with classical turning points.
 - Mathematically,

$$\begin{aligned} E &= V + T & Q(t) &= A \sin \omega_0 t \\ &= \frac{1}{2}kQ^2 + \frac{p^2}{2m} \end{aligned}$$

- Quantum treatment.
 - Discrete energy levels corresponding to specific vibrational states.
 - Vibrational wavefunctions ψ_{vib} of χ_n : Hermite polynomials.
 - Quantum harmonic oscillator.
 - Vibrational energy levels are given by
- $$E_{\text{vib}} = E_\nu = \hbar\nu_e \left(v + \frac{1}{2} \right)$$
- where ν_e can alternatively be expressed in either of the following forms.
- $$\nu_e = c\bar{\nu}_e \quad \nu_e = \frac{1}{2\pi} \sqrt{\frac{k}{m_R}}$$
- The right form relates energy (via ν_e) to the force constant of the harmonic oscillator.
 - Variable definitions.
 - ν_e is the vibrational frequency.
 - $v = 0, 1, 2, \dots$ is the vibrational quantum number.
 - Typically, $\bar{\nu}_e \approx 300 - 3000 \text{ cm}^{-1}$.
 - $\hbar\nu_e$ is our unit of energy (the **quantum** of energy), and $E_0 = \hbar\nu_e/2$ is the zero-point energy.
 - Recall that E_0 is derived by plugging $v = 0$ into the E_{vib} equation.
 - The spacing between adjacent vibrational levels is uniform and given by

$$\Delta E = E_\nu - E_{\nu-1} = \hbar\nu_e$$

- Rotation.

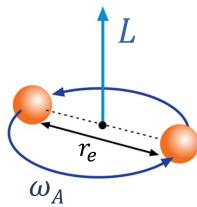


Figure 2.5: Classical rotation.

- Classically, rotation of a free object is governed by its angular momentum L , where

$$L = I\omega_A$$

- For a classical diatomic molecule...
 - The moment of inertia is $I = m_R r_e^2$;
 - The energy of free rotation is purely kinetic, given by $E_{\text{rot}} = \frac{1}{2}I\omega_A^2 = L^2/2I$.
- Quantum mechanically, these expressions still hold. However, rotational angular momentum L is quantized.
- **Quantum rigid rotor:** Rotation occurs without any vibration or other configurational change with respect to the internal coordinates.

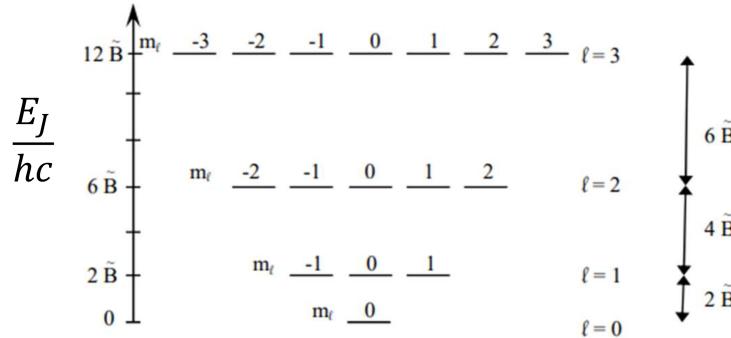


Figure 2.6: Quantum rotation.

- Rotational energy levels are given by

$$E_{\text{rot}} = \frac{L^2}{2I} = \frac{\hbar^2}{2I} J(J+1) = hc\bar{B}J(J+1)$$

- Variable definitions.
 - $J = 0, 1, 2, \dots$ is the rotational angular momentum quantum number.
 - $\bar{B} = h/8\pi^2 c I$ is the rotational constant, which typically has value between 0.1-10 cm⁻¹.
- As J increases, more and more rotational energy levels become available (see Figure 2.6).
 - Precisely, the degeneracy $g(J)$ of the J^{th} rotational energy level is $g(J) = 2J + 1$.
 - Degenerate energy levels are indexed by the azimuthal quantum number $M_J = 0, \dots, \pm J$, which has to do with the projection of the angular momentum onto the axis of rotation.
- The spacing between adjacent rotational energy levels is *not* uniform (see Figure 2.6).
 - The spacing between the M_J levels is uniform.

- Quantum mechanical energies.

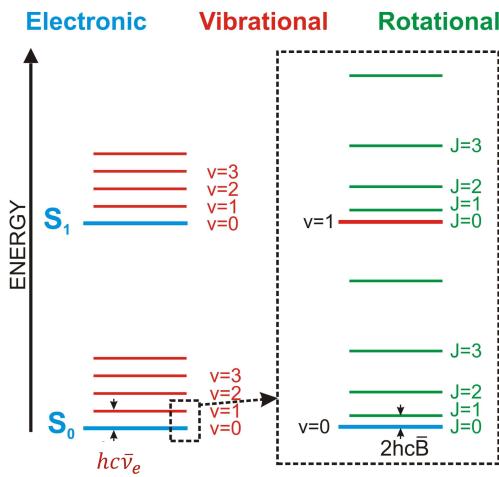


Figure 2.7: Electronic, vibrational, and rotational energy level spacing.

- Given the way that we approached the problem, we have that
$$\begin{aligned} E_{\text{tot}} &= E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + \dots \\ &= E_{\text{elec}} + h\bar{\nu}_e \left(v + \frac{1}{2} \right) + h\bar{B}J(J+1) + \dots \end{aligned}$$

 - The energy can only take on discrete values (see Figure 2.7).
 - Note that the typical energy range for...
 - E_{elec} is 10^4 - 10^5 cm $^{-1}$;
 - E_{vib} is 10^2 - 10^3 cm $^{-1}$;
 - E_{rot} is 10^{-1} - 10^1 cm $^{-1}$.
 - The scale of electronic differences, vs. vibrational differences, vs. rotational differences is shown in Figure 2.7.
 - We can summarize the state of the system from an energy point of view by specifying vibrational and rotational constants ($\bar{\nu}_e$ and \bar{B}) and their associated quantum numbers (v and J).
 - Wrap up.
 - We have taken step one toward a quantum description of spectroscopy.
 - Today: The wavefunction and energy of quantum states.
 - Next time: Add light into the mix.
 - Separation of electronic, vibrational, and rotational motion in molecules leads to independent contributions to the energy via

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} \quad \Psi = \Psi_{\text{elec}} \Psi_{\text{vib}} \Psi_{\text{rot}}$$

- For spectroscopy, we can specify the state of a molecule with E_{elec} relative to the ground electronic state, the vibrational and rotational constants $\bar{\nu}_e$ and \bar{B}_e , and associated quantum numbers.

2.4 Lab 1: UV-VIS

Ocean Optics Procedure

- This is the solution-phase experiment.

- See document for experimental procedure. No theory here (see Rowan's slides for that).
- This experiment allows us to calculate the extinction coefficient of iodine.

Lab Manual

- This is the gas-phase experiment.
- **X state:** The ground electronic state.
- **B state:** An excited electronic state.
- Purpose of the experiment: Take a 500-600 nm UV/Vis absorption spectrum of gaseous I₂, and use it to calculate several spectroscopic constants.
- Introduction to the theory.
 - Refer to Chapter 13 of McQuarrie and Simon [1] for additional context on the following.
- The energy of a spectroscopic transition (in cm⁻¹) is given by

$$\omega(v', v'', J', J'') = T'_e - T''_e + G'(v') - G''(v'') + F'(J') - F''(J'')$$

- Variable definitions (all quantities in cm⁻¹).
 - T_e is the electronic energy.
 - $G(v)$ is the energy of the vibrational energy level with vibrational quantum number v .
 - $F(J)$ is the energy of the rotational energy level with rotational quantum number J .
 - Single primes refer to the upper state (in this case, the B state) and double primes refer to the lower state (in this case, the X state).

- We set the zero of energy by defining

$$T''_e = 0$$

- To account for anharmonicity, vibrational energy levels can be written as a power series expansion in $(v + 1/2)$.

$$G(v) = \omega_e(v + 1/2) - \omega_e x_e(v + 1/2)^2 + \omega_e y_e(v + 1/2)^3 + \dots$$

- In the above equation, $\omega_e = \omega$ is the energy of the transition in wavenumbers, and x_e, y_e, \dots are anharmonicity constants.
- Similarly, rotational energy levels can be written in a power series expansion in $(J(J + 1))$.

$$F_v(J) = B_v J(J + 1) + D_v J^2(J + 1)^2 + \dots$$

- In both the vibrational and rotational expansion, we only retain enough terms to adequately fit the spectroscopic data.
- Under our experimental conditions...

- Resolution will not be good enough to resolve rotational structure. Additionally, the cubic term of $G(v)$ can be neglected. Thus, *our* form of the transition energy is

$$\begin{aligned} \omega(v', v'') &= \omega_{\text{el}} + G'(v') - G''(v'') \\ &= \omega_{\text{el}} + \omega'_e(v' + 1/2) - \omega'_e x'_e(v' + 1/2)^2 - \omega''_e(v'' + 1/2) + \omega''_e x''_e(v'' + 1/2)^2 \end{aligned}$$

where $\omega_{\text{el}} = T'_e - T''_e$.

- v, J in $(v', J'), (v'', J'')$ can take on any integer value in theory, but in practice, only a few show up.
 - Indeed, the most intense transitions will be from level $v'' = 0$ and they will decrease in intensity as v'' increases.
 - Additionally, there will be transitions to several values of v' . No *simple* rules govern the intensities.
- Also expect to see some overlap.
- Several references are listed. These describe how to analyze the spectra in more detail.
- The experimental setup and procedure is described.
- We now move into data analysis.
- We analyze the spacing between electrovibrational transitions to determine the shape of the potential energy surfaces of the X and B states of I_2 .
 - In other words, any absorption peak we observe in our recorded spectrum corresponds to promotion of an electron from some vibrational energy level $v'' = 0, 1, 2$ in the ground electronic (X) state to some vibrational energy level $v' = 0, 1, 2, \dots$ in the first excited (B) state. The spacing between these peaks allows us to calculate the necessary anharmonicity constants. We can then plug these back into a Morse potential.
- The following well-established reference points will allow us to label all peaks in our spectrum.

λ (nm)	541.2	539.0	536.9	571.6	568.6	565.6	595.7	592.0	588.5
v'	27	28	29	18	19	20	13	14	15
v''	0	0	0	1	1	1	2	2	2

Table 2.3: Established reference points in the UV/Vis spectrum of I_2 .

- As per the above, we can calculate that

$$\begin{aligned}
 \Delta\omega(v') &= \omega(v' + 1, v'') - \omega(v', v'') \\
 &= \omega_{el} + \omega'_e(v' + 3/2) - \omega'_e x'_e(v' + 3/2)^2 - \omega''_e(v'' + 1/2) + \omega''_e x''_e(v'' + 1/2)^2 \\
 &\quad - [\omega_{el} + \omega'_e(v' + 1/2) - \omega'_e x'_e(v' + 1/2)^2 - \omega''_e(v'' + 1/2) + \omega''_e x''_e(v'' + 1/2)^2] \\
 &= \omega'_e(3/2) - \omega'_e x'_e(v'^2 + 3v' + 9/4) \\
 &\quad - [\omega'_e(1/2) - \omega'_e x'_e(v'^2 + v' + 1/4)] \\
 &= \omega'_e - 2\omega'_e x'_e(v' + 1)
 \end{aligned}$$

- Thus, a **Birge-Sponer plot** can be used to calculate ω'_e and x'_e .
- **Birge-Sponer plot:** A linear plot of $\Delta\omega(v)$ vs. $v + 1$.
 - As per the above, the line of best fit should have slope $-2\omega_e x_e$ and y -intercept ω_e .
- Similarly,

$$\Delta\omega(v'') = \omega(v', v'' + 1) - \omega(v', v'') = \omega''_e - 2\omega''_e x''_e(v'' + 1)$$
 - Once again, a Birge-Sponer plot enables the calculation of ω''_e and x''_e .
- Relating $\omega'_e, \omega''_e, x'_e, x''_e$ to the Morse potential for the X and B states.

- Consider the general Morse potential function

$$U(r) = D_e(e^{-\beta(r-r_e)} - 1)^2$$

- We will take it as God-given for now that

$$D_e = \frac{\omega_e(1/x_e - x_e)}{4} \quad \beta = \sqrt{\frac{k_e}{2hcD_e}}$$

- Recall that the force constant k_e is equal to the curvature at the bottom of the well, i.e.,

$$k_e = \left(\frac{\partial^2 U(r)}{\partial r^2} \right)_{r_e} = \mu(2\pi c \omega_e)^2$$

where μ is the reduced mass of the system in question and c is the speed of light in cm s^{-1} .

- Describing dissociation.

- Recall that dissociation occurs from the ground vibrational state $v'' = 0$, not the potential energy minimum at $U(r''_e)$.
- Thus, the dissociation energy D_0 is offset from D_e by $G(0)$. In particular,

$$D_0 = D_e - G(0) = \left[\frac{\omega_e(1/x_e - x_e)}{4} \right] - \left[\frac{\omega_e}{2} - \frac{\omega_e x_e}{4} \right] = \frac{\omega_e(1/x_e - 2)}{4}$$

- Calculating the energy difference T_e between the energy minima of the X and B states.

- We have that

$$T_e = D''_e + E(I^*) - D'_e$$

where $E(I^*)$ is the energy of an excited iodine atom produced when the B state of I_2 dissociates.

- Refer to Figure 2.8 to rationalize this expression.

■ $E(I^*) \approx 7603.15 \text{ cm}^{-1}$.

- A plot summarizing all quantities discussed thus far.

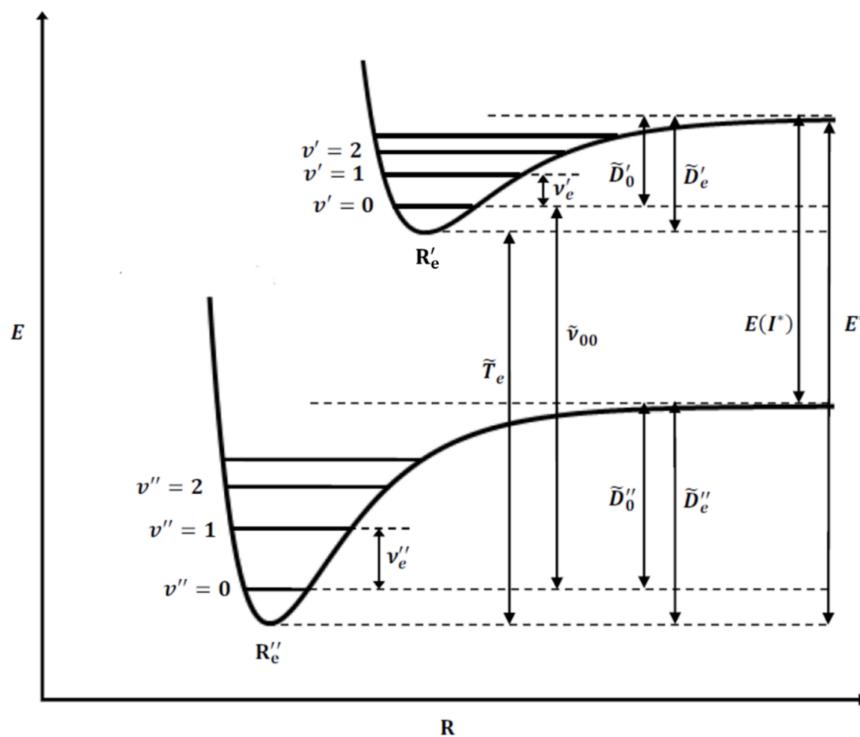


Figure 2.8: The potential curves and spectroscopic quantities pertinent to I_2 .

- The document discusses an alternate way to analyze the data using parabolic least squares regression.
- The document includes instructions for the short lab report.

Rowan's Introduction to the UV-VIS Experiment

- Reviews the basics of absorption spectroscopy, today's experimental setups, and the expected analysis.
- Information on error propagation.

Quantities from the Experiment

- The original concentration of I₂ in CHCl₃ was 0.01 M (0.1357 g in 50 mL).
- We diluted 0.7 mL of this solution to a volume of 25 mL.
 - This brought us into a region where Beer's law is linear.
- The path length (width of the cuvette) is $b = 1 \text{ cm}$.
- **Beer's law:** The following relationship, where A is peak absorbance, ε is the extinction coefficient, b is the path length, and C is the concentration. *Given by*

$$A = \varepsilon b C$$

Week 3

Molecular Parameters from Spectra

3.1 Lecture 5: Quantum Principles for Spectroscopy (Part 2)

1/17:

- Today: How *light* interacts with molecules.
- Review of the classical vs. quantum resonance criterion (driven harmonic oscillator vs. matching energy difference between states).
- Reminder of spectroscopic notation: E'' (ground state) vs. E' (excited state).
- Different types of transitions (electronic, vibrational, rotational) can be observed using different parts of the EM spectrum (UV/Vis, IR/Raman, FIR/ μ wave) as probes.
- What does light actually do?
 - Quantum mechanically, it's coupling to the eigenstates of the system.
 - Quantum eigenstates are stationary.
 - Light couples two states, dragging them together and mathematically creating a superposition.
- Example.

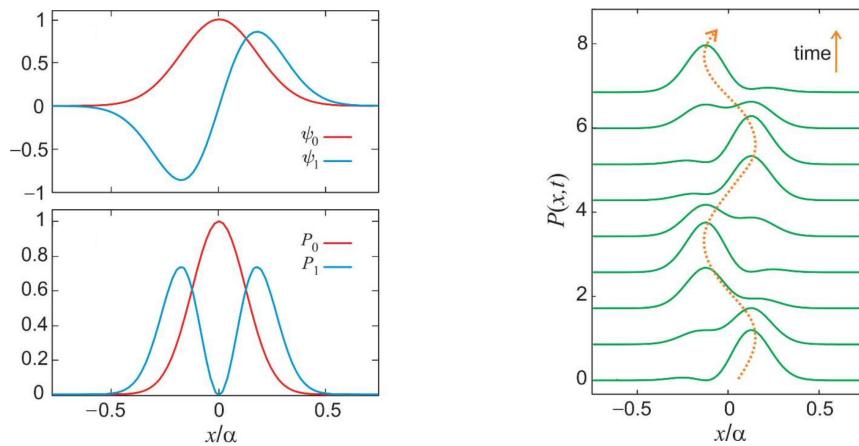


Figure 3.1: Light-induced coupling of quantum eigenstates.

- If we have two solutions to the particle in a box ψ_0, ψ_1 corresponding to the first and second energy levels, what light does is gives you a time-dependent wavefunction

$$\psi(t) = c_0(t)\psi_0 + c_1(t)\psi_1$$

- The probability that the particle is in one state or the other oscillates: Since $c_n(t) = c_n e^{-iE_n t/\hbar}$,

$$P_1 = |c_1(t)|^2 \approx \frac{\sin^2(E_1 - E_0)t}{\hbar} \quad P_2 = |c_0(t)|^2 \approx \frac{\cos^2(E_1 - E_0)t}{\hbar}$$

- Electronic degrees of freedom can be discussed in the same way.
 - Light drives electrons back and forth (as per our classical molecule), but this time, we mathematically represent this change as a coupling of the s orbital and the more elongated p orbital.
- Factors governing absorption strength.
 - Beer's law.
 - Two important factors.
 1. Extinction coefficient.
 2. Concentration.
- Quantum mechanically, absorption strength depends on state population.
 - This is also a thermodynamic/statistical question.
 - Thermal energy is distributed via the Boltzmann distribution.
 - The probability of initially occupying an excited state increases with temperature.
- Thermal energy distributes molecules through states with different rotational and vibrational states.
- Worry if $E''_{\text{rot}}, E''_{\text{vib}} \leq 2k_B T$.
- Populations at higher states will give rise to additional features in the absorption spectrum.
- Final states don't matter for us because $E_{\text{final}} \gg k_B T$.
 - The only place where final energy matters is NMR because changes are so small; this is also why NMR is performed at cryogenic conditions.
- Transition dipole moment.
 - Classical (we need a change to grab onto) v. quantum (we take our transition dipole operator and square its expected value) again.
- Selection rules.
 - Light can drive a molecule to go up or down one vibrational quantum. This is not strictly true because most oscillators are *not* harmonic oscillators. Greater transitions are called **overtones**.
 - Rotations: Same type of thing with $\Delta J = \pm 1$.

3.2 Office Hours (Moe)

- No Results and Discussion / short text summary/response section needed, right?
 - Correct; none.
- Do we need to calculate the extinction coefficient based on the Ocean Optics data?
 - We don't.
- What is the second table requested?
 - Extend the reference data table.

- Birge-Sponer plot for just v' or both v' and v'' ?
 - Do present for the excited state.
 - Create a grouped scatter plot for the ground state (5-6 data points for the value of 1, and the value of 2). Where there is overlap (i.e., everywhere we *can* calculate $\Delta\omega(v'')$, we should).
- Deriving the relationships between the Morse potential and the spectroscopic constants?
 - You would have to do all of the stuff with the Laguerre polynomials and Schrödinger equation.
- Using the NIST database?
 - Multiple database entries, look at the citations therein, and check the references in the manual.
 - Worst case, contact them for values.
- What is the value of the mercury calibration line? 5461 Å? My peak is at 5483 Å. Is this within the realm of possibility?
 - Yes it is.
 - We don't have to show this method now in the short lab report, but we would in the full lab report.
- Help with Excel graph making: IodineHighRes plot.
 - See practice plot.
- Do we need to calculate errors?
 - Yes, to the best of our ability based on what's in the manual.

3.3 Lecture 6: Infrared Vibrational-Rotational Spectroscopy

1/19:

- This is what's directly relevant to our HCl experiment.
- Point of the online lectures: Provide more context on quantum dynamics, which are often glossed over.
- Review of the partitioning of quantum mechanical energies into electronic, vibrational, rotational, etc. DOFs.
 - Different energy scales per DOF.
 - We can treat electrons separately from nuclei using the BO approximation.
 - Tokmakoff: "BO is the most important concept in molecular quantum mechanics."
 - If we zoom into the bottom of the electronic potential well, we can see vibrational and rotational energy levels as per Figures 2.6-2.7.
 - Note that this is only for one nuclear configuration! If we change the bond length, we have to redo the whole calculation.
 - We've been ignoring translational energy; if we want to understand how that influences our HCl spectrum, come talk to Tokmakoff.
- Up to this point, we've talked about how molecular parameters influence structure. Today, we do the opposite: Calculating said parameters from observables.
- Mid-IR light can induce vibrational and also rotational transitions.
- Typically, only one ground vibrational state is populated $v'' = 0$.
 - Several rotational levels may be populated.

- Simplest version of the spectrum.
 - Heteronuclear diatomic molecule modeled as a quantum harmonic oscillator and rigid rotator.
 - Under this approximation, we get equally spaced vibrational energy levels.
 - First information from vibrational spectroscopy: Strength of bonding and shape of the potential well.
 - Next, rotational energy: Gives bond length information.
- Now for the light.
 - Resonance condition: $h\nu = \Delta E$ again. Full formulas from the lab manuals written out.
- Selection rules.
 - $\Delta v = \pm 1$ and $\Delta J = \pm 1$.
 - Differing transition frequency expressions for the R- and P-branches.
 - If we're interested in the Q-branch, come talk to Tokmakoff.
- ν_e is the spacing between the ground and first vibrational energy.
- R-branch and P-branch schematic.

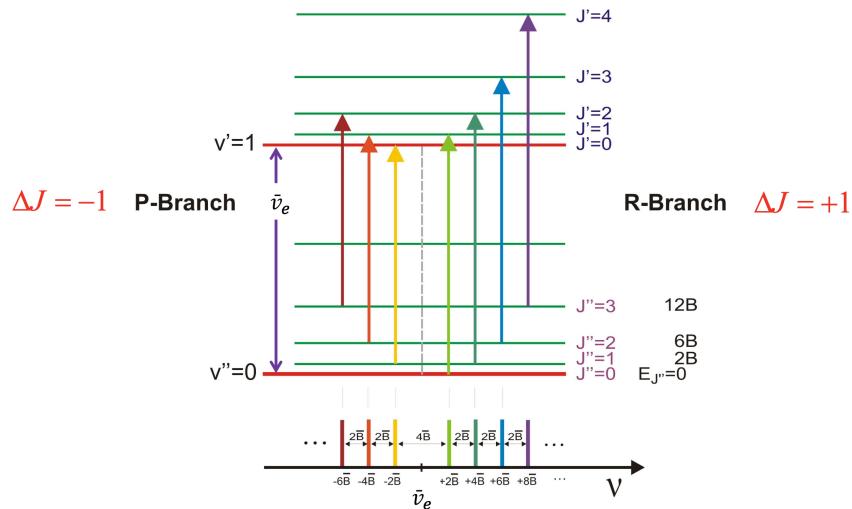


Figure 3.2: Vibrational and rotational excitations.

- Note the relationships between the selection rules and the transitions.
- On a molecular level, we'd expect all lines to have the same intensity.
 - In reality, occupation depends on temperature via the Boltzmann distribution.
 - Great graphical explanation of the rotational energy levels!
- Predicted vibrational-rotational spectrum.
 - See Figure 3.3.
 - The envelope gives you the classical structure (come talk to Tokmakoff about this).
 - There are some other things to consider, e.g., Doppler shifts.

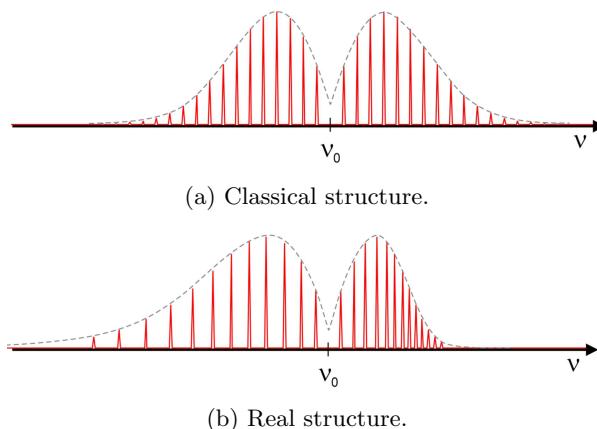


Figure 3.3: Predicted and actual P/R-branch spacing.

- In practice, our dumbbells shapes are not equally distributed. This problem is particularly bad for HCl. Asymmetry induces this.
- Vibration and rotation aren't independent.
 - Vibration-rotation coupling — if we resonantly excite a molecule, the bond length extends, the moment of inertial increases, and thus the molecules rotates more slowly.
 - The equation

$$\bar{B} = \bar{B}_e - \alpha_e \left(v + \frac{1}{2} \right)$$
 is not theoretical; α_e is the experimentalist's fudge factor to get a more accurate molecule.
 - α_e is the vibrational-rotational coupling constant.
 - Alternative: Centrifugal distortion. As the molecule spins faster, the bond length increases.

$$\bar{B} = \bar{B}_e - D_e J(J+1)$$
 – D_e is the centrifugal distortion constant.
- Vibrations aren't harmonic.
 - Especially for strongly heteronuclear molecules such as HCl.
 - Atoms don't want to collide both because of the Coulombic repulsion between nuclei and the Pauli repulsion force between the electrons not wanting to occupy the same space.
 - We account for the anharmonicity difference with another fudge factor.
 - Overtone transitions.
- Analysis of vibrational-rotational transition frequencies.
 - We use a quadratic fit.
 - The index parameter m does allow us to analyze both branches at the same time. Procedure:
 - Assign transition frequencies to J'', J', m .
 - Quadratic fit allows us to extract \bar{v}_e, B_e, α_e .
 - B_e gives you r_e .
- Morse potential.

- It's hard to describe bonding with so few parameters, but the Morse potential does about as good a job as you can do. Additionally, there are analytical expressions relating our experimental parameters to D_e, β .
- Raise in your long report discussion how much you trust (or don't trust) the Morse potential.
 - The potential gives you the dissociation energy D_e of the molecule, but we're making measurements of vibrational energy levels at the very bottom of the well. What might that do?
 - HCl has a fairly long relaxation. More weakly bonded molecules have much steeper slopes (usually $\propto r^{-6}$).
- Next video: Polyatomic molecules, perhaps including CO₂.
- The bending vibration of CO₂ has a Q-branch. Why? We should look into this.
- Another in-person lecture next Tuesday; same thing as today but for the I₂ experiment.

Week 4

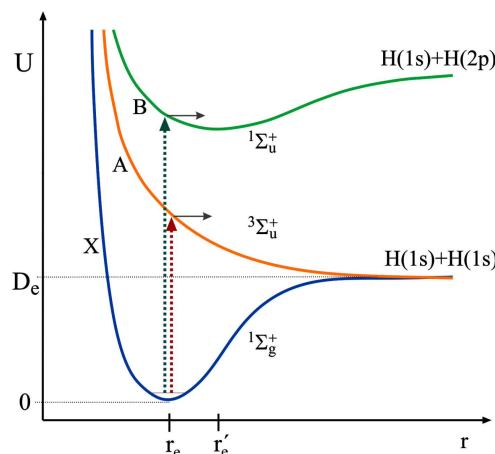
Electronic Spectroscopy

4.1 Lecture 7: Electronic Molecular Spectroscopy

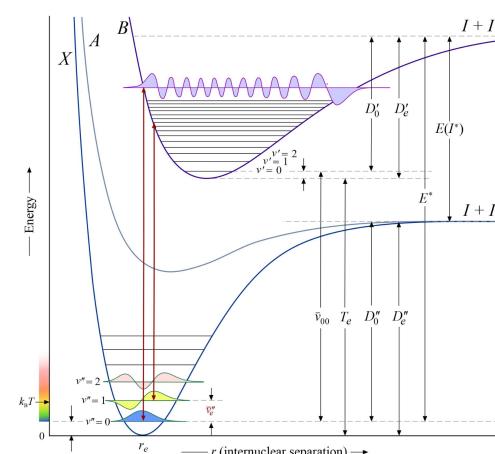
1/24:

- Lant check in on lab.
 - The clean up process is still going on; we're not getting back in the lab for the rest of the quarter. We'll still meet in Jones 108, but not use the PChem lab.
 - When cleaning up the small barometer spill, they found a much larger spill covered in dust that's been there for who knows how many years, so they're having to bring in a professional team and it will take weeks. They don't just have to get it down to OSHA levels; it's an educational environment, so the requirements are even more stringent.
 - They may or may not be able to still offer every lab.
 - Lant is open to questions.
 - Most of us should be totally fine.
 - They found a line of it behind the hood.
- Announcements.
 - No lecture on Thursday; OH then in Searle 240.
 - NMR lecture next week.
 - Detailed guidelines on the long report by the end of the week.
- Today: Electronic spectroscopy and the I₂ absorption data.
- This is electronic *molecular* spectroscopy where electrons are localized, in contrast to electronic *nano-material* spectroscopy for example.
- We focus on valence electrons.
 - These absorb UV/Vis light.
 - Light absorption changes electronic charge distribution around the molecule; a lot of energy allows you to break bonds.
 - Molecules change all states, but start in the electronic ground state.
 - We will not look at core electrons here; we'd need X-rays for that. This is atom specific.
- Types of molecular electronic transitions.
 - In organic compounds, we're usually looking at $\sigma \rightarrow \sigma^*$ or $\pi \rightarrow \pi^*$ transitions, typically in unsaturated compounds.

- In saturated compounds, it is extremely difficult to get excitations, and we have to go into the deep UV.
- Example: Coumarin 153 dye.
 - Which HOMO and LUMO change, as well as the net change in dipole.
- Inorganic spectroscopy.
 - $d \rightarrow d$ and charge transfer; related to $\text{Ru}(\text{bpy})_3^{2+}$.
- Electronic spectra of diatomic molecules.
 - Lots of fine structure: Primarily changes in vibrational quantum number.
 - The rotational constant of massive I_2 is very small; thus, we just can't resolve it here.
- Electronic spectra of diatomic molecules. *picture*
 - Transition to higher energy across potential energy surfaces.
 - **Bound vs. dissociative** surfaces.
 - **Franck-Condon principle:** The big one for electronic spectroscopy. Along the same lines as the BO approximation, we assume that electronic configuration can change/be excited much more quickly than the nuclei can move, so we fix the nuclei when we study electronic changes. Corresponds to *vertical* transitions.
 - Electronic excitation results in unstable configuration. More force on the atom as it tries to lengthen its bond causes it to vibrate more.
- Potential energy surfaces of I_2 .
 - We get a transition from the X state to the B state that increases bond length.
 - I_2 is a massively anharmonic oscillator (hard repulsive wall; softer attractive wall).
 - Vibrational spacing Δv decreases with increasing energy.
 - Different shaped potentials (different bond lengths and different vibrational splittings).
- UV/Vis spectroscopy of I_2 .



(a) Vibrational excitation.



(b) Wavefunction overlap.

Figure 4.1: Franck-Condon factors in electronic spectroscopy.

- Franck-Condon implies a vertical transition; this implies significant vibrational excitation since vertically above the equilibrium is an excited vibrational state.
 - In particular, we get excitation to the classical turning point.
- We need good overlap between vibrational wavefunctions to get excitation (also by Franck-Condon).
- There are resonances with many states, especially since higher-energy vibrational states are so tightly spaced. This is what gives vibrational fine structure.
- The transition spacing converges on the dissociation energy. From the 0-0 transition ($v'' = v' = 0$) and convergence limit, we can get D'_0 .
- Low frequency vibration of the X state implies that $v'' = 1, 2$ will be thermally occupied as well. This allows access to lower vibrational excited states because this wavefunction extends farther and can overlap with lower.
- There is also an excited A state between the X and the B state.
- To measure $v'' = 0$ transitions all the way down, you need to eliminate the hot bands. To do this, cool your sample down to a few degrees kelvin (reduces thermal occupation of higher states).
- Reconstructing a potential from absorption spectra.
 - Can't resolve rotational transitions.
 - The sawtooth structure hides the rotational transitions.
 - Assign transitions.
 - Use spacing to get information.
 - The frequency of the transition is related to the bare electronic transition, plus vibrational fine structure.
- Tons of good stuff on UV-Vis that may be worth rewatching at some point!!!
- Isolate X and B state frequencies.
 - Changes in v' vs. v'' .
 - You can go from frequencies to dissociation constants with additional equations.
- **Birge-Sponer plot:** A plot of the vibrational frequency vs. the final vibrational quantum number.
 - At higher and higher vibrational quantum numbers, we get closer to the dissociation threshold and see deviation from linearity.
 - If it deviates to higher vibrational quantum numbers, the potential is a bit softer; otherwise, it's a bit steeper.
 - The y -intercept also tells you the maximum transition you can get to before dissociating.
- Selection rules for electronic spectroscopy.
 - We won't have to analyze intensity, but it does convey a lot of important information.
 - Absorption requires that resonance creates changes in electronic charge density, i.e.,

$$\frac{\partial \mu}{\partial q} \neq 0$$

- Technically, we need a change in parity/inversion from $u \leftrightarrow g$.
- Transition probability involves nuclear and electronic degrees of freedom.
- Vibrational wave functions are on different electronic surfaces.
- Related to both the electronic transition dipole moment and the Franck-Condon overlap integral.

- Thus, the maximum intensity tells us about the displacement between r_e'' and r_e' .
- Franck-Condon factors (FCF's) for harmonic oscillators are discussed.
- We can talk to Tokmakoff about this if we *want* to do it in our report.
- After absorption.
 - A word on fluorescence (useful for later experiments).
 - Energy has to dissipate to return to equilibrium.
 - Options.
 - Energy transfer and relaxation processes (within and between molecules).
 - Electron transfer.
 - Photochemistry.
 - Radiative relaxation.
 - High probability/fast processes dominate.
- Relaxation of electronic states.

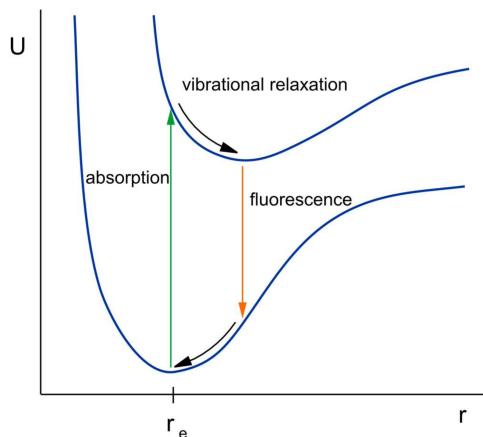


Figure 4.2: UV/Vis fluorescence.

- We get a displacement of charge and a new equilibrium nuclear separation.
- More vibrational energy is dissipated nonradiatively.
- A huge amount of energy is released to the ground state, typically through fluorescence.
- Naturally, fluorescence is always red-shifted relative to absorption.
- We call the red shift the **Stokes shift** and denote it by 2λ .

4.2 Lab 2: FT-IR

Lab Manual

- Plan.
 - Investigate the relationships between the energies of spectral lines and the rovibrational properties of the studied molecules.
 - In particular, study $\text{HCl}_{(\text{g})}$.
 - Determine the bond length of HCl.

- Classical picture of molecules.
 - Picture two point charges $\pm q$ separated by a distance l .
 - By definition, the electric dipole moment is ql .
 - ql changes as the molecule vibrates.
 - If light waves strike the molecule and their frequency ν is equal to the normal vibration frequency of the molecule, they will drive the oscillatory motion and thus light will be absorbed and converted into vibrational energy.
 - Covers the harmonic oscillator treatment/derivation.
- Quantum picture of molecules.
 - There are allowed but discrete amounts of vibrational and rotational energy which a diatomic molecule may have in its stationary nonradiating states.
- Diatomic molecules.
 - Quantum harmonic oscillator: Can exist in the following energy levels, where $\bar{\nu}_e = \nu/c$ is the fundamental frequency of the oscillator expressed in wavenumbers (cm^{-1}) and $v = 0, 1, 2, \dots$ is the vibrational quantum number.

$$E_v(\text{vib}) = hc\bar{\nu}_e \left(v + \frac{1}{2} \right)$$

- Quantum rigid rotator: Can exist in the following energy levels, where $B_e = h/8\pi^2cI$ is the rotational constant (in cm^{-1}), $I = \mu r_e^2$ is the moment of inertia, r_e is the equilibrium internuclear separation, and J is the rotational angular momentum quantum number.

$$E_J(\text{rot}) = hcB_eJ(J+1)$$

- For a diatomic molecule that is vibrating harmonically with an amplitude much smaller than the bond length and rotating as a rigid body, the total energy of vibration and rotation is given by

$$E_{v,J} = E_v(\text{vib}) + E_J(\text{rot}) = hc \left[\bar{\nu}_e \left(v + \frac{1}{2} \right) + B_e J(J+1) \right]$$

- Selection rules determine that for IR rovibrational spectroscopy, v changes by $+1$ and J can change by ± 1 .

■ This leads to the **R-branch** and **P-branch**.

- The R- and P-branch equations are linear in $J'' + 1$ and $-J''$, respectively. Thus, plots of these quantities vs. wavenumbers follow a linear regression, allowing for experimental determination of $\bar{\nu}_e$ and B_e .
- Real vibration potentials are not fully harmonic. We can adjust the vibrational energies with a multiplied term containing a dimensionless positive anharmonicity constant $x_e \ll 1$.

$$E_v = hc\bar{\nu}_e \left(v + \frac{1}{2} \right) \left[1 - x_e \left(v + \frac{1}{2} \right) \right]$$

■ x_e describes how the vibrational energy level spacing decreases as v grows in anharmonic vibrations.

- Similarly, real molecules are not entirely rigid as they rotate. We can adjust the rotational energies by accounting for the extent to which B_e changes as the moment of inertia changes; I will change more at higher v , so we take

$$B_v = B_e - \alpha \left(v + \frac{1}{2} \right)$$

- $\alpha_e \ll B_e$ is a positive number.
- The new rotational energy levels are $E_{J,v}(\text{rot}) = hcB_v J(J+1)$.
- It follows that the corrected...
- Total energy is...

$$E_{v,J} = hc \left\{ \bar{\nu}_e \left(v + \frac{1}{2} \right) \left[1 - x_e \left(v + \frac{1}{2} \right) \right] + B_e J(J+1) - \alpha_e \left(v + \frac{1}{2} \right) J(J+1) \right\}$$

- R-branch expression is...

$$\bar{\nu} = \bar{\nu}_e(1 - 2x_e) + (2B_e - 3\alpha_e) + J''(2B_e - 4\alpha_e) - J''^2 \alpha_e$$

- P-branch expression is...

$$\bar{\nu} = \bar{\nu}_e(1 - 2x_e) - J''(2B_e - 2\alpha_e) - J''^2 \alpha_e$$

– As before, a fit of this plot (this time, a quadratic fit) can be used to calculate $\bar{\nu}_e, B_e, \alpha_e$.

- **R-branch:** The set of rovibrational transitions corresponding to $\Delta J = +1$. *Given by*

$$\bar{\nu} = \bar{\nu}_e + 2B_e(J'' + 1)$$

- Derivation.

$$\begin{aligned} \bar{\nu} &= \frac{\Delta E}{hc} \\ &= \frac{E_{v',J'} - E_{v'',J''}}{hc} \\ &= \left[\bar{\nu}_e \left(v'' + 1 + \frac{1}{2} \right) + B_e(J'' + 1)(J'' + 2) \right] - \left[\bar{\nu}_e \left(v'' + \frac{1}{2} \right) + B_e J''(J'' + 1) \right] \\ &= \bar{\nu}_e + B_e(J'' + 1)[(J'' + 2) - J''] \\ &= \bar{\nu}_e + 2B_e(J'' + 1) \end{aligned}$$

- **P-branch:** The set of rovibrational transitions corresponding to $\Delta J = -1$. *Given by*

$$\bar{\nu} = \bar{\nu}_e - 2B_e J''$$

- A similar derivation to that for the R-branch applies here.

- Fourier transform spectroscopy.

– Difference from a grating spectrometer: All wavelengths are measured simultaneously; computer processing performs an FFT on the raw data later to decompose it into its component wavelengths and their respective intensities.

- Advantages of FT-IR.

1. Substantially better signal-to-noise ratio.
 - Math in here??
 2. The light throughput can be much larger because the Michelson interferometer in an FT-IR machine does not require the narrow entrance and exit slits of the monochromator.
 3. Computers do the data processing.
- FT-IR is useful for samples with very high and very low absorption bands, e.g., catalyst molecules on a surface.

Week 5

Magnetic Resonance Spectroscopy

5.1 Lecture 8: Magnetic Resonance Spectroscopy

1/31:

- Refer to Chapter 14 of McQuarrie and Simon [1].
- There is both NMR (nuclear magnetic resonance) and ESR (electron spin resonance) or EPR (electron paramagnetic resonance).
 - The last two are the same thing.
- Two fields: The static magnetic field, and the probing *electromagnetic* field.
- Derivation of quantized angular momentum.
 - In molecules, there is a multiplicity/degeneracy of states that grows as $2J+1$. They have quantized angular momentum.
 - So is the orbital angular momentum of electrons!
 - Putting atoms into a magnetic field *creates* the anisotropy necessary for discussing the z -component (or any coordinate component) of angular momentum.
 - Spin angular momentum: Just means that the objects (e.g., electrons and nuclei) have a property that looks a lot like spin and/or angular momentum.
 - We say that each nucleon has a spin of $1/2$. Protons and neutrons add separately.
 - Even number of protons and neutrons? Spin 0.
 - Mixed even/odd? We have actual nuclear spin.
 - We need a nucleus like this to detect!
 - Odd/odd? We have 0 spin again.
 - We focus on spin $1/2$ particles. These have two degenerate energy states that split in a magnetic field.
- Classical picture of spin angular momentum.
 - Picture a charged particle with angular momentum. The circulating charge produced a magnetic field which aligns along the direction of the angular momentum.
 - Indeed, a spinning charged particle behaves like a dipole.
 - $\gamma = 2mc$ is the **gyromagnetic ratio**.
- Quantum spin angular momentum.
 - Basically the same thing; we just rephrase everything from before in the language of operators.
- **Zeeman effect:** Two energy levels split with increasing B .

- **Larmor frequency:** The frequency $\nu = \gamma B / 2\pi$ in the radio frequency range that induces a shift.
- Typical operating conditions.
 - NMR vs. ESR: NMR has a stronger magnetic field, longer EM excitation radio waves, and significantly lower gyromagnetic ratios.
 - There is only a tiny difference between nuclear state occupation at room temperature; hence supercooling to get something detectable.
- What is the magnetic dipole doing in the magnetic field?
 - No constraints on the x and y components of I .
 - A dipole in a field experiences a torque.
 - Dipole precesses around B at the Larmor frequency ν .
 - FT-NMR spectrometers use pulsed rf fields to synchronize and detect the procession of spins.
- Lots of good extension material on NMR; also worth rewatching at some point!

5.2 Lecture 9: Magnetic Resonance Spectroscopy 2

- 2/2:
- Summary of last time.
 - The quantity that we're measuring is spin angular momentum \bar{I} , which is a vector quantity.

$$|\bar{I}| = \hbar\sqrt{I(I+1)}$$
 where $I = 1/2$ is the nuclear spin quantum number.
 - The other quantity of concern is the projection $I_z = m_I \hbar$ where $m_i = \pm 1/2$.
 - In a magnetic field, we break degeneracy, getting $E(m_I) = -\gamma_N \hbar m_I B$ and $\Delta E = -\gamma_N \hbar B$.
 - Electromagnetic resonance is achieved when the frequency ν of incident radiation satisfies $\hbar\nu = \Delta E$.
 - The interest in chemistry: Chemical shift.
 - There are small variations in the frequency for different types of protons depending on the surrounding electron density.
 - Measured frequency depends on effective magnetic field.
 - Shielding: The influence of electrons around the nucleus on the effective magnetic field.
 - The effective field is smaller than the applied field.
 - Shielding *decreases* the splitting (this is why nearby highly polar groups lead to large shifts, while alkanes have small shifts).
 - Measuring the chemical shift.
 - We measure the difference in the Larmor frequency relative to a standard (TMS).
 - Shielding is a small effect (on the order of 10^{-6} , so we use ppm δ).
 - Example: 1 ppm at 500 MHz is $\nu = 500$ Hz, which is tiny (on the order of microjoules).
 - Chemical shift charts (from OChem) are included in the slides.
 - FT-NMR spectrometers.
 - How do we make these measurements?
 - NMR spectrometers are almost all working in FT mode these days.

- They use pulsed radiofrequency (r.f.) fields and detect the precession of spins.
 - Precession of one spin in a magnetic field occurs at the Larmor frequency.
 - Applying an excitation field creates a superposition of $m_s = \pm 1/2$ states. The net dipole is now perpendicular, and precesses that way (i.e., in the xy plane) in a mathematically describable fashion.
 - Putting your superconducting coil along the x - or y -axis allows you to detect changes.
- **Magnetization:** The macroscopic alignment of magnetic dipoles $\bar{M} = \sum \bar{\mu}$.
 - At equilibrium, \bar{M} aligns along \bar{B} .
 - An rf field rotates magnetization to x : This is a **$\pi/2$ -pulse** or a **90°-pulse**.
 - We detect precessing magnetization and return to equilibrium during the **free-induction decay**. An FT of the decay then generates our spectrum.
- Relaxation mechanism.
 - Spin state lifetime (T_1).
 - “Spin-lattice” or “longitudinal” relaxation.
 - Recovery of the magnetization along z .
 - A molecular property.
 - Transfer of energy to the environment.
 - The return of magnetization to equilibrium has a characteristic time constant T_1 which appears in the time vs. relaxation plot $1 - e^{-t/T_1}$.
 - Dephasing (T_2).
 - “Transverse” relaxation.
 - Loss of magnetization in the xy -plane of many different sources.
 - We have the loss described by e^{-t/T_2} .
 - These two processes are not independent.
- There are numerous types of NMR experiments.
 - In our lab, we just scratch the surface.
 - We use a population inversion to measure T_1 .
 - **π -pulse** to invert magnetization.
 - Wait for relaxation.
 - Read out following another **$\pi/2$ -pulse**.
 - Two-dimensional spectroscopy.
 - Heteronuclear single quantum coherence spectroscopy (HSQC).
 - Excite ^1H ; transfer its magnetization to ^{13}C , which is nice because ^{13}C is hard to excite on its own.
 - Transfer back to ^1H and detect.
 - Tells us which protons transfer magnetization.

5.3 Lab 3: NMR

Lab Manual

- Modern NMR is performed in the time-domain, and frequency-domain spectra are obtained via Fourier Transformation of the data.
- Goal: Apply FT-NMR to investigate relaxation processes in liquids.

- Use an NMR technique called inversion recovery to determine the spin-lattice relaxation times T_1 for ^{13}C in n-hexanol, hexanoic acid, hexylamine, hexane thiol, or bromohexane.
- NMR basics (misc. notes).
 - Review from Chapter 14 of McQuarrie and Simon [1].
 - Definitions of the **Zeeman Hamiltonian** and **Zeeman levels** are new.
 - $\Delta E = -\gamma\hbar B_0$ gives only a static picture of nuclear interaction with the magnetic field. In reality, a single nucleus remains in a certain state no longer than a time T_1 on average.
 - A nuclear spin exposed to a magnetic field B_0 tends to “align” with said field. It’s not so much aligning, though, as it is acting like a gyroscope in a gravitational field; indeed, it will precess about the direction of B_0 with a characteristic frequency ω .
 - To rigorously treat the populations of the ground and excited spin states, we consider an **ensemble** of nuclei and the resultant thermodynamic argument.
 - The **total magnetization** takes the form of a vector aligned in the direction of B_0 (which is Z; there is no net magnetization in the XY-plane).
 - An alternating transmitter field B_1 “tips” the magnet from its equilibrium position by driving the Larmor precession. The angle α through which \mathbf{M} is tipped depends, via the following relation, on the strength of B_1 and the length of time t_p during which B_1 is applied.

$$\alpha = -\gamma B_1 t_p$$

- Immediately following this process, the transverse components M_X, M_Y decay to zero with a time constant T_2 , and the longitudinal component M_Z is restored to its equilibrium value with time constant T_1 .
- As with general time constants (which tend to be exponential factors), it will take much longer than T_1 for equilibrium to be “restored.”
- **Zeeman Hamiltonian:** The Hamiltonian operator relevant to nuclear magnetic spins. *Denoted by \mathcal{H}_Z . Given by*

$$\mathcal{H}_Z = -\mu \cdot B_0 = -B_0 I \gamma \hbar$$
- **Zeeman levels:** The $2I + 1$ energy levels $E(m) = -B_0 \gamma \hbar m$, where $m = -I, -I + 1, \dots, I$.
- **Spin-lattice relaxation time:** The average time for which a single nucleus remains in a certain state. *Denoted by T_1 .*
- **Spin-spin relaxation time:** A type of interaction that occurs between different spins. *Denoted by T_2 .*
- **Larmor frequency:** The characteristic frequency of a given nucleus at which it precesses in a magnetic field. *Denoted by ω .*
- **Total magnetization:** The vector sum of all the magnetic moments. *Denoted by \mathbf{M} .*
- **FT-NMR (pulsed NMR).**
 - Experiment: A strong transmitter field B_1 is applied for a short time t_p .
 - Specifically, since the transverse magnetization has its maximum when $\alpha = 90^\circ$, we want to choose t_p, B_1 such that $\gamma B_1 \cdot t_p = 90^\circ$. This is called a **90° pulse**. t_p is on the order of a few microseconds in general.
 - After the pulse, the relaxation contains spectroscopic information: The transverse magnetization will decay exponentially to zero due to spin relaxation in a manner that can be picked up by the receiver as a **free induction decay**.

- Differing transmitter and Larmor frequencies: M_Y and B_1 interfere, yielding a sine wave with exponentially decreasing amplitude:

$$M_Y(t) = M_{Y_0} \cos[(\omega_0 - \omega_1)t] e^{-t/T_2}$$

- M_{Y_0} is the transverse magnetization immediately after the pulse. It is given by

$$M_{Y_0} = M_{Z_0} \cos \alpha = M_{Z_0} \cos(\gamma B_1 t_p)$$

where M_{Z_0} is the equilibrium magnetization in the Z-direction.

- In general, a molecule will have multiple chemical environments, each with its own Larmor frequency. All of these will affect the FID, so we will need to use an FT to separate the different contributing frequencies.
- For more on pulsed NMR, see Bloch [2].
- **90° pulse:** An application of a strong transmitter field B_1 over a time t_p sufficiently short such that $-\gamma B_1 t_p = \alpha = 90^\circ$.
- **Free induction decay:** A decay that occurs in the absence of an RF-field. *Also known as FID.*
- Chemical shifts and shielding.
 - Review from Chapter 14 of McQuarrie and Simon [1].
- ^1H vs. ^{13}C .
- Signal processing considerations.
 - Real + imaginary parts of the FT data.
- Locking.
 - Making sure that the magnetic field is what the machine thinks it is.
 - This is like calibration, and we use a substance with a single sharp known NMR line (typically deuterium ^2H) to do the locking.
- Spin decoupling.
 - Using a third magnetic field B_2 to resonate the nuclei to be decoupled.
 - We will use this technique to spin-decouple ^1H and ^{13}C , greatly simplifying the latter spectrum.
- Spin-lattice relaxation.
 - T_1 is the “lifetime” of the first-order rate process that returns the magnetization to the Boltzmann equilibrium along the +Z-axis.
 - The **spin-lattice relaxation rate** depends on the strength of intramolecular interactions and molecular motion.
 - Molecular mobility can be quantified by a **correlation time**.
 - Mechanisms involved in relaxation: Dipolar coupling, quadrupolar coupling, paramagnetic interaction, scalar coupling, chemical shift anisotropy, and spin rotation.
 - Protonated carbons: Dipole-dipole interactions with the attached protons are overwhelmingly dominant.
- **Spin-lattice relaxation rate:** The reciprocal of the spin-lattice relaxation time T_1 . *Given by*

$$\frac{1}{T_1}$$

- **Correlation time:** The time it takes for a molecule (or a molecular fragment) to reorient by a unit angle. Denoted by τ_C .
- Dipole-dipole coupling.
 - Depends on the strength of dipolar coupling, orientation of the interacting nuclei, distance between the interacting nuclei, and molecular motion.
 - Relaxation rate for a protonated carbon.

$$\frac{1}{T_1} = n \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_i^2 \gamma_H^2}{r_{CH}^6} \tau_C$$

- μ_0 is the permeability of a vacuum.
- γ_i is the gyromagnetic ratio of atom i ($i = {}^{13}\text{C}, {}^1\text{H}$).
- n is the number of bonded hydrogens.
- r_{CH} is the average C-H bond distance.
- The above equation only applies in the **extreme narrowing limit**.
- **Extreme narrowing limit:** The case where $1/\tau_C$ is much greater than the resonance frequency.
 - Holds in liquids of low viscosity.
- Inversion recovery technique.

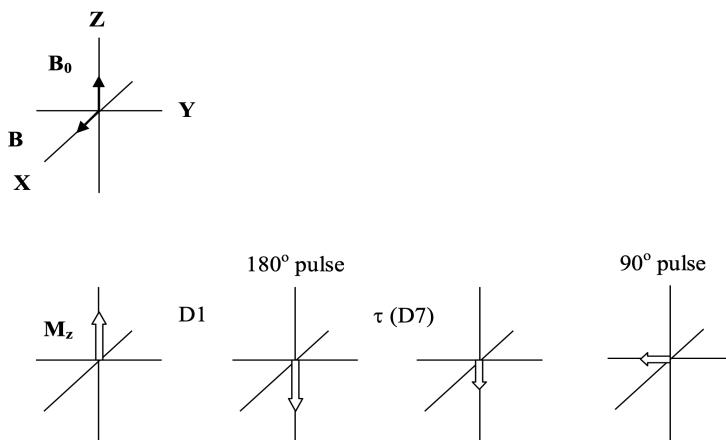


Figure 5.1: NMR inversion recovery.

- Use a multi-pulse NMR technique: Delay \rightarrow 180° pulse \rightarrow delay τ \rightarrow 90° pulse \rightarrow acquisition (FID).
- This has the effect depicted in Figure 5.1.
- The decay of magnetization in the +Z-direction is

$$\frac{dM_Z}{dt} = -\frac{M_Z - M_{Z_0}}{T_1}$$

- Integrating the above yields

$$M_Z = M_0(1 - 2e^{-\tau/T_1})$$

which can be used to calculate T_1 .

- Implications of the above equation.

- After a delay of T_1 , 63% of the magnetization is recovered along the +Z-axis.
- To recover 99% of the magnetization, a delay of at least $5T_1$ is needed.

In-Lab Notes

- To start, create a dataset with proton NMR in CDCl_3 . All of our ^1H NMR experiments will go into this dataset for the rest of the day.
- Create a dataset for carbon NMR as well.
- Any time you approach the instrument, do a mental metal check.
- Remove the dust cap, eject any previous samples, prepare yours, and sit it to float on top. Now click “Insert sample manually.”
- Lock the machine onto the CDCl_3 deuterium peak. There are tons of solvents to choose from, among them fruit juice (for food chemists) and blood plasma (for biologists). Once it starts hovering in a certain region, you’re good.
- We now do tuning. The tuner is made of adjustable capacitors, and it calibrates the receiver.
- We now do shimming. Think carpentry: Making everything level. Here, we introduce a homogeneous field to correct for any inhomogeneities.
- Sarah has a sample tuner and shimmer for us to hold.
 - They are very old devices from a previous, now disassembled NMR.
- Recall what’s showing now from Tokmakoff’s lectures.
- Control suite with some more adjustments.
- That’s it for proton NMR. We now just collect our spectrum.
- Acquisition finished: See bottom left-hand corner.
- We now move on to data analysis. We can follow along with which scan we’re on using the info in the bottom-left hand corner.
- Internal standard: TMS. Was developed here at UChi!
- Moving onto carbon NMR.
- We’ll use 8 scans every time, though more would be better (96 is standard).
- Dummy scans are magnetic scans without data collection. They bring your sample back to a good place for collection after all of the calibration (24 is standard).
- After the scan, go to Process > Process Spectrum.
- We do see 6 peaks, as expected.
- As part of the short report, you’ll need to assign each ^{13}C peak to which carbon on the molecule it is, numerically label the peaks, and create a numerically labeled structure in chemdraw or something.
- Usually, it would take a long time to collect ^{13}C spectra, but we’ve drastically decreased the number of scans, giving us quicker but worse data, and this NMR has a really strong probe that allows fewer scans to accomplish more.
- While we’re waiting for the next spectrum to collect, we can set limits, noting which regions the instrument should measure.
- MNova for data analysis.
- We’re going to plot I vs. τ and do a nonlinear data fitting to determine T_1 .

- After collecting the last few spectra, we'll split up: Some will be doing data analysis, finding our τ, I values. Others will be doing future experiments.
- There's also a 2D rendering of our data that we can do, using ^1H on one axis and ^{13}C on the other.
- We'll start with $\tau = \text{D7} = 0.001\text{ s}$.
- For the lab report, we make the regression plot for each of the six carbons.
- The amount of time you need for a certain material is partially material dependent.
- Phase correction parameters are important.
 - $\text{PHC0} = -172.561$.
 - $\text{PHC1} = -336.042$.
- We're testing $\tau = 0.1\text{ s}$ next.
- Strategy: Augment by 2 orders of magnitude twice and then fill in.
- Command line: "D7" and then enter your value.
- convbin2asc

Week 6

Intro to Long Reports

6.1 Lecture 10: Scientific Visual Communication

- 2/7:
- Long report submissions delayed until Friday.
 - The content of today may be useful!
 - Thursday.
 - Anna Wuttig on the current state of EChem.
 - Tokmakoff will stick around after for us to chat about our reports with him.
 - There are many aspects beyond *visual* communication, but this is one that isn't always seen, so Tokmakoff decided to focus on it today.
 - Take all the guidelines and extra chapters seriously; they're exactly what is being graded for.
 - We should care about communication because it's as important to our career development as anything.
 - Our science must be distributed; otherwise, we're just a hobbyist.
 - We need to convey very complicated, quantitative information to other scientists, management, government agencies, policy makers, investors, and the general public.
 - Reduce complex quantitative data accurately into clear, concise messages: Data interpretation.
 - Often, there are real requirements on content and formatting.
 - Excellence in communication.
 - Content is key, but saying it well will really level you up.
 - It develops *trust* in your methods, results, and communications.
 - A well-communicated report and graphic can change the world, e.g., the hockey stick curve.
 - **Communication:** The means of exchanging information.
 - **Medium:** Any channel of communication.
 - Media we will discuss.
 - Print (text, graphics).
 - Graphics are how people digest scientific information.
 - Oral (in person with visual support).
 - Never use double columns if you want transport to online.

- The common starting point for all communication.
 1. Audience.
 - Identify; sets the objective, expectations, language, and aspects of your work to focus on.
 - You need to know if you're talking to fellow bench scientists, or senior management.
 2. Message.
 - What are you trying to say? Just say what you need to, and get rid of the rest.
 - When your TA or Tokmakoff reads your report, what are they going to think of my magenta line.
 3. Media.
 - What tools are at your disposal, and how are they best employed.
- Visual presentation tips for text and graphics.
 - Our goal: Communicate quantitative information clearly and concisely.
 - Make your viewer's life easy (be consistent, define the purpose of each element, etc.).
 - Simplicity is good; clutter is bad.
 - Color should be chosen with a real focus in mind.
- Typefaces and fonts.
 - The visual representation of language. Its style should help, not interfere, with your communication.
- **Typeface:** The design elements for lettering. A collection of glyphs.
- **Glyph:** A single representation of a character.
- **Font:** A variation of a typeface like size, weight, and spacing.
- Classes of typefaces: **Serif** and **sans serif**.
 - Sans-serif is good for titles, headings, and labels.
 - Serifs are good for presenting large amounts of text.
- History of typefaces.
 - Use legacy typefaces; they're still supported.
 - “Microsoft is your friend.”
 - Computers revolutionized typography; Microsoft drove the development with proprietary stuff, which eventually caused them to lose the edge, and now there's great open-source fonts.
- Typefaces for equations.
 - Times New Roman and Garamond have full math support.
 - Computer modern (\TeX) is probably still the best in terms of being able to distinguish things since it includes so many helpful flourishes.
 - You're probably encountered difficulties with the lab manual (e.g., v vs. ν) because it's not in Computer modern.
- Tokmakoff's recommendations for formatting: Typed 8.5×11 documents should have a...
 - Single column format.
 - 1" margins.
 - 11-12 point type.

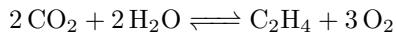
- ~ 90 characters per line including spaces (15 characters per linear inch).
- 4-5 lines per vertical inch.
- Why worry about font size?
 - Legibility vs. readability; too small impacts legibility, and too big impacts readability.
- Why worry about line spacing?
 - $1.5\times$ is Tokmakoff's recommendation.
 - $2\times$ is legacy from typewriters, when single and double were the only options.
- Why worry about margins?
 - White space helps with clarity.
 - Don't just insert figures; make figures break text.
- Equations should be numbered.
- Color.
 - Don't let it distract; let it help you make a cleaner presentation.
 - Really bright colors draw the eye too much.
- Scientific figures.
 - Purpose: To convey quantitative information on the relationship between different physical variables with minimal effort.
 - Each figure should convey information on exactly one topic.
 - Again, know your audience, be aware of your medium (typed vs. oral), clarity, etc.
 - Additional consideration for scientific reports: Often the figure is the only documentation of the data.
 - If the reader wanted to analyze your data, can they read data values off the graph using the axis labels?
 - Raw Excel sheets, other records may not be saved, so the literature report may be the only way for future scientists to reanalyze your data.
- Examples of good and bad figures.
 - As you see scientific figures going forward, take note of what you like and what you don't like and learn.
 - Tokmakoff asks for the class's feedback on his examples.
- You should have 4-6 axis labels and 4-10 tick marks.
 - More tick marks than labels is a good idea!
- Make sure colors translate to black and white, so maybe I should vary both shapes and colors in my Birge-Sponer plot.
- Rowan is very picky about what Excel settings you use.
 - Don't cut and paste into word; stuff gets realigned.
- Tokmakoff doesn't look for units for unitless quantities (e.g., absorbance).
- Use a legend when there are two or more series being plotted.
- Caption.

- Use for report figures.
- It should describe what is plotted and is needed to interpret the data beyond what is in the figure.
- For data, typically quote specific experimental conditions.
- Titles are only for oral presentation graphics.
- Don't mislead! Rescaling your axes can mislead about growth.
- Make everything 300 dpi.
- Publishers use JPG in CMYK color profile.
 - Online: Use RGB color profile.
 - Everything else is up to us.
- Takeaways.
 - Clarity and conciseness.
 - White space is good!
 - Microsoft is (mostly) your friend.
 - Their templates, colors, and fonts have been professionally designed... with everyone in mind.
 - Use recommended formatting, but be aware it isn't for scientists.
 - There are no firm rules — just guidelines. It is an art.

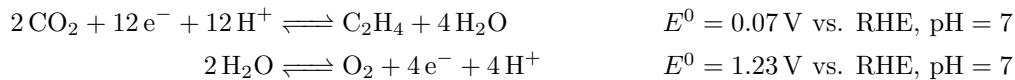
6.2 Lecture 11: Electrochemistry

2/9:

- Guest lecture by Anna Wuttig.
- Ben Masters (our TA) is one of her grad students.
- Electrochem can solve important problems, and we know the mechanisms in principle because we can measure the flow of electrons in it as current.
 - Thus, we can modify whatever we want and have an *in situ* handle on reaction rate.
 - This is why it's important for physical chemistry, which seeks to understand, predict, and rationally design future reactions.
- We will focus on CO₂-reduction today.
 - Wuttig hopes to **upconvert** it to other things.
- We currently do this with the water-gas shift reaction and Fischer-Tropsch chemistry.
 - But this is both energy-intensive and has poor selectivity.
- Alternative: Electrochemistry.
- Example.



- Produces ethylene (used in a lot of things in industry) and O₂ (benign).
- Allows you to store ΔG = 1343 kJ mol⁻¹ of energy, corresponding to ΔE = -1.16 V.
- This involves two electrochemical half-reactions (recall from gen-chem).



- The first one is kinetically very difficult, though — it requires you to input *twelve* electrons.

- In the EChem module, we'll study RHEs and other kinds of electrodes.
 - Essentially, these allow us to pin EChem reactions on a common axis.
 - The axis does move as a function of pH, though.
- We have no electrolyser or catalyst that can run the example reaction right now.
 - Thus, we so far have to put in more energy to store that energy.
 - A focus of the chemistry world: Find catalysts and conditions such that this is possible.
- CO₂ reduction as an energy storage scheme.

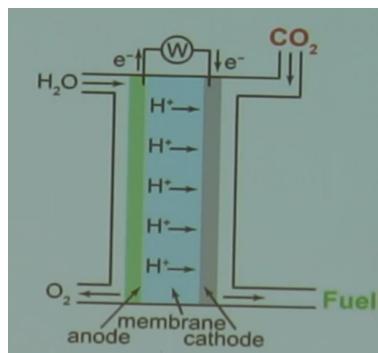


Figure 6.1: CO₂ reduction as an energy storage scheme.

- Use renewable energy sources like wind and solar to drive electrochemical reactions. Specifically, driving the transfer of electrons may facilitate oxidation of water to O₂ at the anode reduction of CO₂ to fuels (such as ethylene) at the cathode. Note that the water's protons will theoretically diffuse through a proton exchange membrane.
- Big idea: Store renewable intermittent electricity in energy-dense chemical bonds.
- Selectivity challenges in CO₂ reduction.
 - One reason we don't know how to do this yet: CO₂ can be reduced to myriad products.
 - A competitive side reaction: Hydrogen evolution.
 - Other carbonaceous products include methanol, ethanol, etc. Some of these may be good, but we don't want to produce all of them at once!
 - Though it might be theoretically possible to pin the ΔE thermodynamically, it's practically virtually impossible.
 - Consequently, selective CO₂RR requires control over the relative rates (kinetics) of competing reactions.
- Understanding of interfacial proton coupling is poor.
 - CO₂ + 2 e⁻ + 2 H⁺ → CO + H₂O is possible.
 - Things like molecular electrocatalysts allow us to access this at a high rate and selectivity.
 - We can boost the rate even further with *intramolecular* proton donors (esp. phenolic groups).
 - *Intermolecular* proton donors can help, too, but make sure not to make it too acidic, or you'll favor hydrogen evolution!
 - Thus, what you really need is precise proton delivery.
 - These homogeneous catalysts are nice and pretty, but in a functional device, we'll need heterogeneous catalysis.

- Possible example: Au catalyst.
- Mathematical models suggest that the concentration profiles at the interface of the solid are higher. Essentially, the pH near the surface becomes much more alkaline very quickly.
- We don't have control over the proton coordinate here, and we don't actually know what the proton donor is (could be water, hydronium, carbonic acid, etc.).
- Thus, we need to understand the role of PCET in dictating CO₂RR vs. HER selectivity.
- This is what Wuttig did her PhD on!
- Electrochemistry is nice because you always know the rate.
 - The velocity v of the reaction is related to the current i , the number of electrons n , and Faraday's constant $F = 96\,485 \text{ C/mol e}^-$ via

$$i = nFv$$
 - You can also measure how many product you're forming either by assuming that all current is going to your reaction, or by using in-line gas chromatography.
 - In the EChem module, we'll assume that everything is going to hydrogen evolution.
 - Knowing how much current is going to hydrogen and CO, we can construct a **Tafel plot**.
- **Tafel plot:** The relationship that describes the log-linear dependence of the reaction rate as a function of the applied potential.
 - We will take the partial current going to CO and plot it vs. the applied potential.
 - This yields direct mechanistic insight: Increasing the overpotential decreases the ΔG^\ddagger .
- Example of using a Tafel plot.
 - Assume CO₂ is reduced in a rate limiting step by combining with an electron.
 - Using kinetics, we would have

$$R_{\text{CO}} = k_1(\theta^*)(a_{\text{CO}_2}) \exp\left(\frac{\beta nF}{RT}\right)$$
 - θ^* is the concentration of the active sites on the gold surface; not every atom on the surface is active, as can be shown via fancy microscopy techniques.
 - a_{CO_2} is the **activity** of CO₂ dissolved in solution.
 - β is the symmetry factor: For reactions in which there is a high reorganizational potential energy, we can take $\beta \approx 1/2$.
 - This yields info on the Tafel slope:

$$\frac{\partial \eta}{\partial \log(j)} = \frac{60 \text{ mV}}{\beta} = 120 - 150 \text{ mV}$$
 - Thus, we check the data: At all potentials in the linear range, check for linear dependence.
 - Tafel data implies ET RLS with slope about 1.
- What if instead, we couple adsorption with proton transfer from?
 - Look at the rate of CO formation vs. the bicarbonate concentration.
 - Nothing here, so it's not this.
 - Moreover, because it's not this charged species, it's not any acidic species (because changes in one would change the pH of all).
 - Nothing for water, too.
 - Thus, the data suggests that there's no proton transfer in the initial step, so it must happen afterwards.

- Note that changing the partial pressure of CO also doesn't change anything, suggesting that as soon as CO is created, it is released and future adsorption is not inhibited.
- Other data complete the mechanism.

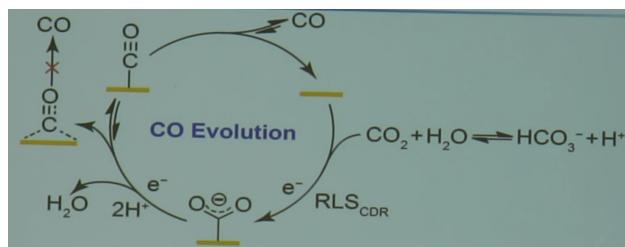
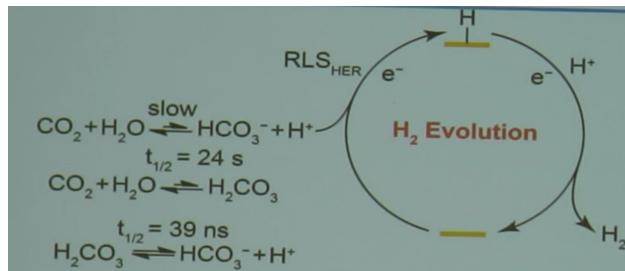
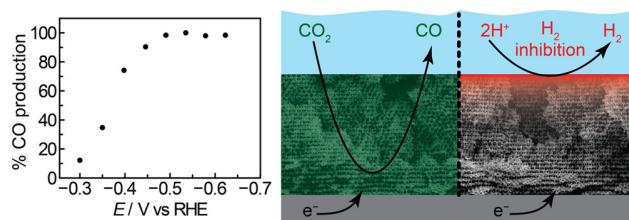


Figure 6.2: CO evolution mechanism.

- Simultaneous hydrogen evolution is dependent on the proton donor environment.

Figure 6.3: H₂ evolution mechanism.

- Mechanism is deceptively simple, but profound all the same.
- We first get adsorption of a proton to a hydride.
 - But Tafel slope is super high, so you may be being limited by the ability of the protons to get to the surface in the first place.
 - Suppose that the protons are special, i.e., donated by the relatively slow dissociation of H₂CO₃.
 - Note that H₂CO₃ dissociates with t_{1/2} = 24 s in real life; it is only super fast in our body because of an enzyme we have that takes it to t_{1/2} = 39 ns.
 - Changing the concentration of H₂CO₃ and rerunning the experiment confirms this.
- We do observe an explicit change in the rate of hydrogen evolution based on the concentration of H₂CO₃, but the relationship is complex and potential dependent.
- This is an independently occurring catalytic reaction on *some* catalytic site (maybe one that was occupied by CO, maybe not, we don't know).
- Utilizing this mechanism to design a better, more selective reaction.

Figure 6.4: Enhancing heterogeneous CO₂RR with mesoporous membranes.

- If we couple the two reactions, because they both depend on $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$, we can increase selectivity by slowing down this equilibration even further.
 - We make the environment at the gold catalysis further out of equilibrium with the bulk.
 - Wuttig teamed up with other scientists to develop a mesoporous gold structure, forcing everything that wants to touch the gold to go through the structure.
 - The CO_2 reaction does not care how thick the structure is, but H_2 does! This leads to near-selective CO formation.
- In our module, however, we need to *increase* H_2 evolution, though!
 - We'll use all the same principles Wuttig just discussed, but it'll be simpler.
 - H_2 evolution is also an important reaction.

6.3 Lab 4: GCMS

Lab Manual

2/9:

- Goal.
 - Use GCMS to quantify how much benzene there is in 87 gasoline.
 - We will use a **standard addition method** with respect to an internal standard reference.
- Why we are interested.
 - Gasoline is a complex mixture of hydrocarbons, and refineries are known to include aromatics such as benzene, toluene, and xylenes to increase the octane rating.
 - However, there is increasing concern about the hazards associated with these compounds.
- **Standard addition method:** The quantitation of a substance of interest in a complex mixture performed by spiking in increasing known amounts of that substance and plotting the resulting signal from this series of samples to determine the original amount.
- Description of how gas chromatography works.
- **Electron ionization** (mass spectrometry): A “hard ionization” source that results in a charged ion likely to fragment into a characteristic fragmentation pattern. *Also known as EI.*
 - As discussed in Labalme [3], electrons are generated via thermionic emission from a hot tungsten filament and then accelerated by applying a large potential between the filament and anode.
- **Chemical ionization** (mass spectrometry): A “soft ionization” source through which the major product is the molecular ion and very little fragmentation occurs. *Also known as CI.*
- EI is more useful for molecular identification against a library of known fragmentation patterns; CI is more useful for calculating the molecular weight of an unknown or newly synthesized compound.
- Common MS peaks in EI spectra.
 - Molecular ion at $m/z = \text{MW}$.
 - $[\text{C}_4\text{H}_3]^+$ at $m/z = 51$, which is often a tell-tale sign that the analyte is an aromatic.
 - $[\text{C}_7\text{H}_7]^+$ at $m/z = 91$, which often arises from the rearrangement of a benzyl fragment and suggests that the analyte contains a benzyl moiety.
- Mass analyzers.
- Methods of mass analysis: Quadrupole, time of flight, ion trap, ion cyclotron, etc.

- Our setup has both a quadrupole and time-of-flight mass analyzer.
- **Quadrupole:** A device that filters out ions with very low or very high m/z ratios.

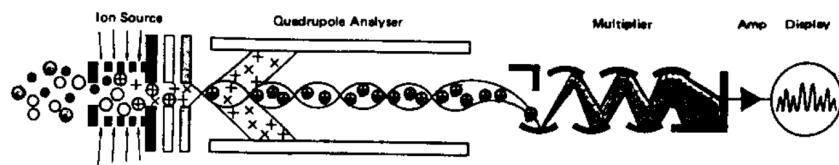


Figure 6.5: Quadrupole mass spectrometer.

- In our setup, it allows ions of our desired m/z range to pass into the time-of-flight tube where they are ultimately detected.
- Can be tuned to scan the atomic mass range or pass only a particular mass/charge of interest.
- Setup: Each parallel plate contains a dc voltage as well as a radiofrequency oscillation with frequency f . How much something moves correlates with its mass. We use one set of plates in the xz -plane, and one in the yz -plane, each meant to filter out an extreme of mass.
- **Time of flight:** A device that accelerates charged particles along a path and measures how long they are in the tube before they crash into a detector. *Also known as TOF.*

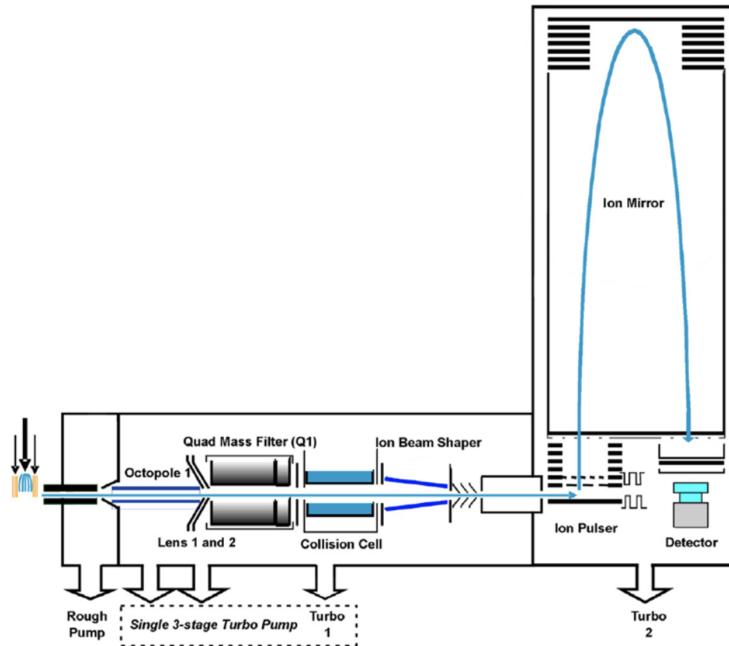


Figure 6.6: Time of flight mass spectrometer.

- We rearrange $E = (1/2)mv^2$ to
$$m = \left(\frac{2E}{d^2} \right) t^2$$
- Smaller ions are accelerated to a higher total velocity and arrive at the detector first.
- Standard addition analysis: Largely to be discussed in lab.
- Error analysis discussed.

In Lab

- We are not actually solving the linear fit for concentration, but for the added concentration. This will be negative since we're concentrating the amount you would have to remove in order for the peak to disappear, which is the opposite of the initial amount.
- Using an internal standard allows us to divide out volume.
 - Let R denote the substance of interest.
 - We have that

$$A_R \propto [R] = V \cdot \eta_R \cdot [R] = V \cdot \eta_R \cdot ([R]_0 + [R]_{\text{add}})$$

where...

- A_R is the GC peak area.
- V is the sample volume.
- $[R]$ is the concentration of R .
- And η_R is the detector efficiency for R .
- Thus, there will be a linear relationship between $[R]_{\text{add}}$ and A_R , the x -intercept of which occurs when $[R]_{\text{add}} = -[R]_0$.
- When V is nonconstant (there will be slight variations in how much sample we add to the GCMS tube each time), we can use an **internal standard** to correct our work.
- In particular, if B denotes benzene and T denotes toluene, we have

$$A_B = V \cdot \eta_B \cdot ([B]_0 + [B]_{\text{add}})$$

$$A_T = V \cdot \eta_T \cdot [T]_0$$

- We can then divide these two equations to obtain

$$\begin{aligned} \frac{A_B}{A_T} &= \frac{\eta_B}{\eta_T} \cdot \frac{[B]_{\text{add}}}{[T]_0} + \frac{\eta_B}{\eta_T} \cdot \frac{[B]_0}{[T]_0} \\ &= \frac{\eta_B}{\eta_T \cdot [T]_0} \cdot ([B]_{\text{add}} + [B]_0) \end{aligned}$$

- Notice that V cancels out!
- **Internal standard:** A substance in a solution that is always at the same concentration.
- These last two points are related to Q3-4 of the lab report.
- 0,2.5,5,7.5,10,12.5 are data points.
- **Extract chromatogram** allows you to find all peaks that have a significant concentration of a certain m/z .
 - For example, you can type in $m/z = 78$ and find all peaks corresponding to benzene (there should only be one).
 - $m/z = 91$ will get you all toluene derivatives.
 - Xylenes come in a pair of three (ortho/meta/para).
 - $m/z = 105$ should yield all xylene derivatives.
- Range of masses: 50-600; Solvent pause time: 4 min.
- 0ppm.
 - Rt: 4.696. Benzene. Integration: 321274.63.
 - Rt: 6.858. Toluene. Integration: 329835.47.
 - Rt: 8.540. *para*-Xylene. Integration: 353207.99.

- Rt: 8.363. Ethyl benzene. Integration: 104551.1.
 - We're now using mesitylene instead of *para*-xylene.
- Notes on how to answer the questions.
 1. Input 0ppm data in to Excel. Plot the regular chromatogram (TIC) vs. retention time.
 2. Plot an EIC for both benzene and toluene. Also plot their extracted mass spectra (peak labels [3-4 per spectrum] should include a name or structure and an *m/z* value). This can be extracted from the 0ppm data as well.
 3. Using integration data for both benzene and toluene at all concentrations (jotted down) and ppm data (given), normalize the benzene data using the toluene data (toluene is an **internal standard** because it's always at the same concentration, so it makes benzene peaks comparable via normalization), make a scatter plot, find the line of best fit, and calculate the concentration.
 4. Use the Student's *t*-test, 95% confidence interval, $n - 2 = 3$ DOFs, to get $t = 3.182$. No need to cite a source. For tabulation, make a very simple 2×2 table with headers "Concentration" and "Error" and then place the values below. To get a volume percentage, use HL's Canvas announcement to convert concentration in ppm (not mol/L) to a mass percentage, and then a volume percentage (using density).
 - Hypothetical: Imagine 1 gram of solution (approximate as pentane density). You can convert it to liters pentane using the density and stoichiometry.
 - Now imagine you have 5 µg benzene. You can convert it to liters benzene using the density and stoichiometry.
 - Divide the latter by the former to obtain a volume percentage.
 5. Plot EICs and MSs for both mesitylene and ethyl benzene. The EICs can be the same in both cases. Peak areas are comparable across EICs, so just compare the peak area of benzene which correlates with its above-derived concentration to estimate the concentrations of mesitylene and ethyl benzene using a simple ratio.

References

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- (2) Bloch, F. Nuclear Induction. *Phys. Rev.* **1946**, *70*, 460–474.
- (3) Labalme, S. CHEM 30200 (Synthesis and Physical Methods in Inorganic Chemistry) Notes <https://github.com/shadypuck/CHEM30200Notes/blob/master/Notes/notes.pdf> (accessed 02/09/2023).