

# 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](http://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*).

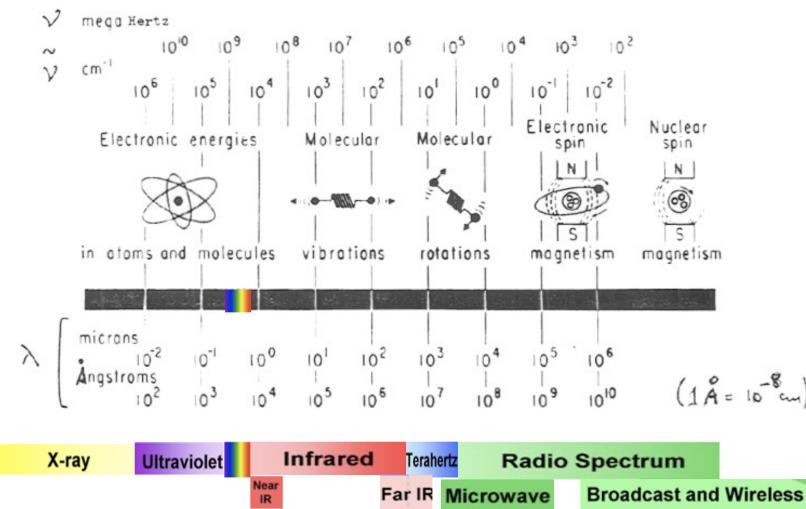


Figure 1.1: Types of light used by different forms of spectroscopy.

- 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.

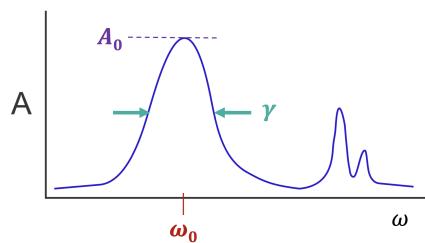


Figure 1.2: Features of an absorption spectrum.

- $x$ -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  $\epsilon$  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  $\omega_0$ , peak height  $A_0$  or peak area, linewidth  $\gamma$  (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  $\lambda$  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  $I = \frac{1}{2}\varepsilon_0|E_0|^2$ .
- $\omega$  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  $\omega$ , not  $\omega_0$ .
    - The particle oscillates  $90^\circ$  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.

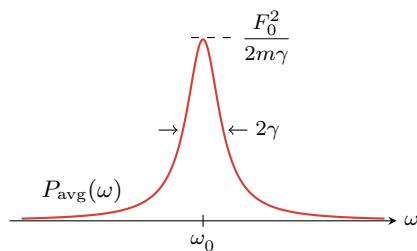


Figure 1.3: Lorentzian lineshape.

- 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  $P_{\text{avg}}$  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  $\omega_0$ .
    - 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  $30 \text{ cm}^{-1}$  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  $k = m_R \omega_0^2$ .
- $\gamma$  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  $\omega_0$  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  $2890\text{ cm}^{-1}$ , we predict that  $\bar{\nu}$  for  $^2\text{H}^{35}\text{Cl}$  is  $2070\text{ cm}^{-1}$ , 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:  $\text{CO}_2$  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.

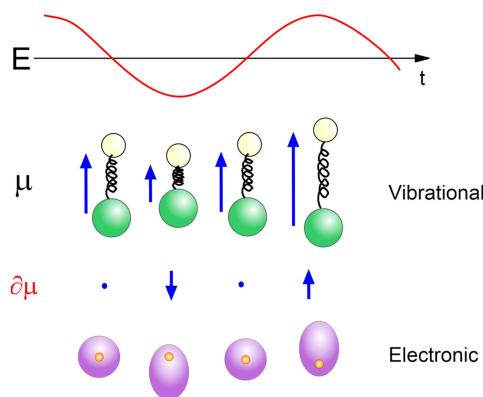


Figure 1.4: Light inducing a dipole change.

- 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  $\omega_0$  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  $\gamma$ : Irreversible chemical relaxation processes and chemical rate processes.
    - Peak amplitude: A proxy for the **extinction coefficient**  $\varepsilon$ .

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

# 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.

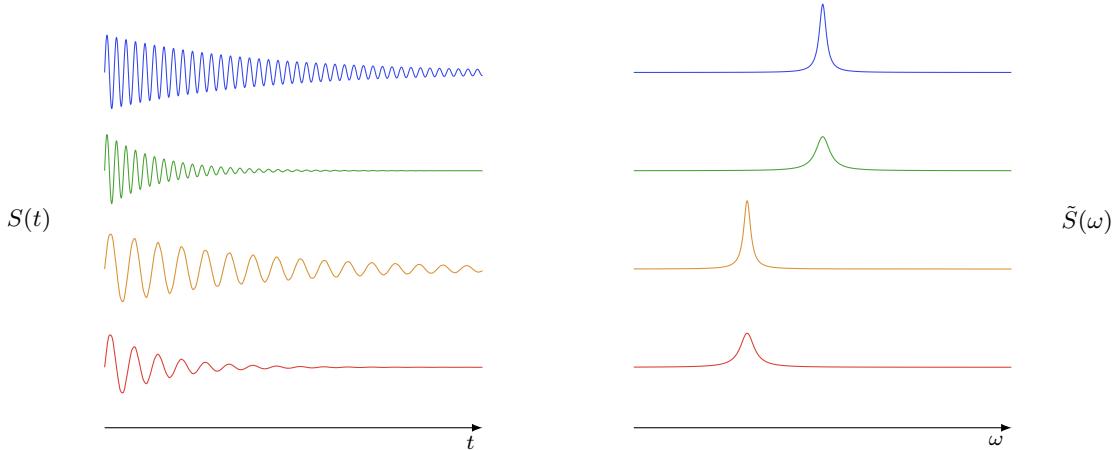


Figure 2.1: Parameters in the time and frequency domains.

Parameter	Time Domain $S(t)$	Frequency Domain $\tilde{S}(\omega)$
Large $\omega_0$	Fast oscillations	High frequency
Small $\omega_0$	Slow oscillations	Low frequency
Large $\gamma$	Fast decay	Broad linewidth
Small $\gamma$	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 (1997) 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  $\psi_i$ ).
      - 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  $(r, \theta, \phi)$  — which are needed to describe the potential and kinetic energy of the particle, as well as any motion and structure.
    - Thus,  $N_{\text{tot}}$  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 ( $\sim 1000$  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  $\text{H}_2$ .

- 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  $\text{H}_2$ , 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  $\text{H}_2\text{O}$ , 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.

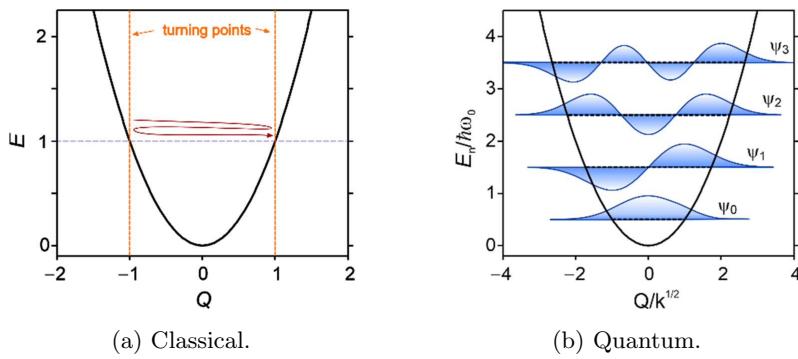


Figure 2.4: Classical vs. quantum picture of vibration.

- 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  $\psi_{\text{vib}}$  of  $\chi_n$ : 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  $\nu_e$  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  $\nu_e$ ) to the force constant of the harmonic oscillator.
  - Variable definitions.
    - $\nu_e$  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  $E_{\text{vib}}$  equation.
    - The spacing between adjacent vibrational levels is uniform and given by

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

- Rotation.

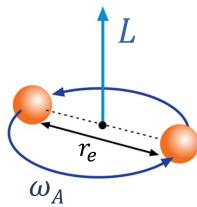


Figure 2.5: Classical rotation.

- 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.

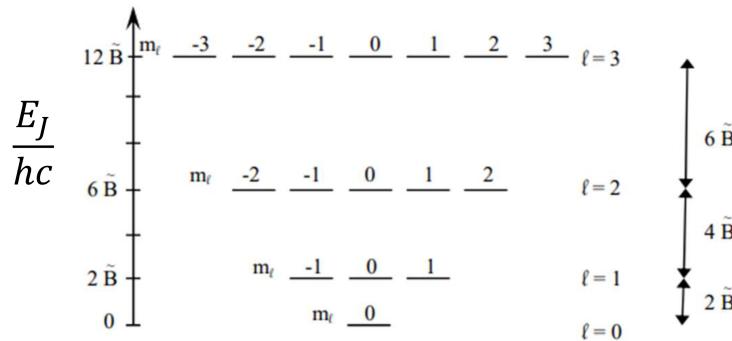


Figure 2.6: Quantum rotation.

- 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<sup>-1</sup>.
- As  $J$  increases, more and more rotational energy levels become available (see Figure 2.6).
  - Precisely, the degeneracy  $g(J)$  of the  $J^{\text{th}}$  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.

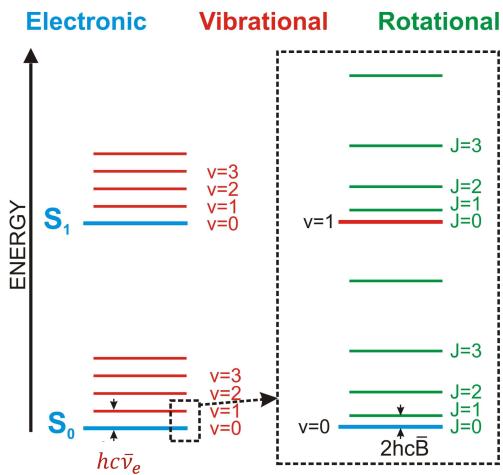


Figure 2.7: Electronic, vibrational, and rotational energy level spacing.

- Given the way that we approached the problem, we have that

$$E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + \dots$$

$$= E_{\text{elec}} + hc\bar{v}_e \left( v + \frac{1}{2} \right) + hc\bar{B}J(J+1) + \dots$$

- The energy can only take on discrete values (see Figure 2.7).
    - Note that the typical energy range for...
      - $E_{\text{elec}}$  is  $10^4$ - $10^5$  cm $^{-1}$ ;
      - $E_{\text{vib}}$  is  $10^2$ - $10^3$  cm $^{-1}$ ;
      - $E_{\text{rot}}$  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 ( $\nu$  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  $E_{\text{elec}}$  relative to the ground electronic state, the vibrational and rotational constants  $\bar{\nu}_e$  and  $\bar{B}_e$ , and associated quantum numbers.

# References

McQuarrie, D. A., & Simon, J. D. (1997). *Physical chemistry: A molecular approach*. University Science Books.