

## 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.

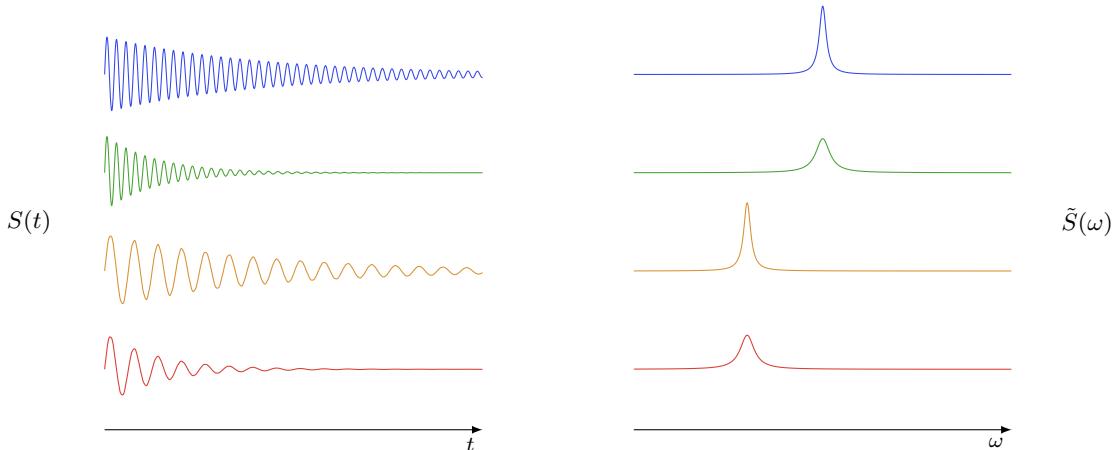


Figure 2.1: Parameters in the time and frequency domains.

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.

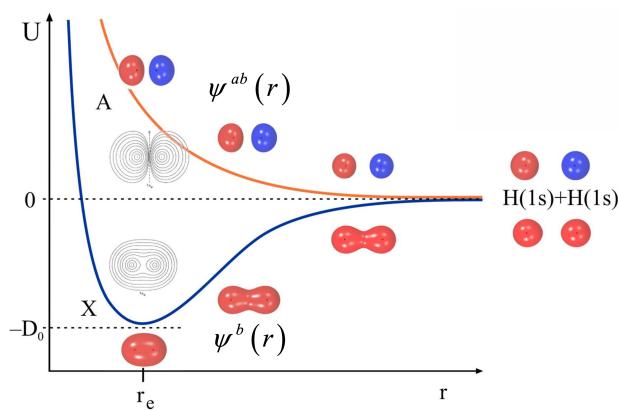


Figure 2.2: Born-Oppenheimer surfaces for  $\text{H}_2$ .

- 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,

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

- 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.

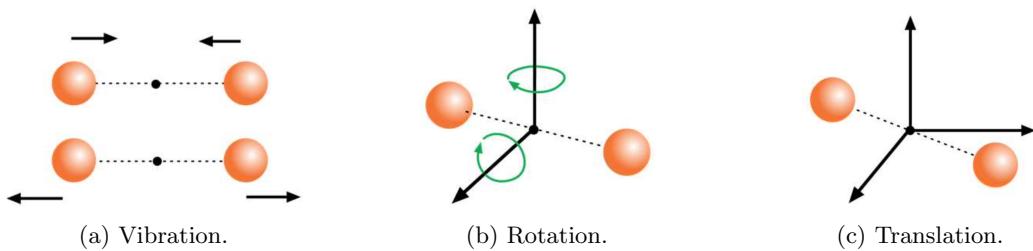


Figure 2.3: Modes of nuclear motion.

- 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.

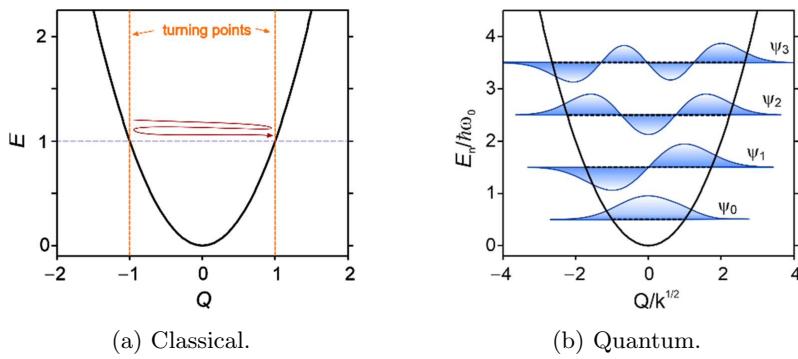


Figure 2.4: Classical vs. quantum picture of vibration.

- 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,

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

- 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.

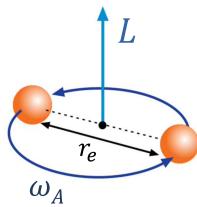


Figure 2.5: Classical rotation.

- 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.

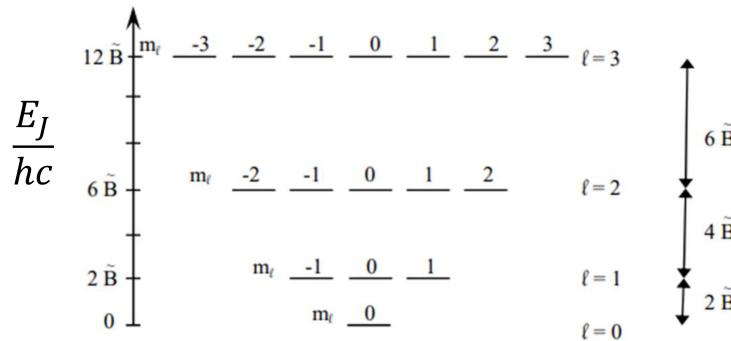


Figure 2.6: Quantum rotation.

- 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.

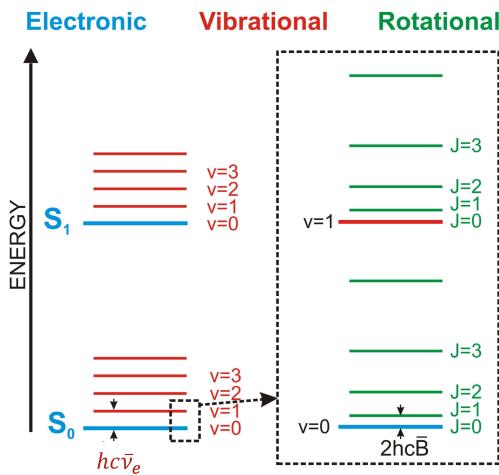


Figure 2.7: Electronic, vibrational, and rotational energy level spacing.

- Given the way that we approached the problem, we have that
$$\begin{aligned} E_{\text{tot}} &= E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}} + \dots \\ &= E_{\text{elec}} + hc\nu_e \left( v + \frac{1}{2} \right) + hc\bar{B}J(J+1) + \dots \end{aligned}$$
- The energy can only take on discrete values (see Figure 2.7).
- Note that the typical energy range for...
  - $E_{\text{elec}}$  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 ( $\nu_e$  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  $E_{\text{elec}}$  relative to the ground electronic state, the vibrational and rotational constants  $\nu_e$  and  $\bar{B}_e$ , and associated quantum numbers.