

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.

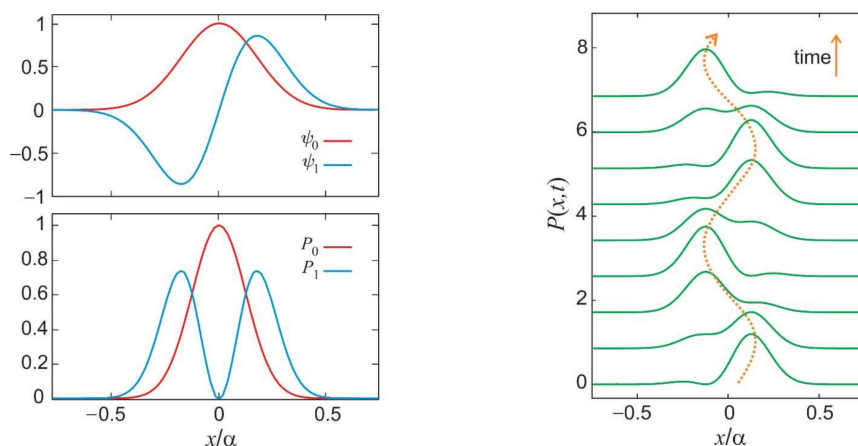


Figure 3.1: Light-induced coupling of quantum eigenstates.

- 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.

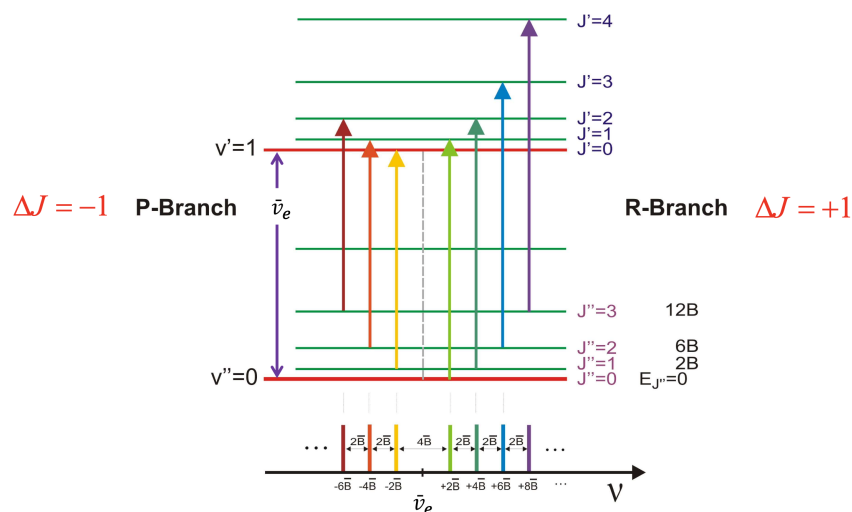


Figure 3.2: Vibrational and rotational excitations.

- 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.

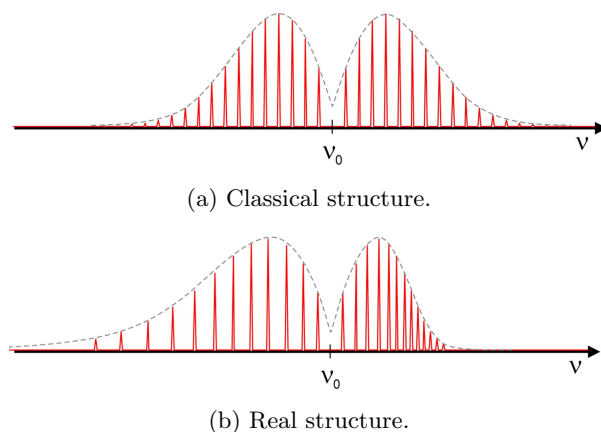


Figure 3.3: Predicted and actual P/R-branch spacing.

- 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 inertia increases, and thus the molecule 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 $\bar{\nu}_e, B_e, \alpha_e$.
 - 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.