Week 4
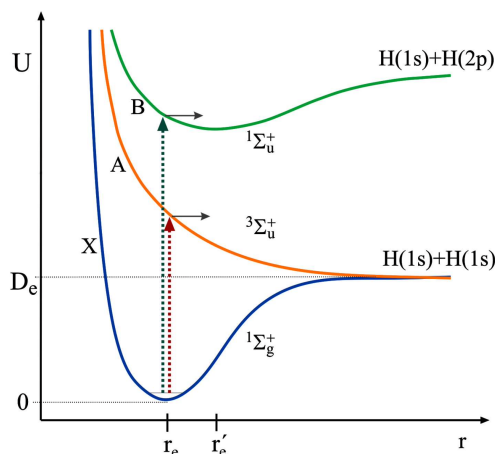
Electronic and Magnetic Spectroscopy

4.1 Lecture 7: Electronic Molecular Spectroscopy

• 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 I_2 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.

  - – $d \to d$ and charge transfer; related to $Ru(bpy)_3{}^{2+}$.

- 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 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.
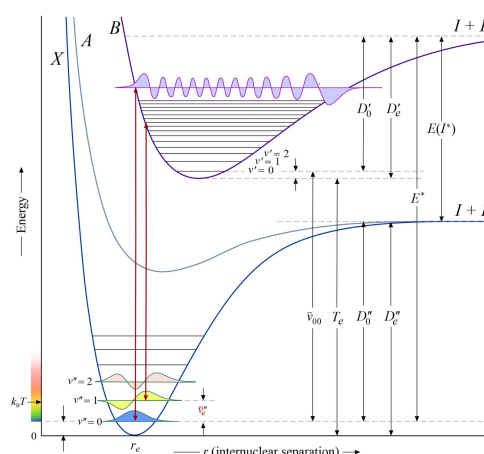
(a) Vibrational excitation.   (b) Wavefunction overlap.

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 processe dominate.

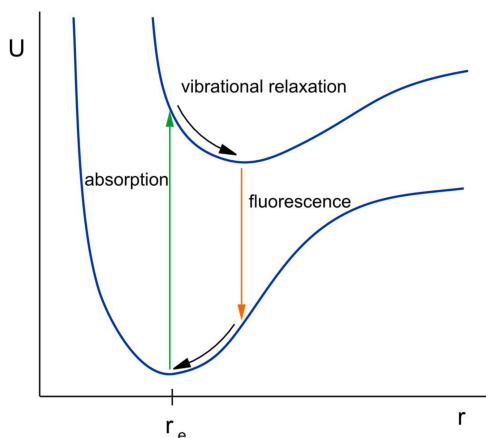- Relaxation of electronic states.

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 flourescence.
    - Naturally, fluorescence is always red-shifted relative to absorption.
    - We call the red shift the **Stokes shift** and denote it by 2λ.

4.2 Lecture 8: Magnetic Resonance Spectroscopy

1/26:   - Refer to Chapter 14 of McQuarrie and Simon (1997).

- 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 *electro*magnetic 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!

4.3   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 $HCl_{(g)}$.

– 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 $v = 0, 1, 2, \ldots$ 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 $B_e = h/8\pi^2 cI$ 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.

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

    – 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.