

## Week 4

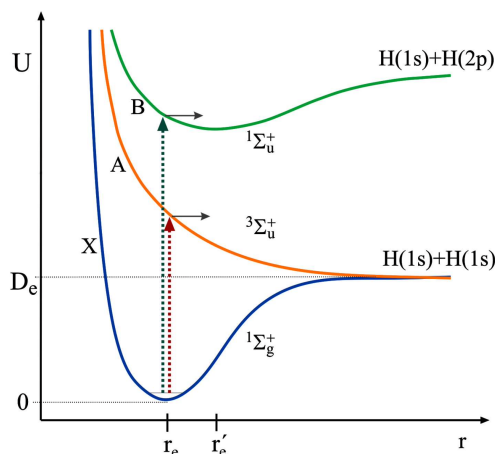
# Electronic and Magnetic Spectroscopy

### 4.1 Lecture 7: Electronic Molecular Spectroscopy

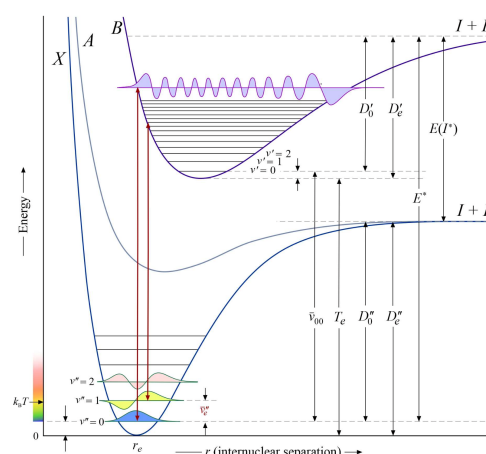
1/24:

- Lant check in on lab.
  - The clean up process is still going on; we're not getting back in the lab for the rest of the quarter. We'll still meet in Jones 108, but not use the PChem lab.
  - When cleaning up the small barometer spill, they found a much larger spill covered in dust that's been there for who knows how many years, so they're having to bring in a professional team and it will take weeks. They don't just have to get it down to OSHA levels; it's an educational environment, so the requirements are even more stringent.
  - They may or may not be able to still offer every lab.
  - Lant is open to questions.
  - Most of us should be totally fine.
  - They found a line of it behind the hood.
- Announcements.
  - No lecture on Thursday; OH then in Searle 240.
  - NMR lecture next week.
  - Detailed guidelines on the long report by the end of the week.
- Today: Electronic spectroscopy and the I<sub>2</sub> absorption data.
- This is electronic *molecular* spectroscopy where electrons are localized, in contrast to electronic *nano-material* spectroscopy for example.
- We focus on valence electrons.
  - These absorb UV/Vis light.
  - Light absorption changes electronic charge distribution around the molecule; a lot of energy allows you to break bonds.
  - Molecules change all states, but start in the electronic ground state.
  - We will not look at core electrons here; we'd need X-rays for that. This is atom specific.
- Types of molecular electronic transitions.
  - In organic compounds, we're usually looking at  $\sigma \rightarrow \sigma^*$  or  $\pi \rightarrow \pi^*$  transitions, typically in unsaturated compounds.

- In saturated compounds, it is extremely difficult to get excitations, and we have to go into the deep UV.
- Example: Coumarin 153 dye.
  - Which HOMO and LUMO change, as well as the net change in dipole.
- Inorganic spectroscopy.
  - $d \rightarrow d$  and charge transfer; related to  $\text{Ru}(\text{bpy})_3^{2+}$ .
- Electronic spectra of diatomic molecules.
  - Lots of fine structure: Primarily changes in vibrational quantum number.
  - The rotational constant of massive  $\text{I}_2$  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  $\text{I}_2$ .
  - We get a transition from the X to the B state that increases bond length.
  - $\text{I}_2$  is a massively anharmonic oscillator (hard repulsive wall; softer attractive wall).
  - Vibrational spacing  $\Delta v$  decreases with increasing energy.
  - Different shaped potentials (different bond lengths and different vibrational splittings).
- UV/Vis spectroscopy of  $\text{I}_2$ .



(a) Vibrational excitation.



(b) Wavefunction overlap.

Figure 4.1: Franck-Condon factors in electronic spectroscopy.

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

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

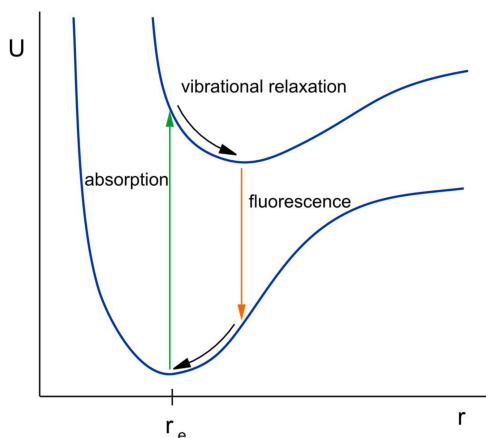


Figure 4.2: UV/Vis fluorescence.

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

## 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 *electromagnetic* field.
  - Derivation of quantized angular momentum.

- In molecules, there is a multiplicity/degeneracy of states that grows as  $2J+1$ . They have quantized angular momentum.
- So is the orbital angular momentum of electrons!
- Putting atoms into a magnetic field *creates* the anisotropy necessary for discussing the  $z$ -component (or any coordinate component) of angular momentum.
- Spin angular momentum: Just means that the objects (e.g., electrons and nuclei) have a property that looks a lot like spin and/or angular momentum.
- We say that each nucleon has a spin of  $1/2$ . Protons and neutrons add separately.
  - Even number of protons and neutrons? Spin 0.
  - Mixed even/odd? We have actual nuclear spin.
    - We need a nucleus like this to detect!
  - Odd/odd? We have 0 spin again.
- We focus on spin  $1/2$  particles. These have two degenerate energy states that split in a magnetic field.
- Classical picture of spin angular momentum.
  - Picture a charged particle with angular momentum. The circulating charge produced a magnetic field which aligns along the direction of the angular momentum.
  - Indeed, a spinning charged particle behaves like a dipole.
  - $\gamma = 2mc$  is the **gyromagnetic ratio**.
- Quantum spin angular momentum.
  - Basically the same thing; we just rephrase everything from before in the language of operators.
- **Zeeman effect**: Two energy levels split with increasing  $B$ .
- **Larmor frequency**: The frequency  $\nu = \gamma B/2\pi$  in the radio frequency range that induces a shift.
- Typical operating conditions.
  - NMR vs. ESR: NMR has a stronger magnetic field, longer EM excitation radio waves, and significantly lower gyromagnetic ratios.
  - There is only a tiny difference between nuclear state occupation at room temperature; hence supercooling to get something detectable.
- What is the magnetic dipole doing in the magnetic field?
  - No constraints on the  $x$  and  $y$  components of  $I$ .
  - A dipole in a field experiences a torque.
    - Dipole precesses around  $B$  at the Larmor frequency  $\nu$ .
  - FT-NMR spectrometers use pulsed rf fields to synchronize and detect the precession of spins.
- Lots of good extension material on NMR; also worth rewatching at some point!