

## Week 4

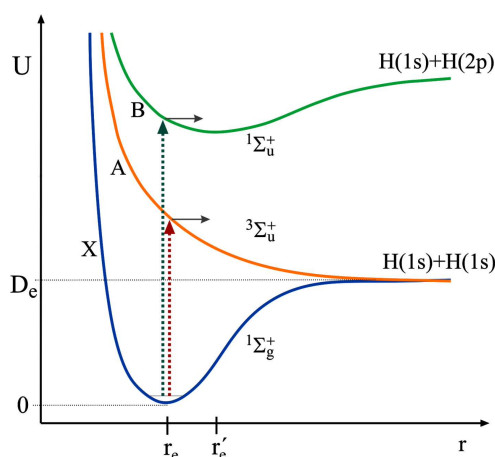
# Electronic Spectroscopy

### 4.1 Lecture 7: Electronic Molecular Spectroscopy

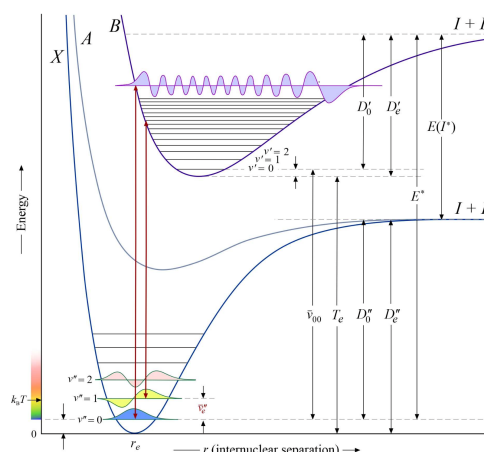
1/24:

- 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.

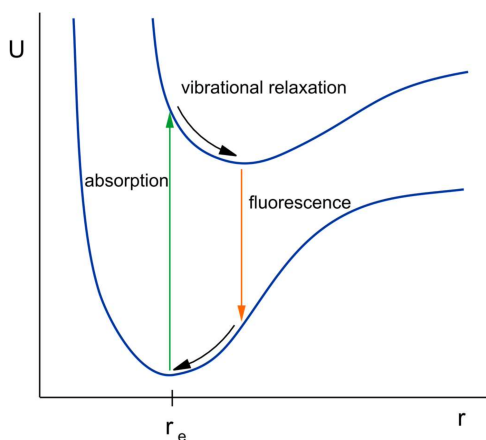


Figure 4.2: UV/Vis fluorescence.

- 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 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  $\text{HCl}_{(g)}$ .
  - 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  $\nu$  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 ( $\text{cm}^{-1}$ ) and  $v = 0, 1, 2, \dots$  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  $B_e = h/8\pi^2cI$  is the rotational constant (in  $\text{cm}^{-1}$ ),  $I = \mu r_e^2$  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  $\pm 1$  and  $J$  can change by  $\pm 1$ .

■ 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.