

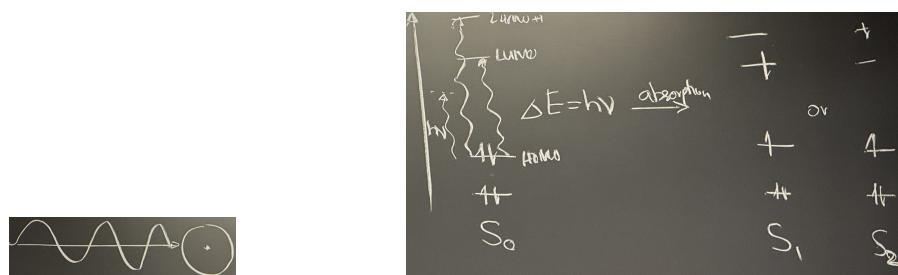
Week 15

Light-Matter Interactions

15.1 Photochemistry

12/10:

- Announcements.
 - Alex plugs the course evaluations again.
 - No class Thursday.
 - On the exam.
 - They wrote the exam, intending for it to be difficult. Alex and Masha respect us as chemists, and wanted to challenge us to explore our full potentials.
 - Regardless of how you did on the exam, if you engaged it seriously, you succeeded per Alex.
 - No single exam is a referendum on our value as a chemist or worth as a human.
 - If it didn't go as planned, feel free to reach out to Alex, Masha, or anybody else in the chemical faculty if you feel that they can help you learn something. We are all in a place of mutual learning, and you should take advantage of that opportunity.
 - On the mechanistic proposal.
 - Jonathan grades Exam 2; Alex grades the mechanistic proposal.
 - They will get our grades back to us before the deadline to submit/lock in grades.
- Today: Light-matter interactions (the photophysics and photochemistry of organic molecules).
 - This is an addendum to electron transfer.
 - In an ideal world, organic photochemistry would not be a final lecture in 5.53; it would be a half- or full-semester course. But alas, they don't have that in the syllabus.
 - Hopefully this gives us some useful context to approach the literature with greater insight, though.
- Consider an atom with a spherically symmetric electron distribution.



(a) Impinging photon.

(b) Orbital effects.

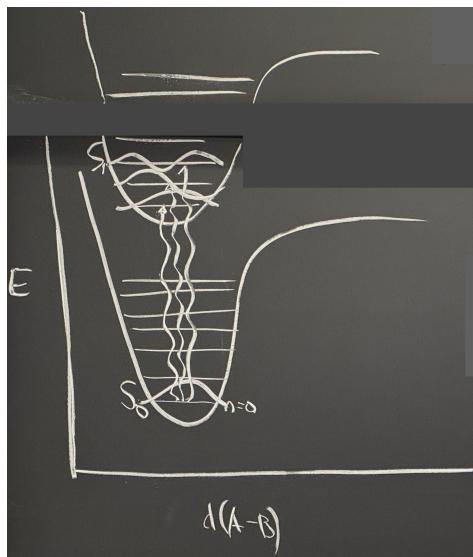
Figure 15.1: Irradiation of an atom with light.

- Suppose we impinge upon the atom with **light**.
- Electrons are charged particles, and thus will interact with the light.
- A bunch of stuff can happen, depending on the energy/wavelength/frequency of the light.

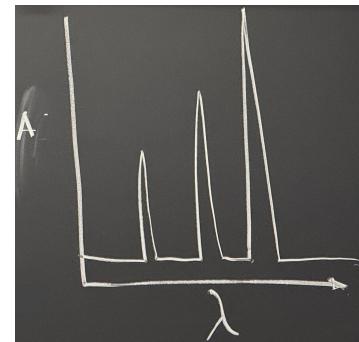
$$E = h\nu = \frac{hc}{\lambda}$$

- Suppose that this atom has some electrons in filled orbitals, and some possible stable electronic states/wavefunctions defined by the nuclear potential.
- If you have a photon of random energy (not corresponding to any orbital gap), it will create a nearly instantaneous virtual state.
 - The atom can elastically or inelastically scatter the photon.
 - Inelastic scattering is the basis for Raman spectroscopy!
- The transit of the photon through the electron cloud can also meet a resonance condition between the energies of the wave functions.
 - This does not lead to scattering of the photon, but to absorption of the photon.
- Because reasons, the spin angular momentum of the electron will not be affected by this absorption.
- The ground state is S_0 (a singlet, ground state).
 - The excited state is S_1 (still a singlet, but no longer a ground state).
 - A doubly excited singlet state is S_2 .

- **Light:** An oscillating electromagnetic field traversing the universe.
- Let's now look at the effect of this excitation on a molecule.



(a) Electronic promotion potential energy surfaces.

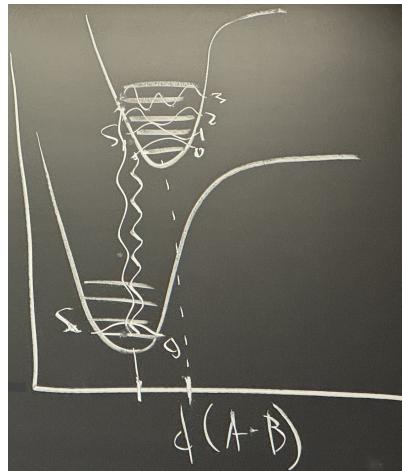


(b) Vibrational spectrum.

Figure 15.2: Irradiation of a molecule with light (simplistic).

- The higher-lying vibrational states (in S_0) will be populated via a Boltzmann distribution.
- When we excite into S_1 , we jump to a different potential energy surface (Figure 15.2a)!
- We can also array absorption vs. wavelength (Figure 15.2b).
 - Slightly different photons can excite into higher vibrational states.
 - We expect more absorption of lower energy photons because there is greater orbital overlap of the S_0 ($n = 0$) state with the S_1 ($n = 0$) state than with any of the S_1 ($n > 0$) states.

- The energy range for these excitations is usually in the UV-Vis range.
 - Visible irradiation: 400-700 nm is equivalent to 75-45 kcal/mol of energy.
 - UV irradiation: 200-400 nm is equivalent to 150-75 kcal/mol of energy.
- Modifying this picture.



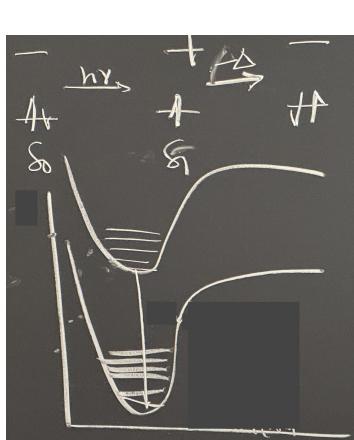
(a) Electronic promotion potential energy surfaces.



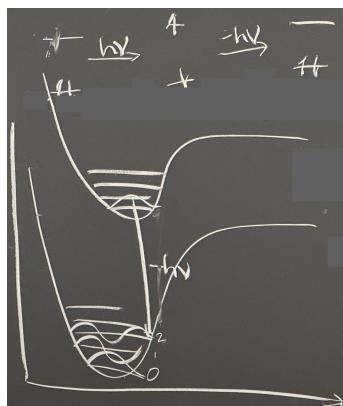
(b) Vibrational spectrum.

Figure 15.3: Irradiation of a molecule with light (real).

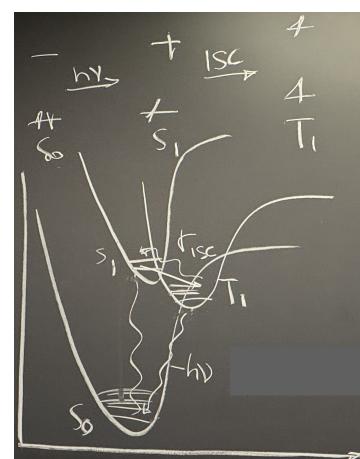
- It's not that the excited electron spends less time between the nuclei; that's too classical.
 - Rather, population of higher-energy, antibonding orbitals leads to decreased bond order in the excited state that shifts the S_1 potential energy surface over to the right.
 - This leads to the **Franck-Condon principle**, which implies that peak distribution flips.
- Franck-Condon principle:** Electronic transitions proceed vertically, irrespective of nuclear motion.
 - Like Born-Oppenheimer, electrons are assumed to move on a timescale where nuclei stand still.
 - Also reflects that we like exciting into wave functions having more overlap with the ground state.
- Once a molecule is excited, what happens? There are several mechanisms of relaxation.



(a) Internal conversion.



(b) Fluorescence.



(c) Phosphorescence.

Figure 15.4: Photochemical relaxation mechanisms.

- Franck-Condon tells us that we can excite into higher vibrational states.
 - And we saw previously that we can excite into higher-lying electronic states (e.g., S_2).
 - What happens is answered by **Kasha's rule**.
 - Possibility 1: Radiationless decay.
 - This is also known as internal conversion.
 - You can distribute energy to the solvent or else.
 - This is a mechanism to generate heat from light, and is relatively useless in terms of preparative photochemistry.
 - So we lose heat to the ground state.
 - Possibility 2: In the microscopic reverse of absorption, we get Franck-Condon-type emission from the lowest excited vibrational state back down to a higher vibrational ground state.
 - This means that we emit a photon of lower energy than we put in!
 - As drawn, this is $S_1 \rightarrow S_0$ emission.
 - Also happens without any change in the angular momentum of the electron.
 - This is known as fluorescence, and occurs with rate constant $k_f \approx 10^6 - 10^9 \text{ s}^{-1}$.
 - In the literature, we'll sometimes see a value called the **fluorescence lifetime**.
 - So we lose light to the ground state.
 - Possibility 3: The excited state undergoes intersystem crossing to a triplet excited state (T_1).
 - Why does this happen?
 - Consider the case of benzene.
 - This does not lead to any bond *cleavage*, but the triplet also has decreased bond order (see Figure 14.13).
 - By moving electrons out of the same orbital, we remove the Coulombic repulsion. Additionally, since they have the same spin, we benefit from losing the **Pauli repulsion**/gaining the **exchange energy**. This means that the triplet is slightly lower energy.
 - But physics hasn't stopped! Where does the momentum go? This has to deal with spin-orbit coupling.
 - In much the same way that molecular orbitals of disparate energies don't mix well, the rate of intersystem crossing is also governed by the similarity in energies between S_1 and T_1 ; the more similar the energies, the faster ISC happens.
 - What can the triplet state do?
 - It could react right back to the singlet!
 - This establishes an electronic equilibrium from the singlet and triplet excited states.
 - The triplet state has a relatively slow rate of electronic emission, but emission from it is called **phosphorescence**.
 - Thus, triplet lifetimes are usually many orders of magnitude longer than singlet lifetimes.
 - Related to TADF organic photoelectronic solar cells.
 - **Kasha's rule:** There is a large driving force for relaxation into lower electronic, and vibrational, excited states relative to any other chemistry that may happen.
 - **Fluorescence lifetime:** The average time a molecule lives in an excited state before fluorescing. *Denoted by τ_f . Given by*
- $$\tau_f := 1/k_f \approx \frac{10^{-4}}{\epsilon_{\max}}$$
- ϵ_{\max} is the **extinction coefficient** from **Beer's law** ($A = \epsilon bC$).
 - This means that in events with strong absorption to the excited state, there's a fast rate at which fluorescence happens.

- Example: The photophysics of benzophenone.

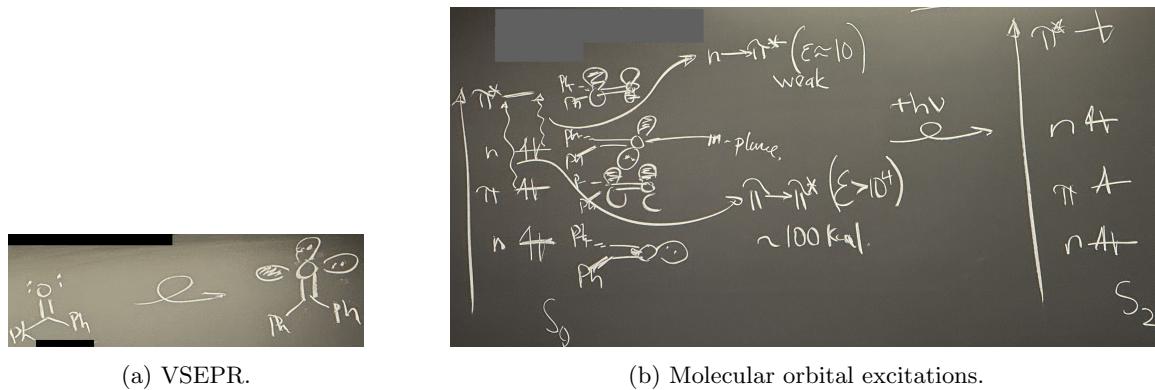


Figure 15.5: Electronic structure of benzophenone.

- The frontier MOs are the carbonyl π and π^* orbitals.
- It's also got nonbonding lone pairs on the oxygen.
 - An sp -hybridized oxygen is more likely than an sp^2 -hybridize one: One lone pair in sp and one in an orthogonal p -orbital.
 - These two nonbonding pairs are nondegenerate: This is molecular orbital theory, as in the nonequivalent electron pairs of H_2O (see Figure III.12 from Labalme (2024)).
 - Technically, this is an excuse by VSEPR purists!
- Consider an $n \rightarrow \pi^*$ transition.
 - Because there is very little orbital overlap, we have an extinction coefficient of $\varepsilon \approx 10$. Thus, this is a weak transition with little absorption, so it tends not to be important and the context of benzophenone.
- Consider the $\pi \rightarrow \pi^*$ transition.
 - Here, $\varepsilon > 10^4$.
 - Thus, we'll preferentially excite this transition.
 - The λ_{\max} for this transition is known; we can look up the exact value, but it's about 315 nm.
 - In effect, the result is an S_2 state because we've excited up two energy levels.
- Let's now look at a diagram that is rigorous energetically but dispenses with the internuclear coordinate. This is a **Jablonski diagram**.

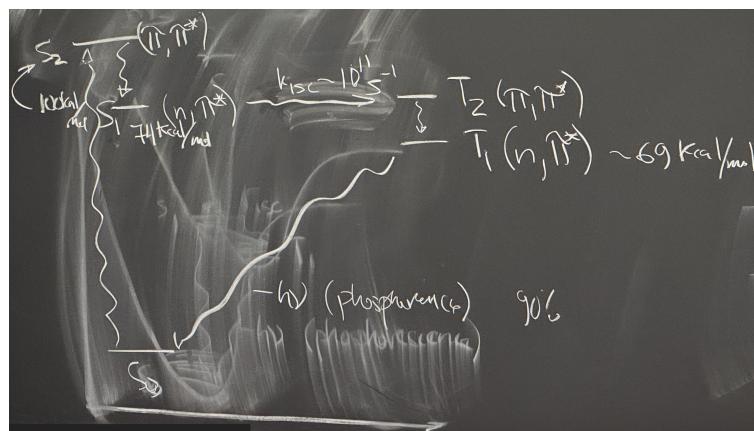
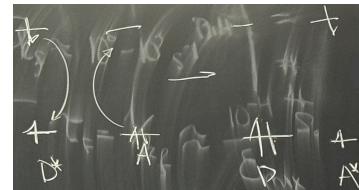


Figure 15.6: Jablonski diagram for exciting benzophenone.

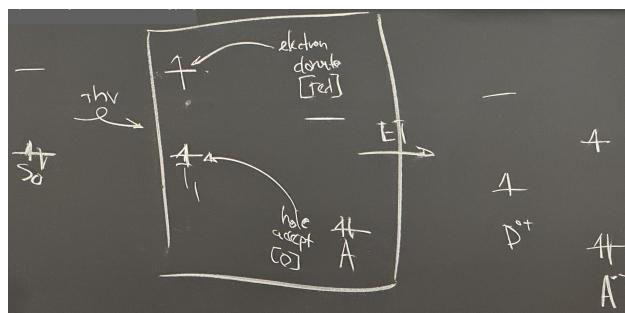
- Excitation to S_2 happens with an energy of about 100 kcal/mol. Occurs with a (π, π^*) transition.
- This then follows with rapid relaxation to the S_1 singlet.
 - This new S_1 state is lower in energy, electronically.
 - We can also show this on our Jablonski diagram!
 - S_1 is at 74 kcal/mol, experimentally.
 - Fluorescence from S_1 (in a right angle array; spectrofluorophotometry!) experimentally gives you the energy of this state.
- Very fast intersystem crossing ($k_{ISC} \approx 10^{11} \text{ s}^{-1}$) from $S_1 \rightarrow T_2$ can then occur.
 - This is because the T_2 state happens to be very similar in energy to S_1 .
- Then we quickly drop to T_1 .
 - We can hang here for a while; long lifetime.
 - Triplets are spin-forbidden to go down to the ground state, with lifetimes on milliseconds to even seconds.
 - This lifetime is comparable to diffusion, so we can do chemistry now!
- Alternatively, phosphorescence back to the ground state.
 - 90% of the energy goes here.
- We care about benzophenone because it's oft-used in preparative photochemistry as a triplet sensitizer.
- Photochemistry.
- Intermolecular energy transfer can occur.



(a) Dexter energy transfer.



(b) Forster energy transfer.



(c) Electron transfer.

Figure 15.7: Intermolecular photochemistry.

1. Donor to acceptor ($D^* + A \longrightarrow D + A^*$).
 - (a) Dexter energy transfer.
 - The triplet excited state relaxes to its singlet and excites the acceptor to its triplet.
 - Example: Triplet benzophenone and singlet naphthalene transfers to singlet benzophenone and triplet naphthalene.

- (b) Forster energy transfer.
 - Energy falling down causes energy up in the acceptor.
 - The rate here is exquisitely dependent on distance ($k_{\text{For}} \propto 1/r^6$).
 - This type of transfer relies on good orbital overlap between the donor and acceptor.
- 2. Electron transfer.
 - A hole can accept electrons from another molecule (oxidation), and the excited electron can donate (reduction).
 - Takeaway: Photoexcited species are better both donors and acceptors.
 - Hole transfer creates a radical cation and radical anion.
- Stuff Alex didn't get to: Stern-Volmer quenching, excited state electron transfer, mechanisms of photoisomerization, and photoluminescence.
- Closing thoughts.
 - Graduate education is a fraught transitional process from learning other people's knowledge to generating your own knowledge.
 - Alex is eager to be a resource to us in future years; door is open.
 - He also hopes to learn from us, because we know some things better than he ever will.