Lecture XII: Introduction to Organic Photochemistry

A vast field, we will cover only the basics: photophysics and selected photochemical reactions. PHOTOPHYSICS is what you should probably remember!

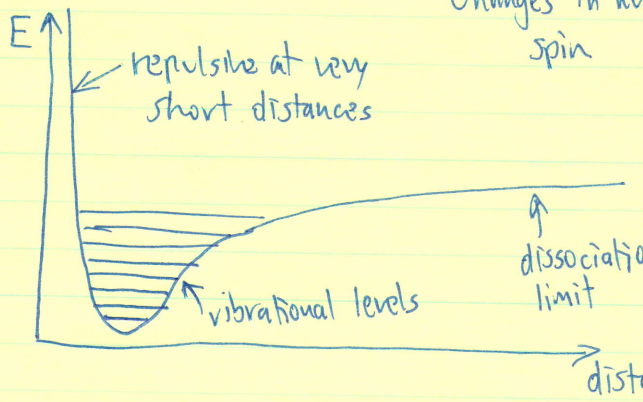
① Photophysics – Jablonski diagram

$E = hc/\lambda = h\nu$

TV

	radio	μwave	IR	Vis	UV	X-ray	Gamma
E (kcal/mol)	$3\cdot10^{-6}$	$\sim10^{-3}$	1–30	30–72	72–140	greater	
	↑ changes in nuclear spin	↑ changes in rotations	↑ change in vibrations	↑ change of valence electronic levels but also bond-breaking		↑ knocking out inner-shell electrons!	

avg. BDE = 40–140 kcal mol^{-1}

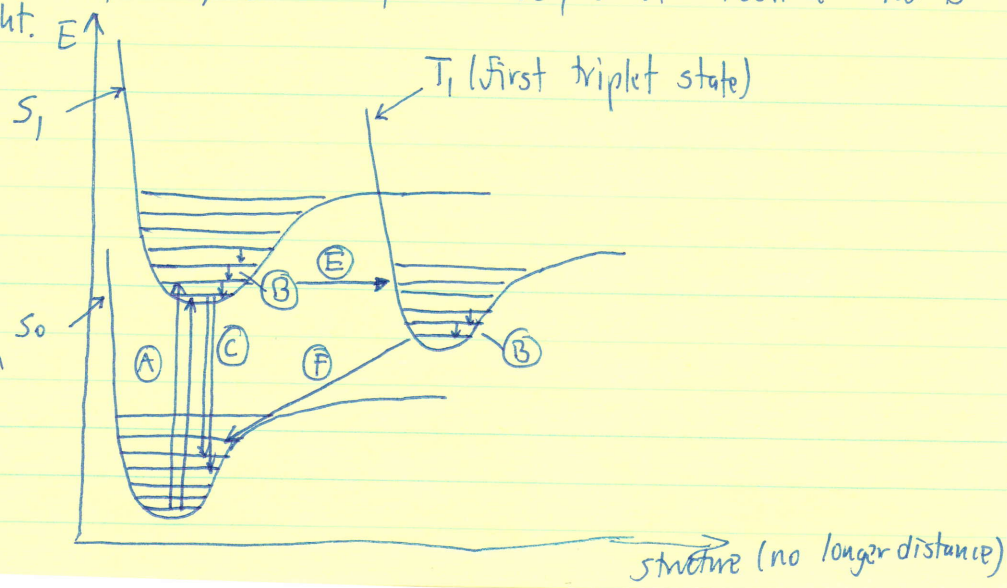


⇐ Electronic surface of ground state A–B bond

Absorption of a photon of light promotes one electron from a high-lying filled orbital (typically HOMO) to a low-lying unfilled orbital (typically LUMO). Whole molecule is then in the 1st excited state (S_1). Since we start with S_0 (singlet ground state) and the spin cannot be changed the first excited S_1 state is also a singlet. Direct excitation into S_2 state can happen, but is very unlikely: requires too much energy! Indirect $S_0 \to S_1 \to S_2$ is unlikely too, since S_1 has very short lifetime and is unlikely to productively absorb light.

Jablonski diagram: summary of unimolecular photophysical processes

- (A) = absorption
- (B) = radiationless vibrational relaxation
- (C) = fluorescence
- (E) = inter-system crossing
- (F) = phosphorescence



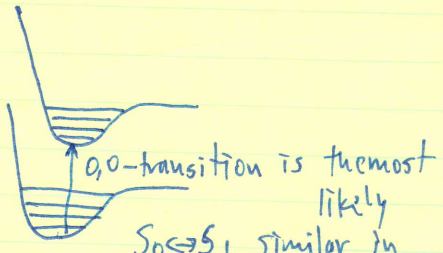
(A) Absorption ($E = hc/\lambda$)

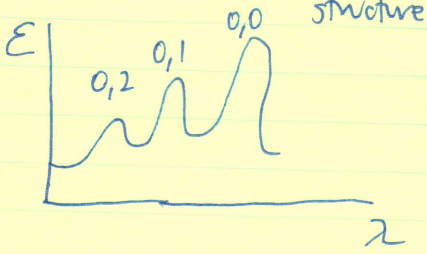
Starting at the lowest vibrational level of S_0, $h\nu$ promotes an electron into S_1. It can end up in either lowest or one of the higher vibrational levels, depending on $h\nu$.

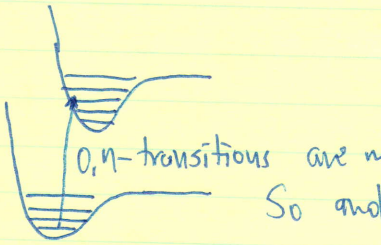
$S_0 \rightarrow S_1$ transition takes only 10^{-16}–10^{-14} s. This is very fast, and nuclei cannot keep up, because they are too heavy. They move on the order of 10^{-13}–10^{-12} s. This means that S_0 and S_1 have very similar structures.

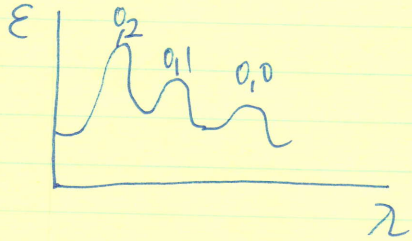
Franck-Condon principle states that electronic transition occur vertically on the potential energy surface. If ground and excited states differ too much in ~~energy~~ structure, excitation is unlikely to happen.

What does this mean in practical terms? UV/Vis spectra have a fine structure which depends on vibrational levels:



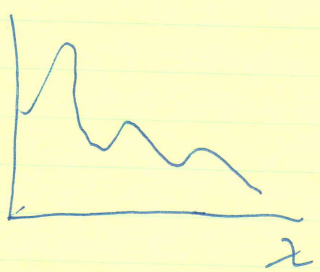






$A = \varepsilon \cdot l \cdot c$ (c: concentration, l: length) — Beer's law!

Typically, because of interaction with the solvent, and because of a huge number of vibrational and rotational levels, this fine structure is not observed, instead very broad spectra are seen:



Chemists often describe transitions in terms of orbitals, since it allows correlations with reactivity:

C–C	$\sigma \rightarrow \sigma^*$	180 nm	vacuum UV region
C=C	$\pi \rightarrow \pi^*$	210 nm	
C=O	$n \rightarrow \pi^*$	280 nm	These chromophores are mostly responsible for photochemical reactivity.
	$n \rightarrow \pi^*$	350 nm	
	$n \rightarrow \pi^*$	270 nm	
	$\pi \rightarrow \pi^*$	260 nm	

$\pi \rightarrow \pi^*$: ALLOWED TRANSITION ($\varepsilon > 10^3$), mostly responsible for pericyclic reactivity
$n \rightarrow \pi^*$: FORBIDDEN " ($\varepsilon < 10^3$), " " " radical additions
" electron transfer
cleavages.

How can you tell the difference between π, π^* and n, π^* transitions? Response in solvent polarity is different. π, π^* increases the polarity of excited state so more polar solvents stabilize it (increased λ_{max}, red shift).

(B) Radiationless Vibrational Relaxation

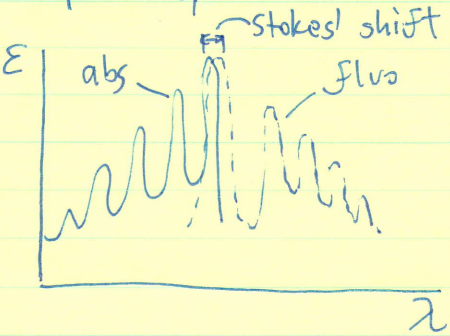
No photons involved. Excited molecule bumps into other molecules and gives them some of its kinetic energy (i.e. heat). Eventually, it comes back down to 0-vibrational level of the excited state.

Rate: $10^{11}-10^{12}\ s^{-1}$: very fast. But quick lasers can "catch" the excited state before it relaxes back and promote it to an even more excited state!

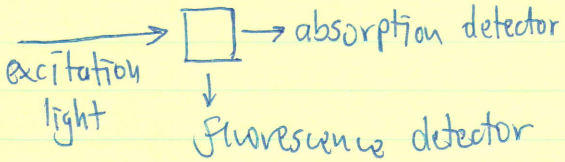
(C) Fluorescence

Radiation: $S_1 \rightarrow S_0$ + emission of $h\nu$
Fluorescence spectrum = emission spectrum
look at Jablonski diagram: Fluorescence occurs from 0 state of S_1 to n state of S_0

Fluorescence spectra are almost always shifted to higher λ, since some energy gets lost in process (B). Also, these spectra look like mirror images of absorption spectra.



very sensitive analytical methods, can be used for single molecule detection



Fast process: $10^8-10^5\ s^{-1}$; but more commonly expressed as a fluorescence lifetime.

(D) Internal Conversion (IC) – radiationless return from S_1 to S_0. Energy is given off as heat to surroundings.

(E) Inter-system crossing (ISC)

Switch from S_1 to T_1. Although forbidden, since it changes spin, it does happ
Through a process known as spin-orbit coupling. For ketones, the rate of this proce
is 10^{11}–$10^{8}\ s^{-1}$, but it gets faster with heavy atoms.

Triplet is lower in energy than singlet — Hund's rule!

(F) Phosphorescence

Switch from T_1 to S_0. Again, forbidden, but it does happen. Phosphorescence and fluorescence are often collectively referred to as luminescence.

n,π^* rate is 10^2–$10^3\ s^{-1}$ π,π^* rate is 10^{-1}–$10^{1}\ s^{-1}$ very slow!

Many glow-in-the-dark objects are based on phosphorescence.

Quantum yield — quantitative measure of likelihood of one of the above processes.

$$\phi_n = \frac{\text{number of molecules that do } n}{\text{number of absorbed photons}}$$

sum of all ϕs should be 1, but it rarely is, because some processes are unknown, or difficult to study.