CHEM 361B - Lecture 19 Activity

Electronic Transitions and Photochemistry

1. Propanone (or acetone, $(CH_3)_2CO$), has a strong absorption at 189 nm and a weaker absorption at 280 nm. Assign these features to n-to-π^* or π-to-π^* transitions.

2. Another way to quantify quantum yield is calculate the number of molecules consumed per photon. The reactant 1,3-cyclohexadiene can be photochemically converted to *cis*-hexatriene. In an experiment, 2.5 mmol of cyclohexadiene are converted to *cis*-hexatriene when irradiated with 100 W of 280 nm of light for 27.0 s. All of the light is absorbed by the sample.

   (a) Show that the total photon energy adsorbed by the sample is 2700 J.

   (b) Show that the energy of a 280 nm photon is 7.095×10^{-19} J.

   (c) Show that the total number of photons adsorbed by the sample is 3.8055×10^{21} photons?

   (d) Show that the quantum yield of this process is 0.396

3. A substance has a fluorescence quantum yield of $\Phi_{F,0} = 0.35$. In an experiment to measure the fluorescence lifetime of this substance, it was observed that the fluorescence emission decayed with half-life of 5.6 ns.

   (a) Show that the observed fluorescence lifetime is 8.08×10^{-9} s.

   (b) Show that the fluorescence rate constant, k_F, of this substance is 4.33×10^7 s-1.

4. The quenching of tryptophan fluorescence by dissolved O_2 gas was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Show that the quenching rate constant for this process from the following data is 1.28×10^{10} s^{-1}:

$[O_2]$ (10^{-2} mol L^{-1})	0	2.3	5.5	8.0	10.8
τ (10^{-9} s)	2.6	1.5	0.92	0.71	0.57

5. You are designing a FRET experiment to determine the magnitude of the structural change introduced by substrate binding to an enzyme. Using site-specific mutagenesis, you have constructed a mutant form of the enzyme that possesses a single tyrosine residue and a single tryptophan residue, and these residues are separated by 11 Å. You would like to determine if the distance between these residues changes with substrate binding. The fluorescence of tyrosine overlaps with the tryptophan absorption; therefore, these two amino acids form a FRET pair for which $R_0 = 9$Å.

   (a) Show that the FRET efficiency at an 11 Å separation is 0.231.

   (b) The detection limit of your experiment is when the FRET efficiency is 80% of what was found in part a. Show that the distance between the two residues at the detection limit is 11.53 Å

6. One method of determining Franck-Condon factors between the $n = 0$ vibrational state of the ground electronic state and the n^{th} vibrational level of an electronic excited state is:

$$FC_{0-n} = \frac{1}{n!}\left(\frac{\delta^2}{2}\right)^n e^{-\delta^2/2}$$

where δ is the dimensionless displacement of the excited state relative to the ground state and can be related to atomic displacements through

$$\delta = \left(\frac{\mu\omega}{\hbar}\right)^{1/2}(r_f - r_i)$$

(a) Determine the Franck-Condon factors for $n = 0$ to $n = 5$ when $\delta = 0.2$ corresponding to the excited-state potential surface being slightly displaced from that of the ground state.

(b) How would you expect the Franck-Condon factors to change if the excited-state displacement increases to $\delta = 2.0$? Verify your expectation by calculating the Franck-Condon factors from $n = 0$ to $n = 5$ for this displacement.