Photochemistry and Photophysics

Michaelmas 2017

Due: 5pm Thursday Week 3

1. **Beer-Lambert Law**

   (a) A solution of $K_3[Fe(C_2O_4)_3]$ of concentration 0.006 mol dm^{-3} is contained in a cell of thickness 1 mm and is irradiated with light of wavelength 400 nm. The natural molar absorption coefficient at this wavelength is 594 dm^3 mol^{-1} cm^{-1}. What fraction of the incident light intensity is absorbed?
   The Fe(III) is reduced to Fe(II) on irradiation and the quantum yield for Fe(II) formation at $\lambda = 400$ nm is 1.13. If the solution is irradiated for 20 minutes with light of $\lambda = 400$ nm, it is found that 3.4×10^{-6} mol of Fe(II) formed. Calculate the intensity of the light incident on the cell (measured in photons s^{-1}).
   Explain how this problem is connected to the idea of a chemical actinometer.

   (b) The decadic molar absorption coefficient for a compound is 3×10^4 dm^3 mol^{-1} cm^{-1} at 313 nm where the compound undergoes a photochemical bleaching reaction. The product does not absorb at 313 nm.
   A 1.5×10^{-3} M solution of the compound in a 1 cm^3 cell of 1 cm^2 cross-section was placed in the path of a light beam of 0.01 mW cm^{-2} at 313 nm. What fraction of the incident intensity is absorbed?
   The absorbance (this quantity is equal to εcl) decreased by 7% of the original value in two hours. Find the quantum yield of the bleaching reaction.

   (c) Ultraviolet radiation photolyses O_3 to O_2 and O. From the following data determine the rate at which ozone is consumed by 305 nm radiation in a layer of the stratosphere of thickness 1 km. The quantum yield for the photodissociation is 0.94 at 220 K, the concentration of O_3 is about 8×10^{-9} mol dm^{-3}, the decadic molar absorption coefficient is 260 dm^3 mol^{-1} cm^{-1}, and the intensity of radiation at this wavelength is about 1×10^{14} photons cm^{-2} s^{-1}.

2. **Symmetry**
   Using the group theory table for D$_{2h}$ symmetry, show that the lowest energy electronic transition of p-benzoquinone ($^1B_{1g} \leftarrow^1 A_g$) is formally forbidden. The transition becomes vibronically allowed in combination with certain vibrational excitations. What are the symmetries of the vibrational modes that can be excited in this way?

Table 1: Character Table

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	x	

Table 2: Direct Product Table

| D_2, D_{2h}	A	B_1	B_2	B_3
A	A	B_1	B_2	B_3
B_1		A	B_3	B_2
B_2			A	B_1
B_3				A

3. **Absorption and Fluorescence**

The absorption and fluorescence spectra of benzene in solution in cyclohexane are shown below. Explain the origin of the approximate "'mirror image symmetry"' in the spectra and comment, qualitatively, on their structure.

The compounds biphenyl, phenol, hexane and tyrosine show no such mirror image relationship in their spectra. Suggest reasons.
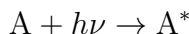
Would the mirror image also be observed for the gas-phase fluorescence/absorption spectra of benzene?

Figure 1: Absorption and Fluorescence spectra of benzene in cyclohexane (source: I. B. Berlman, *Handbook of Fluorescence Spectra of Aromatic Molecules*, Academic Press, New York and London, 1971)
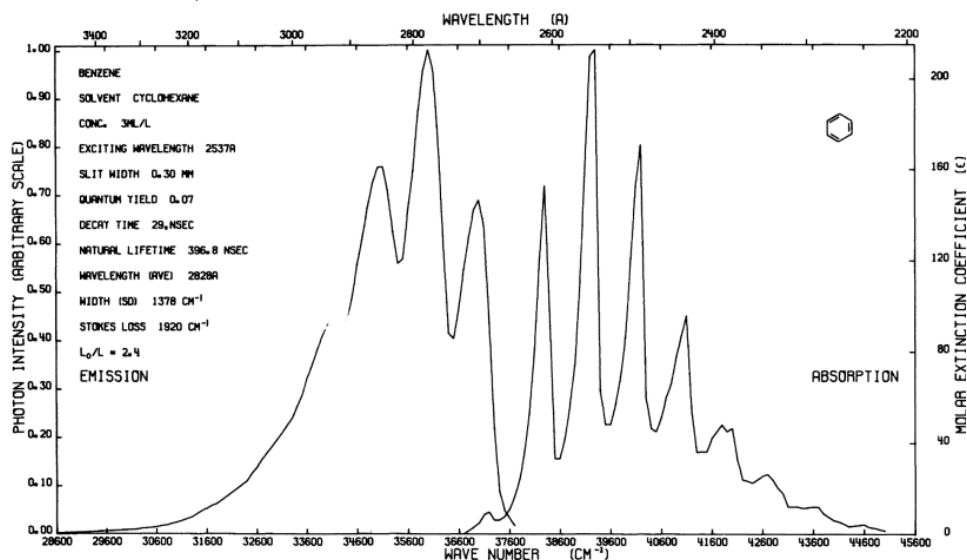
4. Kinetics

(a) The photoreduction of benzophenone (A) may be represented by the reaction scheme shown below:

$$A + h\nu \rightarrow A^*$$

$$A^* \xrightarrow{k_1} A + h\nu \qquad \text{(radiative decay)}$$

$$A^* + Q \xrightarrow{k_2} A + Q \qquad \text{(quenching)}$$

$$A^* + B \xrightarrow{k_3} C \qquad \text{(reaction)}$$

Using the steady state approximation or assuming pseudo-first order kinetics, derive an expression for the quantum yield for the reaction as a function of the concentrations of species Q and B. Show that the data below are consistent with the scheme above and obtain values of the ratios k_1/k_3 and k_1/k_2.

(i) $[Q] = 0$				
[B] / M	1.0	0.2	0.07	0.04
ϕ_3	0.97	0.78	0.52	0.40
(i) $[Q] = 10^{-3}$ M				
[B] / M	0.25	0.09	0.04	0.02
ϕ_3	0.50	0.25	0.125	0.07

Assuming k_2 has the typical diffusion controlled value of about 5×10^9 M^{-1} s^{-1}, calculate k_1 and k_3.

From measurements of the integrated absorption coefficient the true radiative lifetime of the A* singlet state is estimated to be 5×10^{-5} s. Comment on the value you have obtained for k_1 in relation to this.

(b) Naphthalene contained in an alcohol-ether low-temperature glass absorbs light at $\lambda = 315$ nm, and two different emission spectra are observed. The quantum yields and observed lifetimes for the two emissions are (i) $\phi = 0.3, \tau = 3 \times 10^{-7}$ s; (ii) $\phi = 0.03, \tau = 2.3$ s.
How can those observations be interpreted? Estimate as many kinetic parameters as you can for the various processes occurring, assuming that no internal conversion or physical quenching occur. Explain qualitatively the magnitudes of the quantities that you obtain.

(c) Comment on the truth, or otherwise, of the following statement.

> Fast time-scale flash photolysis can be used to determine rate constants for collisional relaxation (quenching) processes of singlet and triplet states. Radiate decay rate constants (Einstein A coefficients) can be determined from such measurements, and can also be calculated from absorption coefficients.

5. **Atmospheric Chemistry**
G. C. G. Wachewsky *et al.* (*J. Phys. Chem.* **100**, 11559 (1996)) examined the UV absorption spectrum of CH_3I, a species of interest in connection with stratospheric ozone chemistry. They found the integrated absorption coefficient to be dependent on temperature and pressure to an extent inconsistent with internal structural changes in isolated CH_3I molecules; they explained the changes as due to dimerization of a substantial fraction of the CH_3I, a process which would naturally be pressure- and temperature-dependent.

(a) Compute the integrated absorption coefficient over a triangular lineshape in the range 31 250 cm^{-1} to 34 483 cm^{-1} and a maximal molar absorption coefficient of 150 dm^3 mol^{-1} cm^{-1} at 31 250 cm^{-1}.

(b) Suppose 1 per cent of the CH_3I units in a sample at 2.4 Torr and 373 K exists as dimers. Compute the absorbance expected at 31 250 cm^{-1} in a sample cell of length 12.0 cm.

(c) Suppose 18 per cent of the CH_3I units in a sample at 100 Torr and 373 K exists as dimers. Compute the absorbance expected at 31 250 cm^{-1} in a sample cell length of 12.0 cm; compute the molar absorption coefficient that would be inferred from this absorbance if dimerization was not considered.

6. **Beer-Lambert Law II**
The Beer-Lambert law states that the absorbance of a sample at a wavenumber $\tilde{\nu}$ is proportional to the molar concentration [J] of the absorbing species J and to the length L of the sample. In this problem you will show that the intensity of fluorescence emission from a sample of J is also proportional to [J] and L. Consider a sample of J that is illuminated with a beam of intensity $I_0(\tilde{\nu})$ at the wavenumber $\tilde{\nu}$.

Before fluorescence can occur, a fraction of $I_0(\tilde{\nu})$ must be absorbed and an intensity $I(\tilde{\nu})$ will be transmitted. However, not all of the absorbed intensity is emitted and the intensity of fluorescence depends on the fluorescence quantum yield, ϕ_f, the efficiency of photon emission. The fluorescence quantum yield ranges from 0 to 1 and is proportional to the ratio of the integral of the fluorescence spectrum over the integrated absorption coefficient. Because of a Stokes shift of magnitude $\Delta\tilde{\nu}_{Stokes}$, fluorescence occurs at a wavenumber $\tilde{\nu}_f$, with $\tilde{\nu}_f + \Delta\tilde{\nu}_{Stokes} = \tilde{\nu}$. It follows that the fluorescence intensity at $\tilde{\nu}_f$, $I_f(\tilde{\nu}_f)$, is proportional to ϕ_f and to the intensity of exciting radiation that is absorbed by J, $I_{abs}(\tilde{\nu}) = I_0(\tilde{\nu}) - I(\tilde{\nu})$.

(a) Use the Beer-Lambert law to express $I_{abs}(\tilde{\nu})$ in terms of $I_0(\tilde{\nu})$, $[J]$, L, and $\varepsilon(\tilde{\nu})$, the molar absorption coefficient of J at $\tilde{\nu}$.

(b) Use your result from part (a) to show that $I_f(\tilde{\nu}_f) \propto I_0(\tilde{\nu})\varepsilon(\tilde{\nu})\phi_f[J]L$.

7. **Non-radiative Processes**
Discuss the following observations concerning non-radiative transitions in photochemistry in as much detail as possible: refer to Fermi's golden rule and its applicability to these processes where appropriate.

(a) The rate constant for intersystem crossing from S_1 to T_1 in propanone is $5 \times 10^8 s^{-1}$, but in benzophenone it is roughly $10^{11} s^{-1}$.

(b) The triplet (T_1) lifetimes for the molecules benzene, naphthalene and anthracene are 16 s, 2.4 s and 0.045 s, respectively. The T_1 to S_0 energy gaps are 29500 cm^{-1}, 21300 cm^{-1} and 14700 cm^{-1}, respectively.

(c) The fluorescence quantum yield of naphthalene in solution in hexane is 0.23, but for 1-bromonaphthalene is is 0.0016.

(d) The quantum yield of phosphoerescence of benzene-h_6 in a rigid glass at 80 K is 0.18, but for benzene-d_6 the yield is 0.24 under the same conditions.

(e) Fluorescence is generally observed only from the first excited singlet state (S_1) but for azulene, fluorescence is observed from the second excited singlet state (S_2) and almost non is observed from S_1.

(f) The fluorescence yield and lifetime of tryptophan fluorescence are both reduced in the presence of dissolved oxygen.

8. **Excimers and delayed fluorescence**

(a) Explain what is meant by the terms 'excimer' and 'delayed fluorescence'; describe the two main mechanisms for delayed fluorescence.

(b) Account for the following observations: When a dilute solution of pyrene (a polynuclear aromatic hydrocarbon) in ethanol is exposed to ultraviolet light it emits a violet fluorescence. Sudden extinction of the ultraviolet source results in the near instantaneous (sub microsecond) extinction of almost all the fluorescence but, at high light intensities in de-oxygenated solutions, the fluorescence decay also displays a delayed component.

In a concentrated solution the violet fluorescence is replaced by an intense sky-blue luminescence which decays near instantaneously when the excitation source is extinguished.

When the concentrated solution is cooled, becoming increasingly viscous and eventually forming a glass, the violet fluorescence returns as the sky blue luminescence fades. Sudden extinction of the light source results in the near instant loss of the fluorescence but in the glassy solution a red afterglow remains decaying with a half-life of ca. 1 s.

9. **Intermolecular Energy Transfer**
   The Förster theory of resonance energy transfer shows that the efficiency of energy transfter, E_T, is given by

   $$E_T = \frac{R_0^6}{R_0^6 + R^6}, \tag{1}$$

   where R_0 is a parameter characteristic of each donor-acceptor pair, and R is the separation of the donor and acceptor. The theory can be tested by performing fluorescence measurements on a series of compounds in which an energy donor and an energy acceptor are covalently linked by a rigid molecular linker of variable and known length. The following data was collected for a family of compounds with the general composition dansyl-(L-prolyl)$_n$-naphthyl in which the distance between the naphthyl donor and the dansyl acceptor was varied by increasing the number of L-prolyl units. Use a graphical procedure to test whether this data is adequately described by the Förster theory; if so, determine a value of R_0 for the naphthyl-dansyl pair.

R / nm	1.2	1.5	1.8	2.8	3.1	3.4	3.7	4.0	4.3	4.6
E_T	0.99	0.94	0.97	0.82	0.74	0.65	0.40	0.28	0.24	0.16

10. **Photoionization and Photoelectron spectroscopy**
    The photoelectron spectrum of HF excited by 40.81 eV photons, shown below, consists of two band systems. Sketch a molecular orbital diagram for HF and identify the orbitals from which the electrons are ejected and the states of HF$^+$ formed by ionization.

    Explain the form of the lower ionization band system and estimate the vibrational constants $\tilde{\omega}_e$ and $\tilde{\omega}_e x_e$ for this state.

    Estimate the dissociation energy of HF$^+$ in the excited electronic state from the higher ionization energy band system and comment on the appearance of this band in the light of your results.
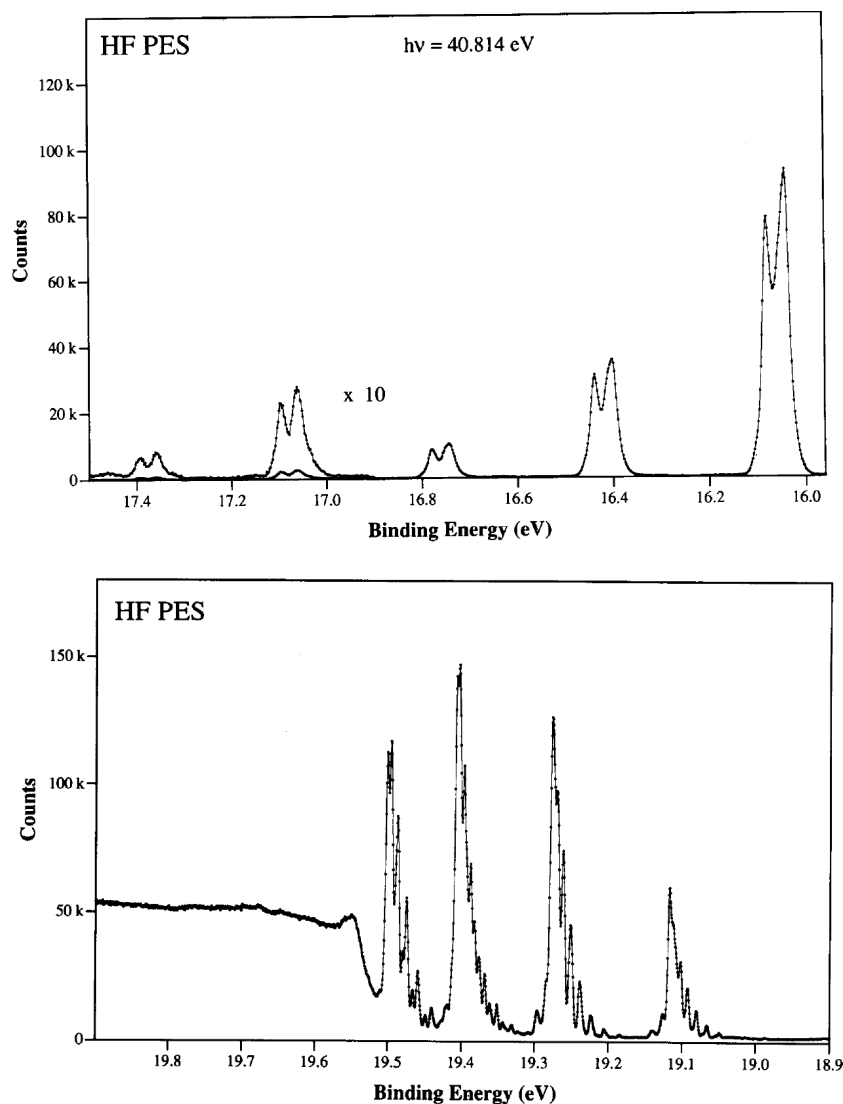
11. Photophysics and Photochemistry (from 2015 PartIB II paper)

(a) Explain the physical basis of gas phase photoelectron spectroscopy applied to atoms and molecules. [5]

(b) What is Koopmans' Theorem? To what extent is it an approximation? [3]

(c) The band corresponding to the lowest ionization energy in the photoelectron spectrum of F_2 molecules shows a long vibrational progression with a vibrational interval that is greater than for the ground state. Explain. [4]

(d) Sketch the molecular orbital diagram of N_2 and use it to predict the photoelectron spectrum of nitrogen, focussing your discussion on the three lowest electronic states of N_2^+. [9]

(e) The photoelectron spectrum of argon shows two peaks with an intensity ratio close to 2:1. Explain. [4]

12. **Atmospheric Chemistry**

The molecule Cl_2O_2 is believed to participate in the seasonal depletion of ozone over Antarctica. M. Schwell *et al.* (*J. Phys. Chem.* **100**, 10070 (1996)) measured the ionization energies of Cl_2O_2 by photoelectron spectroscopy in which the ionized fragments were detected using a mass spectrometer. From their data, we can infer that the ionization enthalpy of Cl_2O_2 is 11.05 eV and the enthalpy of the dissociative ionization,
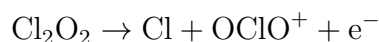
$$Cl_2O_2 \rightarrow Cl + OClO^+ + e^-$$

is 10.95 eV. They used this information to make some inferences about the structure of Cl_2O_2. Computational studies had suggested that the lowest energy isomer is ClOOCl, but that $ClClO_2$ (C_{2v}) and ClOClO are not very much higher in energy. The Cl_2O_2 in the photoionization step is the lowest energy isomer, whatever its structure may be, and its enthalpy of formation had previously been reported as $133 \, kJ \, mol^{-1}$. The Cl_2O_2 in the dissociative ionization step is unlikely to be ClOOCl, for the product can be derived from it only with substantial rearrangement. Given $\Delta_f H^0(OClO^+) = 1096 \, kJ \, mol^{-1}$ and $\Delta_f H^0(e^-) = 0$, determine whether the Cl_2O_2 in the dissociative ionization is the same as that in the photoionization. If different, how much greater is its $\Delta_f H^0$? Are these results consistent with or contradictory to the computational studies?

13. **Transition Dipole Moment**

Estimate the trnasition dipole moment of a charge-transfer transition modelled as the migration of an electron from a H1s orbital on one atom to another H1s orbital on an atom a distance R away. Approximate the transition moment by $-eRS$, where S is the overlap integral of the two orbitals given by

$$S(R) = \left[1 + \frac{R}{a_0} + \frac{1}{3} \left(\frac{R}{a_0} \right)^2 \right] \exp \left(-\frac{R}{a_0} \right), \tag{2}$$

with a_0 being the Bohr radius. Sketch the oscillator strength as a function of R using the curve for S given below. Why does the intensity fall to zero as R approaches zero and infinity?