Advanced class - Photochemistry/Atmospheric chemistry

Q1. <u>Advanced physical chemistry 1998, Q5</u>

Discuss <u>all</u> of the following observations concerning non-radiative transitions in photochemistry in as much detail as possible.

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

b) The radiative lifetime of the first excited singlet state in benzene, of $^{1}B_{2u}$ symmetry, is 414 ns, but its measured lifetime in solution is much shorter. For anthracene the radiative and measured lifetimes of the first excited singlet state are both about 10 ns.

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

d) The quantum yield of phosphorescence 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) The emission spectrum of a solution of pyrene in hexane at room temperature changes as a function of concentration. The emission from such a solution shows two lifetime components, one of the order of ns, the other of the order of ms.

Q2. <u>Advanced physical chemistry 2000, Q10</u>

a) Three processes of absorption and emission of light are absorption, spontaneous emission and stimulated emission.

   i) Describe briefly what happens in each process at a molecular level.
   ii) Indicate the factors determining the rate of each process in a two level system. [equations for the Einstein coefficients are not expected.]
   iii) Which process is dominant in fluorescence and which in laser action?

b) Comment on THREE of the following statements, giving equations and/or examples where applicable:

   i) Beer's law is strictly valid only for light of a narrow range of wavelengths within which the absorption coefficient is constant. At high light intensities it may break down completely. In some circumstances 'negative absorption' may occur, where the transmitted light is more intense than the incident light.

   ii) Kasha's rule, that emission occurs from the lowest state of each multiplicity, is valid for most luminescent substances. It breaks down for very small molecules in the gas phase and for some special polyatomic molecules such as azulene and its derivatives and thiocarbonyls in solution, which emit from S_2.

iii) Fluorescence emission bands generally lie to the red of the corresponding absorption bands, and may relate to the shape of the absorption as mirror images. For some substances the magnitude of the red shift between absorption and emission varies over a wide range according to the nature of the solvent.

iv) The products of a photochemical reaction are often chemically distinct from the products of a thermal reaction with the same reactant(s). The nature of the products may depend on the wavelength of the light used, or on the nature of the solvent. For instance, solvents containing heavy atoms such as ethyl iodide or dibromoethane may favour different products from those produced in a hydrocarbon solvent.

v) Pyrene (and some other compounds) shows fluorescence of different colours in concentrated and dilute solution. In concentrated solution at low temperature, light in the fluorescence wavelength band exhibits a two-component decay, with one short and one long lifetime.

Q3. <u>Advanced physical chemistry 2000, Q11</u>

a) The mean temperature of the Earth's surface is higher than the mean temperature expected from the balance of absorbed and emitted radiation.

i) Explain qualitatively why this is so.

ii) Identify the atmospheric constituents which make major contributions to surface warming.

iii) Discuss whether or not the contributions of different gases are additive, and how the warming effect may depend on their concentrations.

b) i) Explain why the presence of methane in the troposphere is important for the oxidation of NO to NO_2 and thus for the formation of tropospheric ozone.

ii) THe main reaction removing CH_4 is reaction with OH, for which the rate constant is 7.7×10^{-15} $cm^3 molecule^{-1} s^{-1}$. The mean concentration of OH in the troposphere is 6×10^5 molecules cm^{-3}. Estimate the lifetime of CH_4 in the troposphere.

c) The most intense feature in the Earth's dayglow is emission from the transition $O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-)$.

i) How is the excited molecular oxygen $O_2(^1\Delta_g)$ formed?

ii) The v′=0 → v″=0 vibrational band of this system is the most intense as observed from space, but very weak as seen from the ground, whereas the v′=0 → v″=1 band can be observed equally well from outside or within the atmosphere. Suggest a reason.

iii) The infrared atmospheric band originates at altitudes around 50 km, where the gas density is 2×10^{16} molecules cm^{-3}, from the transition $O_2(^1\Delta_g) \rightarrow O_2(^3\Sigma_g^-)$ whose radiative lifetime is 44 min. In a total solar eclipse, the intensity of the band was found to drop

with a half-life of 108 s. Obtain a rate constant for quenching of the excited state and comment on the result.
[Note: a typical quenching rate constant is 3×10^{-11} $cm^3moleule^{-1}s^{-1}$.]