

Photochemistry

Section A

- Q1. a) Obtain expressions for the quantum yields of the following processes:
- Fluorescence of an atom in a low pressure gas.
 - Fluorescence of an atom in a high pressure gas.
 - Photodissociation of a molecule in solution, where fluorescence, quenching and non-radiative decay exist as competing pathways.
- b) What measurements would be needed to determine the rate constant for photodissociation in case iii) above, and how would they be combined?
- c) Is the rate constant for dissociation likely to depend on the exciting wavelength? Explain why or why not.
- Q2. For the gas phase photoreaction $\text{HI} + h\nu \rightarrow \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{I}_2$, the quantum yield at 254 nm is found to be 2.0. Suggest a reaction scheme to explain this result, justifying both the steps you include and those you omit.
- Q3. a) Write down the reaction scheme for relaxation and quenching of a fluorescent excited state (normal 'dynamic' quenching).
- b) Obtain expressions for the ratios of fluorescence intensity and lifetime in the presence of a quencher to the values without quencher (I_0/I and τ_0/τ) in normal quenching of the excited state as in a).
- c) Given that the mechanism of the less common 'static' quenching is reversible formation of a non-fluorescent complex involving the *ground* state of the quenched molecule, obtain expressions for I_0/I and τ_0/τ in pure static quenching, in which the quencher has no effect on the excited state.
- d) Compare the expressions you have obtained, and in view of the comparison suggest one or more ways to distinguish static and dynamic quenching.
- Q4. For a 3.7×10^{-3} M solution of naphthalene in hexane, the peak of the first absorption band is at 301 nm. Light at this wavelength is reduced to a tenth of its initial intensity on passing through 1 cm of the solution; obtain the molar absorption coefficient. The width of the absorption band is estimated as 3000 cm^{-1} , and its shape may be assumed to be triangular; the refractive index of hexane is 1.375. Estimate the radiative lifetime of the S_1 state. The measured fluorescence lifetime and quantum yield are 96 ns and 0.19 respectively; comment.
- Q5. For naphthalene in a glassy matrix at 77 K excited to the S_1 state, the quantum yield of fluorescence is 0.20, the quantum yield of triplet formation is 0.80, and the quantum yield of phosphorescence is 0.018.
- Draw a labelled diagram showing the radiative and non-radiative pathways followed in naphthalene under these conditions.
 - Using the measured lifetime of fluorescence of 96 ns, determine the rate constant for intersystem crossing from S_1 to T_1 .
 - From the measured phosphorescence lifetime of 2.6 s, determine the rate constant for intersystem crossing from T_1 to S_0 .

iv) Comment on the difference between the two lifetimes and the two intersystem crossing rate constants.

Q6. Comment on the following, indicating which parts of the statements are true or false.

- (A) The dispersed fluorescence spectrum of a molecule excited in either the gas phase or solution is independent of excitation wavelength, and is approximately a mirror image of the absorption spectrum.
- (B) The width of an absorption line for a gas phase atom is independent of pressure, and decreases with decreasing temperature. If it was possible to cool the atom to absolute zero in the gas phase, the absorption width would become infinitely narrow.
- (C) In solution the magnitude of the $S_1 - T_1$ splitting influences the rate of intersystem crossing (ISC) from S_1 . Heavy atom substitution increases the ISC rate, and this is shown particularly clearly in the comparative behaviour of hydrogenated and deuterated compounds.
- (D) Fast timescale flash photolysis can be used to determine rate constants for collisional relaxation of singlet and triplet states. Radiative decay rate constants (Einstein A coefficients) can be determined from such measurements, and can also be calculated from absorption coefficients.