

Photoionization of solutes in homogeneous or micellar solutions

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The one-photon ionization of perylene (Pe) and tetracene (Tet) in anionic (NaLS) or neutral micelles (Mi) is compared with the photoionization process in homogeneous solutions (tetramethylsilane or methanol). Two striking results are emphasized.

(a) The shape of the photoionization efficiency curves in the threshold energy region is found to differ markedly for Pe or Tet in NaLS Mi on the one hand and in neutral Mi or homogeneous solutions on the other. It is suggested that such a difference illustrates the reduced recombination of geminate ion pairs in the former case.

(b) The decrease ΔI_{Mi} of the ionization threshold energies of Pe and Tet in Mi relative to their gas phase ionization potentials amounts to 2.3 - 2.35 eV for both solutes. This decrease ΔI_{Mi} is interpreted in terms of the parameters which are currently considered to govern the optical ionization of impurity molecules in condensed media. In such a framework the electric field gradient at the Mi-water interface does not seem to contribute significantly to the observed ΔI_{Mi} value.

The vacuum UV photolysis of 1-butyne

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Molecular oxygen is largely used as a radical scavenger in various photochemical studies. For example, the disappearance of ethane formation observed in the photolysis of 1-butene on addition of 5% - 10% O₂ is good support for a radical mechanism leading to the formation of ethane. This effect is confirmed by the use of nitric oxide. In each case the presence of free electrons gives rise to a free-radical scavenging effect and precludes recombination of organic free radicals ($R_1 + R_2 \rightarrow R_1R_2$).

For 1-butyne the situation is similar to the extent that the ethylene quantum yield is not concerned. For example, at 147 nm the ethane quantum yield decreases from 0.38 to 0.00 on addition of either 10% O₂ or 10% NO at a total pressure of 1 Torr (133 N m⁻²). For ethylene nitric oxide has no noticeable effect: the production of ethylene does not seem to result from a radical-radical

reaction. Conversely, the addition of molecular oxygen increases the ethylene quantum yield from 0.14 to 0.38 at a total pressure of 1 Torr.

From these results it is not obvious what mechanism is responsible for such an effect. However, the involvement of excited *triplet* intermediates may be assumed:



Direct absorption of a photon leads to the formation of a *singlet* excited molecule. This excited molecule decomposes into two *triplet* excited molecules etc. Triplet–triplet annihilation processes are well known in the liquid phase but are not often included in gaseous chemical systems.

Collision-induced radiationless transitions in CS₂

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We measured the quenching rate constants of CS₂ vapour (¹A₂ and ³A₂ states) by laser-induced fluorescence with the gases CS₂, CO₂, O₂, NO, C₂H₅OH, CH₃OH, C₂H₅NO₂, CCl₄ and CH₃CN. The emission was measured in regions centred at 4480 and 5860 Å. The quenching cross sections were obtained for both electronic states. Stern–Volmer plots at 4480 Å for the ³A₂ state show saturation effects for CH₃CN, C₂H₅NO₂ and O₂, whereas only O₂ produces such effects at 5860 Å. The quenching cross sections correlate with the molecular parameters defined in the Thayer–Yardley model for collision-induced radiationless transitions. The decay of CS₂ obeys this model for the two states involved.

Energy selection experiments in glassy matrixes: the fluorescence spectrum of isobacteriochlorin

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The fluorescence spectrum of a synthetic isobacteriochlorin 1 was studied in a glassy matrix at low temperature. It consists of a single strong 0–0 band and very little vibronic structure. Excitation into a region 400 - 900 cm⁻¹ above the