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% O_2 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% O_2 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