

solute (benzene). The compounds which were studied were C_6H_{12} , C_6D_{12} and $C_{10}H_{18}$, with which both intensity and lifetime quenching experiments on the UV emission were performed. At variance with previous results, the quenching rate parameters obtained are consistent with a diffusional mechanism.

Effect of excited state switching on the photophysical characteristics of benzophenone and related molecules

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The study of the phosphorescence emission of a series of aryl ketones in acetic acid solution at liquid nitrogen temperature has shown that it is possible in this solvent to vary the nature of the lowest triplet state progressively from a predominantly n,π^* configuration to a predominantly π,π^* or charge transfer (CT) configuration by changing the substituent from electron withdrawing to electron releasing in nature. This behaviour has been evidenced by the presence of two components in the low temperature spectra, which invert their positions according to the nature of the substituent. This state switching is responsible for the different photophysical characteristics of aryl ketones in fluid solution. In fact, only n,π^* triplets display phosphorescence emission and efficient sensitizing power, whilst ketones with CT triplets neither phosphoresce nor sensitize but act as quenchers of n,π^* triplet ketones.

Two-photon photoionization of substituted anthracenes from the S_1 state: application to the study of intermolecular and intramolecular charge transfer

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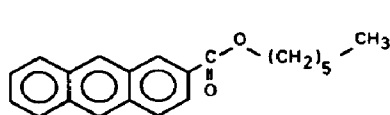
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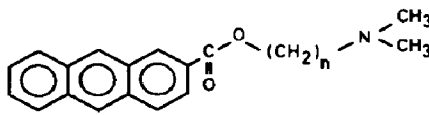
Intermolecular and intramolecular deactivation of the excited states of the following compounds were studied by laser photolysis. Fluorescence quenching of the compounds 2-A(n) ($n = 2, 11$) occurs through the formation of non-fluorescent (or weakly fluorescent) intramolecular exciplexes. In solution a photoion-

ization process was found to take place as well as the formation of exciplexes. In solutions of anthracene, 2-A(0) or 2-A(*n*) in acetonitrile or ethanol excited by a YAG–Nd laser (353 nm; pulse radiation, 3 ns; energy, 5 - 70 mJ), cation–electron pairs are formed. The photoionization process is biphotonic, the second photon being absorbed by an excited singlet state S.

This photoionization process was then used for the study of intermolecular and intramolecular charge transfers. An intramolecular charge transfer was shown to occur from the anthracene cation to the amino group at the opposite end of the molecule in the compounds 2-A(2) and 2-A(11). The influence of chain length on the rate of electron transfer enabled us to determine the mechanism of this transfer.



2-A(0)

2-A(*n*)

Photoionization of tryptophan in aqueous solution

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Photochemical formation of solvated electrons e_{aq}^- from neutral aqueous tryptophan at low light intensities was studied by quantitative determination of Cl^- ions resulting from the reaction of e_{aq}^- with 2-chloroethanol. Cl^- ion liberation at low scavenger concentrations (less than 10^{-2} M) results only from this reaction, since NO_3^- ions or tryptophan reduce the Cl^- ion yield by competition reactions for the electrons between the different scavengers in the system. For $\lambda_{\text{exc}} = 254$ nm a yield $Q(e_{\text{aq}}^-)$ of 0.021 ± 0.002 was found. This yield decreases similarly to the fluorescence yield after addition of Cs^+ ions as singlet quenchers. Electron ejection and fluorescence emission are competitive processes. Studies of excitation wavelength effects, especially on the fluorescence yield, gave no indication of processes originating prior to fluorescence when the excitation wavelength was longer than 248 nm.