

polyene chain, causing the departure from mirror symmetry, an increased Stokes shift, and in the extreme case ( $\theta = 180^\circ$ ) *trans-cis* isomerization. The increase in  $\theta$  reduces the  $^1A_g^*$  energy and increases the  $^1B_u$  energy, so that when  $\theta$  exceeds a critical value  $\theta_c (\geq 0)$  the  $^1B_u - ^1A_g^*$  energy gap  $\Delta E$  becomes positive and increases with  $\theta$ . The fluorescence then corresponds to the forbidden  $^1A_g \rightarrow ^1A_g$  transition (rate  $k_F$ ) which derives its oscillator strength by coupling to the allowed  $^1B_u \rightarrow ^1A_g$  transition (rate  $k_A$ ) so that  $k_F = K^2 k_A / \Delta E^2$

corresponding to

$$\tau_F / \tau_A = \Delta E^2 / K^2$$

where  $K$  is the matrix element coupling the two transitions.  $\tau_F$  and  $\tau_F / \tau_A$  thus depend on  $\Delta E$  and  $\theta$ , which are influenced by the solvent, temperature and polyene chain length. The intramolecular radiationless transitions (intersystem crossing, internal conversion, *trans-cis* isomerization) also depend on  $\theta$ , and they are subject to similar solvent and temperature effects.

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## O6

### Formation of the Excited Triplet, the Excited Singlet and the Excimer of Octafluoronaphthalene in Solution

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The octafluoronaphthalene (OFN) excited triplet is formed by flash photolysis of OFN solutions in methylcyclohexane, acetonitrile, benzene and carbon tetrachloride. Formation of the triplet is photosensitized by phenanthrene and decafluorobenzophenone. The OFN triplet is also formed by pulse radiolysis of solutions of OFN in benzene and methylcyclohexane.

Emission from dilute solutions ( $10^{-4} - 10^{-3} M$ ) of OFN in benzene and methylcyclohexane has been observed by photoexcitation and pulse radiolysis. The emission  $\lambda_{\max}$  is at  $\sim 350$  nm, in reasonable agreement with previously published data

and is attributed to the OFN excited singlet.

The emission  $\lambda_{\max}$  shifts slowly towards the red as the OFN concentration is increased, in both photoexcitation and pulse radiolysis studies. The magnitude of the shift is small ( $\sim 10$  nm). The emission spectra obtained at  $10^{-4} M$  OFN in solutions in benzene and methylcyclohexane are attributed to the OFN excimer.

## O9

### Direct Determination of the Triplet Quantum Yields of Acridine in Polar and Non-Polar Solvents

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The present work reports direct measurement of  $S \rightarrow T$  intersystem crossing (ISC) quantum yield of acridine (the heterocyclic compound isoelectronic of anthracene) in different solvents using the third harmonic of a neodyme laser (352.7 nm). The system to be studied is exposed to a pulse of the laser light and the transient absorption changes in the system (due to triplet population) are recorded. Knowing the extinction coefficient of the triplet ( $\epsilon_{T-T}$ ) and the total light absorbed, an absolute value of the triplet yield is obtained. The number of photons absorbed is determined by using a standard for comparison. In this work anthracene in ethanol has been used: the quantum yield  $\Phi_T$  and the extinction coefficient of the triplet state have been very well established for this molecule:  $\Phi_T = 0.7$  [1] and  $\epsilon_{T-T} = 60.000$  in ethanol at 421 nm.

The method was used to determine triplet yields for acridine in polar and non-polar solvents: Benzene, tert-Butanol and water (pH = 12). Values of the quantum yields are given in the table. The corresponding  $\epsilon_{T-T}$  were determined by a light saturation technique [2].

The different deactivation processes of the excited state  $S^*$  is expressed in the following scheme:

