

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 θ reduces the $^1A_g^*$ energy and increases the 1B_u energy, so that when θ exceeds a critical value $\theta_c (\geq 0)$ the $^1B_u - ^1A_g^*$ energy gap ΔE becomes positive and increases with θ . 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. τ_F and τ_F / τ_A thus depend on ΔE and θ , 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 θ , and they are subject to similar solvent and temperature effects.

This work was supported by NATO grant 630.

O6

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

A. SINGH and M. J. QUINN
Research Chemistry Branch, Atomic Energy of Canada Limited and Whiteshall Nuclear Research Establishment, Pinawa, Manitoba ROE 1L0 (Canada)

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 λ_{\max} is at ~ 350 nm, in reasonable agreement with previously published data

and is attributed to the OFN excited singlet.

The emission λ_{\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 (~ 10 nm). The emission spectra obtained at $10^{-4} M$ OFN in solutions in benzene and methylcyclohexane are attributed to the OFN excimer.

O9

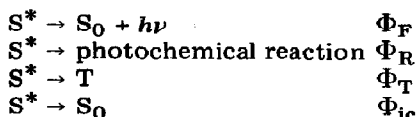
Direct Determination of the Triplet Quantum Yields of Acridine in Polar and Non-Polar Solvents

A. KELLMANN
Laboratoire de Photophysique Moléculaire, Université de Paris-Sud, 91405-Orsay (France)

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 (ϵ_{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 Φ_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 ϵ_{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:



and the sum of the corresponding quantum yields of these processes is unity: $\Phi_{ic} = 1 - \Phi_R - \Phi_F - \Phi_T$.

In benzene and water there is no photochemical reaction from the singlet state, and in tert-BuOH the yield of the reaction is very low. Acridine does not fluoresce in non-polar solvents, in alcoholic solution its quantum yield is very low compared to a high yield in water [3]. The various data are summarized in the table:

Solvent	Φ_T	Φ_R	Φ_F	Φ_{ic}
Benzene	0.71	-	-	0.29
tert-BuOH	0.61	0.01	0.02	0.36
water	0.37	-	0.37	0.26

These data imply an internal conversion from the first excited singlet for acridine in these different solvents. It is significant that even in water where the fluorescence yield is important an internal conversion is present, contrary to the anthracene molecule where no internal conversion occurs. This different behaviour may be due to the lone pair of the nitrogen in the cycle. ISC quantum yields of aromatic heterocycles have not been extensively studied, Hadley [4], however stated similar observations between quinoline and naphthalene.

- 1 A. R. Horrocks, and F. Wilkinson, Proc. Roy. Soc. A, 206 (1968) 257.
- 2 A. Kellmann and L. Lindqvist, in A.B. Zahlan (ed.), The triplet State, Cambridge University Press, London, 1967, p. 439.
- 3 E. J. Bowen, N. J. Holder and G. B. Woodger, J. Phys. Chem., 66 (1962) 2491.
- 4 S. G. Hadley, J. Phys. Chem., 75 (1971) 2083.

O10

The Temperature and Viscosity Dependence of Energy Transfer from Triplet Aromatic Molecules

E. J. MARSHALL, N. A. PHILIPSON, M. J. PILLING, S. A. RICE and P. SPENCER

Physical Chemistry Laboratory, South Parks Road, Oxford (U.K.)

The deactivation of triplet aromatic molecules in alcohols was studied by laser flash photolysis, as a function of temper-

ature. Methanol/water and 2-methyl-2,4-pentanediol were used as solvents. Both form glasses, and a viscosity range of $> 10^{12} \text{ kg m}^{-1} \text{ s}^{-1}$ was available. For exoergic transfer to other aromatic molecules, the reactions are diffusion-controlled, but the rate constant falls less rapidly with temperature than the solvent fluidity. This is in agreement with published results, but the present data cover a wider viscosity range than has previously been reported. For transfer to metal ions, the high temperature rate is less than the diffusion-controlled value, and the temperature dependence of the quenching process itself, exclusive of fluidity effects, may be determined. At lower temperatures the mechanism changes to one of diffusion-control. A theoretical analysis of the effect of an exchange interaction on a diffusion-controlled reaction shows that the encounter distance increases as the solvent fluidity is reduced. The implications of this to the present experimental results are discussed.

O12

Excited State Formation in *p*-Dioxane

AJIT SINGH, S. P. VAISH and M. J. QUINN

Research Chemistry Branch, Atomic Energy of Canada Limited and Whiteshell Nuclear Research Establishment, Pinawa, Manitoba ROE 1L0 (Canada)

Emission from purified liquid *p*-dioxane has been observed by photoexcitation and pulse radiolysis. Solute emission is observed on pulse radiolysis of solutions of naphthalene in *p*-dioxane. At a naphthalene concentration of 10^{-3} M the *p*-dioxane emission is reduced by $\sim 75\%$. However, at a naphthalene concentration of 1 M , the solute emission is ~ 10 times greater than that at 10^{-3} M . This is attributable to energy transfer from higher excited states of the solvent to the solute, in the 1 M solution.

Evidence has been obtained for the formation of the triplet excited state of *p*-dioxane, by pulse radiolysis of solutions of β -carotene. Formation of the solute triplet has been studied as a function of naphthalene concentration (10^{-4} to 1 M) in *p*-dioxane. The dependence of the naphthalene triplet formation on the naphthalene concentration is quite similar to that of the naphthalene emission.