Investigation of Singlet–Triplet Transitions by the Phosphorescence Excitation Method. Spectroscopic Determination of Intersystem Crossing Quantum Yields and Extinction Coefficients of Singlet–Triplet Transitions

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WE previously reported that the phosphorescence excitation method (PEM) is useful for investigation of the singlet–triplet absorption spectra of organic molecules.[1] In that preliminary report we obtained the position and relative intensity of the lowest singlet–triplet transition of 1-bromonaphthalene, but did not determine the absolute magnitude of the singlet–triplet extinction coefficient, ϵ_{ST}. In this Communication, we show how PEM may be used either to determine spectroscopically intersystem crossing yields, ϕ_{IC}, in molecules where ϵ_{ST} can be measured directly, or to measure ϵ_{ST}-values in molecules where ϕ_{IC} is known.

In PEM, the observed intensity of phosphorescence, $I(\lambda)$, is monitored as a function of the wavelength, λ, of the exciting light. If λ corresponds to a singlet–singlet absorption band, $I(\lambda_S)$ will be given by

$$I(\lambda_S) = \epsilon_{SS}(\lambda_S)\cdot C_S\cdot\phi_{IC}\cdot q\cdot L(\lambda_S)\cdot X(C_S) \qquad (1)$$

where $L(\lambda_S)$ is the intensity of the exciting light at

TABLE[a]

Compound	$\epsilon_{SS}(\lambda_S)$	$\epsilon_{ST}(\lambda_T)$	$\gamma(\lambda_S,\lambda_T)$	$\epsilon(\lambda_S)/\epsilon(\lambda_T)$	ϕ_{IC} (calc.)	ϕ_{IC} (lit.)
1-Bromonaphthalene	357 (3190 Å)	0·014 (4400 Å)	25,000	25,500	1·0	(1·0)[b]
Benzophenone	65 (3700)	0·036 (4040)	2200	2000	1·1	1·0[c]
Acetophenone	8·2 (3550)	0·080 (3760)	122	102	1·2	1·0[c]

[a]All absorption and emission measurements in rigid (ether–toluene, 4 : 1) glass at 77°K.
[b]No literature value appears to be available, but the observed fluorescence quantum yield, (ref. 2) $\phi_f = 0{\cdot}0016$ suggests that ϕ_{IC} is near unity.
[c]See reference 3.

wavelength λ_S, C_S is the molar concentration, q is an apparatus constant, ϵ_{SS} (λ_S) is the extinction coefficient for the singlet–singlet transition, and X is the fraction of triplet-state molecules which phosphoresce. If λ corresponds to a singlet–triplet absorption band, $I(\lambda_T)$ will be given by

$$I(\lambda_T) = \epsilon_{ST}\,(\lambda_T)\cdot C_T\cdot q\cdot L(\lambda_T)\cdot X(C_T) \qquad (2)$$

where C_T is the molar concentration. In order for PEM to work properly, the optical density of the sample at the excitation wavelength must be small, and therefore $C_S << C_T$. From Equations 1 and 2, we find that

$$\frac{\phi_{IC}\cdot\epsilon_{SS}(\lambda_S)}{\epsilon_{ST}(\lambda_T)} = \frac{I(\lambda_S)}{I(\lambda_T)}\cdot\frac{C_T}{C_S}\cdot\frac{L(\lambda_T)}{L(\lambda_S)} \equiv \gamma(\lambda_S,\lambda_T) \qquad (3)$$

The quantity ϵ_{SS}, and all of the quantities on the right hand side of Equation 3 can be easily determined experimentally, and thus the only unknown quantity is ϕ_{IC}/ϵ_{ST}. If either ϕ_{IC} or ϵ_{ST} can be measured independently, PEM may be used to determine the other.

In the present work we have measured ϵ_{ST} for 1-bromonaphthalene, benzophenone, and acetophenone at 77°K by conventional absorption techniques, and these results are presented in the Table and the Figure. The phosphorescence excitation spectra, $I(\lambda)$ against λ, for these same compounds are also presented in the Figure and the essential data are collected in the Table. From these data, and Equation 3, we have calculated ϕ_{IC}-values for the three compounds. Since ϵ_{ST} and γ were only measured to within ± 10%, the calculated ϕ_{IC}-values are uncertain by about ± 20%. These results are also presented in the Table, where they are compared with ϕ_{IC}-values from the literature. Within the precision of our measurements, the agreement with previously determined ϕ_{IC}-values is satisfactory.

Because of the recent availability of ϕ_{IC}-values,[3,4] and the difficulty associated with direct measurement of ϵ_{ST}-values, PEM would appear to have its greatest utility in the determination of ϵ_{ST}-values, rather than ϕ_{IC}-values.

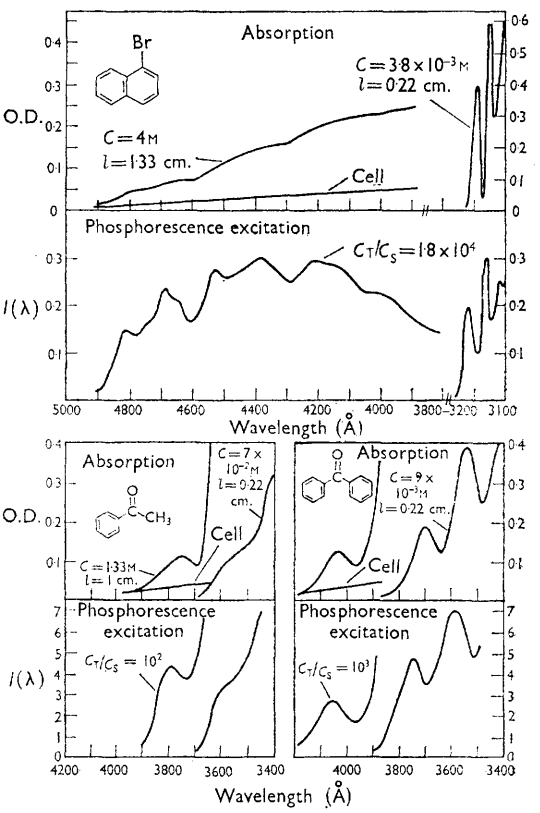

FIGURE. *Absorption and phosphorescence excitation spectra of* 1-*bromonaphthalene, benzophenone, and acetophenone in a rigid ether–toluene glass at* 77°K.

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[1] W. Rothman, A. Case, and D. R. Kearns, *J. Chem. Phys.*, 1965, **43**, 1067.
[2] V. L. Ermolaev and K. K. Svituschev, *Optics and Spectroscopy*, 1959, **7**, 399.
[3] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, 1965, **43**, 2129.
[4] C. A. Parker and T. A. Joyce, *Chem. Comm.*, 1966, 234.