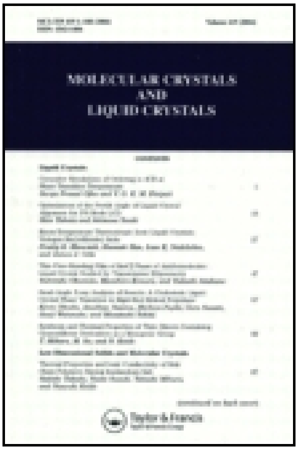

Molecular Crystals

Quantum efficiencies of triplet formation in aromatic molecules

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Quantum efficiencies of triplet formation in aromatic molecules

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Abstract—A knowledge of the quantum yields of fluorescence, φ_F, and phosphorescence, φ_P, alone does not make it possible to separate the two non-radiative processes, $\varphi_{F'}$, and $\varphi_{P'}$, which quench respectively the first excited singlet state, S_1, and the lowest triplet state, T_1. To do this, the quantum yield of triplet formation, φ_T, must be known. We have measured the extinction coefficients, ε_T, of triplet-triplet absorption for a series of aromatic hydrocarbons in EPA at 77°K. From the ε_T data plus chemical actinometry, we have obtained values of φ_T. In addition, we have made accurate absolute measurements of fluorescence yield, φ_F, in solution at 25°C. From our φ_F data and room-temperature values of φ_T reported by Lamola and Hammond, we can calculate values of $\varphi_{F'}$. Benzene, naphthalene, phenanthrene, chrysene and 1,2-benzanthracene have significant values of φ_F. Perdeuteration causes no significant change in the value of $\varphi_{F'}$. We conclude, therefore, that internal conversion from S_1 to S_0 is determined largely by processes other than coupling of the electronic excitation to C-H vibrations. At 77°K, φ_F data to combine with our φ_T values are available only for anthracene. Depending on which of two φ_F values is used, the value obtained for φ_F, is either 0.20 or 0.12 with an uncertainty of ± 0.10. Clearly there is a great need for accurate low-temperature measurements of fluorescence yield in order to determine whether significant internal conversion from S_1 to S_0 occurs at 77°K.

1. Introduction

The energy level diagram for a typical aromatic molecule is shown in Fig. 1. The φ's represent quantum yields and the k's rate constants for the various processes. The suffixes F, P and T refer to fluorescence, phosphorescence and triplet formation respectively. The symbols $\varphi_{F'}$, $k_{F'}$ and $\varphi_{P'}$, $k_{P'}$ refer to the radiationless processes which respectively quench fluorescence and phosphorescence. Several simple relations con-

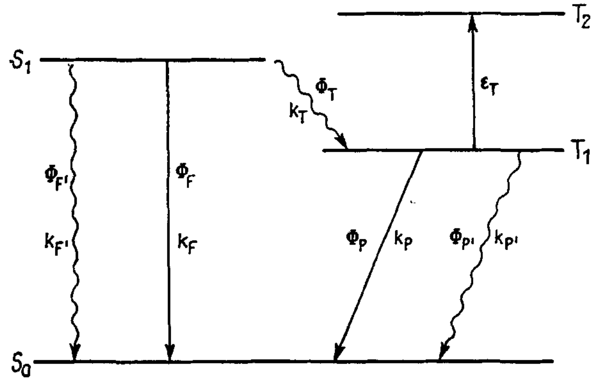

Fig. 1.

nect the quantities shown,

$$\varphi_F + \varphi_{F'} + \varphi_T = 1 \tag{1}$$

$$\varphi_T = \varphi_P + \varphi_{P'} \tag{2}$$

$$k_F = \varphi_F(k_F + k_{F'} + k_T) = \varphi_F/\tau_F^m \tag{3}$$

$$k_{F'} = \varphi_{F'}(k_F + k_{F'} + k_T) = \varphi_{F'}/\tau_F^m \tag{4}$$

$$k_T = \varphi_T(k_F + k_{F'} + k_T) = \varphi_T/\tau_F^m \tag{5}$$

$$k_P = \varphi_P(k_P + k_{P'})/\varphi_T = \varphi_P/\varphi_T\tau_P^m \tag{6}$$

$$k_{P'} = \varphi_{P'}(k_P + k_{P'})/\varphi_T = \varphi_{P'}/\varphi_T\tau_P^m \tag{7}$$

where $\tau_F^m = (k_F + k_{F'} + k_T)^{-1}$ is the measured lifetime of fluorescence and $\tau_P^m = (k_P + k_{P'})^{-1}$ is the measured lifetime of phosphorescence.

A knowledge of the quantum yields of fluorescence and phosphorescence alone does not make it possible to separate the two non-radiative processes, $\varphi_{F'}$ and $\varphi_{P'}$. To do this, the value of the quantum yield of triplet formation, φ_T, needs to be known. Measurements of φ_F and φ_P are fairly extensive[1-6] but values of φ_T are difficult to obtain and little quantitative data exist. Clever methods involving triplet energy transfer have been developed but these are necessarily indirect[7, 8]. The most direct way to obtain quantum efficiencies of triplet formation is an optical determination of the concentration of triplets coupled with chemical actinometry to determine the number of photons absorbed by the system. This is the method used in the present work. It depends for its success on an accurate determination of the extinction coefficient, ε_T, for the T–T absorption band.

2. Experimental

A detailed description of the experimental techniques for measuring ε_T and φ_T is given in a forthcoming publication.[9] The measurement of ε_T is based on obtaining the number of molecules converted to the triplet state from the decrease in the absorption of the ground state when the sample is excited by *uv* light. All measurements were made in frozen glassy solutions of EPA at 77°K.

We have also measured values of φ_F at 23°C by the technique of Weber and Teale[2, 6] for use with the values of φ_T measured at room temperature by Lamola and Hammond.[7]

3. Results and Discussion

Radiationless Quenching of S_1 at Room Temperatures

Present values of φ_F and values of φ_T by Labhart[10] and by Lamola and Hammond,[7] which were all measured at 25°C, appear in Table 1 together

TABLE 1 Quantum yield data at 25°C

Compound	Solvent	φ_T	φ_F	$\varphi_{F'}$ $(1-\varphi_T-\varphi_F)$
Benzene	a	0.24[b] ± 0.01	0.055 ± 0.01	0.705 ± 0.02
Naphthalene-h_8	c	0.40[d] ± 0.01	0.19 ± 0.01	0.41 ± 0.02
Naphthalene-d_8	c	0.38[d] ± 0.01	0.20 ± 0.01	0.42 ± 0.02
Phenanthrene	Benzene	0.76[d] ± 0.01	0.15 ± 0.01	0.09 ± 0.02
Chrysene	Benzene	0.67[d]	0.23	0.10
Fluorene	c	0.31 ± 0.01[d]	0.70 ± 0.03	−0.01 ± 0.04
Triphenylene	c	0.95 ± 0.05[d]	0.066 ± 0.01	−0.016 ± 0.006
1,2-benzanthracene	Hexane	0.55[e]	0.20[e], 0.20	0.25

(a) trans-1,2-dimethylcyclohexane for φ_T measurement and hexane for φ_F measurement
(b) A.A. Lamola, Ph. D. Thesis, Calif. Inst. Tech. (1965)
(c) Benzene for φ_T measurement and absolute ethanol for φ_F measurement
(d) Reference 7
(e) Reference 10
(f) Value of φ_F in absolute ethanol solution

with derived values of the non-radiative component, $\varphi_{F'}$ (Eq. 1). Values of φ_F and φ_T used in this calculation of φ_F should be measured in the same solvent. The measurements of φ_T for naphthalene, triphenylene and fluorene were made in benzene while the φ_F measurements were made in absolute ethanol. However, the values of φ_F are usually only slightly higher in benzene than in ethanol due to the higher index of refraction of benzene and the difference should not be large enough to contribute a serious error in the estimate of $\varphi_{F'}$. Similarly, the different solvents used in measurements of φ_F and φ_T of benzene should result in little error in $\varphi_{F'}$.

Excepting fluorene and triphenylene, the compounds in Table 1 have significant values of $\varphi_{F'}$ that range between 0.09 for phenanthrene and 0.70 for benzene. Consequently at 25°C, there is significant radiationless quenching of S_1 directly to S_0 in 6 of the 8 aromatic hydrocarbons in Table 1.

Values of phosphorescence yield of aromatic hydrocarbons for the perdeuterated form of the molecule are usually much higher than for the perprotonated form of the molecule. A similar increase of φ_F due to perdeuteration is not obtained. Values of φ_F for ethanol solutions at 25°C of the perdeuterated forms of naphthalene, chrysene, triphenylene and 1,2-benzanthracene are only very slightly larger (0.02 or less) than φ_F for the corresponding perprotonated compound. We conclude, therefore, that the rate of $S_1 \rightarrow S_0$ radiationless quenching is determined largely by processes other than coupling of the electronic excitation energy to C–H vibrations.

In the case of naphthalene, the triplet yield φ_T is also independent of deuteration[7] and the corresponding values of $\varphi_{F'}$ for naphthalene-h_8 and naphthalene-d_8 are, therefore, the same within the limits of error (Table 1). The magnitude of $\varphi_{F'}$ (0.41) for naphthalene and its lack of change on deuteration further strengthens the above conclusion.

Triplet Yields and Radiationless Quenching of S_1 at 77°K

Values of ε_T and φ_T for several aromatic hydrocarbons in EPA at 77°K are summarized in Table 2. The estimated accuracy is $\pm 10\%$ for values of ε_T and $\pm 15\%$ for values of φ_T. For anthracene-d_{10} the measurement of ε_T is less accurate because the extent of singlet depletion is much less on account of the much shorter triplet lifetime of this com-

TABLE 2 Extinction coefficients for T-T absorption and quantum yields of triplet formation for several aromatic hydrocarbons

Compound	$\varepsilon_T{}^a$ l. mole^{-1} cm^{-1} EPA: 77°K	λ in nm	φ_T EPA: 77°K
Anthracene-d_{14}	115,000	426	0.53
Chrysene	48,000	585	0.70
Picene	62,000	630	0.36
1,2:5,6-Dibenzanthracene	35,000	585	0.98
1,12-Benzperylene	40,000	467	0.59

(a) Maximum value at wavelength, λ

pound. The estimated accuracy of φ_T for anthracene-d_{10} is consequently ±20%.

Other estimates of ε_T for some of the above compounds have been reported by McClure,[11] Craig and Ross[12] and Porter and Windsor.[13] No other measurements of triplet yields at low temperatures have been reported, however.

We would like to estimate values of $\varphi_{F'}$ at 77°K. However, with the exception of anthracene, low temperature φ_F data are not available for these compounds. Medinger and Wilkinson[8] concluded from quenching measurements that $\varphi_{F'} \approx 0$ for anthracene at room temperature and Laposa *et al.*[14] have come to a similar conclusion for anthracene at 77°K in EPA from the small change in fluorescence lifetime upon deuteration of ordinary anthracene. The low-temperature value of φ_F for anthracene is uncertain. Parker and Hatchard[4] made fairly precise relative measurements of φ_F and converted them to absolute values by assuming Weber and Teale's[2] value of 0.54 for the fluorescence yield of fluorene. This led to a value of 0.27 for the fluorescence yield of anthracene. However, we have recently remeasured φ_F for fluorene and obtain 0.70. This leads to a φ_F value of 0.35 for anthracene. Neither value is likely to be very reliable since Parker and Hatchard made their measurements in EPA at 77°K and both Weber and Teale and we worked in liquid ethanol solution at room temperature; the optical densities in EPA at 77°K may differ considerably from those at room temperature and corrections for polarization effects at low temperature may be quite appreciable. The low temperature φ_F values for anthracene can, therefore, be taken only as a rough guide. Values of $\varphi_{F'}$, for anthracene in EPA at 77°K can be estimated from the values of φ_T for perdeuterated anthracene in Table 1 and the value of φ_F for perprotonated anthracene[15] measured by Parker and Hatchard. Depending on which value of φ_F is used, the value of $\varphi_{F'}$ obtained is either 0.20 or 0.12. However, the uncertainty in these values exceeds ± 0.10. One cannot, therefore, conclude with certainty that $\varphi_{F'}$ is significantly greater than zero for anthracene at 77°K. There is clearly a great need for accurate low-temperature measurements of φ_F in order to determine whether significant radiationless quenching of S_1 to S_0 occurs at 77°K.

By combining in equation 5 the $\varphi_{T'}$ measurements of Table 2 with values of fluorescence lifetimes,[14] the rate constant k_T for intersystem crossing can be evaluated. The values obtained are 9.3×10^7 sec^{-1} for anthracene -d$_{10}$ and 1.4×10^7 sec^{-1} for chrysene.

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