

Intermolecular energy transfer in mixed laser dyes: photophysical properties of triplet states

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Abstract. Triplet-singlet energy transfer in laser dyes have been studied in EPA at 77 K using N₂ laser as an excitation source. Phosphorescence of the donor (D) and the delayed fluorescence of the acceptor (A) and their lifetimes have been measured for coumarin 102 (D)–rhodamine B(A) and 9(10H)–acridone (D)–rhodamine 6G(A) dye systems as a function of acceptor concentration. These data yield energy transfer rate constants of $\sim 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the donor acceptor combinations, consistent with the Forster mechanism. The phosphorescence quantum efficiency and other spectral parameters are also reported.

Keywords. Phosphorescence; delayed fluorescence; energy transfer rate constant; phosphorescence quantum efficiency; quantum yields; lifetimes; critical transfer distance.

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1. Introduction

Triplet states, being long-lived, play an important role in many photophysical and photochemical processes and also in the performance of the dyes as laser media. In dye lasers, the accumulation of dye molecules in the triplet state quenches lasing by triplet–triplet absorption, unless effective measures are taken to reduce the triplet population in the gain medium. Therefore, an understanding of the triplet properties is essential in these applications. The literature survey for information on the triplet state of molecules shows that much work has been done on aromatic molecules using flash photolysis and other techniques, but for laser dyes, only limited information is available. In our laboratory, we have undertaken a programme on the spectroscopy of low-lying excited states of dyes at low temperature under conditions of laser excitation. As a part of this programme, we have reported (Math *et al* 1991) the first observation of intense phosphorescence from several commonly employed laser dyes in EPA at 77 K with an N₂ laser excitation. The present communication deals with the triplet properties of coumarin 102 and 9(10H)–acridone dyes on the basis of the study of triplet-singlet energy transfer (TSET) technique applied to two pairs of dyes: Pair I, coumarin 102 (donor)–rhodamine B (acceptor); Pair II, 9(10H) acridone (donor)–rhodamine 6G(acceptor). In each system, the phosphorescence spectrum of the donor (D) overlaps with the absorption spectrum of the acceptor (A). Such a triplet-singlet energy transfer by Forster (1948) has been experimentally demonstrated earlier in organic molecules (Bennett *et al* 1964; Kellogg and Bennett 1964; Kellogg

1967 and Vaudo and Hercules (1970) and inorganic molecules (Ermolaev and Svshnikova 1963) at 77 K. The main cause of the T-S energy transfer is known to be dipole-dipole interaction between the excited triplet molecule (energy donor) and the ground state molecule (energy acceptor) over distances larger than the molecular diameter. Here, the transfer luminescence from the singlet-state of the acceptor acts as an indicator of the population of the triplet state of the donor.

2. Experimental

Spectral grade dyes (Eastman-Kodak and Exciton) and solvents (Merck and Fluka) were used without further purification. Degassing of solutions by the freeze-pump-thaw cycles did not produce any measurable effect on luminescence. The solutions were prepared in EPA (ether/isopentane/ethanol in volume ratio of 5:5:2 at room temperature). Luminescences were measured with a fixed donor concentration and variable acceptor concentration for each system. The concentrations of the acceptor were sufficiently low to minimize the effect of reabsorption. A cylindrical quartz cell (10 mm path length) containing the solutions was quickly immersed in liquid nitrogen to produce a clear rigid glass without any cracks. Specially fabricated quartz dewar with parallel windows between which the cell snugly sits was used to keep the liquid nitrogen. N_2 laser (f.w.h.m. ca 6.0 ns, peak power ca 150 kW, repetition rate ca 30 Hz) was used as the excitation source. The spectra of the luminescence were recorded at

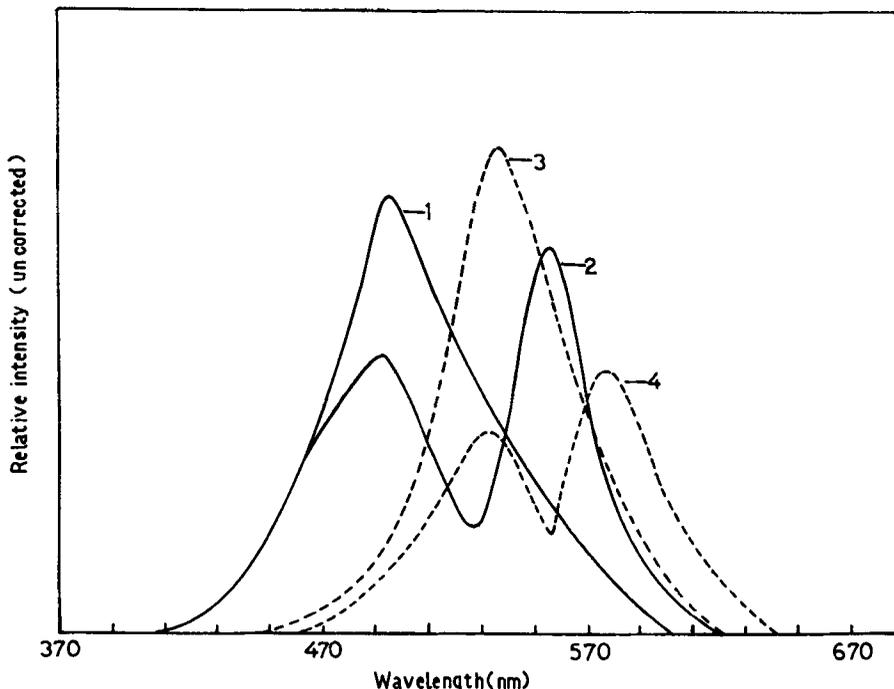


Figure 1. 1. Phosphorescence spectrum of acridone ($5 \times 10^{-4} \text{ mol dm}^{-3}$); 2. Delayed luminescence spectrum of acridone ($5 \times 10^{-4} \text{ mol dm}^{-3}$) + Rh 6G ($2.5 \times 10^{-5} \text{ mol dm}^{-3}$); 3. Phosphorescence spectrum of C 102 ($8.3 \times 10^{-3} \text{ mol dm}^{-3}$); 4. Delayed luminescence spectrum of C 102 ($8.3 \times 10^{-3} \text{ mol dm}^{-3}$) + Rh B ($3.13 \times 10^{-5} \text{ mol dm}^{-3}$).

right angles to the direction of excitation with the help of a monochromator, an RCA 931 A photomultiplier operated at 1000 V and an X-Y recorder (Riken Denshi Co. Ltd., Model F-3DG, dynamic response *ca* 0.01 s/mm. The set up was also used to determine decay times for phosphorescence and delayed fluorescence. The triplet decay curves were almost of first order, the reproducibility being 5%. Fluorescence of the donor was measured using an oscilloscope. Integrated intensities corrected for spectral sensitivity were used in analyzing the data. Typical luminescence spectra are shown in figure 1.

3. Results and discussion

The intensity of the donor fluorescence did not change in presence of the acceptor indicating the absence of any energy transfer from the donor singlet to that of the acceptor. In both the pairs, an increase in the acceptor concentration results in the reduction of the donor phosphorescence, and the appearance of fluorescence of the acceptor (delayed fluorescence, d.F.) with a lifetime close to that of the donor phosphorescence and shortening of the donor triplet lifetime. The values of phosphorescence intensities and triplet lifetimes of donor dyes measured at different acceptor concentrations were found to fit the following relationship:

$$I_p^{D^0}/I_p^D = \tau_p^{D^0}/\tau_p^D = 1 + k_{et}\tau_p^{D^0}[A] = 1 + k_q[A] \quad (1)$$

where $I_p^{D^0}$ and I_p^D are the intensities of phosphorescence of the donor in the absence and presence of acceptor respectively, k_{et} is the energy transfer rate constant, k_q is the quenching constant, $\tau_p^{D^0}$ and τ_p^D are the lifetimes of the donor in the absence and presence of the acceptor and $[A]$ is the acceptor concentration. Plots of $\tau_p^{D^0}/\tau_p^D$ vs $[A]$ are straightlines, the slopes of which yield $k_q = 0.84 \times 10^4$ and $1.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ respectively for I and II pairs. Plots of $I_p^{D^0}/I_p^D$ vs $[A]$ are also linear and yield k_q values of 0.62×10^4 and $1.2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1}$ respectively and these are in close agreement with the above values. This establishes that any of the two methods is adequate for using TEST. A typical plot of $\tau_p^{D^0}/\tau_p^D$ vs $[A]$ is presented in figure 2.

From these plots, half quenching concentration $[A]_{\frac{1}{2}}$, the concentration at which $\tau_p^{D^0}/\tau_p^D = 2$, was determined for each pair. The experimental value of the critical transfer distance, R_0 , for which excitation transfer from $^3D^*$ to A and simultaneous deactivation of $^3D^*$ are of equal probability, was calculated from the relation (Turro 1965)

$$R_0 = \frac{7.35}{\sqrt{[A]_{\frac{1}{2}}}} \text{ in } \text{\AA} \quad (2)$$

The values of R_0 are 153 Å and 185 Å respectively for I and II pairs.

The measured phosphorescence intensities were also used to evaluate the phosphorescence quantum efficiency (q_p^D) of the donor dyes. In terms of rate constants, q_p^D is given by the

$$q_p^D = \frac{k_p}{k_p + k_{GT}} \quad (3)$$

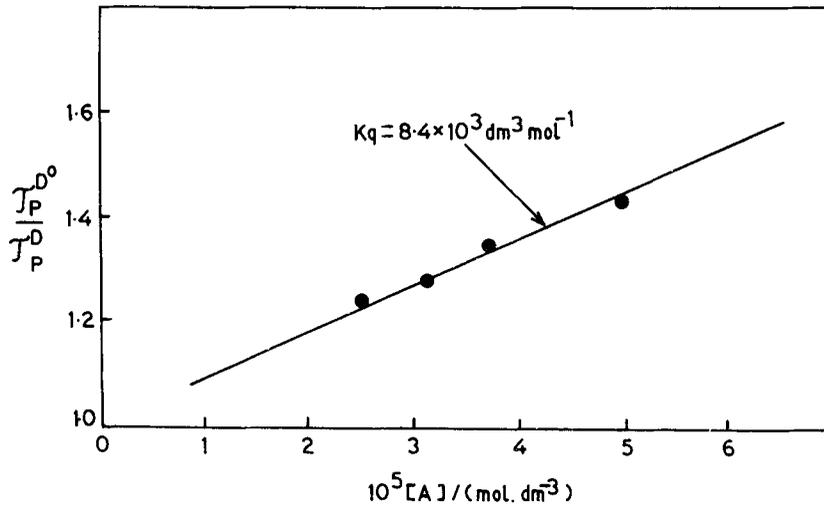


Figure 2. Plot of $\tau_P^{D^0}/\tau_P^D$ vs Rh B concentration in EPA 77 K.

where k_p and k_{GT} are the rates for $T_1 \rightarrow S_0$ radiative and $T_1 \rightsquigarrow S_0$ nonradiative processes respectively. The process of TSET can be used to determine q_p^D . To understand TSET through an analysis of the donor and acceptor luminescences, we have adopted the nomenclatures of Birks (1970) with suitable modifications. Determination of quantum yields (Φ) is difficult and time-consuming. However, the ratios of quantum yields lead to the ratios of intensities when measured simultaneously. Therefore, Φ_p , relative phosphorescence yield defined as Φ_p/Φ_F becomes equal to I_p/I_F when phosphorescence and fluorescence are measured simultaneously i.e. the intensity measurements relative to the fluorescence intensity of the donor which does not change with acceptor concentration become essentially phosphorescence yields, delayed fluorescence yields etc. Therefore, for the present experimental conditions, to distinguish between the donor and acceptor luminescences, the following symbols are introduced and these are also connected to quantum yields as indicated above.

$\phi_p^{D^0}$ (relative phosphorescence yield of the donor = $I_p^{D^0}/I_p^{D^0}$ in the absence of the acceptor)

ϕ_p^D (relative phosphorescence yield of the donor = $I_p^D/I_p^{D^0}$ in the presence of the acceptor)

$\phi_{d,F}^A$ (relative delayed fluorescence yield of = $I_{d,F}^A/I_p^{D^0}$ (the acceptor)).

If a fraction x of molecules in the triplet of the donor [$^3D^*$] transfers its energy to the singlet of the acceptor, the reduction in the relative phosphorescence yield of the donor i.e., $\phi_p^{D^0} - \phi_p^D$ is given by $xq_p^D[{}^3D^*]$ and the corresponding relative delayed fluorescence yield of the acceptor, $\phi_{d,F}^A$ is given by $xq_F^A[{}^3D^*]$ where q_F^A is the fluorescence quantum efficiency of the acceptor. Therefore,

$$\frac{\phi_p^{D^0} - \phi_p^D}{\phi_{d,F}^A} = \frac{xq_p^D[{}^3D^*]}{xq_F^A[{}^3D^*]} = \frac{q_p^D}{q_F^A} \quad (4)$$

Equation (4) reduces to (5) in terms of measured intensities:

$$q_p^D = \frac{I_p^{D^0} - I_p^D}{I_{d,F}^A} \cdot q_F^A \quad (5)$$

Taking the value of q_F^A for each acceptor to be unity (Birks 1970) the values of q_p^D were calculated.

If the internal conversion rate constant k_{GS} from $S_1 \rightsquigarrow S_0$, a nonradiative process is assumed to be zero, a reasonable assumption for the rigid media at 77 K, the triplet quantum yield of the donor (Φ_T^D), the fluorescence quantum yield of the donor (Φ_F^D) and the phosphorescence quantum yield of the donor (Φ_p^D) may be evaluated from the following expressions which are derivable from standard expressions

$$\Phi_T^D = \frac{\phi_p^{D^0}}{q_p^D + \phi_p^{D^0}} \quad (6)$$

$$\Phi_F^D = \frac{q_p^D}{q_p^D + \phi_p^{D^0}} \quad (7)$$

and

$$\Phi_p^D = q_p^D \cdot \Phi_T^D \quad (8)$$

The intersystem crossing rate constants k_{ST} for the $S_1 \rightsquigarrow T_1$, the nonradiative process for donors were estimated from

$$k_{ST} = \Phi_T^D / \tau_F^D \quad (9)$$

where τ_F^D is the donor fluorescence lifetime and the values at room temperature were taken from literature [for C 102 = 4.8 ns (Jones *et al* 1985)] and for acridone = 15 ns (Birks 1970) as the fluorescence lifetimes do not change appreciably with temperature. The values of k_p and k_{GT} were also calculated from the following relations:

$$k_p = q_p^D / \tau_p^D \quad (10)$$

and

$$k_{GT} = \frac{1 - q_p^D}{\tau_p^D} \quad (11)$$

All the significant data are presented in table 1.

The values of k_{et} are of the order of $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and R_0 values are above 100 \AA which are much higher than other reported values but sufficiently below the theoretically predicted value of 1000 \AA by Perrin (1927) and Perrin (1932). These results establish that energy transfer process by Forster mechanism is effective over long separation between $^3D^*$ and A. If the optical transition is forbidden in the donor but allowed in the acceptor, larger transfer distances are expected when the phosphorescence yields are high. This results from the fact that the lower transfer rate is compensated by longer lifetimes of the excited donor. Such TSET processes may play an important role in chemiluminescence, bioluminescence and photochemical reactions as do other sensitized luminescence processes.

Table 1 contains amongst other data on triplet state energies, the associated quantum yields and energy transfer rates. As can be seen from this table, these two donor dyes exhibit high phosphorescence quantum yields and long triplet lifetimes.

Table 1. Triplet characteristics of dyes.

Acceptor concentration ($\times 10^5 \text{ mol dm}^{-3}$)	$\tau_p^D(\text{s})$	q_p^D	Φ_F^D	Φ_T^D	Φ_p^D	$k_{ST}(\text{s}^{-1})$	$k_p(\text{s}^{-1})$	$k_{GT}(\text{s}^{-1})$
<i>C 102 (D) – Rh B (A)</i>								
Donor concentration = $8.3 \times 10^{-3} \text{ mol dm}^{-3}$ (fixed), $\tau_p^{D^0} = 4.28 \text{ s}$, $E_T = 54 \text{ kcal mol}^{-1}$								
5.00	3.00	0.84	0.33	0.67	0.56	1.39×10^8	0.28	0.05
3.70	3.17	0.81	0.36	0.64	0.52	1.31×10^8	0.26	0.06
3.13	3.36	0.79	0.33	0.67	0.53	1.39×10^8	0.24	0.06
2.50	3.43	0.76	0.30	0.70	0.53	1.40×10^8	0.22	0.07
<i>Acridone (D) – Rh 6G(A)</i>								
Donor concentration = $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ (fixed), $\tau_p^{D^0} = 5.56 \text{ s}$, $E_T = 57 \text{ kcal mol}^{-1}$								
3.75	3.57	0.58	0.50	0.50	0.30	3.2×10^7	0.23	0.05
2.50	3.99	0.60	0.46	0.54	0.32	3.6×10^7	0.15	0.10
0.50	4.96	0.63	0.45	0.55	0.35	3.6×10^7	0.13	0.07
0.25	5.35	0.55	0.52	0.48	0.26	4.6×10^7	0.10	0.08

These findings indicate excitation energy availability of these dyes for photophysical and photochemical reactions. The knowledge of quantum yields and lifetimes of triplets are also useful for improving the performance of dye laser. Particularly, in dye lasers under flashlamp excitation, the triplet effects are important in addition to the effect produced by the duration of the pump light pulse. Therefore, under such conditions, the population of the triplet must be controlled either by chemical additives or rapid flow of the dye through the excited region, otherwise the accumulation of molecules in the triplet state gives rise to triplet-triplet absorption, thereby preventing the laser action. In energy transfer dye lasers (ETDL) the locations of the singlet and triplet states determine the efficiency of the dye laser. Thus for example, the mixture of coumarin 102 (donor) and acridine orange (acceptor) under an N_2 laser excitation produces lasing in acridine orange with high efficiency (Savadatti *et al* 1986). It may be noticed that acridine orange does not lase on its own with an N_2 laser excitation but lases efficiently at very low concentration of $1 \times 10^{-5} \text{ mol dm}^{-3}$ in the presence of C 102. Such a high laser efficiency may be explained as follows. The singlet and triplet energies for acridine orange are $52.8 \text{ kcal mol}^{-1}$ and $46.8 \text{ kcal mol}^{-1}$ respectively (Rapoport *et al* 1979). These values are lower than the triplet energy of C 102 ($E_T = 54.5 \text{ kcal mol}^{-1}$). It is therefore quite likely that the singlet state of acridine orange is populated not only by the singlet of C 102 ($E_S = 62.00 \text{ kcal mol}^{-1}$) but also by the triplet-triplet annihilation process of the type: $T(D) + T(A) \rightarrow S_1(A) + S_0(D)$. There are also cases where the triplet quenching by triplet-triplet energy transfer improves the dye laser operation. For example, in trans-stilbene (D) – C 102 (A) combination (Priyadarsini *et al* 1989), trans-stilbene not only acts as a donor for C 102 singlet but also acts as quencher for C 102 triplets which otherwise could have impaired laser operation followed by triplet-triplet absorption.

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