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STUDY OF EXCITATION TRANSFER IN LASER DYE MIXTURES BY DIRECT MEASUREMENT OF FLUORESCENCE LIFETIME

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ABSTRACT

By directly measuring the donor fluorescence lifetime as a function of acceptor concentration in the laser dye mixture Rhodamine 6G–Cresyl violet, we found that the Stern-Volmer relation is obeyed, from which the rate of excitation transfer is determined. The experimental results indicate that the dominant mechanism responsible for the efficient excitation transfer is that of resonance transfer due to long range dipole-dipole interaction.

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1. Introduction

The concept of radiative transfer has been applied [1,2] to improve the pumping efficiency of Neodymium lasers. By circulating fluorescent dye solutions between the flashlamp and the laser rod the light conversion is enhanced since the dyes absorb the visible and UV radiation strongly and then transfer the excitation to the Nd^{+3} ions by emission and reabsorption. Similar improvement in the efficiency of flashlamp-pumped dye lasers has also been reported [3]. Excitation transfer in laser dye mixtures has also been utilized to achieve better dye laser performance at the desired wavelengths. For example, Rhodamine 6G-Cresyl violet mixtures are reported [4,5] to have enhanced the laser efficiency of Cresyl violet, and Rhodamine B-DODC mixture has enabled the generation of tunable near infrared radiation with nitrogen laser pumping[6]. This type of excitation transfer is called "sensitized fluorescence" and is well known in photochemistry [7]. Study of laser dye mixtures using gain spectroscopy [8] indicated that the excitation transfer in the case of Rhodamine 6G-Cresyl violet mixture is very efficient, although the mechanism responsible has not been determined. In this paper we report experimental work for determining the dominant excitation transfer mechanism in such laser dye mixtures.

2. Excitation Transfer Mechanisms

The main mechanisms for the intermolecular, singlet-singlet electronic energy transfer in dye mixtures, or donor-acceptor pairs, are [7,9,10]:

(a) radiative transfer--emission of donors absorbed by acceptors (so-called "trivial mechanism");

(b) diffusion controlled collisional transfer;

(c) resonance transfer due to long-range dipple-dipole interaction.

Mechanisms (b) and (c) are also called nonradiative transfer because the excitation transfer takes place before the excited donor emits, in contrast to mechanism (a). Mechanism (c) occurs with donor-acceptor separation much greater than collisional diameters. The quantum mechanical treatment of resonance transfer is due to Förster [17]. The origin of such resonance transfer is the long-range dipole-dipole Couloumb interaction. The probability of energy transfer due to such interaction is large if the emission spectrum of the donor overlaps strongly with the absorption spectrum of the acceptor-i.e., precisely the conditions required of mechanism (a), the purely radiative emission-reabsorption.

Although all these mechanisms contribute to the donor fluorescence quenching and enhance the acceptor flourescence yield, they can be experimentally distinguished [11] by noting that (i) the radiative transfer does not affect the donor fluorescence lifetime; (ii) the diffusion-controlled collisional transfer rate should decrease with the rigidity of the environment, or more specifically should be inversely proportional to the solvent viscosity; (iii) theory and experiments have indicated clearly that the long-range resonance transfer rate is at least ten times faster than that of collisional transfer. Thus, by simply measuring the donor fluorescence lifetime as a function of acceptor concentration distinction can be made between the various mechanisms. For example, if the donor lifetime is little affected by the acceptor molecules, then mechanism (a) can be considered the dominant one.

3. Experimental

The fluorescence lifetimes of organic laser dyes are typically in the 1-10 nsec range, which can be directly measured [12,13,14] by using picosecond or subnanosecond optical pulse excitation and observing the fluorescence decay with a fast electronic detection system. The conventional phase-shift method and other systems for measuring nanosecond radiative lifetimes are less accurate and not as simple to use.

In this experiment the output of a ruby laser, mode-locked with DDI in methanol, is frequency doubled in a KDP crystal. The resultant UV pulses are 8 psec in duration and are separated by the 9.4 nsec cavity round trip time. These pulses are passed through a tilted dye sample cell close to the cell wall and after proper filtering the flourescence is detected from a near perpendicular direction. The beam size of the excitation is about 2.5 mm. A fast vacuum photodiode and a Tektronix 7904 oscilloscope with the amplifier plug-in unit are used. With this detection system the combined time resolution is approximately 0.9 nsec (fall time). This is somewhat longer than the resolution obtainable if a direct access oscilloscope is used [12,13,15]. However, the sensitivity (20 mv/cm) is 20 times better so that much weaker fluorescence signals can be detected. The possibility of decay time shortening with high excitation intensity [13] is thus avoided. The lifetime data are obtained by fitting the decay curve to a straight line on semi-log plots. Within the experimental error the decay curves were found to be simple exponentials. Lifetimes were measured in pure Rhodamine 6G solutions and in solutions of Rhodamine 6G-Cresyl violet mixtures for a fixed Rhodamine 6G concentration (5×10^{-3} M) and different Cresyl violet concentrations. Both methanol and ethylene glycol were used as solvents. The results are shown in Table 1 and Figure 1. Typical error is ~10% except for lifetimes shorter than 1 nsec where accurate measurements become difficult.

4. Discussion

Table 1 shows that concentration quenching [21] in pure Rhodamine 6G solutions is quite important. Similar observation has been previously reported [15]. The reduction in lifetime for very low concentrations as observed here is also noted in [15]. It is possible that the effect of radiation trapping (self-reabsorption-reemission), which tends to lengthen the observed lifetime [16], is present and superimposed on the effect of concentration quenching which reduces the lifetime.

Figure 1 shows a plot of $(\tau_f)^{-1}$ versus Cresyl violet concentration, where τ_f is the observed decay time of the Rhodamine 6G fluorescence. The Rhodamine 6G concentration was fixed at 5×10^{-3} M. The plots are straight lines, apparently obeying the Stern-Volmer relation [7]

$$\frac{\tau_{fo}}{\tau_f} = 1 + K_{et}A, \tag{1}$$

where τ_{fo} is the measured lifetime in the absence of acceptor molecules, K_{et} is the excitation transfer rate and A is the acceptor concentration. Equation (1) can be obtained from the rate equation

$$\frac{dD^*}{dt} = P(t) - \frac{D^*}{\tau_{fo}} - K_{et}AD^*, \tag{2}$$

assuming δ-function excitation for P(t). D^* is the excited donor concentration. Although Förster's theory indicates a deviation from simple exponential decay, it has been observed [18] that both Förster's formulation and Vavilov's phenomenological treatment [19], which uses a simple exponential decay with an effective time constant τ_f, fit experimental results with slightly different decay time constants.

From Figure 1, we obtain $A_{\frac{1}{2}}$, the acceptor concentration at which $\tau_f = \frac{\tau_{fo}}{2}$. K_{et} is calculated from

$$K_{et} A_{\frac{1}{2}} = \frac{1}{\tau_{fo}} \qquad (3)$$

R_o, the critical separation of donor and acceptor molecules for which energy transfer from D^* to A and emission from D^* are equally probable, can be calculated from [7].

$$R_o = \sqrt[3]{\frac{3000}{4\pi N A_{\frac{1}{2}}}} = \frac{7.35}{\sqrt[3]{A_{\frac{1}{2}}}} \text{ in Å} \qquad (4)$$

where N is Avogardro's number. This corresponds to an average of one molecule of A in a sphere of radius R_o with D^* as the center. The values obtained are shown in Table 2.

Note that the values of R_o obtained agree well with those obtained in resonance transfer studies of other donor-acceptor pairs using different techniques [10,20] and are considerably greater than the value for the collisional excitation transfer, which is 4-6 Å [7]. In terms of K_{et}, the excitation transfer rate obtained here is typical of resonance transfer [9,10,20]. This is in contrast to the values for the case of collisional transfer (10^9 - 10^{10} liter mole^{-1} sec^{-1}) as observed experimentally or calculated from the Debye equation [7,9]. It is also seen that the excitation transfer rate does not decrease with a more than twenty times increase in solvent viscosity. On the contrary, K_{et} is found to be greater in ethylene glycol than in methonol, which might be due to the so-called "cage effect" [21].

We conclude that although radiative and collisional processes probably contribute to the energy transfer in the Rhodamine 6G-Cresyl violet laser dye mixture, resonance transfer due to long-range dipole-dipole interaction is the dominating mechanism responsible for the efficient excitation transfer. The technique described here is simple and can be applied to studies of other excitation transfer processes.

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Table 1

Fluorescence lifetimes of pure Rhodamine 6G solutions

Concentration (M)	τ_f in methanol (nsec)	τ_f in ethylene glycol (nsec)
10^{-2}	2.4	2.5
5×10^{-3}	2.7	2.9
10^{-3}	3.5	4.1
5×10^{-4}	6.1	6.4
10^{-5}	9.3	9.7
10^{-6}	6.2	6.4

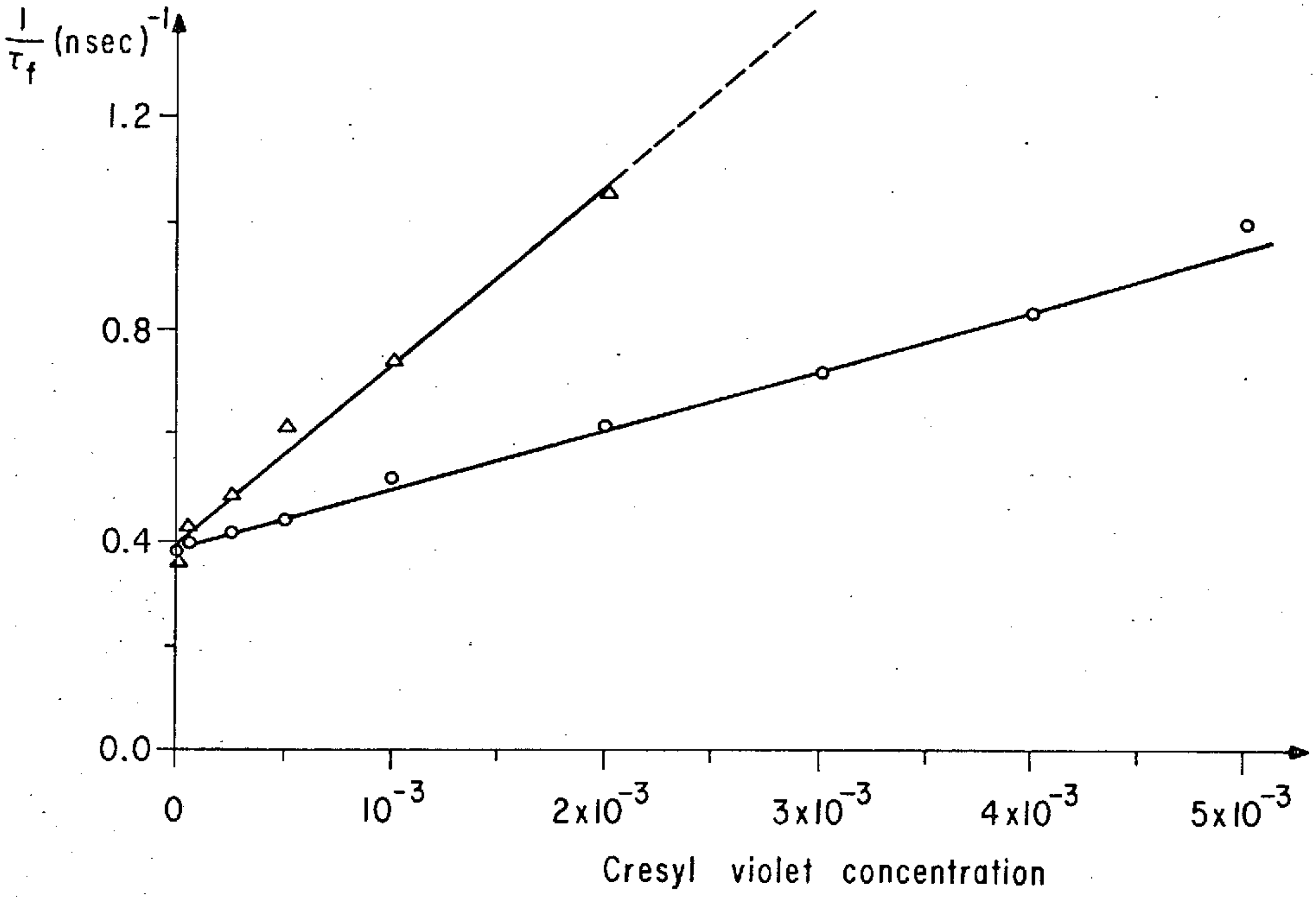
Table 2

$A_{\frac{1}{2}}$ ("half-quenching concentration"), K_{et} (excitation transfer rate), and R_o ("critical separation") calculated from Fig. 1.

Solvent	$A \frac{1}{2}$ (M)	K_{et}(liter mole^{-1} sec^{-1})	R_o(Å)
Methanol	2.6×10^{-3}	1.4×10^{11}	53
Ethylene glycol	1.5×10^{-3}	2.2×10^{11}	64

Figure Caption

Fig. 1. $(\tau_f)^{-1}$ versus Cresyl violet concentration for fixed Rhodamine 6G concentration 5×10^{-3} M in two solvents: o for methanol, Δ for ethylene glycol. Dotted section corresponds to $\tau_f < 1$ nsec where accurate measurement is not obtained.



$\frac{1}{\tau_f}$ (nsec)$^{-1}$
1.2
0.8
0.4
0.0
0
10^{-3}
2×10^{-3}
3×10^{-3}
4×10^{-3}
5×10^{-3}
Cresyl violet concentration