

## Influence of experimental parameters on dominant energy transfer mechanisms

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**Abstract.** Three pairs of dyes which operate as efficient energy transfer dye lasers in ethanol have been investigated to understand the dominant energy transfer mechanisms taking place in them. Special attention is given to the experimental configuration which is expected to influence the energy transfer rate constants over an order of magnitude or two. Fluorescence lifetimes have also been studied using time correlated single photon counting technique. It is found that apart from the excitation source and the concentration of dyes, the experimental configuration has a crucial role to play in determining the dominant energy transfer mechanism.

**Keywords.** Energy transfer dye lasers; energy transfer; fluorescence lifetimes; front surface and perpendicular configuration.

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### 1. Introduction

Energy transfer dye lasers (ETDLs) have generated considerable interest as they are useful in obtaining enhanced laser output, wide tuning range, reduced concentration and pump threshold, and ultrashort pulsewidths, in contrast to their single dye counterpart (Berlman *et al* 1973; Kaschke *et al* 1986; Marason 1982; Muto and Ito 1981; Savadatti *et al* 1986). Many studies have shown that the energy transfer (ET) mechanisms operating in ETDLs and sensitized fluorescence are basically the same (Hilborn and Brayman 1974; Muto and Ito 1981; Terada and Ohba 1983). The principal ET mechanisms are: (i) radiative transfer, (ii) resonance transfer and (iii) collisional transfer. The rate constants for mechanism (ii) are much higher ( $\sim 10^{11} \text{ LM}^{-1} \text{ s}^{-1}$ ) than those for mechanisms (i) and (iii), and enhance the fluorescence (and hence the ability to lase) even when fluorescence quantum yields of donor (D) and/or acceptor (A) are low (Inamdar 1989).

In most of the reports on ETDLs, efforts were made to estimate rate constants and to propose the energy transfer mechanisms occurring in dye mixtures at high (lasing) concentration (Savadatti *et al* 1986). The method was to study the fluorescence (measured in perpendicular configuration) at low concentrations and the ET rate constants determined from these were taken as valid for the actually high concentrations used for ETDLs (Muto *et al* 1984; Cox and Matise 1980). The pump sources used for the two experiments were also different (Hg lamp and laser respectively). Hence the general conclusion was that the dominant mechanism was the same for low as well as lasing concentrations.

## 2. Experiments

In the present study, we emphasize on the fact that dominant energy transfer mechanism depends not only on the concentrations of the component dyes (Birks and Kuchela 1961) and temperature (Ebeid *et al* 1985) but also on the experimental configuration and excitation source (Inamdar and Savadatti 1989). The principal experiments carried out are: study of (a) sensitized fluorescence of dye mixtures excited by 365 nm Hg line, (b) N<sub>2</sub> laser pumped ETDL output and (c) direct fluorescence lifetimes of donor (D) in presence of acceptor (A). The three pairs of dyes studied are: (i) coumarin 1 (C1) + uranine (Ur), (ii) coumarin 102 (C102) + uranine (Ur) and (iii) coumarin 1 (C1) + acridine orange (AO).

(a) Sensitized fluorescence: Dye mixtures are excited by 365 nm line of Hg lamp and the sensitized fluorescence is detected both in the perpendicular (transverse) and front surface configurations for medium (non-lasing) and high (lasing) concentrations. The experimental set up consisted of a 400 W Hg lamp, an excitation monochromator, a photomultiplier and a recorder. The ET rate constants were determined using the equation

$$I_D^0/I_D = 1 + k_{ET}[A]\tau_D^0 \quad (1)$$

where  $I_D^0$  and  $I_D$  are the donor fluorescence intensities in absence and presence of the acceptor,  $\tau_D^0$  is the fluorescence lifetime of the donor in the absence of acceptor and  $k_{ET}$  is the rate constant for ET from D to A.

(b) A 400 W TEA N<sub>2</sub> laser was employed to pump the dye mixtures and the ETDL outputs (transverse configuration) were detected and measured by a fast photodiode and a calibrated oscilloscope. The dye laser cavity consisted of a grating, a tuning mirror and an output coupler in GIG configuration. ETDL outputs for a fixed donor concentration and varying acceptor concentrations were monitored.\* Equation 1 was used to calculate the ET rate constants where  $I_D^0$  and  $I_D$  were donor dye laser output intensities in the absence and presence of acceptor.

(c) Fluorescence lifetimes of donor with ( $\tau_D$ ) and without ( $\tau_D^0$ ) acceptor were measured on Edinburgh's model 199 time domain fluorescence spectrometer wherein the samples are excited by a flashlamp and time correlated single photon counting technique is employed to determine the  $\tau$  values.

## 3. Results and discussion

Our primary interest is to understand and compare the dominant ET mechanisms operating in high and low concentration solutions, excited by a conventional source or a laser in front surface or transverse configuration. The values of the ET rate constants, determined for all the three cases discussed above, are compiled in table 1. Fluorescence lifetimes of D are determined in front surface configuration and the ETDL measurements are obviously in transverse configuration although the concentrations employed in both these cases are high and identical with those used for fluorescence intensity measurements in front surface configuration (i.e., in the range

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\* Donor dye laser output monitored in presence of very low concentrations of acceptor.

**Table 1.** Energy transfer rate constants ( $k_{ET}$ ).

Pair	Donor (D)	Acceptor (A)	$k_{ET} \times 10^{-11} (\text{LM}^{-1} \text{s}^{-1})$ measured from				
			Fluorescence intensity (Hg excited)		Fluorescence lifetime (flashlamp excited)	ETDL output (N <sub>2</sub> laser pumped)	
			P**	F*	F*	L*	S*
I	C1	Ur	51.80	3.12	0.54	39.90	59.10
II	C102	Ur	99.60	3.82	0.51	—	—
III	C1	AO	78.70	1.13	0.85	—	—

\*Concentration range  $10^{-3}$ – $10^{-2}$  M/L; \*\*Concentration range  $10^{-5}$ – $10^{-4}$  M/L; P–Perpendicular configuration; F–Front surface configuration; L–Laser emission; S–Superradiance.

of  $10^{-3}$ – $10^{-2}$  M/L). The range of concentrations used for fluorescence measurements in transverse configuration was  $10^{-5}$ – $10^{-4}$  M/L. The above values of rate constants indicate a crucial role of configuration, concentration of dyes and excitation source, in proposing the dominant ET mechanism. And one should be cautious about drawing inferences without taking these into account. Sensitized fluorescence data and fluorescence  $\tau$  data, both measured in front surface configuration ( $k_{ET} \sim 10^{11} \text{LM}^{-1} \text{s}^{-1}$ ) agree and suggest a dominant resonance transfer mechanism. Interestingly, ETDL output (laser/superradiance) lead to rate constants of the same order of magnitude as those obtained from sensitized fluorescence in perpendicular configuration, indicating that the same ET processes operate in lasers too. However it is difficult to assess the contribution of radiative transfer in ETDLs. This fact stresses the importance of experimental configuration.

In view of the above results it is felt that whenever one is interested in determining the fundamental constants like rate constants of energy transfer for lasing (high) concentrations, one should prefer front surface configuration. Otherwise it would lead to misleading inferences as drawn by Berfman *et al* (1973). These authors studied energy transfer dye laser action in a pair of dyes bisMSB and perylene, and assigned a lasing band at 447 nm to the donor bisMSB saying that it is redshifted by the presence of acceptor perylene. Later, Kleinerman and Dabrowski (1978) studied fluorescence of the same mixture in front surface geometry and observed that the 447 nm band is really blue shifted band of perylene itself. Pant *et al* (1982) and Kushwaha and Pant (1984a, b) also determined rate constants for energy transfer in acriflavine and rhodamine systems and obtained rate constants for resonance energy transfer of the order of  $10^{12}$  and  $10^{13} \text{LM}^{-1} \text{s}^{-1}$  whereas in all other reports this value does not exceed  $10^{11} \text{LM}^{-1} \text{s}^{-1}$ . Hence we feel that front surface configuration for measurement of fluorescence should be preferred in case of high concentrations.

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