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Energy transfer in Rh 6G:Rh B system in PMMA matrix under cw laser excitation

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Abstract

Energy transfer of Rh 6G:Rh B dye–mixtures in a poly methyl methacrylate (PMMA) matrix was studied by investigating the emission spectral characteristics under argon ion laser excitation. The fluorescence behaviour of the acceptor dye (Rh B) was investigated for various concentration of the donor (Rh 6G) and excitation powers. The energy transfer rate constants (k_f), transfer probability (P_{da}) and the transfer efficiency (η) have been evaluated and their concentration dependence on donor molecules was studied. The observed decrement in the emission peak wavelength of the acceptor dye with donor concentration is attributed to the formation of complexes in the dye–mixture and also to the result of cross-relaxation taking place in the donor dye system. The blue shift in the emission wavelength of the acceptor was also investigated for various donor concentrations. A significant enhancement of fluorescence intensity of the acceptor (Rh B) of the order of 226% and a transfer efficiency of 90% were observed in the present dye–mixture system as compared with pure Rh B, both in PMMA matrices. Further the experimental results revealed the non-radiative type energy transfer for the dye system in the PMMA matrix.

Keywords: Dye–mixture; Energy transfer; Poly methyl methacrylate

1. Introduction

The excitation of dye lasers through energy transfer processes provides one of the means of extending the lasing wavelength region and improving the efficiency. Energy transfer dye lasers (ETDLs) using numerous donor–acceptor dye pairs have been reported by various workers during the last three decades. In 1968, soon after the discovery of organic dye laser, Peterson and Snavely [1] demonstrated the feasibility of a dye–mixture laser with flash lamp excitation. In 1971 Moller et al. [2], using N_2 laser pumping, obtained effective excitation transfer from Rh 6G to Cresyl violet (CV) and observed an increase in the power output. A simple theoretical model developed by Dienes and Madden [3] was found to be in good agreement with experimental observations for the CV–Rh 6G mixture, a dye commonly used for most ETDL studies [1–4]. Dienes et al. could explain the variation of gain with acceptor concentration using this theoretical model. These gain measurements done by them on Rh 6G:CV mixtures and on CV alone clearly show a higher gain in the mixture as compared to CV alone. This high gain of ETDL systems was demonstrated in other donor–acceptor pairs such as Rh 6G:Rh B [5], Coumarin 30:Rh 6G [6], Coumarin 485:RhD [7], Uranine:DAMC [8], Coumarin 440:Coumarin 485 [9] and Rh 610:Nile Blue 690 [10]. Recently Kumar and Unnikrishnan [11] have also observed an enhancement of optical gain by many times for the FDS:Rh B dye–mixture due to energy transfer. A conversion efficiency of about 200% for the dye–mixture Rh 6G:Rh B was observed whereas for Rh B alone it was only 7% [5]. As a result of this high gain, the conversion efficiency of the dye laser was improved considerably. It should be noted that dyes like perydine can be made to lase by energy transfer pumping though they do not lase otherwise. This high gain, which is a result of an enhanced lifetime of the acceptor [6], produces a blue shift in the emission peak of the acceptor. Investigations showed pronounced blue shifts in the peak superradiant emission wavelengths of Rh 6G, Rh B, Coumarin 1 and perydine [6,12,13].

Most of the studies conducted so far report investigations of energy transfer between dyes in liquid media. The use of a solid matrix for the dye laser gets rid of many of the common problems associated with static or flowing liquid systems such as convective Schlieren, evaporation, flow fluctuation, stagnant films, solvent or dye poisoning and even explosions

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[14]. Organic polymers used as host materials for dye lasers provide an alternative to the conventional liquid dye lasers. One of the important advantages of transparent polymers, compared with traditional optical materials, is that it is possible to introduce organic dyes or other compounds that play the role of active components into the polymers, which appreciably changes the characteristics of the polymer matrix. Different organic polymers can be used as solid host materials, the most frequently used polymer material is poly methyl methacrylate (PMMA) because of its best optical transparency. Dye doped PMMA is important in that it provides initial observations that may help interpreting the behaviour of dyes in a PMMA matrix. We therefore in the present work made an attempt to elucidate the mechanism of energy transfer between Rh 6G and Rh B in a solid matrix of PMMA.

2. Experimental

The dye doped PMMA samples were prepared using standard experimental techniques [15]. In all the samples prepared the acceptor concentration was kept constant at 10^{-3} M/l whereas the donor concentration was given the values 10^{-4}, 5×10^{-4}, 10^{-3}, 3×10^{-3} and 5×10^{-3} M/l.

Optical absorption spectra of the samples were recorded on a Hitachi U2000 spectrophotometer.

In order to record the emission spectra, the 488 nm line of an argon ion laser of the LICONIX 5300 series was used as the excitation source. The fluorescence emission from the sample was focused onto the entrance slit of a 0.2 m concave holographic monochromator (McPherson model 275) which has a wavelength accuracy of ±0.1 nm. The output of the monochromator was fed to a photomultiplier (Oriel model 7068) for detection, and finally the emission spectrum was recorded on a chart recorder. All the spectra were recorded with a scanning speed of 1000 Å/min.

To study the dependence of fluorescence emission on the excitation intensity, fluorescence spectra were recorded at various pump intensities, viz. 20, 40, 60, 80 and 150 mW.

3. Theoretical tools

The energy transfer probability from donor to acceptor (P_{da})and the transfer efficiency (η) are evaluated using the known expressions [16]

$$\eta = 1 - \frac{I_{\mathrm{d}}}{I_{0\mathrm{d}}} \tag{1}$$

$$P_{\mathrm{da}} = (\tau_{0\mathrm{d}})^{-1}\left(\frac{I_{0\mathrm{d}}}{I_{\mathrm{d}} - 1}\right) \tag{2}$$

where $I_{0\mathrm{d}}$ and I_{d} are the fluorescence intensities of the donor in the absence and presence of the acceptor, respectively, and $\tau_{0\mathrm{d}}$ the decay time of the donor in the absence of the acceptor which is evaluated using the well known Strickler–Berg formula [17]

$$\frac{1}{\tau} = \frac{8\pi c \int_{\mathrm{em}} E(\lambda)\,\mathrm{d}\lambda \int_{\mathrm{abs}} \sigma_{\mathrm{l}}(\lambda)\,\mathrm{d}\lambda}{\int_{\mathrm{em}} E(\lambda)\lambda^3 n^{-3}(\lambda)\,\mathrm{d}\lambda\,\lambda n(\lambda)} \tag{3}$$

where c is the speed of light, $n(\lambda)$ the refractive index of the medium at wavelength λ, and $\sigma_{\mathrm{A}}(\lambda)$ the absorption cross-section. The integration extends over the $\mathrm{S}_1 \rightarrow \mathrm{S}_0$ fluorescence band (em) and $\mathrm{S}_0 \rightarrow \mathrm{S}_1$ absorption band (abs).

The non-radiative energy transfer rate constant (k_{f}) can be evaluated using the Stern–Volmer equation [18]

$$\frac{I_{0\mathrm{d}}}{I_{\mathrm{d}}} = 1 + k_{\mathrm{f}}\tau_{0\mathrm{d}}[\mathrm{A}] \tag{4}$$

where [A] represents the acceptor concentration. The half quenching concentration $[\mathrm{A}]_{1/2}$ can be obtained under the condition

$$\frac{I_{0\mathrm{d}}}{I_{\mathrm{d}}} = 2 \tag{5}$$

The critical distance R_0 can be evaluated by the expression

$$R_0 = 7.35([\mathrm{A}]_{1/2})^{1/3} \tag{6}$$

4. Results and discussion

A typical absorption spectrum of the sample corresponding to 10^{-3} M/l concentration of the dye is presented in Fig. 1, where (a) and (b), respectively, represent the absorption lineshapes of the pure Rh 6G and Rh B dye molecules in the PMMA matrix. In order to ascertain the possibility of energy transfer process the respective emission spectra are also recorded and plotted along with the absorption spectrum. In Fig. 1 curves (c) and (d) represent the emission lineshapes of Rh 6G and Rh B molecules. Since most of the area under the emission lineshape of Rh 6G overlaps with the absorption lineshapes of Rh B, energy transfer from Rh

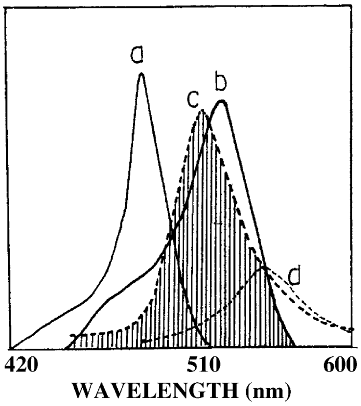

Fig. 1. Overlapping of the absorption spectra of Rh B and Rh 6G with the emission spectra of Rh 6G and Rh B: (a) absorption spectrum of Rh 6G; (b) absorption spectrum of Rh B; (c) emission spectrum of Rh 6G; (d) emission spectrum of Rh B.

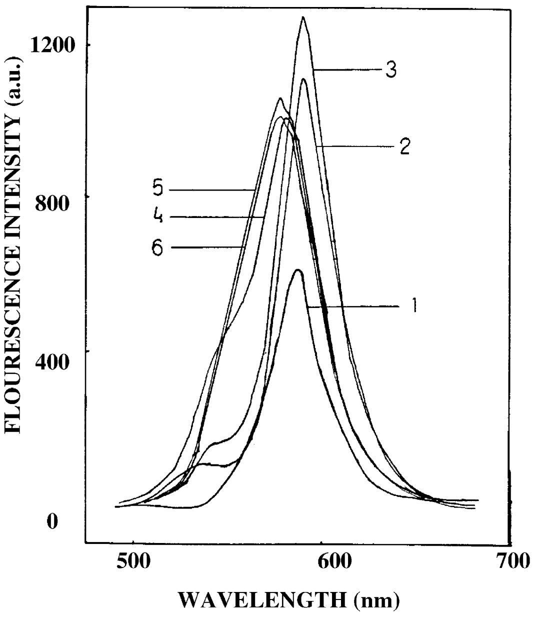

Fig. 2. Dependence of the acceptor fluorescence intensity on donor concentration for 40 mW pump intensity: (1) acceptor only—10^{-3}; (2) 10^{-4}; (3) 5×10^{-4}; (4) 1×10^{-3}; (5) 3×10^{-3}; (6) 5×10^{-3} M/l.

6G to Rh B is clearly possible, the extent depending on the overlapping area which is shown as a shaded region in Fig. 1. In Fig. 2 the emission spectra of the mixed dye system in a PMMA matrix are shown for several donor concentrations, all for a fixed acceptor concentration (10^{-3} M/l) and for 40 mW pump intensity. From the figure it can be clearly noticed that the emission intensity of the donor dye (Rh 6G) is continuously decreasing while that of the acceptor dye (Rh B) is continuously increasing. This is clearly a manifestation of the energy transfer processes occurring in the Rh 6G:Rh B system in the PMMA matrix.

4.1. Dependence of peak wavelength (λ_P) on donor concentration

Fig. 3 shows the dependence of the peak emission wavelength (λ_P) of the dye–mixture on Rh 6G concentration for different pump intensities. All the curves show almost the same behaviour for different pump intensities. From the nature of the curves some important conclusions can be drawn. Except for the concentration 10^{-4} M/l, a blue shift of the emission peak from the donor-sensitized Rh B was observed. The shift is about 12.5 nm for a pump intensity of 20 mW. The donor-sensitized system was observed to have a higher gain compared to the unsensitized system due to an increase in the effective lifetime [6]. As a result of this, the gain maximum is shifted towards the blue [19]. The lifetime of the acceptor will be appreciably increased at low donor concentrations ($<10^{-3}$ M/l) as reported by Urisu and Kajiyama [6]. A similar blue shift had been reported in Rh 6G:Rh B dye–mixtures in methanol [5] and also in other dye–mixtures [13,20]. Fig. 3 also shows that the blue shift was affected by the donor concentration. At very low donor concentration, only partial energy transfer takes place, since when the intermolecular distance is high, the donor–acceptor interaction is weak. Hence the long wavelength tail of the Rh 6G emission, where Rh B has no absorption as can be seen from Fig. 1, is superimposed on the Rh B emission and a blue shift is observed. In addition to this spectral overlap, the enhancement of lifetime due to partial energy transfer may also contribute to blue shift. But this blue shift is smaller than that caused by the enhanced lifetime due to energy transfer process.

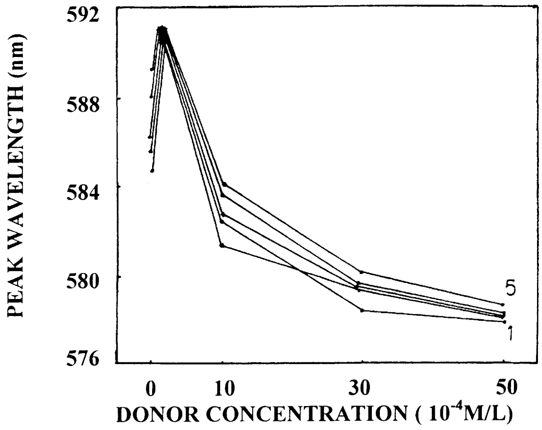

Fig. 3. Dependence of peak emission wavelength (λ_P) on donor concentration for various pump powers: (1) pump power = 20; (2) 40; (3) 60; (4) 80; (5) 150 mW.

4.2. Variation of the peak fluorescence intensity with donor concentration

In Fig. 4 the variation of the peak fluorescence intensity with donor concentration is shown. The maximum of the

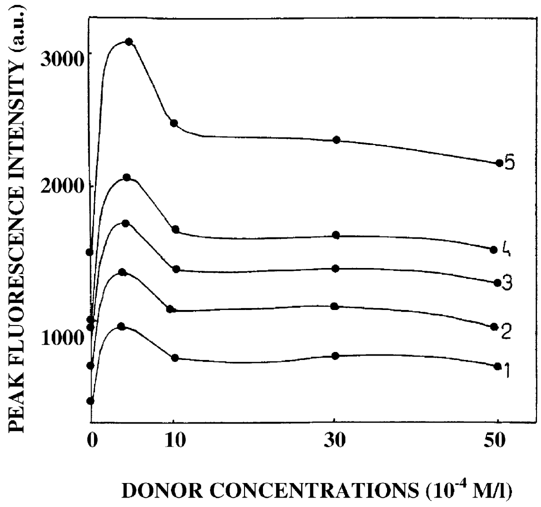

Fig. 4. Plot of peak fluorescence intensity vs donor concentration for various pump powers: (1) pump power = 20; (2) 40; (3) 60; (4) 80; (5) 150 mW.

peak fluorescence intensity was observed at the donor concentration of 5×10^{-4} M/l for all the pump intensities. Above this concentration the peak fluorescence intensity shows a decrease and becomes independent of the donor concentration at higher values. The decrease in fluorescence intensity of Rh B above 5×10^{-4} M/l may be attributed to the effect of a non-radiative fluorescence-quenching interaction between the donor molecules. As the concentration of the donor molecules increases the effective distance between the donor molecules decreases and thereby causes energy transfer to takes place within the donor system itself [20]. In other words, increasing the donor concentration above a particular value will not in any way enhance energy transfer to the acceptor.

4.3. *Dependence of peak fluorescence intensity on pump intensity*

In order to understand the variation of the fluorescence intensity (I_{Lmax}) with pump intensity (I_{P}), peak fluorescence intensity was measured for each of the pumping intensities corresponding to each donor concentration and the variations are shown graphically in Fig. 5. The efficiency (ε) of the system can be defined as the ratio of the peak fluorescence intensity to the pump intensity, i.e. $1 = \varepsilon_{\mathrm{Lmax}}/\varepsilon_{\mathrm{P}}$. In Fig. 5 all the plots show almost a linear dependence of I_{Lmax} and hence efficiency upon pump intensity with a noticeable change of slope at higher concentration. A clear observation from the above plot is that as the donor molecules are added to the acceptor dye efficiency of the acceptor dye molecules increases considerably and in the present case maximum efficiency is obtained for a donor concentration of 5×10^{-4} M/l. Above this concentration the efficiency decreases with donor concentration and hence the value 5×10^{-4} M/l can be considered as the optimum concentration in the present ETDL system consisting of Rh 6G and Rh B.

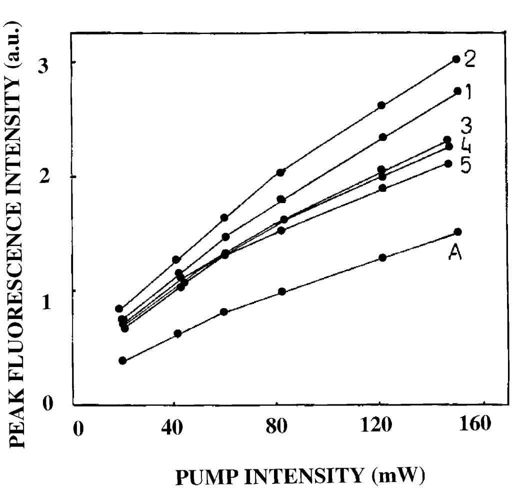

Fig. 5. Variation of peak fluorescence intensity with pump intensity for various donor concentrations: (1) 10^{-4}; (2) 5×10^{-4}; (3) 1×10^{-3}; (4) 3×10^{-3}; (5) 5×10^{-3} M/l. (A) acceptor only (10^{-3} M/l).

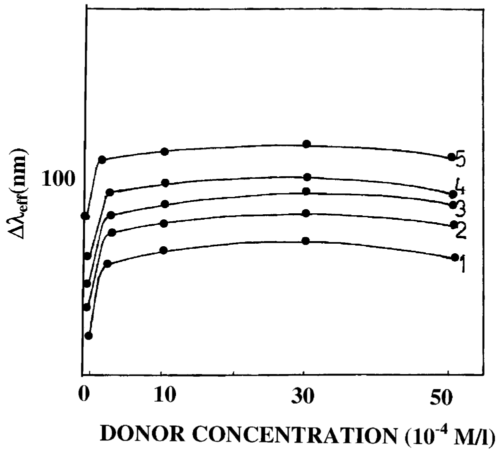

Fig. 6. Variation of the effective fluorescence linewidth with donor concentration: (1) 20; (2) 40; (3) 60; (4) 80; (5) 150 mW.

4.4. *Effect of donor concentration on the effective fluorescence linewidth of the acceptor*

Another way of finding the efficiency of the mixed dye system is to measure the effective area under the emission lineshape of the acceptor in the absence and presence of the donor molecule and thereby evaluate the fluorescence branching ratio. Since most of the time the emission lineshapes are inhomogeneously broadened, a better way of evaluating the area under the emission line shapes is to compute the effective fluorescence linewidth $\Delta\lambda_{\mathrm{eff}}$ [19] which is obtained by integrating the area under the emission lineshape and then dividing by the peak intensity. Fig. 6 shows the variation of these areas with donor concentration for each of the pump intensities.

Table 1 summarizes the relative fluorescence branching ratios of the present ETDL system for different pump intensities and donor concentrations. In calculating these branching ratios the area of the emission spectrum of the pure acceptor dye is compared with that of the combination. From the results given in Table 1 it is clear that, due to the addition of the donor molecules to the acceptor dye, its relative fluorescence branching ratio is increased up to a maximum of 239% compared to the unsensitized system. On an average the present ETDL system is found to be more efficient than the conventional dye lasers by a factor of about 2.2.

In all the fluorescence spectra recorded at different pump intensities the peak fluorescence intensity was observed to occur at a concentration of 5×10^{-4} M/l. Above and below this value the peak intensity does not follow a linear dependence on donor concentration. This nonlinear dependence of the fluorescence peak intensity on donor concentration is in contrast to the observations of Speiser and Katraro [21] who predicted a linear dependence of peak intensity with donor concentration for the anthracene–perydine system. Earlier observations on Rh 6G:Rh B system in methanol [5] also show a nonlinear dependence of fluorescence peak intensity

Table 1
Relative fluorescence branching ratios for different pump intensities and donor concentrations

Donor concentration ($\times 10^{-4}$ M/l)	Relative fluorescence branching ratio (%)				
	$I_p = 20$ mW	$I_p = 40$ mW	$I_p = 60$ mW	$I_p = 80$ mW	$I_p = 150$ mW
1	180	174	168	172	178
5	222	205	184	208	182
10	212	204	184	202	183
30	239	226	212	220	210
50	229	218	207	209	194

upon donor concentration as in the present case. Those investigations have shown that the fluorescence intensity of the acceptor acquires a maximum value at a donor to acceptor molar concentration ratio of unity. Contrary to the results reported earlier [5], we have observed that the fluorescence intensity from the acceptor has a maximum molar donor concentration of 5×10^{-4} at a 5:1 donor to acceptor molar ratio. The decrease in fluorescence intensity from the acceptor at higher donor concentrations, i.e. above 5×10^{-4} M, may be owing to the following reasons. As the donor concentration is increased the intermolecular separation between these dye molecules decreases correspondingly and this results in cross-relaxation between the donor molecules, thereby decreasing the excitation energy considerably. As a result of this phenomenon, above a concentration of 5×10^{-4} M the donor system does not have sufficient energy to excite the acceptor dye molecules. Another cause for the reduction in fluorescence intensity above 5×10^{-4} M may be the formation of donor–acceptor charge transfer (CT) complexes in the system [22]. It was observed that the rate of this complex formation depends on the concentrations of the dye molecules. If the excited complex is nonfluorescing, the addition of donors results merely in the quenching of fluorescence of the acceptor molecule.

4.5. Variation of transfer probability, transfer efficiency and non-radiative rate constant with donor concentration and pump intensity

In order to study the extent of the energy transfer between the donor and acceptor dye molecules, the three most important energy transfer parameters, the transfer efficiency (η) (Eq. (1)), transfer probability (P_{da}) (Eq. (2)) and the non-radiative rate constant (k_f) (Eq. (4)) have been evaluated. The transfer efficiency assumes maximum values (≈95) at the lowest donor concentration and thereafter decreases with increase of donor concentration and assumes minimum value (≈60) at the highest concentration.

Fig. 7 depicts the variation of the transfer probability with the sum of the donor and acceptor concentration for the pump intensity 60 mW. A similar behaviour can also be observed for all other pump powers. Fig. 8 illustrates the dependence of the non-radiative rate constant k_f on the donor concentration showing a decreasing tendency of k_f

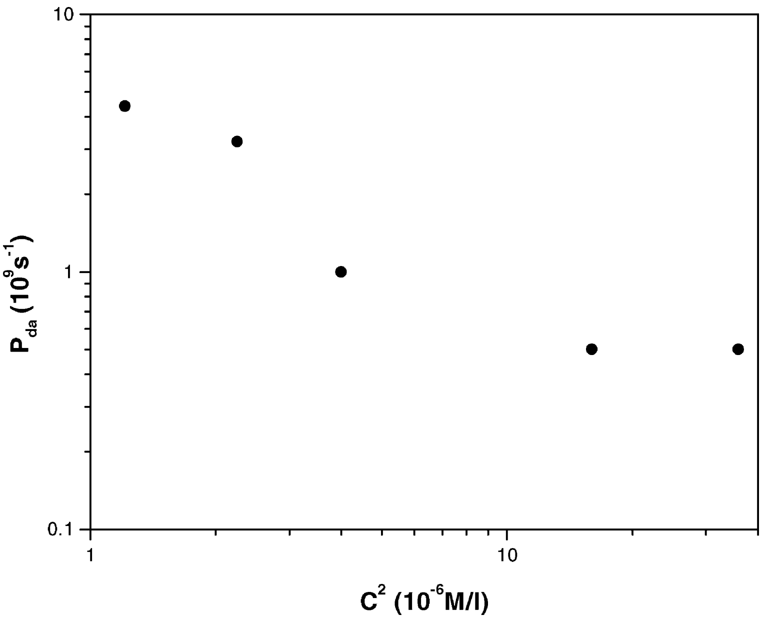

Fig. 7. Plot of transfer probability (P_{da}) with square of the donor plus acceptor concentration (C^2).

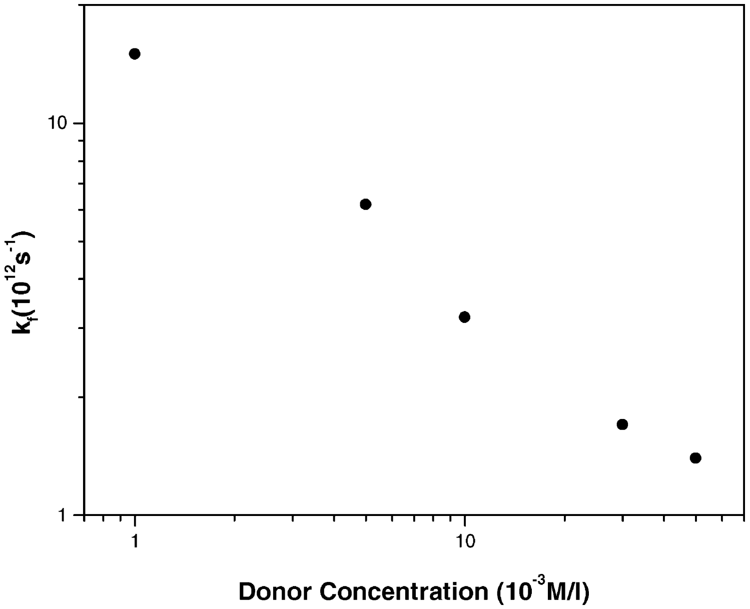

Fig. 8. Variation of the non-radiative rate constant (k_f) with donor concentration.

with donor concentration. The observed variation of these parameters with donor concentration can be interpreted as follows. As the donor concentration increases the effective distance between donor and acceptor molecules decreases. This should enhance the energy transfer between the donor and acceptor molecules and thereby effect an increase in the transfer efficiency, transfer probability and non-radiative rate constant. But, in the present case since the donor molecules are excited first, increasing the donor concentrations will result in the cross-relaxation process between these molecules and thereby decrease their energy. In other words if we are increasing the donor concentration instead of acceptor, then this will result in a reduction in the donor to acceptor transfer parameters. It is also observed that when the acceptor concentration is fixed and donor concentration is changing a reduction in the fluorescence peak intensity of the acceptor with donor concentration is expected and this explains the reason for the reduction in the peak fluorescence intensity of Rh B molecules above 5×10^{-4} M/l concentration of Rh 6G. On the other hand, if we are fixing the donor concentration and allowing the acceptor concentration to vary continuously then one can clearly elucidate the type of energy transfer occurring in the system. In fact we have carried out such measurements also and a typical Stern–Volmer plot resulted out of this study is shown in Fig. 9. We obtain the values of half quenching concentration $[A]_{1/2}$ as 6.3×10^{-4} M/l required to fulfill Eq. (4). Thus knowing $[A]_{1/2}$ and τ_{od} (2.85 ns), k_f the non-radiative

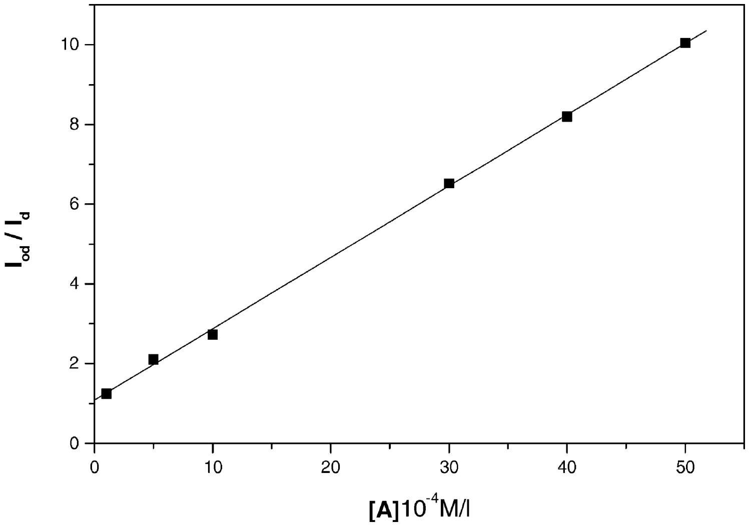

Fig. 9. Stern–Volmer plot for the Rh 6G:Rh B system.

transfer rate has been evaluated as $6.2 \times 10^{12}\,\mathrm{s}^{-1}$. Also knowing $[\mathrm{A}]_{1/2}$, R_0 the critical distance has been calculated to be 86.5 Å typical of a non-radiative energy transfer.

5. Conclusion

The process of non-radiative energy transfer plays an important role in increasing the fluorescence efficiency of the lasing species in most dye molecule systems. The present investigations of the energy transfer between Rh 6G (donor) and Rh B (acceptor) clearly show that the relative fluorescence branching ratio of Rh B has been increased by a factor of 2.21 compared with that of the unsensitized system. This demonstrates that the efficiency of the laser can be increased to a considerable extent by a suitable choice of the donor. Study of the donor concentration dependence on the acceptor fluorescence efficiency, shows that even though the fluorescence intensity increases with donor concentration up to the critical concentration (5×10^{-4} M/l) the non-radiative energy transfer parameters decrease with donor concentration. We have elucidated quantitatively the non-radiative energy transfer in the present system by keeping the donor concentration fixed while varying the acceptor concentration. In addition to this, a comparison of the fluorescence efficiency of Rh 6G:Rh B (200%) based ETDL system in methanol with that of the present system in PMMA (226%) shows that there is an overall enhancement of the efficiency by 26%. This enhancement is primarily due to the immobilization of the dye molecules in PMMA which inhibits the undesirable triplet state formation for laser action. Thus PMMA based Rh 6G:Rh B ETDL system can be considered as an efficient dye laser medium capable of giving superior optical amplification.

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