Energy transfer and optical gain studies of FDS: Rh B dye mixture investigated under CW laser excitation

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ABSTRACT
Radiative and non radiative (Forster type) energy transfer processes in a dye mixture of FDS and Rh B in methanol under CW Ar ion laser excitation were investigated for fixed donor concentration and varying acceptor concentration. It is found that most of the pump power absorbed by FDS is transferred to Rh B as a useful pump power. Transfer probability (PDA), transfer efficiency both radiative ($\eta_R$) and non radiative ($\eta_{NR}$) and optical gain (G) of the system was studied for various pump powers. The gain characteristics of Rh B are found to alter due to the change in the effective fluorescence lifetime caused by energy transfer reaction. Theoretical calculations were also done to find the total transfer efficiency ($\eta_T$) at various acceptor concentrations to identify the appropriate energy transfer mechanism responsible for gain enhancement in Rh B. Both radiative and non-radiative transfer processes are taken into consideration in all the calculations. Various energy transfer parameters viz. radiative rate constant ($K_R$), non radiative rate constant ($K_{NR}$), critical concentration ($C_0$), critical radius ($R_0$) and half quenching concentration ($[A]_{1/2}$) are calculated by using the Stern-Volmer plots and concentration dependence of radiative and non radiative transfer efficiencies. Concentration and pump power dependence of the peak gain and lasing wavelengths of the ETDL have also been studied. The experimental results shows that the dominant mechanism responsible for the efficient energy transfer in this mixture is of radiative nature where as the long range dipole-dipole (d-d) and dipole-quadrupole (d-q) interactions (Forster type) are comparatively smaller.

Keywords: Dye laser, Energy transfer, Stern-Volmer plot

1. INTRODUCTION
In the field of photonics, the use of dye lasers through energy transfer process can provide ways of extending the lasing wavelength regions and improving the efficiency. Energy transfer dye lasers (ETDL) using numerous donor acceptor dye pairs have been reported by various investigators during the last three decades[1-4]. A simple theoretical model developed by Dienes[5] was found to be in good agreement with experimental observations for the Rh6G-CV mixture. He could explain the variation of gain with acceptor concentration because of the higher gain of Rh 6G-CV mixture in comparison with that of CV alone. Such high gain ETDL system has been reported in other donor acceptor pairs such as Rh 6G:Rh B[5], C 30:Rh 6G[6], Coumarin 485:Rh B[7],Uranine:DAMC[8]and C440:C485 etc. This high gain, which is a result of the enhanced lifetime of the acceptor, produces a blue shift in the emission peak of the acceptor and enhancement of the conversion efficiency of the dye laser.

Generally energy transfer process can be classified as (1) radiative and (2) non radiative, depending upon the nature of energy transfer from donor to acceptor. In radiative energy transfer process, photons emitted by the donor molecules were absorbed by the acceptor molecule. Non-radiative energy transfer process involves the interaction between the donor and acceptor molecules during the lifetime in the excited state of the donor, prior to its emission of a photon. This is possible through the following two processes (a) diffusion controlled collisional transfer and (b) resonance transfer due to long-range dipole-dipole interaction.

Diffusion controlled collisional transfer occurs in intermolecular distances which is comparable to the molecular separation mechanism depends on the solvent viscosity and temperature. The other process occurs at a much longer donor acceptor separations than collisional diameters. A good overlap of the donor emission spectrum and the acceptor absorption spectrum is required for radiative transfer and resonance transfer due to long-range dipole-dipole interaction. The radiative transfer mechanism is often the dominant mechanism in dilute solutions and its occurrence cannot be
neglected in the studies of radiation less energy transfer. These two mechanisms can be distinguished by the donor fluorescence lifetime as a function of the acceptor concentration.

2. EXPERIMENTAL

The excitation source used for the present study was an Ar ion laser (LICONIX 5000 Series) whose 488nm line is employed to pump the donor molecule. The dyes used were Laser grade supplied by Exciton Company and the solvent was spectroscopic grade methanol. In all the experiments, the donor concentration was kept fixed at 10-4 m/l where as the acceptor concentration varies. The dye solution was taken in a quartz cuvette of width 1cm and the solution is pumped by the laser beam. As shown in Fig.1, fluorescence emission from the solution was focused on to the entrance slit of a 0.2m concave holographic monochromator (McPherson Model 275) which has a wavelength accuracy of ±0.1nm. The output of the monochromator was fed to a photomultiplier (Oriel Corp.,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 1000A/min. Experiments were repeated for different pump intensities viz 80mW, 110mW, 140mW and 170mW. Optical absorption spectra of the samples were recorded on a Hitachi U 2000 spectrophotometer.

![Figure 1: 1. Ar ion laser 2. Focusing lens 3. Sample 4. Monochromator 5. PMT 6. X-Y Plotter](image1)

3. RESULTS AND DISCUSSION

A typical absorption spectrum of FDS and Rh B corresponding to 10⁻⁴m/l concentration is presented in Fig 2. To confirm the energy transfer process the respective emission spectra are also recorded and plotted along with the absorption spectra. In Fig 2, curves c and d represent the respective emission line shapes. Since most of the area under the emission spectrum of FDS overlaps with the absorption spectrum of Rh.B, energy transfer from FDS to Rh.B is definitely possible, the extend of which is shown as a shaded region in Fig 2. Various physical phenomena that are occurring in the dye mixture due to energy transfer and their functional dependence on a number of parameters are described in detail.

![Figure 2: Spectral characteristic of fluorescence and absorption. Graphs a and b respectively represent the absorption line shapes of FDS and RhB dye molecules. Graphs c and d represent the corresponding emission line shapes. The shaded area is the region of energy transfer.](image2)
3.1 Nature of transfer probability function ($P_{DA}$)

Figure 3 portraits the emission intensity variations of donor and acceptor molecules for different pump powers corresponding to $10^{-4}$ [D] and $10^{-5}$ [A]. The nature of energy transfer process between donor and acceptor atoms can be studied by evaluating the probability function. In the present experimental observations a value of $\theta \sim 6$ is obtained for the $\ln P_{DA}$ Vs $\ln[A]$ plot corresponding to acceptor concentration $< 0.01 \times 10^{-3}$ m/l whereas for the higher concentration ($> 0.03 \times 10^{-3}$ m/l) a slope of $2.7 (\theta = 8)$ is obtained. This confirms the fact that at lower acceptor concentration ($< 0.01 \times 10^{-3}$ m/l) the transfer process is dipole-dipole in nature whereas at higher acceptor concentration ($> 0.03 \times 10^{-3}$ m/l) transfer process is dominated by a dipole quadrupole process (Fig 4a and 4b).

3.2 Variation of transfer efficiency ($\eta$) with acceptor concentration

Energy transfer efficiency (radiative and non radiative) and rate constants for the present ETDL system in methanol solution have been calculated by studying the relative fluorescence intensities of donor ($I_0/I_d$) and relative quantum yield of donor ($\phi_0/\phi_d$) as a function of the acceptor concentration [A] and the critical transfer radius $R_0$. 

![Figure 4(a) Dependence of transfer probability on [A] for d-d interaction B-80mW, C-110mW, D-140mW, E-170mW](image1)

![Figure 4(b) Dependence of transfer probability on [A] for d-q interaction B-80mW, C-110mW, D-140mW, E-170mW](image2)
In the presence of acceptor dye, the fluorescence intensity of the donor dye is reduced from $I_0d$ to $I_d$ by energy transfer to acceptor. The total transfer efficiency ($\eta_T$) was calculated at different acceptor concentrations and is shown in Fig. 5a and 5b respectively for the d-d and d-q processes.

Non radiative transfer efficiency ($\eta_{NR}$) was calculated and is plotted in fig 6a and 6b for the d-d and d-q processes.

These calculations indicate that both radiative and non-radiative processes are important in the present ETDL system, even though the non radiative contribution is negligibly small compared to the radiative part. The radiative transfer efficiency is found to have direct dependence on the acceptor concentrations whereas the non radiative transfer efficiency is observed to play its important role at high acceptor concentration ($>0.07 \times 10^{-3} \text{m/1}$). The variation of $\eta_R/\eta_{NR}$ Vs $[A]$ shown in fig 7 clearly reveals that at acceptor concentration $< 0.07 \times 10^{-3} \text{m/1}$ radiative contribution is far exceeding the non radiative part whereas at higher acceptor concentrations ($>0.07 \times 10^{-3} \text{m/1}$) the radiative contribution will tend to decrease.
The pump power dependence of the transfer efficiency (radiative and non radiative) is graphically shown in fig 8a and 8b. In both the plots all the curves corresponding to different acceptor concentration show negative slopes indicating that pump power has a negative dependence on the transfer efficiency.

The variation of $I_d/I_0$ Vs $[A]$ is always linear in nature as shown in fig 9a for (d-d) and 9b for (d-q). Knowing the value of $[A]_{1/2}$ the half quenching concentration of the acceptor at which $I_d=I_0/2$ the value of $R_0$ can be evaluated. The calculated values of $R_0$ and $[A]$ for d-d and d-q interactions for different pump intensities are tabulated in table.1.
Table 1: Calculated radiative parameters of the dye mixture

<table>
<thead>
<tr>
<th>Pump Power (mW)</th>
<th>Accept. Conc. (10^{-3} m/l)</th>
<th>Absorption Cross-section ( \sigma_{A}^{d}(10^{-19} \text{cm}^2) )</th>
<th>Emission Cross-section ( \sigma_{A}^{e}(10^{-16} \text{cm}^2) ) ( \tau )</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>1248</td>
<td>0.16</td>
<td>5.53</td>
</tr>
<tr>
<td>110</td>
<td>959</td>
<td>0.03</td>
<td>5.3</td>
</tr>
<tr>
<td>140</td>
<td>919</td>
<td>0.005</td>
<td>1.6</td>
</tr>
<tr>
<td>170</td>
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</tbody>
</table>

The results clearly show that the value of R0 for d-q interaction is smaller than that of d-d interaction. Results also show an inverse dependence of pump power on critical radius R_0.

By knowing the values of \( \eta_{NR} \) at different acceptor concentrations for different pump powers the value of \( \phi_{0A}/\phi_{A} \) can be calculated at various[A] values using Eq.13 where \( \phi_{0} \) and \( \phi_{A} \) are quantum yields of donor molecule with and without acceptor. The variation of \( \phi_{0A}/\phi_{A} \) with [A] is also a straight line obeying the Stern-Volmer expression and are shown in Figs.9(c) and 9(d) for d-d and d-q interactions.
Assuming the value of $\tau_{od}$ to be ~ 6ns the values of $K_{NR}$ can be calculated for various pump powers corresponding to d-d and d-q interactions and are summarized in the table 1.

Similarly the curve $I_0/I$ Vs $[A]$ in fig.9(a) and 9(b) give the values of $K_T\tau_{od}$ for different pump powers where $K_T=K_R+K_{NR}$. Again by putting the value of $\tau_{od}=6$ns the total energy transfer rate constant $K_T$ can be calculated for the four pump powers studied. Knowing the values of $K_T$ and $K_{NR}$, radiative transfer rate $K_R$ can be directly evaluated and the values obtained are collected in table 1.

Observations of these results show that non-radiative transfer due to d-d interaction is comparatively less important than the radiative transfer mechanism in the present ETDL system in the acceptor concentration range < 0.01x10^{-3} m/l. At acceptor concentration greater than >0.03x10^{-3} m/l a similar tendency was observed (i.e; $K_R> K_{NR}$) whereas the value of $K_{NR}$ observed is comparatively smaller than that of the d-d interaction. In general both at lower and higher acceptor concentrations radiative transfer process is contributing to the energy transfer mechanism in the present ETDL system.
The pump power dependence of the transfer rate shown in fig 10 reveals that it is having a negative dependence in the transfer rate.

By knowing the values of $\tau_{od}$ and $\phi_0d/\phi_d$, the value of $\tau_d$. The fluorescence life time of the donor in the presence of acceptor at various acceptor concentrations can be evaluated using the equation $\phi_0d/\phi_d = \tau_{od}/\tau_d$. The values of $\tau_d$ at $[A] = 10^{-3}$ m/l are 4.704 ns, 5.49 ns, 5.586 ns and 5.598 ns respectively for 80 mW, 110 mW, 140 mW and 170 mw pump powers.

3.3 Dependence of gain on $[A]$ and pump power

Acceptor concentration and pump power dependence of optical gain $G(\lambda)$ of the acceptor emission is graphically shown in figures 11 and 12.

![Figure 11: Dependence of peak gain on $[A]$ in the absence of energy transfer B-80mW, C-110mW, D-140mW, E-170mW](image1)

![Figure 12: Dependence of peak gain on pump power in the absence of energy transfer B-10^{-6} m/l [A]; C-3\times10^{-6} m/l [A]; D-5\times10^{-6} m/l [A]; E-7\times10^{-6} m/l [A]; F-10^{-5} m/l [A]; G-3\times10^{-5} m/l [A]; H-5\times10^{-5} m/l [A]; I-7\times10^{-5} m/l [A];](image2)

Fig 11 infers that in the absence of energy transfer the gain of the acceptor system varies over a small range of 0.36 cm$^{-1}$ to 0.38 cm$^{-1}$ whereas the pump power has no dependence on the net gain value. Variation of optical gain with acceptor concentration and pump power after energy transfer process is graphically shown in fig 13 and 14.

(In evaluating the optical gain the dependence of the absorption and emission cross section of the acceptor on the concentration is also taken into account and the calculated cross section values are presented in table 2)
From these figures it can be noticed that due to the addition of donor, optical gain of the acceptor system is increased many times, the maximum being observed at 0.01 x 10^{-3} m/l acceptor concentration. It was also noticed that at this concentration acceptor gain increased by 9, 51, 127 and 362 times corresponding to 80 mW, 110 mW, 140 mW and 170 mW pump powers. Figure 13 also show a second gain maximum at 0.05 x 10^{-3} m/l acceptor concentration. 

Pump power dependence of the optical gain shows that at low acceptor concentrations, gain shows almost a saturation effect whereas at high acceptor concentration it shows a linear dependence.

4. CONCLUSIONS

We have analysed in detail the energy transfer process between FDS and Rh.B dye mixture in methanol. We recognise that our results could forecast suitable concentration regions for the wavelength shifts with the acceptor concentration for the dye mixture. Concentration dependence of the acceptor on the energy transfer clearly shows that radiative transfer process is having the major contribution in the present ETDL system, both at lower and higher acceptor concentrations. It was also noticed that at lower acceptor concentration (0.01x10^{-3} m/l) non-radiative transfer is mainly due to the Forster type d-d interaction whereas at higher acceptor concentration (>0.03x10^{-3} m/l) d-q process is contributing to the non-radiative process. Analysis also shows that the optical gain of the acceptor dye can be increased several times due to the energy transfer process. Optical gain is also observed to a direct dependence on the pump power.

REFERENCES


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