4.1 INTRODUCTION

Many attempts have been made in studies aimed to improve dye lasers efficiency and to extend their spectral range of operation. Energy transfer dye lasers (ETDL) have generated considerable interest as they are useful in obtaining enhanced laser output, wide tuning range, reduced concentration and pump threshold requirements and ultrashort pulse width in contrast to their single dye counterpart. Energy Transfer Dye Lasers using numerous donor-acceptor dye pairs have been reported by various investigators during the last three decades. Peterson and Snavely first suggested in 1968 that dye laser efficiency could be enhanced though the use of mixtures of dyes and demonstrated some improvement in lasing for combinations of Rhodamines. After examination of a larger set of paired dyes, Pavlopoulos showed that, although the down-shifting of emission through energy transfer between dyes could be advantages in principle, adjustments of concentrations, aggregation and other complications make most simple combination of dyes unsuitable for efficient energy transfer and wavelength shifting. Schafer and Liphardt et al. have reported energy transfer dye systems not requiring alteration in dye concentration. A simple theoretical model developed by Dienes was found to be in good agreement with experimental observations for Rh 6G-CV mixture, a pair commonly used for ETDL studies. The variation of gain with acceptor concentration is explained using this model. Gain measurements on
these mixtures show a higher gain in the mixture as compared to CV alone. This high gain ETDL systems were successfully demonstrated in other donor-acceptor pairs. As a result of this gain enhancement, the conversion efficiency of the system was improved considerably. The dye mixture is excited where the excitation energy is transferred from an absorbing donor (D) to an acceptor (A). The type of excitation transfer is called sensitised fluorescence\(^{13}\) and has become the subject of intense study.

Most of the earlier studies on energy transfer have been done using a pulsed laser (N\(_2\) laser) as the exciting source. It was later showed that the use of Argon ion laser, which is conveniently and widely used pump source, may be practically extended through energy transfer mechanism to a number of dyes.\(^{14}\) In this chapter, the excitation energy transfer mechanism of two pairs of binary dye mixture systems, Sodium fluorescein-Rhodamine B and Sodium Fluorescein- Cresyl Violet in ethanol, using argon ion laser excitation, is discussed.

### 4.2 EXCITATION TRANSFER MECHANISMS

Mechanisms of energy transfer\(^{15}\) are as follows: (a) radiative energy transfer\(^{16}\) involving the emission of a photon by the donor molecule and its subsequent absorption by the acceptor molecule, (b) resonance transfer due to long-range dipole-dipole interaction\(^{17,18}\) and (c) diffusion-controlled collisional transfer. Mechanisms (b) and (c) are also called non-radiative transfer\(^{19}\) because the excitation transfer takes place before the excited donor emits. Mechanism (c) occurs over donor-acceptor separation of the order of molecular distances. This mechanism is dependent on the solvent viscosity and temperature. Its probability is very small in the concentration range studied.\(^{19,20}\) In mechanism (a), emitted photons of the donor are absorbed by
the acceptor and is called 'trivial mechanism'. The quantum mechanical treatment of resonance transfer is due to Forster. The origin of such resonance transfer is the long-range dipole-dipole interaction. The probability of energy transfer due to such interaction is large if the emission spectrum of the donor strongly overlaps with the absorption spectrum of the acceptor which is precisely the requirement for mechanism (a), the purely radiative emission and reabsorption.

Although all these mechanisms contribute to the donor fluorescence quenching and enhance the acceptor fluorescence yield, these various mechanisms may be theoretically and experimentally distinguished by measuring the donor fluorescence as a function of acceptor concentration. If the donor life time is little affected by the acceptor molecules, then the mechanism by radiative transfer can be considered to be the dominant one. One can also distinguish these mechanisms by comparing the fluorescence spectra and efficiencies. The diffusion controlled collisional transfer rate should decrease with the rigidity of the environment and is inversely proportional to the solvent viscosity. Its probability is very small in the concentration range studied.

### 4.3 THEORETICAL CONSIDERATIONS

To understand the quantitative idea of energy transfer mechanism, the kinetic scheme shown in Figure 4.1 is used. This scheme corresponds to the singlet states of donor and acceptor, coupled by an energy transfer rate constant $K_{D\rightarrow A}$ to account for transfer from the first excited singlet state ($S_1$) of the donor to the ground state ($S_0$) of the acceptor. Each singlet state is pumped with a laser beam of intensity $I_p$ at the rate $\sigma_{01}(P)I_p$. Lasing occurs in the acceptor molecule at the rate $\sigma_v I_L$ where $I_L$ is the generated laser
intensity. Absorption losses at the dye laser frequency are represented by the rate $\sigma_{01} (L) I_L$.

Figure 4.1 Kinetic Scheme for an ETDL

In the case of CW laser pumped ETDL the triplet state effects cannot be neglected. The following assumptions are made, to get the gain expression that can be used in the design of a CW energy transfer dye laser: (1) the triplet-state-effect on the gain equation will be considered for the donor and the acceptor and (2) the effect of excited state absorption or other non-linear quenching processes on the acceptor gain will be disregarded.

The rate equations of the donor-acceptor dye mixture at threshold are given by

$$\frac{dN_{ID}}{dt} = N_{0D} \sigma_D W(t) - K_F N_{ID} N_{0A} - N_{1D}/\tau_D - K_{ST} N_{1D}$$

(1)
\[
\frac{dN_{1A}}{dt} = N_{0A} \sigma_A W(t) - (K_F + K_R) N_{1D} N_{0A} - N_{1A}/\tau_A - \mathcal{A} K_{ST} N_{1A}
\] (2)

\[N_D = N_{0D} + N_{1D}\]

\[N_A = N_{0A} + N_{1A}\]

\[N = N_A + N_D\]

where \(N\) represent population densities, the subscript 0 and 1 for the ground and first excited singlet states respectively, \(W(t)\) is the pump rate (photons cm\(^{-2}\) s\(^{-1}\)), the subscript \(D\) and \(A\) for donor and acceptor respectively. \(\sigma\) is the absorption cross section at the pumping wavelength (488 nm) and \(\tau\) is the decay time in the absence of energy transfer. \(\tau_D\) and \(\tau_A\) are the decay times of the singlet states of the donor and acceptor respectively in the absence of energy transfer. The gain coefficient for the dye mixture system at wavelength \(\lambda\) in terms of stimulated and absorption cross section is given by\(^{22}\)

\[g(\lambda) = \sigma_e^A N_{1A} - \sigma_a^A N_{0A} - \sigma_T^A N_{1A} + \sigma_D^D N_{0D} - \sigma_T^D N_{1D} - \sigma_T^D N_{1D}\]

where \(\sigma_T^D\) and \(\sigma_T^A\) are the triplet state absorption cross-sections of the donor and the acceptor molecules respectively. Since the absorption and emission of the donor molecule can be assumed to be negligibly small in the fluorescence spectrum of the acceptor, the gain coefficient can be written as

\[g(\lambda) = \sigma_e^A N_{1A} - \sigma_a^A N_{0A} - \sigma_T^A N_{1A} - \sigma_T^D N_{1D}\]

(5)

The rate equations (1) and (2) gives

\[\frac{dn_{1D}}{dx} = n_{0D} \alpha_D - K_F \tau_A n_{1D} n_{0A} N_A - \tau_A n_{1D}/\tau_D - \mathcal{A} K_{ST} \tau_A n_{1D}\]

(6)

\[\frac{dn_{1A}}{dx} = n_{0A} \alpha_A - (K_F + K_R) \tau_A n_{0A} n_{1D}/N_A - n_{1A}/\tau_A - \mathcal{A} K_{ST} \tau_A n_{1A}\]

(7)

where

\[x = t/\tau,\]
\[ n_{1D} = \frac{N_{1D}}{N_A} \]
\[ n_{0D} = \frac{N_{0D}}{N_A} \]
\[ \alpha_D = \sigma_D W(t) \tau_A \]
\[ \alpha_A = \sigma_A W(t) \tau_A. \]

Since we are measuring the unsaturated gain, groundstate populations are negligibly perturbed.

Hence \( N_{0A} \equiv N_A \)
\[ \therefore n_{0A} = 1, \]
\[ n_{0D} = \frac{N_D}{N_A} \]
\[ F = \frac{F_D}{1-F_D} \]

where
\[ F_D = \frac{N_D}{(N_A+N_D)} \]

Under steady state approximation
\[ \frac{dn_{1D}}{dx} = \frac{dn_{1A}}{dx} = 0. \] (8)

Hence the above equations can be written as,
\[ n_{1A} = \left\{ \frac{\alpha_A + F_D}{(1-F_D)} \frac{(K_F + K_R)N_A\alpha_D}{(K_F N_A + K_D + K^D K_{ST})} \right\} \frac{1}{(1+K_{ST} \tau_A)} \] (9)

where
\[ k_D = \frac{1}{\tau_D} \] is the natural decay rate of the donor.

Thus the final gain equation of the binary system under CW excitation becomes
\[
g(\lambda) = \left\{ \sigma_e^A \alpha_A / \alpha_D + \frac{F_D}{(1-F_D)} \frac{(K_F + K_R)N_A\sigma_e^A}{(K_F N_A + K_D + K^D K_{ST})} \right\} \frac{\alpha_D N_A}{(1+K_{ST} \tau_A)} \\
- \sigma A^N A - \sigma_T^D N_{1D} - \sigma_T^A N_A \] (10)
Emission cross-sections are calculated using the relation

\[ \sigma_e(\lambda) = \frac{\lambda^4}{8\pi c n^2 \tau_{OD} \lambda_{eff}} \]  

(10a)

where \( \Delta \lambda_{eff} \) is the effective fluorescence line width.

\[ \Delta \lambda_{eff} = \frac{\int I_d \lambda \lambda}{I_p} \]  

(10b)

\( I_p \) is the peak emission intensity of the acceptor and \( \int I_d \lambda \) are obtained from the respective emission spectrum.

Equation (10) shows that the gain per acceptor molecule of the mixture is increased with the addition of the donor by a factor,

\[ \left( \frac{F_D}{1 - F_D} \right) \frac{(K_F + K_R)\sigma_D}{K_F N_A + K_D + D K_{ST}} \sigma_e A N_A^2 \frac{1}{(1 + K_{ST} \tau_A)} \]  

(11)

From equation (10) it is clear that \( g(\lambda) \) is proportional to the pump power and a plot between the two will be a straight line with a slope given by equation (11).

The rate constraints for total \( (K_T) \) and non-radiative \( (K_{NR}) \) energy transfer processes are given by the Stern-Volmer expressions.\(^*\)

\[ \frac{I_{od}}{I_d} = 1 + K_T \tau_{od} [A] \]  

(12)

\[ \frac{\phi_{od}}{\phi_d} = 1 + K_{NR} \tau_{od} [A] \]  

(13)

where

\( I_{od} \) and \( I_d \) are fluorescence intensities of donor in the absence and presence of the acceptor respectively.

\( \phi_{od} \) and \( \phi_d \) are the corresponding quantum yields.
\( \tau_{od} \) is the fluorescence life time of the donor without acceptor and 

\([A]\) is the acceptor concentration.

Knowing the value of \( \tau_{od} \), \( K_T \) and \( K_{NR} \) can be directly evaluated from the corresponding Stern-Volmer plots.

The critical transfer radius \( (R_0) \), for which energy transfer from the excited donor \( (D^*) \) to the acceptor \( A \) and emission from \( (D^*) \) are equally probable, is obtained\(^{24} \) as

\[
R_0 = 7.346 \left( [A]_{1/2} \right)^{-1/3} \text{ where}
\]

\([A]_{1/2}\) is the half-quenching concentration.

\([A]_{1/2}\) is obtained from the \((I_{od}/I_d)\) vs.\([A]\) graph.

According to the Forster-Dexter theory, \( R_0 \) is related with the energy transfer probability \( P_{DA} \) as

\[
P_{DA} = 1/\tau_{od} \left( R_0/R \right)^s
\]

where

\( s = 6, 8, 10 \) respectively for d-d, d-q and q-q interactions.

(d – dipole; q – quadrupole)

The respective critical radii are defined by the expressions\(^{25} \)

\[
R_0^6 \ (d-d) = \frac{3h^4c^4}{4\pi n^4} Q_A \int \frac{f_{S}(E)F_{A}(E)dE}{E^4}
\]

\[
R_0^8 \ (d-q) = \frac{135\pi h^5c^5}{4n^4} Q_A \int \frac{f_{S}(E)F_{A}(E)dE}{E^8}
\]

\[
R_0^{10} \ (q-q) = \frac{225\pi h^{11}c^{10}}{2n^6} \int \frac{f_{S}(E)F_{A}(E)dE}{E^8} \quad \text{for q-q interaction}
\]
where

\[ fs(E) \] is the normalised emission line shape function of the acceptor,
\[ FA(E) \] is the normalised absorption line shape function of the acceptor.

\[ QA \] is the oscillator strength of the absorption band of the acceptor which is in resonance with the donor emission transition and \( E \) is the average energy of the overlapping transition. Total energy efficiency (\( \eta_T \)) is written as the sum of two parts, radiative and non-radiative.

\[ \eta_T = \eta_R + \eta_{NR} \]  \hfill (19)

where

\[ \eta_T = 1 - \frac{I_0}{I_{OD}} \]  \hfill (20)
\[ \eta_{NR} = 1 - \frac{\phi_D}{\phi_{OD}} \]  \hfill (21)

For long range dipole-dipole energy transfer\(^{26}\)

\[ \eta_{NR} = \pi^{1/2} X \{ \exp \left( X^2 \right) \} \left( 1 - \operatorname{erf} X \right) \]  \hfill (22)

where

\[ X = \frac{[A]}{[A]_0} \] is the molar concentration expressed relative to the critical molar concentration of the acceptor.

\[ [A]_0 = \frac{3000}{2\pi^{3/2}} NR_0^{3/2} \]

\[ \operatorname{erf} X = \frac{2}{\sqrt{\pi}} \int_0^X \exp \left( -t^2 \right) \, dt \]

An equivalent expression for \( \eta_{NR} \) is given by

\[ \eta_{NR} = 1 - \frac{\tau_D}{\tau_{OD}} \]  \hfill (23)

The radiative transfer efficiency \( \eta_R \) is obtained by subtracting \( \eta_{NR} \) from \( \eta_T \) using equation (19).

The dipole-dipole nature of the non-radiative transfer from \( D^* \) to \( A \) can be confirmed by plotting a graph between transfer probability \( P_{DA} \) and acceptor concentration \([A]\) on a logarithmic scale. The straight-line graph obtained can very well be fitted with the theoretical expression.
\[ \ln P_{DA} = K + \theta/3 \ln[A] \]  
\[ \text{where} \]
\[ \phi = 6, 8, 10 \text{ respectively for } d-d, d-q \text{ and } q-q \text{ interactions} \]
\[ P_{DA} = 1/\tau_{OD} \left( l_{OD}/l_D - 1 \right) \]  
\[ \text{where} \]
\[ \tau_{OD} \text{ is given by Strickler-Berg equation}^{28-30} \]
\[ \frac{1}{\tau_{OD}} = 8\pi c_0 \frac{\int E(\lambda)d\lambda}{\int E(\lambda)\lambda^3 n^2(\lambda)d\lambda} \int \frac{\sigma_A(\lambda)d\lambda}{\lambda n(\lambda)} \]  
\[ c_0 \text{ is the speed of light in vacuum, } n(\lambda) \text{ is the refractive index of the solution at wave length } \lambda \text{ and } \sigma_A(\lambda) \text{ is the absorption cross section distribution of the dye. } \int E(\lambda)d\lambda \text{ is the fluorescence line shape function.} \]

4.4 EXPERIMENTAL

Two pairs of dyes were chosen such that the absorption spectrum of each acceptor dye overlapped the fluorescence spectrum of the donor dye separately. In the experiments performed, sodium fluorescein (SF) was chosen as the donor, and Rhodamine B (RhB) and Cresyl Violet (CV) as acceptors. Ethanol was used as the solvent. The dyes are obtained from Exciton Inc., Ohio, USA and the solvent (ethanol) used was of optically pure. For excitation, the 488 nm output of the Argon ion laser was used which excited only the donor. The dye solutions were taken in a quartz cuvette of width 1 cm and pumped by the laser beam. Fluorescence emission from the solution was focussed on to the entrance slit of a 0.2 m concave holographic monochromator (Mc Pherson Model 275) which has a wavelength accuracy of ±0.1 nm. The output of the monochromator was fed to a photomultiplier (Oriel Corpn. 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. Experiments were repeated for different pump powers and concentrations of the acceptor. The block diagram of the experimental arrangement is given in Figure 4.2.

The optical absorption spectra of the samples were recorded using Shimadzu UV 160 A uv/vis spectrophotometer.

All the observations were taken at room temperature.

![Block Diagram of the Experimental Arrangement](image)

Figure 4.2  Block Diagram of the Experimental Arrangement

4.5 RESULTS AND DISCUSSION

The conditions favouring energy transfer are (i) a large overlap between the absorption spectrum of the acceptor and the emission spectrum of the donor, (ii) high fluorescence yield of the donor molecule and (iii) the singlet energy of the acceptor is less than that of the donor.
Absorption spectra of Sodium Fluorescein (SF), Rhodamine B (RhB) and Cresyl Violet (CV) are presented in Figure 4.3. To confirm the energy transfer process, the emission spectrum of the donor is plotted along with the absorption spectrum of the acceptor. The extent of energy transfer depends on the area of overlap. The overlap of the emission spectrum of SF and absorption spectrum of RhB (Figure 4.4) and that of SF and CV (Figure 4.5) are given. Since the area under the emission spectrum of SF overlaps with the absorption spectrum of RhB and CV, separately, energy transfer from SF to RhB and from SF to CV is possible, the extent of energy transfer depending on the overlapping area which are shown as shaded region in Figures 4.4 and 4.5.

Figure 4.3  Absorption Spectra of SF, RhB and CV in Ethanol
Figure 4.4  Emission Spectrum of SF and Absorption Spectrum of RhB

Figure 4.5  Emission Spectrum of SF and Absorption Spectrum of CV
It was observed that the emission spectra of SF, RhB and CV in ethanol are red shifted compared to their absorption spectra. Absorption takes place from the lowest vibrational level of the ground state and emission from the lowest vibrational level of the first excited state. Hence transitions in absorption require more energy than all the transitions observed in the emission spectrum.

Various physical phenomena that are occurring in each dye mixture pairs due to energy transfer, their functional dependence on a number of parameters and quantitative analyses of the phenomena are described in detail in the following sub-sections.

4.6 ENERGY TRANSFER AND OPTICAL GAIN STUDIES IN SF-RhB DYE MIXTURE

4.6.1 Dependence of peak fluorescence intensity of the donor \( I_D \) and Acceptor \( I_A \) on acceptor concentration \([A]\)

Figures 4.6 and 4.7 show the variation of the peak emission intensity of the donor and acceptor molecules in the dye mixture system with the acceptor concentrations at various pump powers. All the curves show a sharp reduction in the fluorescence intensity of the donor \( I_D \) compared to that of the isolated donor system. At higher acceptor concentration \((0.4 \times 10^3 \text{ M/L})\), it is observed that the donor emission is either completely quenched or so weak that it cannot be noticed.
**Figure 4.6** Peak Emission Intensity of SF vs. [RhB]

**Figure 4.7** Peak Emission Intensity of RhB vs. [RhB]
This is because of the fact that the donor system is continuously transferring its energy to the acceptor system. At these acceptor concentrations, the separation between the donor and acceptor molecule will be so small that effective coupling and thereby efficient energy transfer became possible. In this case the photons emitted by the excited donor is completely absorbed by the ground state acceptor molecules. Another manifestation of the energy transfer process is the increase in the emission intensity of the acceptor molecule at lower concentrations as compared to the unsensitised system. It is observed that at lower acceptor concentration (10^{-5} \text{ M/L}) the fluorescence intensity of acceptor was increased. At [A] = 0.8 \times 10^{-4} \text{ M/L}, the fluorescence intensity of the acceptor is found to be decreased and at [A] = 0.4 \times 10^{-3} \text{ M/L}, it is abruptly decreased. At higher acceptor concentration, the acceptor emission shows a reduction in intensity due to the self-quenching acceptor-acceptor interaction referred to as the concentration quenching. In this case, the energy transferred to the acceptor molecules are undergoing vibrational relaxation with the surrounding like-molecules and is converted into heat. Even if the acceptor is emitted, the photons are reabsorbed by the ground state acceptor atoms.

4.6.2 Pump power dependence on emission intensity

It is observed that under all conditions, the emission intensity of the donor as well as that of the acceptor increases with pump power. To understand the pump power dependence on the emission intensity and thereby on the efficiency, \( \varepsilon = I_{(\text{max})}/I_{\text{p}} \) of the donor as well as the acceptor emission is plotted for different pump intensities and the variations are shown graphically in Figures 4.8 and 4.9.
The plots show almost linear dependence of $I_{\text{max}}$ and hence efficiency upon pump intensity with a change of slope at higher concentration of the concentration range studied. Fluorescence efficiency of both the donor and the acceptor are reduced with increase in pump power. It is observed that the slopes if the curves are reduced for both the donor and acceptor and attains a saturation at higher concentrations. This may be due to other competitive
quenching process like excited state absorption, singlet to triplet transition etc. at higher pump powers. Fluorescence efficiency of the acceptor is found to be a maximum when the acceptor concentration is $4 \times 10^{-5}$ M. In Rhodamine B in ethanol, the fluorescence efficiency is dependent on the temperature. Figure 4.10 and 4.11 give the graphical variation of the emission intensities of donor and acceptor with pump power.

**Figure 4.10**  Peak Emission Intensity of SF vs. Pump Power

**Figure 4.11**  Peak Emission Intensity of RhB vs. Pump Power
The increase in emission intensity of the donor as well as the acceptor with pump power is prominent at lower concentrations of the acceptor. At higher concentrations the slope of the curves are found to be decreased. At [RhB] = 0.4 \times 10^{-3} \text{ M/L}, the emission intensity is found to be almost a constant with change in the exciting pump power.

4.6.3 Dependence of peak wavelength ($\lambda_p$) of the donor and acceptor emission on acceptor concentration

Figures 4.12 and 4.13 show the dependence of the peak emission wavelength of the donor ($\lambda_p^D$) and that of the acceptor ($\lambda_p^A$) on the acceptor concentration [A].

![Figure 4.12 Peak Emission Wavelength of SF vs. [RhB]](image1)

![Figure 4.13 Peak Emission Wavelength of RhB vs. [RhB]](image2)
All the curves show the same behaviour irrespective of the pump power. An important observation is that the donor dye always shows a blue shift whereas the acceptor dye shows a red shift enhancing the wavelength range of tunability when used as laser active medium. In the concentration range of the acceptor dye used (from $0.5 \times 10^{-5}$ M/L to $8 \times 10^{-5}$ M/L) the blue shift of the peak wavelength of emission of donor is found to be 42.8 Å. The shift in peak wavelength is greater at lower concentrations. This blue shift observed in the donor emission can be accounted as follows. As the concentration of the acceptor molecules increases, the intermolecular separation between the donor and acceptor molecules decreases. The collisional heat energy generated in the acceptor system will be sufficient to populate the higher excited singlet state of the donor molecule which in turn causes the emission to be shifted to the higher energy region. Here the upper vibrational levels of the first excited singlet states are more populated and transition takes place from these excited vibrational levels to the ground electronic level. The red shift observed in the case of acceptor emission is 27 nm as the concentration of the acceptor is increased, in the concentration range studied. In RhB, the amino groups are potentially mobile because of the variation in the excited state $\pi$- electron density within the $C=\!N$ bond. This non-rigidity in the excited state of RhB tends to twist it away from the planar rigid nature leading to loss of energy and hence the red shift. Also at higher concentration of the acceptor, ground state absorption becomes prominent leading to overlapping of absorption and emission spectra.

4.6.4 Nature of energy transfer and probability function ($P_{DA}$)

The nature of energy transfer process between donor and acceptor is studied by evaluating the transfer probability function using equation (25) and observing the functional dependence of the transfer probability function on acceptor concentration using equation (24). In the present experimental
observation a value of $\theta < 6$ is obtained for the ln ($P_{DA}$) vs. ln [A] plot (Figure 4.14) corresponding to acceptor concentration range from $10^{-5}$ M/L to $8 \times 10^{-5}$ M/L. This confirms the fact that at these concentrations the energy transfer process is not dipole-dipole in nature.

![Figure 4.14 ln $P_{DA}$ vs. ln[A]](image)

4.6.5 Energy transfer efficiency ($\eta$) and rate constants

Energy transfer efficiency (radiative-$\eta_R$ and non-radiative-$\eta_{NR}$) and rate constant for SF-RhB binary dye system in ethanol have been calculated by studying the relative fluorescence intensities of donor ($I_{OD}/I_D$) and relative quantum yields of donor ($\phi_{OD}/\phi_D$) as a function of acceptor concentration [A]. In the presence of the acceptor dye (RhB), the fluorescence intensity of donor dye (SF) is reduced from $I_{OD}$ to $I_D$ by energy transfer from donor to acceptor.

The total energy transfer efficiency ($\eta_T$) was calculated using equation (20) at different acceptor concentrations and is shown in Figure 4.15. Non-radiative transfer efficiency $\eta_{NR}$ was calculated using equation (21). Calculations show that the dominant mechanism in the energy transfer is radiative in the concentration range studied. At these concentrations of the acceptor dye, simultaneous laser emission at two separate spectral regions
may be expected. Non-radiative transfer efficiency ($\eta_{NR}$) is found to increase with increasing acceptor concentration $[A]$ (Figure 4.16).

**Figure 4.15** Total Energy Transfer Efficiency vs. [RhB]

**Figure 4.16** Ratio of Radiative to Non-Radiative Energy Transfer Efficiency vs. [RhB]
The variation of $I_{OD}/I_D$ vs $[A]$ is almost linear in nature (Figure 4.17). The half quenching concentration of the acceptor $[A]_{1/2}$ (at which $I_{OD}/I_D = 2$) is obtained as $1.5 \times 10^{-5}$ M/L.

![Graph of $I_{OD}/I_D$ vs. [RhB]](image)

**Figure 4.17** $I_{OD}/I_D$ vs. [RhB]

The value of $R_0$ is calculated using equation (14) and this comes out to be equal to 297.87 Å.

From the values of $\eta_{NR}$ at different acceptor concentrations, the value of $\phi_{OD}/\phi_D$ was calculated at various $[A]$ using equation (21).

The graph connecting $\phi_{OD}/\phi_D$ and $[A]$ is found to be a straight line obeying the Stern-Volmer expression (Figure 4.18).
The slope calculated from $(\phi_D/\phi_0) \text{ vs } [A]$ plot is

$$K_{NR} \tau_{OD} = 1.05 \times 10^3 \text{ LM}^{-1}$$

$\tau_{OD}$ is the fluorescence lifetime of the donor (SF) without acceptor. Assuming $\tau_{OD}$, the value of $K_{NR}$ calculated is $1.7213 \times 10^{10} \text{ LM}^{-1} \text{ s}^{-1}$.

The curve $I_{OD}/I_D \text{ vs } [A]$ in Figure (4.17) gives the value

$$K_T \tau_{OD} = 1.8394 \times 10^5 \text{ LM}^{-1}.$$ 

The total rate of energy transfer, $K_T = 0.308 \times 10^{14} \text{ LM}^{-1} \text{ s}^{-1}$. The difference in these values of $K_T$ and $K_{NR}$ gives the value of $K_R$.

$$K_R = 0.3076 \times 10^{14} \text{ LM}^{-1} \text{ s}^{-1}.$$ 

These values show that the radiative transfer mechanism is more significant than the non-radiative transfer mechanisms in the (SF-RhB) dye mixture in the concentration range studied.
Using equation (23), fluorescne life times of the donor ($\tau_D$) at various acceptor concentration were determined.

The value of $\tau_D$ at $[A] = 0.5 \times 10^{-5}$ M/L is 6.0968 ns and at $[A] = 8 \times 10^{-5}$ M/L is 6.049 ns.

Thus the life-time of the donor is only slightly affected by the acceptor concentration concluding that the radiative transfer is the dominant energy transfer mechanism involved. The variation of life-time of SF with $[\text{RhB}]$ is found to be linear. The variation is caused by the interaction between the SF and RhB molecules.

4.6.6 Effective Fluorescence line width of the Acceptor in Dye Mixture

The effective fluorescence line width of RhB in the dye mixture is calculated using equation (10 b) for different concentrations of RhB at various pump powers. The values are tabulated in Table 4.1.

$$\int I d\lambda$$ is evaluated from the emission spectrum of the acceptor using the trapezoidal method.

$$\int I(\lambda)d\lambda = \frac{h}{2} [1+2 (y_0+y_1+\ldots+y_n)].$$

Table 4.1 Fluorescence line Width of RhB in SF: RhB Dye Mixture System ($10^{-7}$ cm)

<table>
<thead>
<tr>
<th>[RhB] 10^{-4}M/L</th>
<th>Pump power (mw)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td>0.05</td>
<td>33</td>
</tr>
<tr>
<td>0.1</td>
<td>37</td>
</tr>
<tr>
<td>0.4</td>
<td>30</td>
</tr>
<tr>
<td>0.8</td>
<td>27</td>
</tr>
<tr>
<td>4.0</td>
<td>37</td>
</tr>
</tbody>
</table>
It was observed that the fluorescence line width is much more affected by the variation in the concentration of RhB rather than by the changes in pump power. At lower pump powers (<100 mW), the fluorescence line width is maximum at [RhB] = 10^{-5}M/L. But at higher pump powers (>100 mW), fluorescence line width is found to be maximum for much lower concentrations of RhB (0.5 \times 10^{-5}ML). At higher pump powers, the decrease in fluorescence line width with increase in [RhB] is attributed to the increased collision between the molecules and the non-radiative relaxation processes.

4.6.7 Emission Cross Section of the Acceptor

Emission cross section of the acceptor (RhB) is determined for different acceptor concentrations at various pump powers. The values are tabulated in Table 4.2.

**Table 4.2** Emission Cross section of RhB (10^{-16} cm^2)

<table>
<thead>
<tr>
<th>[RhB]10^{-5}M/L</th>
<th>Pump power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td>0.5</td>
<td>5.9</td>
</tr>
<tr>
<td>1.0</td>
<td>5.4</td>
</tr>
<tr>
<td>4.0</td>
<td>6.9</td>
</tr>
<tr>
<td>8.0</td>
<td>8.2</td>
</tr>
</tbody>
</table>

Emission cross section remains almost a constant with change in pump power. There are slight variations in the values with change in the concentration of RhB. As the concentration of RhB is increased, the interaction between donor and acceptor molecules increases. This may change in the orientation of the molecules and hence their dipole moment.
4.6.8 Dependence of gain on $[A]$ and pump power

The pump power dependence of optical gain $g(\lambda)$ of the acceptor emission in the unsensitised system is graphically shown in Figure 4.19. It is evident that in the absence of energy transfer, the gain of the acceptor system is not appreciably changed by changes in the pump power. The extrapolated Y-intercept should be equal to the ground state loss.

Variation of the optical gain with acceptor concentration and pump power after energy transfer process (donor sensitised dye system) is graphically shown in Figures 4.20 and 4.21. In evaluating the optical gain, the dependence of the absorption and emission cross sections of the acceptor on the concentration is considered. The calculated optical gain at different concentrations and pump powers are summarised in Table 4.3. From these figures, it is observed that due to the addition of donor, optical gain of the acceptor system is increased many times. It is observed that in the concentration range used, the gain is gradually decreasing with concentration at low pump powers. For higher pump powers, the gain is increasing with acceptor concentration. This may be due to the increased dimer formation at higher concentrations. The optical gain is found to be increasing with pump power at all the concentration used. A comparison of the gain in the two cases show that different photoquenching mechanisms like TICT formation in the excited state, excited state absorption, intersystem crossing etc. are very much reduced by the energy transfer mechanism. The change of the gain spectrum due to the energy-transfer reaction is attributed to the change of effective fluorescene life-time.$^{28}$
Figure 4.19  Variation of Gain with Pump Power (Unsensitised System)

Figure 4.20  Variation of Optical Gain with [RhB]
4.7 ENERGY TRANSFER AND OPTICAL GAIN STUDIES IN SF-CV DYE MIXTURE

4.7.1 Dependence of the peak fluorescence intensity of the donor ($I_D$) and acceptor ($I_A$) on acceptor concentration

Figure 4.22 and 4.23 show the variation of peak emission intensity of the donor and acceptor molecules in SF-CV dye mixture system with the acceptor concentrations at various pump powers.
All the curves show a sharp reduction in the fluorescence intensity of the donor \( (I_D) \) compared to that of the isolated donor system. At higher acceptor concentration \( (2 \times 10^{-4} \text{ M/L}) \), it is observed that the donor emission is appreciably quenched. This is because of the fact that the donor system is
continuously transferring its energy to the acceptor system. As the acceptor concentration is increased, the separation between the donor and acceptor molecule will be so small that effective coupling and thereby efficient energy transfer becomes possible. In this case the photons emitted by the excited donor is almost absorbed by the ground state acceptor molecules. Another significance of the energy transfer process is the increase in the peak emission intensity of the acceptor as compared to the unsensitized system at lower concentrations. In the concentration range $0.4 \times 10^{-4}$ M/L to $10^{-4}$ M/L it remains almost a constant. This is due to the self-quenching acceptor-acceptor interaction. In this case, the energy transferred to the acceptor molecules is undergoing vibrational relaxation with the surrounding like molecules and is converted into heat. Even if the acceptor is emissive, the photons are reabsorbed by the ground state acceptor molecules.

**4.7.2 Pump power dependence on emission intensity**

It is observed that under all conditions, the peak emission intensity of the donor as well as the acceptor increases with pump power. Figure 4.24 and 4.25 give the graphical variation of peak emission intensities of the donor and acceptor with pump power at different concentrations. The variation of efficiency ($\varepsilon = I_{\text{max}}/I_p$) with pump power is studied at different concentrations (Figures 4.26 and 4.27). For the donor it is observed that efficiency decreases with acceptor concentrations at lower pump powers. For the acceptor, efficiency first increases (in the range $10^{-4}$ to $2 \times 10^{-4}$ M/L concentration of the acceptor) and then it decreases with pump power. At very low concentrations of CV, its fluorescence efficiency is found to be almost independent of pump power.
Figure 4.24  Variation of Peak Emission Intensity of SF vs. Pump Power

Figure 4.25  Variation of Peak Emission Intensity of CV vs. Pump Power
Figure 4.26  Variation of Fluorescence Efficiency of SF with Pump Power

Figure 4.27  Variation of Fluorescence Efficiency of CV with Pump Power
4.7.3 Dependence of peak wavelength, \( \lambda_p \) of the donor and acceptor on acceptor concentration

Figures 4.28 and 4.29 show the dependence of the peak emission wavelength of the donor \( \lambda_p^D \) and that of the acceptor \( \lambda_p^A \) on the acceptor concentration \([A]\).

**Figure 4.28** Peak Emission Wavelength of SF vs. \([CV]\)

**Figure 4.29** Peak Emission Wavelength of CV vs. \([CV]\)
An important observation is that the donor dye always shows a blue shift whereas the acceptor dye shows first a red shift as the acceptor concentration is increased. The blue shift observed for the donor fluorescence is about 60 Å in the range of acceptor concentration from $0.4 \times 10^{-4}$ to $2 \times 10^{-4}$ M/L. The blue shift observed in the donor emission can be accounted as follows. As the concentration of the acceptor increases, the intermolecular separation between the donor and acceptor molecules decreases. The collisional heat energy generated in the acceptor molecules will be sufficient to populate the higher excited singlet vibrational states of the donor molecule which in turn causes the emission to be shifted to the higher energy region. In addition to this, being the CW nature of excitation some triplet effects should also have some observable contribution to the emission spectrum. From $0.4 \times 10^{-4}$ M/L to $2 \times 10^{-4}$ M/L, it is observed that the peak wavelength of acceptor emission is red shifted. The red shift of the peak wavelength of the acceptor emission is owed to the increase in dimer formation between the acceptor molecules as its concentration is increased. The red shift of the peak wavelength of acceptor emission is found to be about 40 Å in the concentration range from $0.4 \times 10^{-4}$ M/L to $1.1 \times 10^{-4}$ M/L of the acceptor. The slight blue shift is due to the decrease in the number of dimers formed as the acceptor concentration is increased (not shown in the graph).

4.7.4 Nature of Transfer Probability Function ($P_{DA}$)

The nature of energy transfer process in between donor and acceptor can be studied by evaluating the transfer probability function using equation (25) and observing the functional dependence of the transfer probability function on the acceptor concentration using equation (24). In the present experimental observations, a value of $\theta < 4$ is obtained for the $\ln (P_{DA})$ vs $\ln (C_D)$ plot (Figure 4.30). But at higher concentrations near to $2 \times 10^{-4}$ M/L of the concentration ranges studied, the value of $\theta$ approaches 6 showing the dipole-dipole nature of interactions.
4.7.5 Variation of Transfer Efficiency ($\eta$) with acceptor concentration $[A]$ and Energy transfer rate constant

Energy transfer efficiency (radiative and non-radiative) and rate constants for the binary dye system in ethanol have been calculated by studying the relative fluorescence intensities of the donor ($I_{OD}/I_D$) and its relative quantum yield ($\phi_{OD}/\phi_D$) as a function of the acceptor concentration $[A]$.

In the presence of the acceptor dye (CV), the fluorescence intensity of the donor dye (SF) is reduced from $I_{OD}$ to $I_D$ because of energy transfer from the donor to the acceptor.

The total transfer efficiency ($\eta_T$) was calculated using equation (19) at different acceptor concentrations and is shown in Figure 4.31. It is found that the total energy transfer efficiency is increased as the concentration of CV is increased. Non-radiative transfer efficiency ($\eta_{NR}$) was calculated using equation (22). Radiative energy transfer efficiency is plotted with $[A]$ in Figure 4.32.
It is observed that non-radiative transfer efficiency is two orders of magnitude less than that of radiative transfer efficiency. The non-radiative as well as radiative transfer efficiency is found to be increased with increase in acceptor concentration. The variation of \((\eta_R/\eta_{NR})\) vs \([A]\) is shown in Figure 4.33.
The ratio is found to decrease at higher concentrations showing that non-radiative energy transfer is increased at higher acceptor concentrations of the concentration range studied. The ratio is found to be decreased from 570 to 252 when the concentration is increased from $0.4 \times 10^{-4}$ M/L to $2 \times 10^{-4}$ M/L at 60 mw pump power. It is also observed that the pump power has no effective dependence on the ratio ($\eta_R/\eta_{NR}$). The pump power dependence of transfer efficiency (total and radiative) is graphically shown in Figures 4.34 and 4.35.
Figure 4.35 Pump Power Dependence of Radiative Energy Transfer Efficiency

The half quenching concentration of the acceptor, $[A]_{1/2}$ for which $I_{0_d}/I_d = 2$ is obtained from the $I_{0_d}/I_d$ vs [A] graph (Figure 4.36).

$[A]_{1/2} = 0.9373 \times 10^{-4} \text{ M/L}$

Critical transfer radius $R_0$ is calculated using equation (14).

$R_0 = 161.72 \text{ Å}$

Using the value of $R_0$, the critical molar concentration of the acceptor is found as

$[A]_0 = 1.0575 \times 10^{-4} \text{ M/cm}^3$

Figure 4.36 $I_{0_d}/I_d$ vs. [CV] Graph
Knowing the values of $\eta_{NR}$ at different acceptor concentrations, $\phi_{OD}/\phi_D$ is calculated at various $[A]$ using equation (13). The variation of $\phi_{OD}/\phi_D$ with $[A]$ is found to be a straight line obeying Stern-Volmer relation (Figure 4.37).

![Figure 4.37 \(\phi_{OD}/\phi_D\) vs. [CV] Graph](image)

The slopes calculated from these plots are $K_{NR} \tau_{OD} = 17 \text{ LM}^{-1}$. Assuming the value of $\tau_{OD}$, the value of $K_{NR}$ is calculated.

$$K_{NR} = 2.7869 \times 10^9 \text{ LM}^{-1} \text{ s}^{-1}$$

The curve $I_{OD}/I_D$ vs $[A]$ in Figure 4.36 gives the value of $K_T \tau_{rel}$.

$K_T \tau_{OD} = 2.386, 1.524, 1.702$ and $2.224 (10^4 \text{ LM}^{-1})$ respectively for the pump powers 60 mw, 70 mw, 80 mw, and 90 mw.

Using $K_T = K_R + K_{NR}$, the average rate of radiative energy transfer ($K_R$) is calculated to be $3.909, 2.495, 2.788$ and $3.646 (10^{12} \text{ LM}^{-1} \text{ s}^{-1})$ for the respective pump powers studied.
The different values show that radiative energy transfer is the prominent mode of energy transfer in the SF-CV binary dye system in the concentration range considered.

Comparing equations (21) and (23), the life time of the donor $\tau_d$ at various acceptor concentrations can be evaluated. The value of $\tau_d$ at $0.4 \times 10^{-4}$ M/L is found to be 6.0961 ns and at $2 \times 10^{-4}$ M/L is 6.0805 ns. Hence the fluorescence life-time of the donor is not appreciably affected by variation in concentration of the acceptor. Hence the nature of energy transfer in the present dye mixture, in the range of acceptor concentration studied is almost purely radiative.

4.7.6 Dependence of gain on [A] and pump power

Acceptor concentration and pump power dependence of optical gain coefficient, $g(\lambda)$ of the acceptor emission is graphically shown in Figures 4.38 and 4.39. It is observed that the effect in the variation of pump power on optical gain is only very small compared to that in the variation of acceptor concentration. It is also observed that the gain of the binary dye system is very much enhanced by the presence of the donor.

![Figure 4.38 Gain vs. [CV]](image-url)
As the pump power is increased the gain is found to be increased slightly at lower concentrations of CV. But as the concentration of the acceptor is increased, optical gain of the system is found to be decreased. This may be due to the increased dimer formation or aggregates of donor molecule with solvent molecule at higher concentrations of the acceptor. The fluorescence line width and emission cross-section calculated are shown in the Tables 4.3 and 4.4. The fluorescence line width is found to be almost constant under different pump powers and acceptor concentrations used. The value ranges from 0.2 to 0.35 (10^{-5} \text{ cm}).

The emission cross section is found to be slightly varying ranging from 1 to 2 (10^{-16} \text{ cm}^2). It is observed that the emission cross section remains to be a constant at $1.4 \times 10^{-15} \text{ cm}^2$ at $0.76 \times 10^{-4} \text{ M/L}$ acceptor concentration at different pump powers used.
Table 4.3  Fluorescence line width of CV in SF:CV dye mixture (10^{-5} \text{cm})

<table>
<thead>
<tr>
<th>[CV] \times 10^{-4} \text{M/L}</th>
<th>Pump power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td>0.3816</td>
<td>0.3475</td>
</tr>
<tr>
<td>0.7632</td>
<td>0.2806</td>
</tr>
<tr>
<td>1.1448</td>
<td>0.2993</td>
</tr>
<tr>
<td>1.5264</td>
<td>0.3563</td>
</tr>
<tr>
<td>1.908</td>
<td>0.3071</td>
</tr>
</tbody>
</table>

Table 4.4  Emission cross section of CV in SF : CV dye mixture (10^{-15} \text{cm}^2)

<table>
<thead>
<tr>
<th>[CV] \times 10^{-4} \text{M/L}</th>
<th>Pump power (mW)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60</td>
</tr>
<tr>
<td>0.3816</td>
<td>1.0554</td>
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<tr>
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<td>1.5264</td>
<td>1.0653</td>
</tr>
<tr>
<td>1.908</td>
<td>1.2226</td>
</tr>
</tbody>
</table>

4.8  CONCLUSIONS

We have analysed in detail the energy transfer process in the two pairs of binary dye system (1) SF-RhB and (2) SF-CV. In both cases radiative energy transfer is more significant compared to non-radiative energy transfer. But it is important that one should not completely overlook contributions due to the non-radiative transfer mechanisms. The solution used has a dilute concentration (that is, the average distance between the donor and acceptor molecules is much larger than molecular dimensions) and the donor life-time
is very short (that is, diffusion effects are negligible). Hence it is concluded that contributions due to diffusion controlled collisional mechanisms are minimal.\textsuperscript{19}

The energy transfer is proportional to the overlap area between the emission of donor and absorption of the acceptor. The first pair SF-RhB has a greater overlap compared to that of the second pair SF-CV. It is underlined by the fact that the optical gain for the first binary system is very much greater compared to the second binary system. By the use of the dye mixture, the range of tunability is increased. Also, the efficiency is found to be increased.

The shift in peak wavelength of emission is observed both in the case of the two pairs of the binary dye systems. These have been explained on the basis of different laser induced photophysical processes taking place in the dye system. The fluorescence line width and emission cross section were calculated and found to have only slight variations in the range of pump powers and acceptor concentrations used. The slight variations in emission cross-section is attributed to the variation in the fluorescence line width which is due to the difference in peak intensities of emission at different acceptor concentrations. These values can be used to find the optimum pump power and the acceptor concentration for efficient energy transfer. The different parameters determined above have a greater dependence on the acceptor concentration compared to the pump power in both the dye systems studied.
REFERENCES


