CHAPTER IV

ENERGY TRANSFER STUDIES IN DYE LASERS
ABSTRACT

The lasing characteristics of the mixed dye systems of Rhodamin 6G - Safranin T, Rhodamin 6G - Rhodamin B and Coumarin 120 - R hodamin 6G were studied using $\text{N}_2$ laser as the pumping source. Laser action was obtained from Safranin T in the mixed dye system with a concentration tuning range of 31 nm. The lasing peak wavelengths as a function of the concentration of the donor and the acceptor were studied for all the three systems. The observed donor concentration dependence on the emission peak wavelengths was attributed to the formation of a complex in the dye mixtures. The blue shift of the emission peaks as a result of donor sensitization was investigated. This blue shift also was found dependent on donor concentration. An enhancement of the power output of the order of 200% in Rh-6G - Rh-B mixture and 55% in C 120 - Rh-6G mixture was observed. A 1:1 molar concentration of donor and acceptor was found to give the maximum efficiency. The degree of polarization of the ETL output was measured as a function of the concentration of the donor and the acceptor. The amount of depolarization introduced by energy transfer mechanism was experimentally obtained.
4.10 Introduction

The increasing applications of dye lasers in spectroscopy and photochemistry demand the improvement of efficiency and extension of spectral region of operation of the dye lasers. Much work has been reported recently in this direction by the excitation of dyes by energy transfer processes. Nitrogen laser pumped dye lasers are limited to dyes which absorb the N₂ laser or to pumping schemes where the excitation energy is transferred from an absorbing donor to an acceptor. Therefore, energy transfer dye laser (ETDL) and laser induced intermolecular and intramolecular processes have become the subject of intense study. In the present chapter a short review of the work done on ETDL and the characteristics of some specific donor-acceptor pairs are reported.

4.20 A Review of the Work on ETDL

Several reports concerning the theoretical and experimental aspects of excitation transfer have appeared during the last decade, but only recently extensive discussions of its applications in ETDL systems have been reported. In 1968, soon after the discovery of organic dye solution lasers, Peterson et al. demonstrated the feasibility of a dye mixture laser with flash lamp excitation. In 1971 Heiler et al.
obtained effective excitation transfer from Rh–6G to Cresyl violet by $N_2$ laser pumping and observed an increase in power output. A simple theoretical model developed by Dienes et al. is found to be in good agreement with the experimental results obtained for Cresyl violet–Rh–6G mixture, a common pair used for most of the ETDL studies. They could also explain the gain variation with acceptor concentration with this theoretical model. The gain measurements done by them on Rh–6G–Cresyl violet mixture and Cresyl violet alone clearly show a high gain in the mixture as compared to Cresyl violet alone.

This high gain of ETDL system was demonstrated in other donor-acceptor pairs also such as Rh–6G–Rh–B, Coumarin 30–Rh–6 and Rh–68–MSB–Perylene. As a result of this high gain, the conversion efficiency of dye laser will be improved much. Recently, the author obtained a conversion efficiency of 21% for the dye mixture Rh–6G–Rh–B at a bandwidth of 1 Å whereas the same for Rh–B alone was only 7%. It is interesting to note that dyes like perylene could be lased by energy transfer mechanism which otherwise would not have been possible. This high gain, which is the result of an enhanced life time of the sensitized acceptor, produces a blue shift in the emission peak of the dye. Recent investigations on $N_2$ laser pumped ETDL showed pronounced blue shift in the superradiant peak emission wavelengths of Rh–6G, Rh–B, Brilliant sulphaphleavin, Coumarin–1 and Perylene. If the fluorescent
levels of donor and acceptor are closely located, this blue shift makes it difficult to identify the lasing species. In such systems, as suggested by Kusumoto et al., the lasing species is identified as the one whose emission peak is independent of the other. But the author showed that this rule cannot be applied, since in many mixture systems the emission peak is dependent on donor concentration.

Many authors have tried to determine the prominent mechanisms of energy transfer in ELDL systems. The prominent mechanisms of energy transfer are the radiative transfer, resonance transfer due to long range dipole - dipole interaction and the collisional transfer. Lin and Diem, by measuring the acceptor concentration and solvent dependence of the fluorescence lifetime of the donor in Rh-6G - Cresyl violet mixtures, determined the reaction rate constant of resonance transfer and concluded that this mechanism was dominant compared to the collisional transfer. Eilborn and Brynan reported a significant contribution of radiative transfer by measuring the spatial distribution and the time dependence of simultaneous two-wavelength output in Rh-6G - Cresyl violet mixture. A quantitative study corresponding to radiative transfer and resonance transfer is reported by Urisu and Kajiyama. From the concentration dependence of the effective fluorescence lifetime they determined the rate constants for both the processes and have shown that radiative
transfer is prominent in Coumarine 30 - Rh-6G mixture. The dominance of these energy transfer mechanisms in a given dye mixture may depend on the concentration and the solvent. 10, 14

One of the main advantages of ETDL systems over conventional dye lasers is the extension of the spectral region of operation. An efficient energy transfer process occurs in a dye mixture when the wavelength region of emission of the donor overlaps the absorption of the acceptor. In order to get laser action from a dye by N₂ laser pumping, either the donor or the acceptor need be a lasing dye under N₂ laser pumping as in the case of Rh-6G - Safranin T, 17

Anthracene - Perylene 10 and Coumarin - Acriflavrin, 16 Pavlopoulos 15 has discussed the requirement for an efficient donor dye for flash lamp pumped ETDL. Dunning and Stokes 19 have reported near infrared laser emission from DCDC with Rh-6 as the donor under N₂ laser pumping. The author could get an enhanced tuning range for Rh-6G by energy transfer mechanism because of the low threshold lasing in ETDL.

In an energy transfer process, it is usual that the donor fluorescence will be quenched by the acceptor. But by a proper selection of the dyes and their concentration it is possible to get simultaneous laser action from both the donor and the acceptor. Ahmed et al. 16 demonstrated the feasibility of a white light dye laser by energy transfer mechani
He obtained simultaneous lasing at three primary colours from 7-diethylamino-4-methylcoumarine, Acriflavin and Rh-B, thus showing that a cascade process of energy transfer is efficient. Many of the spectroscopic applications require simultaneous multiple wavelength laser lines from a laser system. A suitable design of the resonator will permit such an operation of a dye laser, but the wavelength will be within the range of a single dye. For widely separated multiple wavelength operation of a dye laser energy transfer mechanism using mixed dyes is the only possible solution reported so far.

The various advantages of energy transfer mechanism in dye lasers attracted the attention of many researchers. However, a proper theoretical approach to the problem is yet to be worked out in detail. An attempt was made by Dienes and Madden to give a simple theoretical model for the performance of an ETDL. But a more accurate treatment on the performance of an ETDL was given by Weiss and Speiser and a computer simulation applied to the Anthracene - Perylene system by Speiser and Katraro shows good agreement with experimental results.

4.30 Studies on some specific systems and their performance

A detailed investigation on the performance characteristics of Rh-6G - Safranin T, Rh-6G - Rh-B and C 120 -
Rh-6G dye mixture systems are presented here. Since the acceptors in all the three mixtures are found to be lasing under energy transfer conditions, all the experimental observations are based on the lasing mode of the dyes.

4.31 Rh-6G — Safranin T

The molecular structures of Rh-6G (C_{20}H_{31}ClH_{2}O_{3}, molecular weight 479.02) and Safranin T (C_{20}H_{15}N_{4}Cl-molecular weight 326.1) are shown in Fig. 4.1 and 4.2 respectively. Both the dyes belong to the Xanthene group of dyes. Laser action from Safranin T, was reported previously using 532 nm second harmonic radiation of Nd — glass laser as the pump source. But for the present investigations initial attempts made to lase Safranin T using H_{2} laser were unsuccessful. The most important criteria for an efficient energy transfer in a dye mixture is the overlap of the emission spectrum of the donor and absorption spectrum of the acceptor. The studies on spectral characteristics of Rh-6G emission and Safranin T, absorption showed a good spectral overlap and laser action was obtained from Safranin T, by energy transfer process with Rh-6G as the donor using H_{2} laser as the pump source.

Rh-6G (LOBA — India) and Safranin T (Riedel — Germany) were used without further purification.
Fig. 4.1. Molecular structure of Rh 6G.

Fig. 4.2. Molecular structure of Safranin T.

Fig. 4.3. Absorption spectrum of Safranin T (A) and Emission spectrum of Rh 6G (B).
grade methanol was used as the common solvent. The absorption spectrum of Safranin T was obtained with a systromics spectro calorimeter for an absorption path length of 1 cm and concentration of 0.013 gram/litre and is shown in Fig. 4.3(A). The absorption peak was found to be at 515 nm and the spectrum extended up to 625 nm.

The dye solution was transversely pumped and laser in a superradiant manner by 337.1 nm radiation from a pulsed \( \text{N}_2 \) laser (CEL - HL 103) with an output peak power of 100 kW at a repetition rate of 90 pps. The fluorescence spectra of 0.6 gram/litre Rh-6G in methanol and the superradiant emission peaks (\( \lambda_{\text{max}} \)) of Rh-6G alone and Rh-6G - Safranin T mixture were measured by a prism monochromator, an ELK 9504 D3 photomultiplier and a nanometer. The fluorescence emission spectrum of Rh-6G is shown in Fig. 4.3 (B) which shows a good spectral overlap with the absorption spectrum of Safranin T.

The concentration effect of Rh-6G on the \( \lambda_{\text{max}} \) is shown in Fig. 4.4 (A). Fig. 4.4 (B) represents the change in \( \lambda_{\text{max}} \) of Safranin T with concentration for a fixed Rh-6G concentration of 1.2 grams/litre while Fig. 4.4 (C) gives \( \lambda_{\text{max}} \) for different concentrations of Rh-6G with a fixed concentration of Safranin T (1 gram/litre).
Fig. 4.4. Plots of lasing $\lambda_{\text{max}}$ versus concentration.

(A) Rh 6G alone. (B) Safranin T with a fixed concentration of 1.2 grams/litre. (C) Rh 6G with a fixed Safranin T concentration of 1 gram/litre.
Fig. 4.4 (C) clearly demonstrates that the $\lambda_{\text{max}}$ depends only on the concentration of Safranin T establishing the fact that the lasing takes place in Safranin T. Thus most of the excitation energy absorbed by $\text{Cu}^{2+}$ is transferred to Safranin T as a useful pump power making excitation transfer quite efficient. Moreover the fact that an $\text{H}_2$ laser of 100 kW is used to lase Safranin T by energy transfer with the concentration tuning range of 31 nm further demonstrates that the ETDL system can work efficiently, even at very low pump powers.

The $\lambda_{\text{max}}$ value of Safranin T in the ETDL system at the concentration of 2 gram/litre is at 609 nm. Further increase in the concentration of Safranin T stopped the lasing action even at higher donor concentrations. Safranin T alone is reported to lase at 610 nm. But in the present investigations the 610 nm peak emission could not be obtained. The reason for this may be the blue shift of a donor sensitized laser system compared to an unsensitized system. Such an effect was observed by Klenerman et al. and theoretically explained by Urisu et al. But a quantitative estimate of this blue shift could not be obtained since Safranin T alone was not lasing under $\text{H}_2$ laser pumping.
Unlike the Rh-6G - Safranin T system the dye pair Rh-6G - Rh-B is a well known system for its efficiency of transferring energy from Rh-6G to Rh-B and both the dyes can be lased individually by H₂ laser pumping. Hence the system was used to study the performance of a typical ETDL. The molecular structure of Rh-B (molecular weight 472) is shown in Fig. 4.5.

The donor and acceptor concentration dependence on the super radiant emission peaks of the ETDL system was obtained with the setup described in 4.31. with a modification that the prism monochromator was replaced by a Jarrell - Ash 0.5 H scanning monochromator and the nanometer by a Fisher-Recordall 5000 chart recorder. Fig. 4.6 (A) shows the concentration variation of \( \lambda_{\text{max}} \) values for Rh-B alone while Fig. 4.6 (B,C and D) represents the shifts in the Rh-B emission peak for different Rh-6G concentrations (0.2 g/l to 3 g/l) with three fixed Rh-B concentrations (3 g/l, 2 g/l and 1 g/l).

Two important results are evident from these observations. One is the blue shift of the emission peaks of donor sensitized Rh-B and the other is the donor concentration dependence of the emission peaks. A donor sensitized system is shown to have a higher gain compared to unsensitized system.
Fig.4.5. Molecular structure of Rh B.
Fig. 4.6. Plots of lasing $\lambda_{max}$ versus concentration. (A) Rh B alone. (B) Rh 6G-Rh B mixture with a fixed concentration of 3 g/l. (C) Rh 6G-Rh B mixture with a fixed Rh B concentration of 2 g/l. (D) Rh 6G-Rh B mixture with a fixed Rh B concentration of 1 g/l.
Fig. 4.7. Absorption and 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.
system because of an increase in the effective life time of
the acceptor.\(^9\) As a result, the gain maximum will be
shifted to blue region.\(^{35}\) The life time of the acceptor will
be appreciably increased at very low concentrations (<10\(^{-3}\) \(\mu\)l) as reported by Urisu et al.,\(^9\) But this enhanced life time will
remain approximately a constant at higher concentration of
the acceptor as is evident in the case of Rh-6G - Rh-B where
the maximum blue shift remains a constant (~5 nm) in the
concentration range 2 \(\times\) 10\(^{-3}\) \(\mu\)l to 6 \(\times\) 10\(^{-3}\) \(\mu\)l (1 \(\mu\)l to 3
\(\mu\)l). Similar blue shifts have been reported in other dye
mixture systems also.\(^{11}\)

Fig. 4.6 (B, C and D) shows that this blue shift can be affected by the donor concentration. At very low
concentrations of the donor only partial energy transfer is
taking place. Since the intermolecular distance is very high
the donor-acceptor interaction is very weak. Hence the long
wavelength tail of Rh-6G emission where Rh-B has no absorption,
as can be seen from Fig. 4.7 (the absorption and emission
spectra of Rh-6G and Rh-B), is super imposed 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 also may contribute to this blue shift. But
this blue shift is less compared to that caused by the enhanced
lifetime due to complete energy transfer. It can been seen
that when the donor-acceptor concentration approaches 1:1 ratio the energy transfer becomes maximum and the blue shift due to enhanced life time also becomes maximum.

Another important observation is the red shift from the maximum blue shifted wavelength (Δλ) at higher Rh-B concentrations. This red shift may be attributed to a complex formation as it is evident from the nature of the red shift for different Rh-B concentration. Such a red shift due to complex formation, as in the case of a methanol solution of pyrylium and dimethyl aniline is not uncommon. The experimental evidences are not in favour of a ground state interaction of organic dye molecules when organic solvents are used. Hence these complexes are the result of excited state interactions (exciplex). A detailed investigation of the absorption and fluorescence properties of these exciplexes is necessary to explain its role in the observed red shift. The nature of Δλ variation at higher Rh-B concentrations than 3 g/l could not be obtained since under the present experimental conditions the system was not lasing. The rate of complex formation is limited by the diffusion of the two constituents and is proportional to the product of the concentrations of the constituents. The slopes of the red shift portion of B, C and D are different. This indicates that the phenomenon depends on the concentration of donor as well as
the acceptor. The decrease in the maximum blue shifted region with increasing Rh-D concentration further supports the complex formation. This study shows that in the Rh-6G - Rh-D ETDL system the lasing $\lambda_{\text{max}}$ of Rh-D is dependent on Rh-6G concentration due to the formation of a complex. A similar donor concentration dependence of $\lambda_{\text{max}}$ of the acceptor was seen in the system C 120 - Rh-6G.

The tuning range that can be obtained with concentration variation of the lasing species was studied. Fig. 4.8 (A) shows the concentration variation of $\lambda_{\text{max}}$ values for Rh-D alone while Fig. 4.8 (B) represents the same for donor sensitized Rh-D. It can be seen that the tuning range for the ETDL system is approximately the same as that for non-sensitized system except for the blue shift. In Fig. 4.8 (B) the $\lambda_{\text{max}}$ values were obtained by keeping $\frac{[D]}{[A]} = 1$ since it was the concentration ratio at which maximum efficiency could be obtained. Moreover this ratio allows the operation of the system on the maximum blue shifted region shown in Fig. 4.6 (BCU). In order to get laser action at acceptor concentration above 3 g/l the N₂ laser power had to be increased from 100 kW to 150 kW whereas the Rh-D alone system was lasing up to 5 g/l with 100 kW N₂ power. The reason for this decreased efficiency of the donor sensitized system at higher donor and acceptor concentrations is fluorescence quenching by the formation of complexes.
Fig. 4b. Tuning range of Rh B alone (A) and donor (Rh 6G) sensitized Rh B (B).
Fig. 4.9. Efficiency of Rh 6G - Rh B ETDL.

(A) Rh B alone 1.5 g/l.
(B) Rh B 1.5 g/l + Rh 6G 1 g/l.
(C) Rh B 1.5 g/l + Rh 6G 1.25 g/l.
(D) Rh B 1.5 g/l + Rh 6G 2 g/l.
(E) Rh B 1.5 g/l + Rh 6G 8 g/l.
The efficiency of the ETDL system, in terms of intensity, as a function of donor concentration is shown in Fig. 4.8. It can be seen that as the donor concentration increases, the intensity of the peak emission wavelength increases. When the donor acceptor concentration approaches a 1:1 ratio, the peak intensity becomes maximum. A further increase in the donor concentration decreases the peak intensity. This shows that the linear dependence of intensity on donor concentration, as predicted by Speiser et al., is valid only at lower concentrations of the donor. At higher donor concentrations, this linear dependence is disturbed and shows a decrease in intensity due to complex formation. A 200% increase in intensity for the sensitized system (Fig. 4.9(C)) compared to the unsensitized system (Fig. 4.7(A)) was observed. This shows that the ETDL is more efficient than the conventional dye laser.

The studies on the polarization properties of the ETDL, Rh-6G-Rh-B, has given the extend of depolarization introduced by energy transfer mechanism which is a well known depolarizing factor. The degree of polarization of the Rh-B emission as a function of concentration was measured with the monochromator, PMT, chart recorder and the perpendicular and parallel polarizing filters. The ETDL was operated in a superradiant manner and the degree of polarization $P = \frac{I_{III} - I_{II}}{I_{III} + I_{II}}$.
was measured at the emission peaks. The pumping \( \text{N}_2 \) laser power was monitored by a photodiode and oscilloscope. No correction factor was applied to the calculated \( 'P' \) values for the degree of polarization introduced by the monochromator since it will be less than 1%. The partially polarized \( \text{N}_2 \) laser used for the excitation of the dye was having a degree of polarization \( P = +0.33 \). The solvent was methanol.

Fig. 4.10(A) shows the variation of the degree of polarization of Rh-B with concentration and Fig. 4.10 (B) shows that for the dye mixture Rh-6G - Rh-B for a fixed concentration of 2.4 g/l of Rh-6G. The drop in the degree of polarization at higher concentration of Rh-B is due to the concentration depolarization. The relative orientation between the absorbing and emitting dipole causes the depolarization. At higher concentration the absorbed quantum of light is transferred from one oscillator to another with a certain angle between them. This further enhances the depolarization. In the mixed dye system it can be seen that the polarization changes in a complicated manner with increasing acceptor concentration for a fixed donor concentration. Energy transfer takes place preferentially between parallel dipoles, but nonparallel dipoles also undergo transfer with resulting depolarization. This effect can be observed from Fig. 4.10 (A,B) which shows a drop in the degree of polarization of the donor.
Fig. 4.10. The degree of polarization as a function of concentration. (A) Rh B alone. (B) Rh 6G-Rh B mixture for a fixed Rh 6G concentration of 2.4 g/l.

Fig. 4.11. Molecular structure of Coumarin 120.
sensitized system compared to the unsensitized system. However at very high acceptor concentration compared to that of the donor this drop in polarization is zero. To give a satisfactory explanation for this and the complicated variation of polarization with acceptor concentration, further investigations are needed.

4.33 $\text{C}_{120} - \text{Rh-6G}$

The system $\text{C}_{120} - \text{Rh-6G}$ is a best example for efficient energy transfer between a Coumarin derivative and a Xanthene dye. The molecular structure of $\text{C}_{120}$ (Molecular wt. 175) is shown in Fig. 4.11. The ETDL performance of the system was found in good agreement with that of $\text{Rh-6G} - \text{Rh6B}$.

Fig. 4.12 (B) shows the concentration dependence of $\lambda_{\text{max}}$ of Rh-6G for a fixed $\text{C}_{120}$ concentration of 0.35 g/l in methanol and Fig. 4.12 (A) that of Rh-6G alone. At lower concentrations of Rh-6G the blue shift introduced due to donor sensitization is small whereas the same at higher concentration is comparatively large. This indicates that the change in life time of donor sensitized Rh-6G from nonsensitized Rh-6G at higher concentration is large compared to the change at lower concentration since the blue shift is due to the enhancement of acceptor life time. It is a well known fact
Fig. 4.12. Plots of laser $\lambda_{max}$ versus concentration.

(A) Rh 6G alone. (B) C 120 – Rh 6G mixture with a fixed C 120 concentration of 0.35 g/l.
(C) C120 – Rh 6G mixture with a fixed Rh 6G concentration of 2 g/l.
Fig. 4.14. The concentration dependence of the effective fluorescence lifetime $\tau_{ef}$ of donor (C 30) sensitized Rh 6G in methanol. $\tau_{ef}$ is normalized by the fluorescence lifetime $\tau_a$ of pure Rh 6G.

Fig. 4.13 Concentration dependence of the fluorescence lifetime of Rh 6G.
that Rh-6G in Methanol shows an increase in life time with increasing concentration up to $5 \times 10^{-4}$/l due to radiation trapping and then a decrease with further increase in concentration due to concentration quenching. The nature of this dependence is shown in Fig. 4.13. The concentration dependence of the life time of the donor (C30) sensitized Rh-6G in methanol is shown in Fig. 4.14 where $\tau_{ef}$ is the life time of donor sensitized Rh-6G and $\tau_a$ is that of pure Rh-6G. It is evident from Fig. 4.13 and 4.14 that donor sensitized Rh-6G shows the maximum change in life time at concentrations in which life time of pure Rh-6G is the least. Since the blue shift of $\lambda_{max}$ in ETDL is due to the enhancement of life time of acceptor the maximum blue shift will be observed when the change in life time is a maximum. In the lower concentration range ($10^{-4}$ to $2 \times 10^{-3}$/l) of C30 + Rh-6G this effect was confirmed by Urisu et al. But from the increasing blue shift in the range $1.25 \times 10^{-3}$ to $6.25 \times 10^{-3}$/l observed, in the present investigations, it is evident that the life time of donor sensitized Rh-6G enhances with respect to that of pure Rh-6G in the concentration range.

Fig. 4.12 (C) shows the donor concentration dependence of Rh-6G peak emission wavelength. Rh-6G concentration is fixed at 2 grams/litre ($4 \times 10^{-3}$/l) and this concentration of pure Rh-6G has the $\lambda_{max}$ at 581 nm. The blue shift due to
Donor sensitization reaches a maximum only at a ratio of 1:1 molar concentration of C 120 and Rh-6G. (i.e., at C 120 concentration 0.7 grams/litre = $4 \times 10^{-3}$ M/l,) as in the case of Rh-6G. The gradual increase of this blue shift is only due to the enhancement of life time as a result of partial energy transfer since there was no overlap between the emission spectra of Rh-6G and C 120. The maximum blue shift remains a constant in the range $4 \times 10^{-3}$ to $10^{-2}$ M/l. The red shift with further increase in donor concentration suggests the possibility of formation of complexes in the dye mixture.

The measured output intensity of the ETDL was found to be a maximum when the molar concentration of C 120 and Rh-6G were approximately equal and was about 50% larger than that of pure Rh-6G.

The donor and acceptor concentration dependence of the degree of polarization of the system was studied and is shown in Fig. 4.15 (A) and 4.15 (B) respectively. The degree of polarization of the N\textsubscript{2} laser was + 0.33, C 120 alone was + 0.26 at a concentration of $2 \times 10^{-3}$ M/l and that of Rh-6G alone at a concentration of $5 \times 10^{-3}$ M/l was - 0.27. C 120 and Rh-6G alone systems did not show any appreciable change in the degree of polarization in the concentration range investigated. Even though the nature of donor and acceptor concentration dependence cannot be explained, it is quite interesting...
Fig. 4.15. The degree of polarization as a function of concentration. (A) C 120-Rh 6G mixture with a fixed Rh 6G concentration of 1 g/l. (B) C 120-Rh 6G mixture with a fixed C 120 concentration of 0.35 g/l.
to see that the difference in the degree of polarization between donor and acceptor concentration dependence has an approximately constant value throughout the concentration range studied.

4.34 Discussion

Since the first report on N\textsubscript{2} laser pumped ETDL by Hoeller et al., the art of ETDL has developed very rapidly. But even now the performance of ETDL is not fully known owing to the complexity of the quantum mechanical problem associated. Many authors have tried to give more or less simple models that are capable of explaining many experimental observations. The present investigations aimed at revealing many of the unattended or partially attended fields of ETDL was fruitful to a certain extend. The results of the investigations on the three specific ETDL systems can be summarized as follows.

The studies on Rh-6G - Safranin T shows that even if the acceptor dye has little or no absorption in the N\textsubscript{2} laser wavelength it can be lased by energy transfer mechanism with a suitable donor. The selection of donor should be such that its emission spectrum must overlap the absorption spectrum of the acceptor. Because of the low threshold lasing in ETDL even if the acceptor dye has a fluorescence quantum efficiency substantially below unity laser action can be obtained from
the dye. On the other hand if the acceptor can be lased by direct excitation with N₂ laser it can be lased with a lower pump power in ETDL as observed in the case of Rh-6G – Rh-B.

Even though Rh-6G, Safranin T and Rh-B are all from the Xanthene group of dyes, C 120 is from a different family. The C 120 – Rh-6G ETDL shows that efficient energy transfer is possible between a Coumarin derivative and a Xanth dye for laser action.

It can be seen that in all the three systems donor sensitization causes a blue shift in the emission peaks of the acceptor due to an enhancement of life time of the acceptor. Hence it has to be believed that the energy transfer mechanism effectively competes with the life time reducing mechanisms like concentration quenching. From the present investigations and the observations of Urisu et al.⁹ it is clear that when the change in the effective life time of the acceptor is a maximum the blue shift is also a maximum. Hence the extent of blue shift can be taken as a measure of the change in life time.

If the fluorescent levels of donor and acceptor are closely located, the blue shift makes it difficult to identify the lasing species. In such systems, usually the
lasing species is identified as the one whose emission peak is independent of the concentration of the other. But the present investigations show that the lasing peak wavelength of the acceptor can be dependent on the donor concentration also. Hence an investigation of the donor dependence on the acceptor emission becomes necessary prior to the identification of the lasing species. The donor concentration dependence on \( \lambda_{\text{max}} \) have similar nature both in Rh:6G - Rh-B mixture and C 120 - Rh:6G system and this dependence is attributed to the formation of 'exciplex' in the systems eventhough its role on the donor dependence is not known.

The concentration tuning range of the ETDL systems is approximately the same as that of conventional dye lasers. However ETDL have the advantage that the acceptor can be lased even at very low concentrations, which otherwise would not have been possible, there by obtaining the shorter wavelength operation of the acceptor. This can be seen in the case of Rh:6G - Rh-B and C 120 - Rh:6G.

The most attractive feature of an ETDL is its power conversion efficiency. A 200% increase in the superradiant output power, in the case of Rh:6G - Rh-B system, and a 50% increase in the case of C 120 - Rh:6G was observed compared to the non-sensitized systems. In both the cases the maximum efficiency was obtained when the donor
acceptor molar concentration ratio was 1:1. This shows that even if a dye can be directly pumped by N₂ laser it is better to use with a suitable donor for higher efficiency.

Eventhough the observed polarization properties of the ETDL systems can not be explained at this stage it gives us a measure of the depolarization introduced by energy transfer mechanism.
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