Energy Transfer Dye Laser Study of Influence of Various Coumarin Dyes on the Laser Performance of Rh590(Cl) Dye

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Abstract: Different coumarin dyes (C440, C460, C480, C485, C500 and C540A) are mixed with Rh590(Cl) in ethanol. The effect of coumarin dyes and their concentration on the laser gain properties and photostabilities of Rh590(Cl) is studied and discussed by investigating the gain characteristics at various concentrations and pump powers of N2–laser. It is found that for C480 and C540A dyes at optimized concentration, most of the absorbed pump power is transferred to Rh590(Cl) as a useful pump power. The gain characteristics of Rh590(Cl) are found to be changed due to change in the fluorescence lifetime. The mechanism responsible for the improvement in the laser performance and gain characteristics of Rh590(Cl) resulted from the energy transfer from these coumarin dyes. This improvement in the laser efficiency of Rh590(Cl) varied sharply depending upon the kind of coumarin dye. The theoretical calculations are also done to find the total transfer efficiency at various donor concentrations to identify the appropriate energy transfer mechanism responsible for gain enhancement in Rh590(Cl) dye. These calculations take into account the contribution due to both radiative and non-radiative energy transfer. In these dye mixtures the energy transfer excitation was found to overcome the inner filter effect and other losses such as photoquenching. The concentration dependence of peak gain and the lasing wavelengths of ETDL have been studied. The experimental results indicate that the dominant mechanism responsible for the efficient excitation transfer in these mixtures is of non-radiative nature due to long range dipole-dipole interaction. A broader tunable range is also provided by energy transfer.

Keywords: Coumarin dyes, Laser study, Dye Laser
1. INTRODUCTION

Compared with other commercially available multi-wavelength laser sources, dye laser has its obvious advantages such as low cost and high conversion efficiency for a variety of applications, particularly some medical applications involving the removal of pigmented lesions or photodynamic therapy, remote sensing or military applications, which require tunable high power pulsed beams [2,6]. The excitation of dye lasers through energy transfer process can provide ways of extending the lasing wavelength regions and improving the laser efficiency. Even more, under a specific pump condition, the laser oscillations could be observed for some dyes by energy transfer though they did not lase previously [15]. ETDLs have become the subject of intense study because N$_2$ laser pumped dye lasers were, otherwise, limited only to the dyes which absorb the N$_2$ laser light at 337.1 nm. Energy transfer can be achieved by selecting a donor dye absorbing strongly at the pump wavelength and subsequently transferring its energy to the lasing acceptor dye. The main mechanisms proposed for such an energy transfer are [1,13]:

1. Radiative energy transfer involving the emission of a photon by the donor molecule and its subsequent absorption by the acceptor molecule. Effective rate of spontaneous emission gets slowed down due to this mechanism.

2. Radiationless energy transfer due to interaction between the donor and the acceptor molecules during the excitation lifetime of the donor, prior to its emission of a photon. This mechanism is further divided into two parts:
   a. Diffusion controlled collisional transfer which occurs over intermolecular distances of the order of molecular diameter. This mechanism is dependent on the solvent viscosity and temperature. Its probability is very small in the concentration range studied in this work [4,10,11]. At higher concentrations, when dimer formation occurs in excited state, dissociation of these dimers provides a mechanism of radiationless energy transfer.
   b. Resonance energy transfer which occur at much greater donor-acceptor separations than the collisional diameters. The origin of such resonance transfer is the long range dipole-dipole Coulomb interaction. The conditions for dipole-dipole energy transfer are similar to those for radiative transfer, namely an overlap of the donor emission spectrum and the acceptor absorption spectrum, and an allowed transition from the acceptor. The radiative energy transfer mechanism is often the dominant mechanism in dilute solutions and its occurrence cannot be neglected in the studies of radiationless energy transfer. It has been shown by some authors that if the donor lifetime remains unaffected by the change in concentration of acceptor molecule,
radiative energy transfer can be considered dominant [1,12]. All these processes contribute to the donor fluorescence quenching and enhance the acceptor fluorescence yield. However, the mixing of two dyes is not as simple as it appears, and a number of factors, including dye concentration, optical densities and T-T absorption conspire so that only in some cases does a dye mixture successfully lase.

In our previous work, the gain enhancement and photostability for C485 dye had been observed in the presence of C440 dye. A blue shift in the gain region of C485 in presence of C440 dye was observed as compared to neat C485 solution. Increase in concentration of acceptor dye resulted in red shift of gain region. It was also observed that at acceptor concentration [A] <10^{-4} M/L, radiative energy transfer was dominant mechanism while the non-radiative transfer mechanism was dominant at [A] >10^{-4} M/L [8]. In this work, three fluorinated (C485, C500, C540A) and three non-fluorinated coumarin dyes (C440, C460, C480) were taken to act as donor dyes for Rh590(Cl) acceptor dye. The molecular structures of these dyes are given in Ref.1 and 8. The laser gain and tunable properties of Rh590(Cl) were investigated. The effects of coumarin dye concentration on the laser performance of Rh590(Cl) were also studied and mechanism involved is discussed. Concentration of all coumarin dyes has been optimized for better performance of ETDL.

2. EXPERIMENTAL DETAILS

The experimental setup for the measurement of optical gain values at different donor concentrations is described in our previous report [3,8,9] and is shown in Fig.1. The dyes were pumped by 337.1nm light from pulsed N_{2}-laser [Molectron UV-24] which delivers pulses of 900KW peak power and pulse duration of 10 ns. A cylindrical lens of focal length 20cm was used to focus the rectangular beam of cross section 0.6cm x 3.2cm at the exit onto a quartz dye cell of internal area of cross section 8mm x 8mm. The cell was used into two sections so that the length of gain region may be varied from L to L/2 by blocking half of the pumping beam. This is provided by a micrometer arrangement having the least count of 0.005mm attached to a movable screen to expose the dye solution at different cell lengths. The output from the dye cell is obtained at right angle to the incident beam so that the system operates in transverse mode. A number of thin attenuators of glass acting as neutral density filters were introduced in between the lens and the dye cell to attenuate the pump power from N_{2}-laser. One filter attenuates the intensity by 13.6 %.

The output from the dye cell was passed through Jarrell Ash 0.5m monochromator to select the various wavelengths of interest. A fast and
The sensitive photomultiplier tube (Philips XP2020) was fitted at the end point of monochromater, very close to it to prevent any stray light. The pre-amplifier output of PM tube was again amplified by linear amplifier (PA521type) before being recorded. The amplified signal was recorded on the 100 MHz oscilloscope (OS-768Atype).

The dyes used in the experiment were obtained from Exciton INC (Ohio, USA) and were used without further purification. The ethanol used as solvent was spectroscopically pure and the observations were taken at room temperature.

The basic gain equation is the same as already used in [14], i.e.

$$\gamma = \frac{2}{L} \ln \left( \frac{I_L}{I_{L/2}} \right) - 1$$

where $\gamma$ is intensity gain co-efficient, $L$ is the dye cell length, $I_L$ is the light intensity entering the monochromator at full length of the dye cell, and $I_{L/2}$ is the intensity at half length of the dye cell.

3. RESULT AND DISCUSSIONS

Effect of kind of coumarin and its concentration on the gain spectrum of Rh590(Cl) :
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Figure 2: Variation of Gain spectra of different dye mixtures with wavelength.

Figure 3: Variation of gain spectra of different dye mixtures with wavelength.
The gain spectra of binary solution containing 1 x 10^{-3} M/L of Rh590(Cl) and 1 x 10^{-5} to 1 x 10^{-2} M/L of various coumarin dyes in ethanol have been studied. The laser performance such as optical gain and threshold pump power of Rh590(Cl) in absence and presence of coumarin dyes and their dependence on the concentration of each kind of coumarin dye were also investigated. These results are shown in Fig.2 and Fig.3. at optimum concentration of donor and summarized in the Table-I. Higher laser efficiency i.e. higher gain value and lower laser threshold intensity of Rh590(Cl) in the presence of coumarin dyes were observed in nearly all these dyes.

However, the improvement in the laser efficiency of Rh590(Cl) in the presence of coumarin dyes varied sharply depending on the kind of coumarin dye and their concentration. These results are explained by taking coumarin dyes in two groups:

(i) **Non-fluorinated group of dyes:**

Gain spectra of Rh590(Cl) in presence of non-fluorinated dyes i.e. C440,C460,and C480 in ethanol at various concentrations mixed with Rh590(Cl) at 1 x 10^{-3} M/L display dual fluorescence but that the emission from rhodamine is also enhanced due to energy transfer. Dual fluorescence is much more pronounced in C440 as compared to C460, while first peak was almost missing for C480 dye showing that optical gain from this dye is suppressed in presence of Rh590(Cl). The optical gain of Rh590(Cl) in presence of C480 dye
Figure 4: Variation of peak gain of different dye mixtures with concentration.

Figure 5: Variation of peak gain of different dye mixtures with concentration.
at concentration varying from $1 \times 10^{-5}$ M/L to $1 \times 10^{-2}$ M/L was observed only in long wavelength region, but the laser gain of Rh590(Cl) increased sharply for this dye. No maxima in peak gain vs. concentration curve was obtained in presence of C440 and C460 dye solutions while a clear peak at small concentration $1 \times 10^{-4}$ M/L was observed in presence of C480 dye. From these results, we can conclude that most of the pump power absorbed by C480 dye is transferred to Rh590(Cl) dye as a useful pump power. This different behavior of C480 dye in this group is attributed to its molecular structure \([3,5,7,8,9]\) which is rigidized at 6th and 8th position of coumarin ring. In rigid coumarin structure, there is no possibility of amino group rotation at ring position 6 and 8 to form TICT excited states and gain region is shifted to longer wavelength side resulting in good overlap of fluorescence spectrum of C480 dye solution and absorption spectrum of Rh590(Cl) dye. Slightly better performance of Rh590(Cl) dye in presence of C460 donor dye solution as compared to the case of C440 donor dye solution, can be attributed to N\((C_2H_5)_2\) substitution at 7th position of C460 dye while there is NH\(_2\) group in C440 dye. The effect of these groups was explained in our previous report \([7]\).

\(\text{(ii) Fluorinated group of dyes:}\)

The laser performance of Rh590(Cl) dye at $1 \times 10^{-3}$ M/L, in absence and presence of various fluorinated coumarin dyes C485, C500 and C540A at concentrations ranging from $1 \times 10^{-5}$ to $1 \times 10^{-2}$ M/L was investigated. The dependence of peak gain on the concentration of various coumarin dyes and their structure is shown in Fig.4 and Fig.5. The percentage increase in peak gain value of Rh590(Cl) and optimum concentration for each donor dye is represented in Table-I. However, unlike the non-fluorinated dyes, enhanced laser gain of Rh590(Cl) dye in the presence of fluorinated coumarin dyes at all concentrations is quite prominent. Maximum increase in laser gain value of Rh590(Cl) in this work was 150 % using C540A as donor dye at concentration $5 \times 10^{-3}$ M/L. As the observed optimum concentration for this dye is very small, the concentration quenching effects are negligible resulting in large gain value for this dye. Again as the fluorescence region of C540A dye in ethanol \([4]\) completely overlaps with the absorption region of Rh590(Cl) dye[11], large enhancement of optical gain from Rh590(Cl) dye is observed due to almost complete energy transfer from donor to acceptor dye. No optical gain is observed in fluorescence region of all fluorinated coumarin dyes except for the C500 donor dye where a small peak is also observed in the lower wavelength region for some concentrations other than optimum concentration.

The red shift of gain spectra and high gain value with C540A as donor dye are due to its rigidized structure at 6th and 8th position of coumarin ring, just
Figure 6: Variation of peak wavelength of different dye mixtures with concentration.

Figure 7: Variation of peak wavelength of different dye mixtures with concentration.
like C480 dye in non-fluorinated group. The percentage increase in peak gain is small in case of C500 donor dye as compared to C485. This can be attributed to the NH(C_{2}H_{5}) group at 7th position of C500 than N(CH_{3})_{2} group of C485. Gain spectra of these dyes also show similar results [7].

Comparing the structures of rigid dyes from both the groups i.e. C480 and C540A, there is only difference of CF_{3} group at 4th position of C540A dye which results in high peak gain value and large shift in fluorescence region of this dye. This CF_{3} group is an electron withdrawing group which increases the electron acceptor capabilities of the coumarin ring and stabilizes the charge transfer states in polar solvents.

Variation in the peak wavelength of Rh590(Cl) at 1 x 10^{-3} M/L with donor concentration is shown in Fig.6 and Fig.7. It is observed that a donor sensitized system is found to have a high gain value as compared to unsensitized system, because of an increase in effective lifetime of the acceptor dye [15]. Highest value of peak gain is observed at optimum concentration of the donor dyes which, in fact, depends on the molecular structure of the dyes. The effect of replacement of CH_{3} group at 4th position of donor coumarin dyes by CF_{3} group can be understood by comparing the maximum value for peak gain of Rh590(Cl) in presence of C480 and C540A dyes (Fig.4 and Fig.5). It has large value with C540A dye, but the optimum concentration for both the dyes is very low compared to all other coumarin dyes due to their rigidized structure.

It is observed that lasing wavelength of Rh590(Cl) is shifted towards shorter wavelength side in the presence of all coumarin dyes studied. This blue shift can be attributed to the reduction in dye aggregation in the acceptor molecule due to formation of new donor acceptor dimers as the donor was added [10]. Concentration of donor dye has little effect on the variation of peak wavelength value for a given coumarin dye. Optimum concentration is studied in each case because too high a coumarin concentration leads to more light scattering and optical loss [15].

**CONCLUSION**

The effect of Coumarin dyes and their concentrations on laser gain properties and photostabilities of Rh590(Cl) dye is studied. The optimum concentration of donor dye and ideal molar ratio is found to be different for different dye pairs. In case of most stable dye C-540A as donor dye for Rh590(Cl) acceptor dye, this concentration is found to be minimum and ideal molar ratios least. Again the percentage increase in gain and peak wavelength shift is maximum with this fluorinated dye. The experimental results indicate that the dominant
mechanism responsible for the efficient excitation transfer in these mixtures is of non-radiative nature due to long range dipole-dipole interaction.

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