ENERGY TRANSFER RATES IN A 7-DIETHYLAMINO-4-METHYLCOUMARIN–RHODAMINE 6G BINARY DYE MIXTURE LASER

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Summary

In this paper an attempt is made to calculate the radiative and non-radiative Förster-type energy transfer rates in a binary dye mixture laser. The dyes used were 7-diethylamino-4-methylcoumarin (DAMC) and rhodamine 6G (R6G) and the solvent employed was 2-methoxyethanol. The Förster transfer rate was found to be almost five times as large as the radiative transfer rate in this DAMC–R6G dye laser system.

1. Introduction

Laser dyes generally have broad and intense absorption bands. However, some dyes display only weak absorption. Thus, in these dyes considerable portions of broad spectral band pump radiation such as that from a flash lamp are not well absorbed, leading to poor laser efficiency. Increasing the dye concentrations to increase absorption has its practical limits, since at high concentrations, concentration quenching will reduce quantum fluorescence yields, which in turn give reduced laser efficiency.

To improve the efficiency of dye lasers, Peterson and Snavely [1] proposed the use of acceptor–donor dye mixtures as a simple method of achieving more efficient conversion of a fixed pump radiation into dye laser radiation. The donor dye has its lowest energy absorption band located at shorter wavelengths than the dye which acts as the acceptor and the fluorescence spectrum of the donor dye must overlap the absorption band of the acceptor dye.

Energy transfer dye lasers have been studied previously by various researchers [2 - 5] by monitoring the laser intensities. The laser intensities are dependent on the laser medium, the optical resonator and the detector characteristics. The gain, however, is a parameter intrinsic to the laser medium and unmodified by the resonator or the detector. Hence the gain is of greater value in assessing energy transfer in a dye mixture laser. In this

paper we have made a detailed study of gain as a function of pump power, for different donor–acceptor concentrations, for a 7-diethylamino-4-methyl-coumarin (DAMC) (donor) and rhodamine 6G (R6G) (acceptor) dye mixture laser, pumped with a nitrogen laser working at 337.1 nm. Rate equations for the dye mixture laser were set up and solved numerically to determine the variation in gain at various wavelengths for different donor–acceptor concentration ratios and as a function of pump power. The gain was also measured experimentally, and the theoretical and experimental results were compared.

2. Experimental details

The dyes DAMC and R6G were both of laser grade supplied by SERVA International, Heidelberg. The solvent used was spectroscopic grade 2-methoxyethanol. This solvent was chosen because of its low evaporation rate. The experimental set-up used to measure gain has been described previously [6]. The pump source was a pulsed nitrogen laser built by us, radiating at 337.1 nm and operated at a repetition rate of 1 pulse s^{-1}, with a pulse duration of 10 ns. The dye solution was placed in a quartz cuvette which was kept canted to avoid optical feedback. The dye solution was pumped with a focused line image of the nitrogen laser radiation, which was produced by a cylindrical lens of focal length 4 cm. The length of the pumped region of the dye solution could be varied from 0 to 12 mm by using a beam-block mounted on a micrometer. The pumped region of the dye had a uniform intensity of pumping. Care was taken to see that there was no unpumped region of the dye at the monitored end of the cuvette thus preventing reabsorption of the emitted light.

To determine the gain at any wavelength λ, the amplified spontaneous emission intensities $I_1(\lambda)$ and $I_2(\lambda)$ for active lengths l_1 and l_2 respectively of the pumped region of the dye solutions were measured using a mono-chromator (CEL 3134), photomultiplier (RCA 931A) and oscilloscope (ECIL-05-768A). The active lengths of the dye solution used were in the range 6 - 12 mm, always ensuring that the gain was unsaturated. The gain is computed using the equation

$$\frac{I_1(\lambda)}{I_2(\lambda)} = \frac{\exp\{G(\lambda)l_1\} - 1}{\exp\{G(\lambda)l_2\} - 1}$$

where $G(\lambda)$ is the gain at wavelength λ. The absorption and fluorescence spectra of R6G and DAMC were determined using a UVIKON 810/820 UV–visible absorption spectrophotometer and an Aminco–Bowman spectro-fluorimeter respectively. The quantum yields of R6G and DAMC were also determined by us using standard methods [7].

3. Theory

An energy transfer dye laser consists of a binary mixture of two dyes in solution in which energy absorbed by one dye, known as the donor dye,

is transferred to the other dye, known as the acceptor dye, thereby increasing the laser efficiency of·the acceptor dye.

Förster [8] classified energy transfer from donor to acceptor molecules as (a) radiative transfer (reabsorption), (b) non-radiative dipole–dipole transfer, also called Förster-type transfer, (c) collisional transfer and (d) molecular complexing. Radiative and non-radiative transfer can occur when the emission spectrum of the donor overlaps the absorption spectrum of the acceptor. In radiative transfer, the acceptor dye reabsorbs photons emitted by the donor and radiative transfer can be increased by using larger volumes of the mixture solution. The Förster-type transfer decreases the fluorescence lifetime of the donor dye.

Collisional transfer is dependent on the viscosity of the solvent and is significant only for molecular separations of the order of the contact distances. The concentrations of the donor and acceptor were quite low, less than 5×10^{-3} M, and hence collisional transfer of energy can be neglected.

Complexing changes the spectra of the donor and acceptor. No such spectral changes were observed in the DAMC–R6G mixtures studied here at the concentrations used in our experiments.

Time–rate equations can be set up for the populations as described in ref. 9 and the gain per acceptor molecule is obtained as

$$g(\lambda) = \left\{ \sigma_{\mathrm{SEA}}(\lambda) \frac{\gamma_A}{\gamma_D} + (k_F + k_R)\sigma_{\mathrm{SEA}}(\lambda) \frac{F_D}{1 - F_D} \frac{N_A}{k_F N_A + k_D} \right\} \gamma_D - \sigma_{\mathrm{SAA}}(\lambda)$$

Here $\sigma_{\mathrm{SEA}}(\lambda)$ and $\sigma_{\mathrm{SAA}}(\lambda)$ are the singlet stimulated emission and absorption cross-sections respectively of the acceptor at the wavelength λ, and $\gamma_j = \sigma_j{}^L P(t)\tau_A$ where $\sigma_j{}^L$ is the absorption cross-section at the pump wavelength λ_P, $P(t)$ is the pumping rate (photons cm^{-2} s^{-1}) and τ_A is the decay time of the acceptor singlet state. F_D is the fractional donor population $N_D/(N_A + N_D)$ where N_D and N_A is the population per cubic centimetre of the donor and acceptor respectively. k_F and k_R are the Förster and radiative transfer rates respectively, and k_D is the reciprocal of the donor lifetime τ_D.

The gain of the acceptor molecule is thus increased by

$$(k_F + k_R)\sigma_{\mathrm{SEA}}(\lambda) \left(\frac{F_D}{1 - F_D} \right) \left(\frac{\gamma_D N_A}{k_F N_A + k_D} \right)$$

owing to energy transfer from the donor.

The Förster transfer rate [8] is given by $k_F = 1/\tau_D c_{1/2}$ where τ_D is the lifetime of the donor molecule in its first excited singlet state, and $c_{1/2}$ is the half-quenching concentration given by $c_{1/2} = 0.4908 c_0$. The critical concentration c_0 can be calculated as given by Förster [8] from the absorption spectra of the acceptor, the fluorescence spectra of the donor and the quantum yield of the donor. The stimulated emission cross-section $\sigma_{\mathrm{SEA}}(\lambda)$ of the acceptor is given by (see ref. 9) $\lambda^4 E(\lambda)/8\pi cn\tau_A$, where $E(\lambda)$ is the fluorescence line shape function normalized so that $\int E(\lambda)\mathrm{d}\lambda$ is equal to the quantum yield ϕ, and n is the refractive index of the dye solution.

4. Results and discussion

4.1. Gain spectra

The DAMC donor concentration was kept fixed at 5×10^{-3} mol l^{-1} and the gain spectra delineated (a) without any acceptor, (b) using 2.8×10^{-4} mol l^{-1} of R6G as acceptor and (c) using 7.5×10^{-4} mol l^{-1} of R6G as acceptor. These gain spectra are displayed in Fig. 1. Curves (B) and (C) show that the dye mixture exhibits gain simultaneously over two different wavelength regions and the process of energy transfer reduces the gain on the 460 nm band and increases the gain on the 550 nm band in the dye mixture.
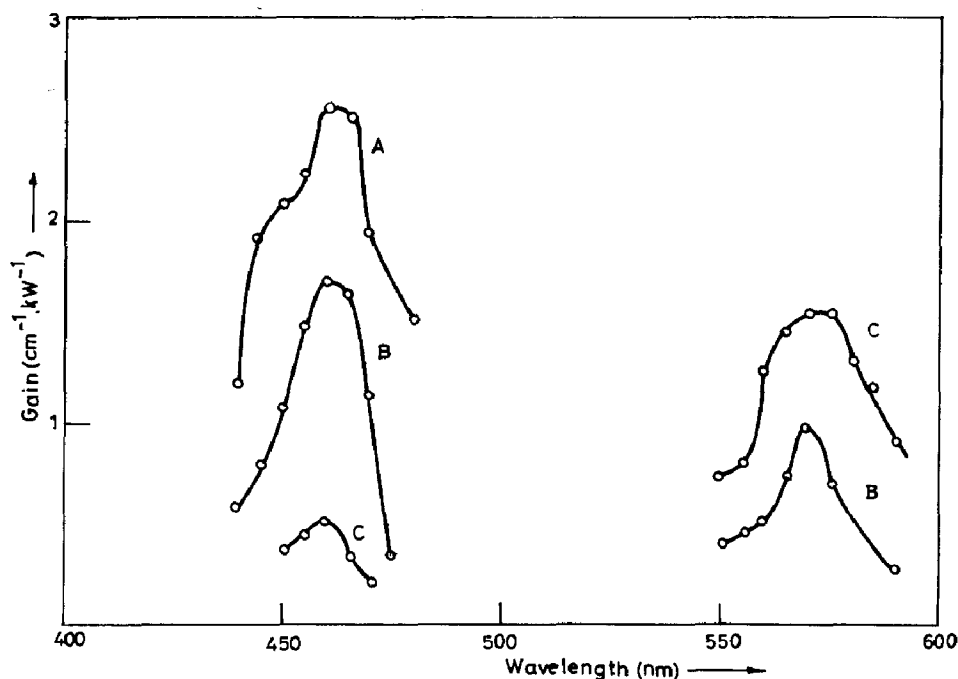

Fig. 1. Gain spectra for a DAMC–R6G dye mixture laser at various R6G concentrations (pump power, 6.5 kW; [DAMC] = 5×10^{-3} M): curve A, 0.0 M; curves B, 2.8×10^{-4} M; curves C, 7.5×10^{-4} M.

4.2. Variation in gain with pump power

Figure 2 shows the variation in the gain of the acceptor molecule with pump power at 575 nm for various concentrations of the acceptor and donor, keeping the ratio $F_D/F_A = N_D/N_A$ fixed at 2.0. At this wavelength of 575 nm, donor emission is negligible. The slopes of these plots of gain vs. pump power give the gain per acceptor molecule per unit pump power for the dye mixtures at λ = 575 nm. In order to calculate the gain enhancement per acceptor molecule per unit pump power resulting from energy transfer processes alone, the slopes of the gain plots for the acceptor dye at 575 nm resulting from its direct pumping with the pump laser at 337.1 nm have to be subtracted from the above values of the slopes of the gain plots for the
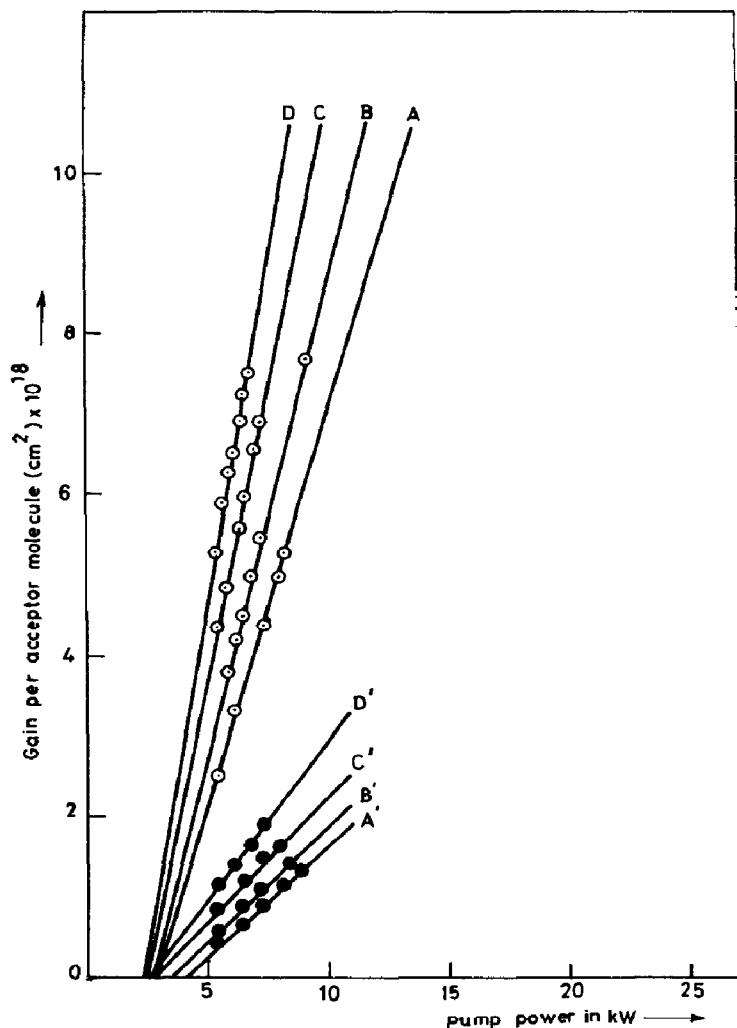
Fig. 2. Variation in acceptor gain with pump power at various concentrations of donor and acceptor (λ = 575 nm): curve A, $N_D = 1 \times 10^{-3}$ M, $N_A = 0.5 \times 10^{-3}$ M; curve B, $N_D = 1.5 \times 10^{-3}$ M, $N_A = 0.75 \times 10^{-3}$ M; curve C, $N_D = 2 \times 10^{-3}$ M, $N_A = 1 \times 10^{-3}$ M; curve D, $N_D = 3 \times 10^{-3}$ M, $N_A = 1.5 \times 10^{-3}$ M; curve A', $N_D = 0$, $N_A = 0.5 \times 10^{-3}$ M; curve B', $N_D = 0$, $N_A = 0.75 \times 10^{-3}$ M; curve C', $N_D = 0$, $N_A = 1.0 \times 10^{-3}$ M; curve D', $N_D = 0$, $N_A = 1.5 \times 10^{-3}$ M.

dye mixtures. Figure 2 also shows the gain vs. power curves measured at 575 nm, for the acceptor molecule R6G alone without any donor, using the same concentration of R6G as used in the DAMC–R6G dye mixture study. The slopes of these graphs give the gain per molecule per unit pump power for the acceptor (R6G) alone. The reason for the slight increase in slope with increasing concentration is the overlap of the absorption and emission spectra for R6G. This overlap causes reabsorption of the photons emitted at short wavelength in the overlap region and re-emission at longer wavelengths. This effect increases with the concentration of R6G, for the concentrations used here, at which concentration quenching is negligible.

TABLE 1

Experimental and computed variation in gain per acceptor molecule per kilowatt at 575 nm with acceptor concentration

Concentration N_A (M)	Measured slope for mixture ($\times 10^{-19}$ cm² kW⁻¹)	Measured slope for acceptor alone ($\times 10^{-19}$ cm² kW⁻¹)	Corrected slope[a]	Corrected slope[b]	Relative value of $N_A/(k_F N_A + k_D)$[c]	Ratio of corrected slope to $N_A/(k_F N_A + k_D)$ ($\times 10^{-8}$)[d]
0.5×10^{-3}	9.44	2.71	6.73	43.9	44.9	46.74
0.75×10^{-3}	12.08	2.77	9.31	60.8	62.0	46.78
1.0×10^{-3}	14.44	2.92	11.52	75.2	76.6	46.83
1.5×10^{-3}	18.47	3.15	15.32	100.0	100.0	47.73

[a](Column 2 − column 3) $\times 10^{19}$ cm² kW⁻¹.
[b]Corrected slope as percentage of slope for $N_A = 1.5 \times 10^{-3}$ M.
[c]100% for $N_A = 1.5 \times 10^{-3}$ M.
[d]Mean value, 47.02×10^{-8}.

Table 1 gives the slopes of the gain plots of the dye mixture and the acceptor molecules alone and the corrected slopes of the gain plots as a function of the acceptor concentration using the graphs of Figs. 1 and 2. Column 5 of this table gives the relative variation in this experimentally determined corrected slope of the enhancement of gain of the acceptor owing to energy transfer as a percentage of the slope for $N_A = 1.5 \times 10^{-3}$ M. Column 6 gives the relative variation in $N_A/(k_F N_A + k_D)$ as a percentage of that for $N_A = 1.5 \times 10^{-3}$ M.

Column 7 gives the ratio of the corrected slope to $N_A/(k_F N_A + k_D)$ which theoretically represents $\sigma_{SEA}\{F_D/(1 - F_D)\}\gamma_D(k_F + k_R)$. The average value of this is 47.02×10^{-8}. k_F and k_D have been computed from our spectral data and are displayed in Table 2.

TABLE 2

Calculated spectral parameters for DAMC (donor) and R6G (acceptor)

Donor lifetime DAMC	$\tau_D = 3.5$ ns
Acceptor lifetime R6G	$\tau_A = 4.5$ ns
Critical transfer radius	$R_0 = 43.5$ Å
Critical concentration	$c_0 = 4.82 \times 10^{-3}$ M
Half-quenching concentration	$c_{1/2} = 2.37 \times 10^{-3}$ M
Förster-type transfer rate	$k_F = 1.21 \times 10^{11}$ l mol^{-1} s^{-1}
Absorption cross-section at 337 nm for the acceptor dye R6G	$\sigma_A{}^L = 2.28 \times 10^{-17}$ cm^2
Absorption cross-section at 337 nm for the donor dye DAMC	$\sigma_D{}^L = 4.38 \times 10^{-17}$ cm^2
Pump rate $P(t)$ per kilowatt	5.65×10^{22} photons cm^{-2} s^{-1}
Emission cross-section for R6G	$\sigma_{SEA}(575) = 1.45 \times 10^{-16}$ cm^{-2}

Substituting for $\sigma_{SEA}(575)$, F_D, γ_D, k_F and k_D enables k_R to be calculated. For the DAMC–R6G binary dye mixture laser k_R works out to be 2.52×10^{10} l mol^{-1} s^{-1} which is one fifth of the Förster rate of energy transfer.

5. Conclusion

The radiative transfer rate in a dye mixture laser can be determined by experimentally measuring the gain of the laser. In the DAMC–R6G system studied here the Förster transfer rate is five times greater than the radiative transfer rate.

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