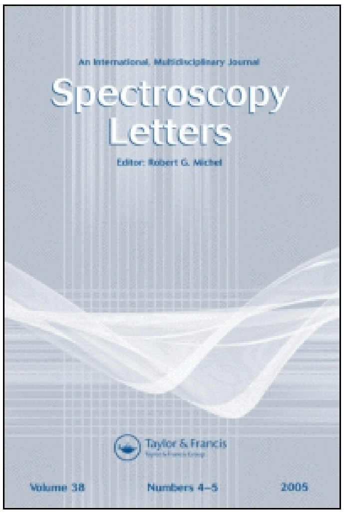

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FLUORESCENCE AND LASER EMISSION FROM COUMARIN-ACRIDINE ORANGE MIXTURES

Keywords: Sensitized fluorescence, lifetimes, energy transfer rates, penetration depth

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ABSTRACT

The sensitized fluorescence and laser emissions of dye mixtures; (I) coumarin 102 (donor) and acridine orange (acceptor) and (II) coumarin 47 (donor) and acridine orange (acceptor) with Hg-lamp and N_2 laser, have been measured as a function of dye concentration and of the pump power (N_2 laser). Acridine orange which does not lase by itself on excitation with N_2 laser, lases efficiently in the presence of 7-amino-coumarins via singlet-singlet energy transfer . Energy transfer rate constants and critical distances have been estimated from fluorescence intensity and lifetime measurements.

The performance of energy transfer dye lasers (ETDLs) are discussed in terms of spectral characteristics of the dyes and their penetration depths.

INTRODUCTION

Acridine orange (AO) is a biologically and medically interesting and active molecule. Its usefulness as a fluorescence probe for diagnostics has been realized. Luminescence studies of this dye, both at room and low temperatureshave been reported(1,2) Dienes and Madden(3) have reported that AO exhibits a peak gain of 1.52 cm^{-1} in the presence of coumarin 47 (C.47) as a sensitizer. We have found efficient laser emission from AO through energy transfer from excited singlet state of coumarin 102 (C.102) and C.47, under N_2 laser excitation. This is of interest because AO does not lase by itself with N_2 laser excitation due to its low quantum yield (Q=0.20(4)) and very low molar extinction coefficient (ε=140 $dm^3 mol^{-1} cm^{-1}$) at 337.1 nm. We present in this paper the results of our measurements on energy transfer in two pairs of dyes: pair I, coumarin 102 (donor, D) - acridine orange (acceptor, A); pair II, coumarin 47 (D) - acridine orange (A). The donors lase efficiently upon N_2 laser pumping because of their high Q values (0.74(5), 0.95(6) for C.102; 0.59(5), 0.79(6) for C.47) and high ε values (0.5×10^4 $dm^3 mol^{-1} cm^{-1}$ for C.102; 0.9×10^4 for C.47). Although the inconsistancies are apparent in

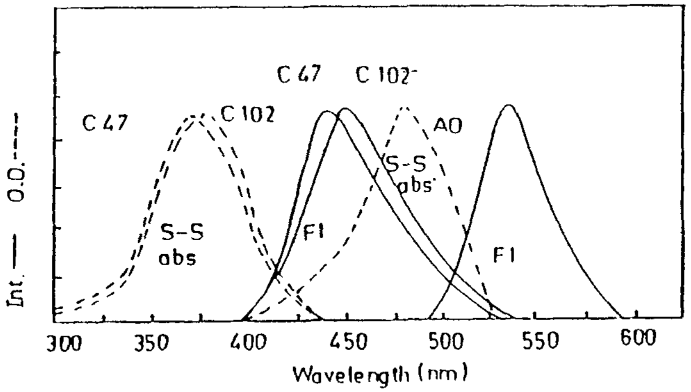

Fig. 1 Absorption and emission spectra of C.102 and C.47

the data on Q of donors: Q of C.102 is higher than that of C.47 in ethanol solutions under the same experimental conditions. The differences in Q and ε values are expected to influence the performance of ETDLs. These two laser dyes serve as good sensitizers for AO to lase, since their emissions overlap adequately with the absorption of AO. Sensitization of organic dyes through energy transfer (ET) process is a highly significant feature of photochemistry in the condensed matter. Possible mechanisms for singlet-singlet energy transfer include radiative transfer, collisional transfer and long range dipole-dipole resonance transfer (Forster type(7)). The relative positions of absorption and emission spectra are illustrated in Fig. 1.

EXPERIMENTAL

Laser grade coumarin dyes (Exciton Chemical Co., USA) and spectral grade acridine orange (West Germany) were used without further purification. The solutions were prepared in spectral grade ethanol (Fluka, West Germany) and contained in a quartz cuvette of path length 1 cm. A 400 kW TEA N_2 laser (EG&G PARC) with a pulse width of 1.2 ns was employed for intensity measurements of ETDLs. The ETDL outputs were detected and measured using a fast photodiode (ITT, risetime <500 ps) and a calibrated oscilloscope (Tektronix). Neutral density filters were employed to vary the optical outputs of the N_2 laser. Appropriate attenuators were used to avoid the saturation effects in the photodiode. Fluorescence emission bands were recorded using Hg source (400 W), a monochromator, a photomultiplier (RCA 931A) and an X-Y recorder (Riken-Denshi, Model F-3DG). The fluorescence lifetimes were measured using a Time Domain Fluorescence Spectrometer (Edinburgh's Model 199) which uses single photon counting technique and appropriate reconvolution method. For the measurement of penetration depths, a home-made TEA N_2 laser (peak power 250 kW; pulsewidth 6 ns) was used.

RESULTS AND DISCUSSION

Fluorescence measurements:

To avoid reabsorption, fluorescence measurements

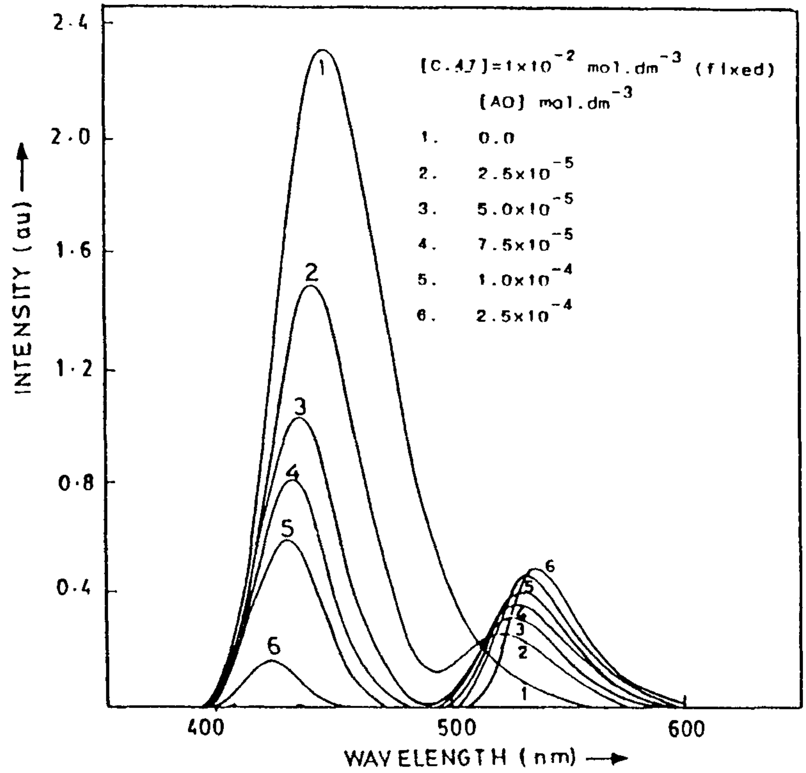

Fig.2 Uncorrected fluorescence spectra of C.47-AO

were made in front surface and corrected for the spectral sensitivity of the apparatus. Integrated intensities of donor emissions were measured for fixed [D] of 5x10^{-3} mol.dm^{-3} (C.102) and 1x10^{-2} mol.dm^{-3} (C.47) and for varying [A] of 2.5x10^{-5} to 2.5x10^{-4} mol.dm^{-3} Also, corrections for radiative transfer and direct absorption of the excitation by the acceptor, were applied to the intensities using the expressions given by Conte and Martinho[18] and the results show that the nett contributions from these two processes is negligibly small. Typical fluorescence spectra of pair I is presented in Fig. 2.

The intensity values obeyed the Stern-Volmer relationship:

$$I_D^0/I_D = 1 + k_{et}\tau_D^0[A] = 1 + K_Q[A] \qquad ...(1)$$

where I_D^0 and I_D are the intensities of donor emission in the absence and presence of acceptor, k_{et} is the energy transfer rate, K_Q is the quenching constant, and τ_D^0 is the lifetime of D in the absence of A. Plots of I_D^0/I_D versus [A] were found to be linear. From the slopes of these plots and using the experimentally determined τ_D values (4.36 ns for C.102; 3.18 ns for C.47), k_{et} values were calculated to be 1.2×10^{11} $mol.dm^3s^{-1}$ for pair I and 1.0×10^{11} $mol.dm^3s^{-1}$ for pair II. The experimental values of critical transfer distance R_0 were determined to be 51 and 50 Å respectively for pairs I and II, using the relation

$$R_0 = 7.35/\ ([A]_{1/2})^{1/3} \text{ in Å} \qquad ...(2)$$

Here, $[A]_{1/2}$ is the half quenching concentration i.e., the concentration of acceptor at which τ_D reduces to $\tau_D^0/2$. The R_0 values were also calculated using the formula given by Forster(8) and these agree with the experimental values. The values of k_{et} and R_0 determined for the two dye mixture systems are given in Table 1.

Table 1.

Rate parameters

Dye pairs	$k_{et} \times 10^{-11}$ mol dm^{3}s^{-1}	R_0 (Å) Cal.	R_0 (Å) Expt.
C 102 - AO	1.20	46.00	51.00
C 47 - AO	1.00	47.00	51.00

Fluorescence lifetimes

Fluorescence decays of donor (C 47), with and without the acceptor were measured and used to determine lifetimes using single photon counting technique. The results show that the lifetime of C 47 drops from 3.18 ns to 2.54 ns when [A] is varied from 1.25×10^{-4} to 1×10^{-3} mol.dm^{-3} for a fixed [D] = 1×10^{-3} mol.dm^{-3}. The data follow Stern-Volmer relation yielding $k_{et} = 0.8 \times 10^{11}$ mol.dm^{3}s^{-1} and R_0 = 47 Å for C.47 - AO pair. In case of C.102 - AO, however, the results were not satisfactory due to the interference of the acceptor emission.

The mean diffusion length 'l_d' in solution also provides information about the dominant energy transfer mechanisms in a mixture. The diffusion length(9) is defined as

$$l_d = [(D_D + D_A)\tau_D^0]^{1/2} \quad \ldots(3)$$

where D_D and D_A are the diffusion co-efficients of the donor and the acceptor which are given by Stokes-Einstein relation

$$D = k_B T/6\pi\eta r \quad \ldots(4)$$

where η is the viscosity of the solvent, r is the radius of diffusing molecule, k_B is the Boltzmann constant and T is the absolute temperature. We found values of l_d = 28.10 and 31.19 Å respectively for pairs I and II. When l_d is smaller than R_0, the probability of collision becomes small and ET by resonance interaction takes place from D to A before their collision(10).

ETDL Characteristics

(1) Effect of concentration

The ETDL outputs and peak wavelengths were measured for a fixed [D] (C.47: 5×10^{-3} mol.dm^{-3}; C.102: 1×10^{-2} mol.dm^{-3}) and varying [A] (5×10^{-3} – 5×10^{-5} mol.dm^{-3}). AO lased in the mixture for the concentration range 5×10^{-3} – 2.5×10^{-4} mol.dm^{-3} with a wide range of 30 nm from 516 to 546 nm. The peak wavelength (λ_L) shifts towards longer wavelengths with increasing [A] (figure 3). However, at the highest concentration no shift is observed in λ_L and the

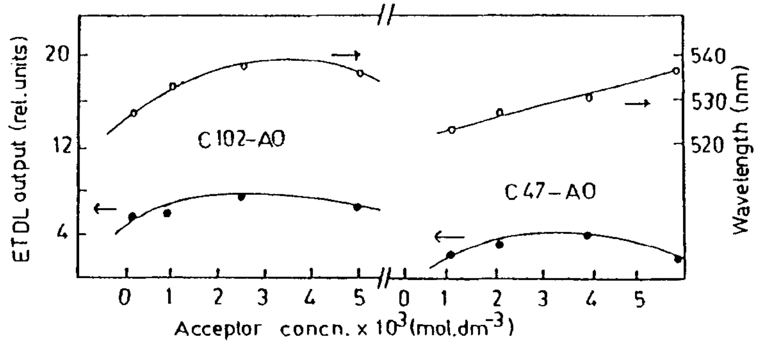

Fig.3 Plots of ETDL output and peak wavelength vs acceptor concentration

tuning range widens with increasing [A].The peak intensity, I_L, passes through a maximum implying complete utilisation of pump radiation and then falls off due to self absorption. The lowest concentration of AO required for lasing in pair I is 2.5 x 10^{-4} mol dm^{3} which is almost four times lower than that needed in pair II.

The measurements were also made for a fixed [A] of 1×10^{-3} mol.dm^{-3} and varying [D] (1×10^{-3} - 1×10^{-4} mol.dm^{-3}). Here, results show that λ_L and tuning range do not change but ETDL output is enhanced. The fact that λ_L does not vary with [D] infers that the acceptor alone lases in ETDL(11).

(2) Effect of pump power

The ETDL outputs at peak wavelength (λ_L) were measured for various pump powers ranging from 47 to 400 kW for a given concentration of donor and

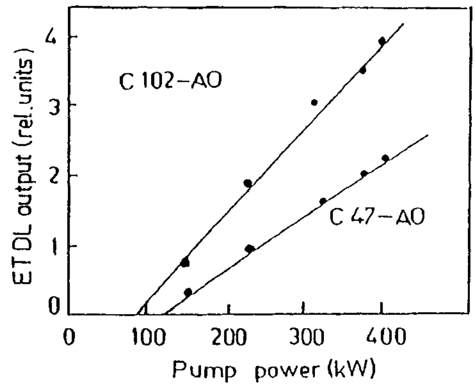

Fig.4 A plot of ETDL output vs pump power

acceptor. As can be seen from figure 4, the peak ETDL outputs do not show saturation tendency, the lasing threshold for AO is lower for C.102 compared to C.47 and conversion efficiency for C.102 - AO is higher than that of C.47 - AO. In our experimental conditions no simultaneous laser emission was observed for any [D]/[A] ratio due perhaps to insufficient pump power.

Penetration depth

Extinction depth, *d*, of the dye solution at the pump wavelength is defined as the distance at which the intensity of the incident light becomes 1/e times the original and helps to estimate the photon density in dye solutions of higher concentrations as the pump light is totally absorbed. This definition coupled with the expression $I = I_0 e^{-\varepsilon C d}$, gives $\varepsilon C d = 1$, where ε is the molar extinction coefficient and C is the concentration and d would then be the extinction depth given by $d = 1/\varepsilon C$. Obviously this is a fixed quantity for a given concentration and indicates that higher concentrations leading to lower extinction depths, lead to higher photon density and better laser output. It may be noted that this concept though useful, does not show any dependence on the intensity of the incident light which should play a significant role. Urisu & Kajiyama[9] have also applied this concept for the determination of average photon density of the pump light $\bar{q}_0(t)$, which is given by

$$\bar{q}_0(t) = \frac{P_0}{c} \; \frac{1-\exp(-1)}{\delta L} \qquad \ldots(5)$$

where P_0 is the input pump power (photons/s), δ is the width of the focussed laser beam, L is the length of the active region and c is the velocity of light. Although this expression does lead to the dependence of the pump power, it is independent of the concentration and extinction depth. This does not relate to the actual situation in any recognizable way. Hence to develop a tangible concept which can be identified with the actual situation, the concept of penetration depth is employed, which is defined experimentally as the distance up to which the pump light absorbed is emitted as superradiant emission in the transverse pumping mode. This concept would define the depth over which the photon density is adequate for stimulated emission to occur. Further, it would depend on the intensity of incident light and can be experimentally measured.

When dye solutions lase under N_2 laser excitation, the cross section of the active region (bright filament) takes a crescent shape. The distance between the front surface of the solution and the tip of the crescent gives the penetration depth which can be measured conveniently using a travelling microscope or by optical method.

To understand the behaviour of penetration depth in relation to extinction depth, an experiment was performed on a single dye (C 47). Penetration depths for this dye in ethanol were measured for various concentrations in the range 2.5×10^{-4} - 1×10^{-2} mol.dm^{-3}. These values when plotted against 1/C lead to a straight line which confirms that the penetration depth is a useful concept and follows the relation $\varepsilon C l$ □ x, where $x = \ln(I_0/I)$. The slope gives $e^{-x} = 0.30$, indicating that 70% of the pump light has been used up in the superradiance. However, if extinction depths are used, $e^{-x} = 0.37$ irrespective of the incident intensity which does not convey the actual state of affairs. Therefore, to calculate photon density penetration depths should preferably be used instead of extinction depths.

Table 2

Penetration depths

Pair	*Penetration depth, mm*			*Extinction depth for mixtures, mm*
	D	*A*	*D–A*	
I	*0.31*	*10.00*	*0.44*	*0.108**
II	*0.24*	*10.00*	*0.34*	*0.102**

* *sum of extinction depths of D at pump frequency and of A at peak of donor emission*

The penetration depths for D (1×10^{-2} mol.dm^{-3}) and A (5×10^{-3} mol.dm^{-3}), and their mixtures at the same concentrations were also measured. These values along with extinction depths are given Table 2. The *7* values for the dye mixtures (Table 2) are nearer to those of donor, thus providing a high density of excited states of acceptors in a small volume needed for superradiance and lasing. This very well explains the effectiveness of high ε for donor which gives low penetration depths and effectively provides a high density of excited state acceptors leading to population inversion. Average photon density of the pump radiation (337.1 nm) was calculated from the pump power in a simple manner. For the N_2 laser, say of 250kW peak power, the number of photons/sec at the peak would be 4.2×10^{23}. This gives 1×10^{15} photons per pulse for a 6 ns pulse. All of these are absorbed in the solution and more than 70% within the penetration depth. Taking a concentration of 5×10^{-3} mol.dm^{-3} (for C.47) and typical (L = 0.8 cm, l = 0.044 cm, w = 0.045 cm) values as experimentally measured, we find that the number of molecules in the active volume are around 4.7×10^{15}. This number is highly sensitive to the values of l and w, in the determination of which significant errors are possible because of filamentisation of the focussed beam and non-uniform distribution of light in the active volume. Inspite of these limitations. it is heartening to see that the number of photons absorbed is of the same order of magnitude as the number of molecules available for excitation in the active volume. Note that for stimulated emission to take occur, there will still be a smaller volume within this volume, which will have higher excitation density, resulting in the population inversion leading to stimulated emission. The combined effect of the ϵ, and Q, of the donor and the acceptor is essentially to achieve this effect and it seems possible only when pump power density is of the same order of magnitude as the number of molecules per cubic cm.

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The inferences drawn from the above studies are:

AO lases efficiently via singlet-singlet excitation transfer dominated by resonance transfer.

Higher ETDL output, wider tuning range, lower pump threshold and concentration threshold for pair I compared to pair II, could be due to higher value of Q of C.102 and stronger overlap of its emission with the absorption of AO. The present ETDLs will be of interest for many applications since the number of compounds lasing in this spectral region is limited.

The concept of penetration depth is a useful parameter which helps to estimate photon density in the acive volume.

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