

Dual ASE from laser dyes with rigidised electron donors

D SASTI KUMAR¹ and V MASILAMANI*²

¹Department of Physics, Regional Engineering College, Tiruchirappalli 620015, India

²Department of Physics, Anna University, Madras 600025, India

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Abstract. The laser dyes coumarin 102 (C 102) and LD 473 exhibit dual amplified spontaneous emission (ASE) in inert solvents like benzene under nitrogen laser pumping. The results indicate that the twisting of the electron donor group of the dye molecule, as envisaged earlier, is not an essential prerequisite for the presence of dual ASE. Specific solute–solvent interactions such as H-bonding or exciplex also may not be very important.

Keywords. Coumarin 102; LD 473; fluorescence spectra; dual ASE; solute–solvent interactions.

1. Introduction

Alkylaminocoumarin laser dyes such as coumarin 1 (C1) and coumarin 2 (C2) exhibit dual ASE bands though the fluorescence spectra contain only one maximum (Masilamani *et al* 1986, 1987). Since the electron donor–acceptor property of these dyes is similar to dimethylamino benzonitrile (DMABN) (Grabowski *et al* 1979), which is well-known for its dual fluorescence phenomenon, the dual ASE was attributed to two conformations of the coumarin dye in the excited state. In one conformation, the amino group of the molecule is in plane with the molecular skeleton, and in the other, the amino group is twisted by 90° with respect to the skeleton. The non-planar conformation is stabilised by complexation with the solvent molecule containing a functional group. In continuation of the study (i.e. effects of molecular structure and solvents on dual ASE), we found some structurally similar laser dyes, but with rigidised amino groups, such as coumarin 102 (C 102) and LD 473 which exhibit dual ASE similar to C1 and C2. These results are presented here.

2. Experimental

A nitrogen laser (100 kW and 10 ns) was used as an excitation source and the dye solution was pumped in a transverse configuration. The wavelength maximum of the ASE band was measured using a constant deviation spectrometer which was calibrated with Hg spectrum as reference. The intensity of the ASE band was measured with photomultiplier–oscilloscope combination.

The dyes C 102 and LD 473 (see figure 1) were purchased from the Exciton Chemical Co., USA. The TLC test did not show the presence of any impurity. The dyes were used

*For correspondence

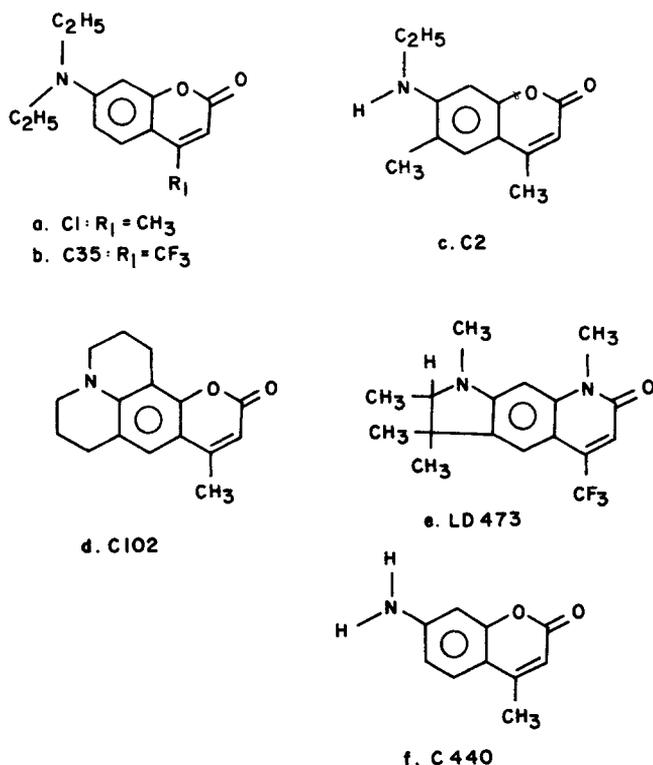


Figure 1. Molecular structures of different laser dyes.

as received. Solvents used were of spectroscopic grade. Absorption and fluorescence spectra were obtained using a Hitachi U2000 spectrophotometer and a Kontron 25 spectrofluorimeter respectively.

3. Results and discussion

LD 473 exhibits dual ASE in benzene, toluene and trichloroethylene. In toluene, ASE bands appear around 438 and 468 nm. The fluorescence maximum appears around 436 nm (figure 2).

The effect of concentration on the relative intensity of two ASE bands of LD 473 in trichloroethylene is shown in figure 3. This shows that the intensity of the longer wavelength ASE band (I_a) increases with increase in the concentration of dye. This is very similar to the behaviour of the longer wavelength ASE of C1. Change in temperature of the solution has only marginal influence on dual ASE (figure 4).

In benzene, C 102 shows only one ASE band which is considerably red-shifted from the fluorescence band maximum (figure 5). In this solvent, the ASE appears around 448 nm and the fluorescence maximum around 428 nm. However, when the temperature of the benzene dye solution is increased to 310 K, a new ASE band starts appearing around 430 nm, i.e. corresponding to the fluorescence band maximum. As the temperature is further increased, the intensity of the shorter wavelength ASE (I_b) increases and

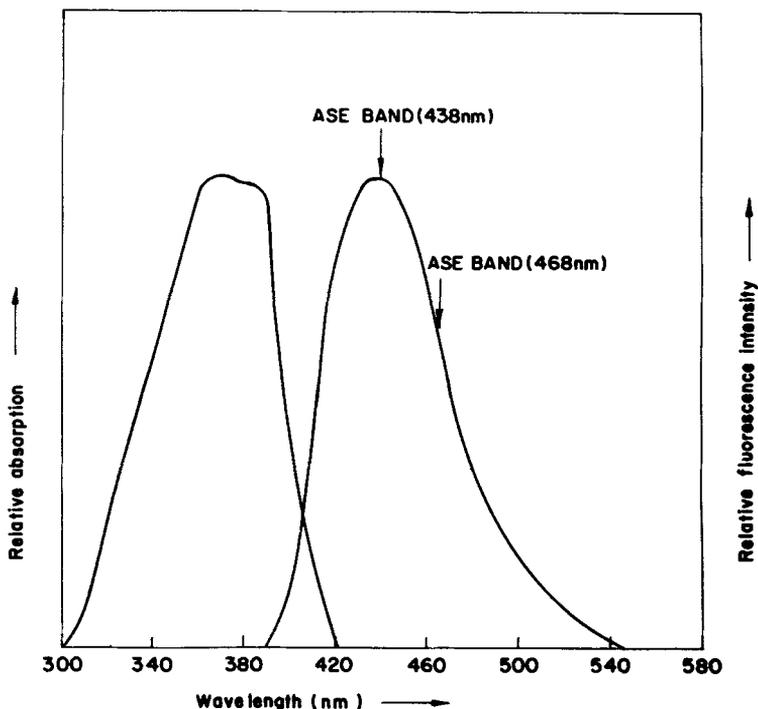


Figure 2. Absorption and fluorescence spectra of LD 473 in toluene at 8 mM concentration.

that of the longer wavelength ASE (I_a) decreases (figure 4). The dye C1 also exhibits similar temperature-dependence for the two ASE bands (figure 4).

The above results in benzene dye solution show that the species emitting the shorter wavelength and longer wavelength ASE's are in dynamic equilibrium at a temperature of about 310 K.

In cyclohexane/acetone (5% v/v) solvent mixture, C 102 exhibits dual ASE. One appears around 420 nm and the other around 455 nm. The intensity of the longer wavelength ASE (455 nm) increases with increase in acetone concentration. The fluorescence peak however is observed only at 417 nm which corresponds to shorter wavelength ASE (figure 5).

Thus, the dual ASE phenomenon observed for LD 473 and C 102 is similar to that of C1. In C1 dye molecule, intramolecular charge transfer occurs in the excited state (Loboda *et al* 1984; Guo and Feng 1987). The amino group acts as an electron donor and the coumarin moiety acts as the electron acceptor. Since in C1 the amino group may undergo rotation with respect to the plane of the molecule, it was proposed that C1 molecules could exist in two conformations in the excited state. In one conformation, the diethylamino group is in plane with the molecular skeleton. The shorter wavelength ASE band was attributed to the emission from these species. In another, the amino group is twisted perpendicular to the molecular skeleton and the longer wavelength ASE was attributed to the emission from these species (Masilamani *et al* 1986).

The molecular structure of C 102 is similar to C1 with the alkylamino group rigidised with respect to the molecular skeleton as shown in figure 1. The molecular structure of

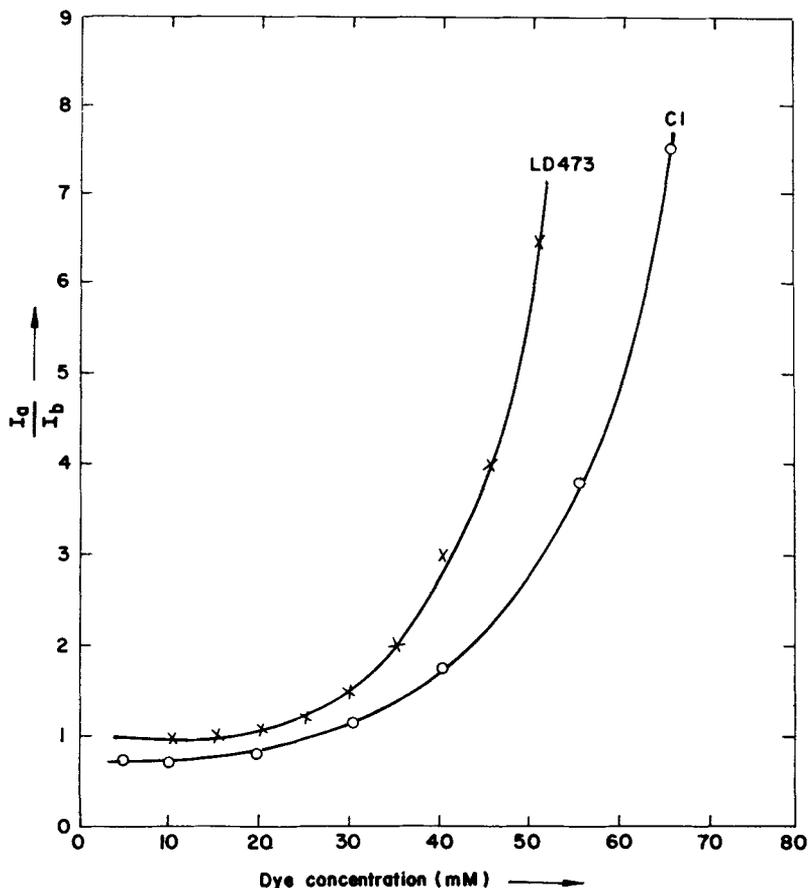


Figure 3. Effect of dye concentration on I_a/I_b . C1 in isobutylmethylketone and LD 473 in trichloroethylene.

LD 473 is also similar to C1 with the ester oxygen replacing the N-CH₃ group. LD 473 has a trifluoromethyl group at the fourth position which increases the electron-acceptor property of the molecule (Gho and Feng 1987). In LD 473 also the alkylamino group is rigidised. Since the electron donor group is rigidised in C 102 and LD 473, a twisted conformation as proposed for C1 cannot exist. However, the appearance of longer wavelength ASE for these dyes suggests that the twisting of the amino group, which is possible for C1, is not necessary for the presence of the longer wavelength ASE band.

Since C 102 and LD 473 exhibit longer wavelength ASE (or dual ASE) even in benzene, H-bonding as in solvents containing hydrogen (Korol'kova *et al* 1987; Yip and Wen 1990, 1991) or exciplex formation (Masilamani *et al* 1986, 1987) (as observed for C1) are not necessary for manifestation of dual ASE. In C 102, rigidisation allows better flow of electrons from the amino group to the coumarin moiety in the excited state, which makes C 102 more polar than C1 (Reynolds and Drexhage 1975). The appearance of dual ASE for C 102 in benzene indicates that the polarity of the dye molecule considerably influences the dual ASE characteristics.

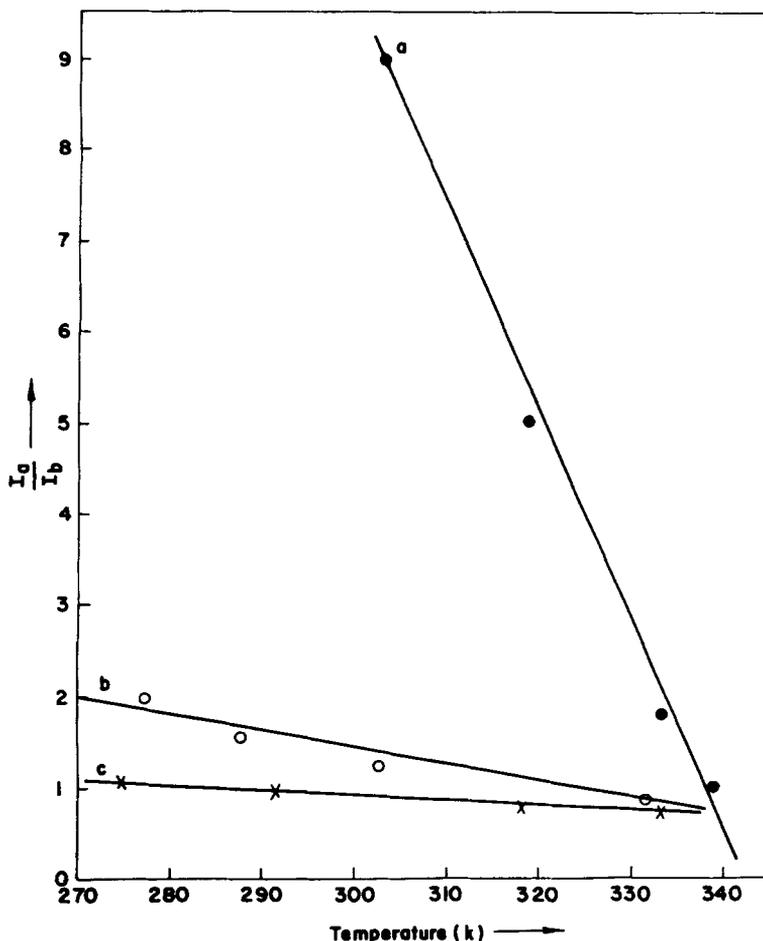


Figure 4. Plot of I_a/I_b as a function of temperature, (a) C 102 in benzene, (b) C1 in isobutylmethylketone and (c) LD 473 in toluene

The dyes C 102 and LD 473 exhibit only one ASE band in polar solvents (alcohols or amides) corresponding to the fluorescence maximum.

Several laser dyes such as coumarin 1 (Masilamani *et al* 1986), coumarin 2 (Masilamani *et al* 1987), coumarin 35 (Sasti Kumar and Masilamani 1995), coumarin 440 (Ramalingam *et al* 1989), coumarin 102 and LD 473 exhibit dual ASE. The general dual ASE characteristics of these dyes are as below.

(a) Species emitting the longer wavelength ASE are not observed under steady-state fluorescence measurements but are observed only under optical gain conditions. This means that the presence of a large number of excited dye molecules is a prerequisite for dual ASE.

(b) All these dyes have a large Stokes's shift; this means that they become considerably more polar in the excited state than in the ground state. This is due to charge transfer from a strong electron donor moiety (alkyl amino group) to a strong electron acceptor moiety (coumarin).

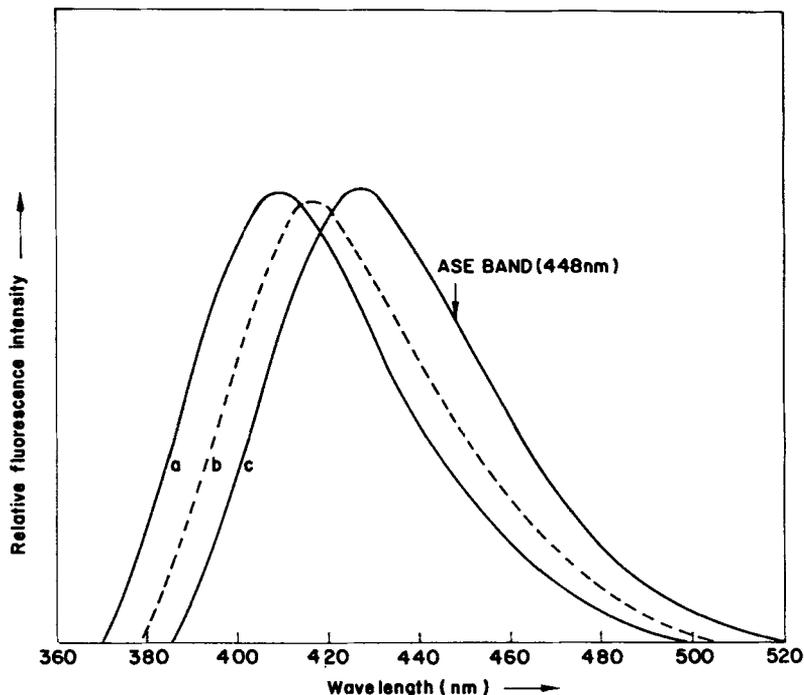


Figure 5. Fluorescence spectra of C 102 at 8 mM concentration in (a) cyclohexane, (b) cyclohexane + acetone (5% v/v) and (c) benzene.

(c) Intensity of the longer wavelength ASE increases with increase in the concentration of the dye.

(d) Intensity of longer wavelength ASE decreases with increase in the temperature of the dye solution.

The above characteristics can very well be explained if we assume that the longer wavelength ASE is due to a new molecular species formed by two excited dye molecules. We may call it a “super-exciplex”. The formation of this super-exciplex may be explained as follows:

On absorbing photons from a pulsed laser, the dye molecules get excited. From the Franck–Condon state, they go to the thermally relaxed polar excited state. When a large number of excited dye molecules exist in a crowd, they polarise the intervening

Table 1. Fluorescence (Flu) and ASE maxima of LD 473 in different solvents. Concentration 8 mM; wavelength in nm

Solvents	Flu	ASE
Benzene	437	438, 467
Toluene	436	438, 468
Trichloroethylene	434	435, 468

Table 2. Fluorescence (Flu) and ASE maxima of C 102 in different solvents. Concentration 8 mM; wavelength in nm

Solvents	Flu	ASE
Benzene	428	448
Toluene	427	448
Cyclohexane	410	—
Cyclohexane + acetone (5% v/v)	417	420, 455
Cyclohexane + dioxane (20% v/v)	421	422, 452
Cyclohexane + xylene (50% v/v)	425	425, 450

medium. The solvent, with or without a functional group, can form a loose bond interlinking two polar excited dye molecules.

When the excited dye molecules are not highly polar (e.g. C1 and C2), they require solvents which contain the functional groups for the formation of the super-excimer. The dyes C1 and C2 become sufficiently polar in the excited state due to the rotation of the amino group which gives rise to large charge-separation (i.e. TICT states). For some dye molecules, e.g. C 102 and LD 473 which are highly polar, even nonpolar solvents are sufficient for super-excimer formation.

Such a super-excimer is an entirely new molecular species, different from the excimer or excimer, which is a combination of one excited and one ground state molecule. More detailed study is needed to characterise the species exhibiting longer wavelength ASE and we are working on this.

4. Conclusion

The observation of dual ASE from laser dyes with rigidised electron donor groups suggests that twisting of the electron donor groups of the dye is not necessary for the formation of dual ASE. The results show that the presence of dual ASE in any type of solvent is dependent upon the polarity of the excited dye molecule.

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