

## Influence of solvents on amplified spontaneous emission characteristics of 7-diethylamino-4-methylcoumarin

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**Abstract.** 7-Diethylamino-4-methylcoumarin (coumarin 1) exhibits two amplified spontaneous emission (ASE) bands in certain solvents under pulsed laser excitation though there is only one maximum in the fluorescence spectrum. In some solvents, it exhibits only one ASE band corresponding to the fluorescence maximum, while in other solvents, the ASE band is largely red-shifted from this maximum. These laser characteristics were studied in various solvents and also in binary solvent mixtures. The study shows that the above characteristics of coumarin 1 are due to the formation of a new type of emitting species under pulsed laser excitation and that this depends upon the properties of the solvent.

**Keywords.** Coumarin 1; fluorescence; dual ASE; solvent effects.

### 1. Introduction

Lasing wavelengths of dyes in a given solvent depend upon their photophysical properties, which can generally be inferred from their fluorescence characteristics. Fluorescence studies are usually carried out using a spectrofluorimeter. Recently, several 7-aminocoumarin laser dyes, e.g. coumarin 1 (Krashakov *et al* 1984; Masilamani *et al* 1986; Korol'kova *et al* 1987; Yip and Wen 1991), coumarin 2 (Masilamani *et al* 1987), coumarin 440 (Ramalingam *et al* 1989), coumarin 485 (Mohan *et al* 1991), coumarin 35 (Sastikumar and Masilamani 1995) and coumarin 102 (Sastikumar and Masilamani 1995), have been found to exhibit two ASE bands in certain solvents under pulsed laser excitation. The important feature is that they exhibit only one fluorescence maximum which corresponds to the shorter wavelength ASE band. Normally, one ASE band would be observed corresponding to the fluorescence maximum. The photophysical properties of several 7-aminocoumarin laser dyes have been studied in various solvents under spectrofluorimeter measurements (Loboda *et al* 1984, 1989; Jones *et al* 1985; Rettig and Klock 1985; Guo and Feng 1987) and the fluorescence spectrum does not show any anomalous bands. It appears that the photophysical properties of dyes in certain solvents under laser excitation are different from those observed under spectrofluorimetric measurements. Therefore, a study was carried out to understand the emission characteristics of one of the 7-aminocoumarin laser dyes such as coumarin 1 (C1) in various solvents and binary solvent mixtures under both excitation conditions. This paper presents the results of the study.

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## 2. Experimental

The laser dye coumarin 1 was obtained from Exciton Chemical Co., USA and was used as received. The TLC test did not show the presence of any impurity. The solvents used were of spectroscopic grade. A nitrogen laser (peak power 100 kW and 337.1 nm) was used as a pump source and the dye solution was excited transversely. The ASE bands were studied using a constant deviation spectrometer which was calibrated using the Hg spectrum. The relative intensity of the ASE bands were measured using a photomultiplier-oscilloscope combination.

Fluorescence spectra were obtained using a Kontron SFM 25 spectrofluorimeter. The concentrations of dye solutions used were about 8 mM. The fluorescence spectrum of each solution gave only one fluorescence peak without any shoulder or hump. The fluorescence spectra taken before and after irradiation with the laser were the same.

## 3. Results and discussion

Table 1 gives the spectral parameters of Coumarin 1 (C1) in various solvents and solvent mixtures. C1 exhibits dual ASE in ethylacetate, 1, 2 dichloroethane and isobutylmethylketone. In these solvents, C1 exhibits only one fluorescence maximum corresponding to shorter wavelength ASE. For example, C1 exhibits ASE bands around 425 nm and 450 nm in isobutylmethylketone. However, the fluorescence maximum occurs around 424 nm.

In acetone and ethylmethylketone, C1 exhibits only one ASE band, which is largely red-shifted from the fluorescence maximum and appears in the longer wavelength ASE region. For instance, the ASE band appears around 450 nm in acetone, whereas the fluorescence maximum is around 430 nm. It therefore appears that the species emitting the shorter wavelength ASE are fully converted into longer wavelength ASE emitting species within the excited-state lifetime in these solvent environments.

**Table 1.** Spectral characteristics of coumarin 1 in various solvents.

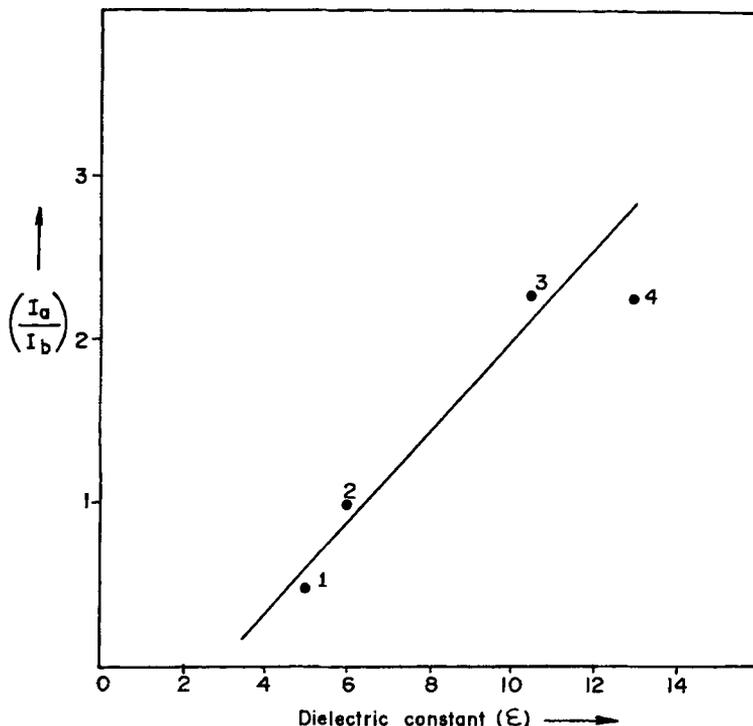
Solvents	Dielectric constant	Flu.* (nm)	ASE* (nm)	(nm)
Benzene	2.28	414	415	—
Toluene	2.38	414	415	—
Xylene	2.38	414	414	—
<i>n</i> -Butylacetate	5.01	415	416	450
Ethylacetate	6.02	417	417	450
1,2-Dichloroethane	10.36	421	423	451
Isobutylmethylketone	13.11	424	425	450
Ethylmethylketone	18.51	427	—	450
Acetone	20.70	430	—	450
Dimethylformamide	36.71	443	—	450
Acetonitrile	37.50	436	—	450
Dimethylsulphoxide	46.68	447	—	450
Benzene + acetone (10% v/v)	3.4	416	417	447
Benzene + DMSO (1% v/v)	—	415	416	447

\*For 8 mM concentration

The relative intensity of the ASE bands in a given solvent depends upon the polarity of the solvent environment (figure 1). Figure 1 indicates that the intensity of the longer wavelength ASE ( $I_a$ ) increases with increase in the polarity of solvent whereas the intensity of the shorter wavelength ASE ( $I_b$ ) decreases. This suggests that the formation of the species emitting longer wavelength ASE is accelerated by the polar environment. This may be the reason for not observing an ASE band corresponding to the fluorescence maximum in acetone and ethylmethylketone, whose dielectric constants are relatively higher than that of ethylacetate or 1, 2 dichloroethane. It appears that the polarities of acetone and ethylmethylketone are sufficient to convert all shorter wavelength ASE emitting species into longer wavelength ASE emitting species, whereas in less polar solvents (ethylacetate and 1, 2 dichloroethane) the species emitting the shorter wavelength ASE and longer wavelength ASE are in dynamic equilibrium, leading to the occurrence of dual ASE.

The shorter wavelength ASE band maximum exhibits considerable red shift as the polarity of the solvent environment increases, whereas the longer wavelength ASE band remains almost the same (figure 2). The different nature of the slopes indicates the existence of two types of emitting species under laser excitation.

In polar aprotic solvents (acetonitrile and dimethylsulphoxide (DMSO)), C1 exhibits only one ASE band which appears in the longer wavelength ASE region. In DMSO, the ASE band appears around 450 nm and the fluorescence maximum around 447 nm.



**Figure 1.** Dependence of the  $I_a/I_b$  value on the dielectric constant of the solvent (1-*n*-butylacetate, 2-ethylacetate, 3-1, 2 dichloroethane and 4-isobutylmethylketone).

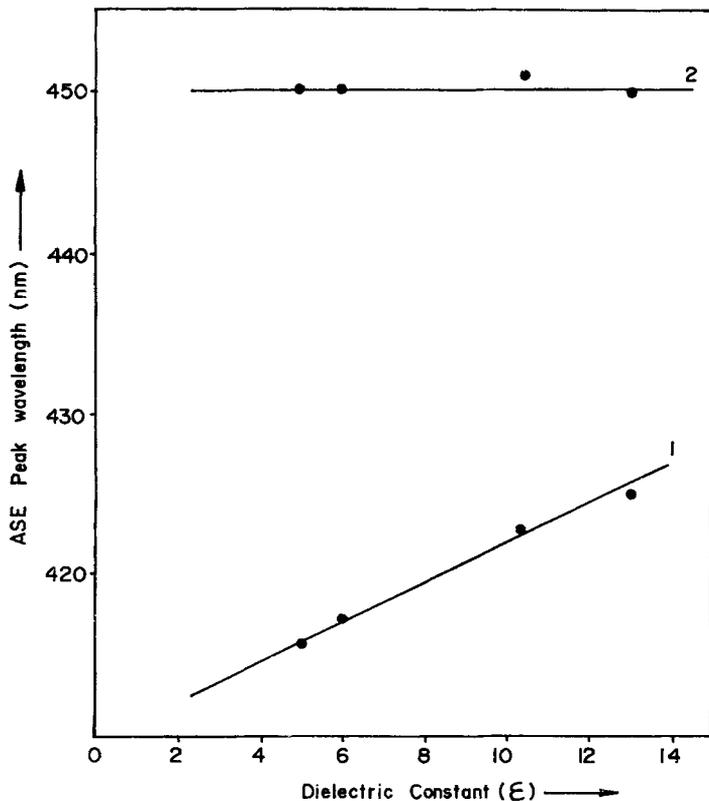
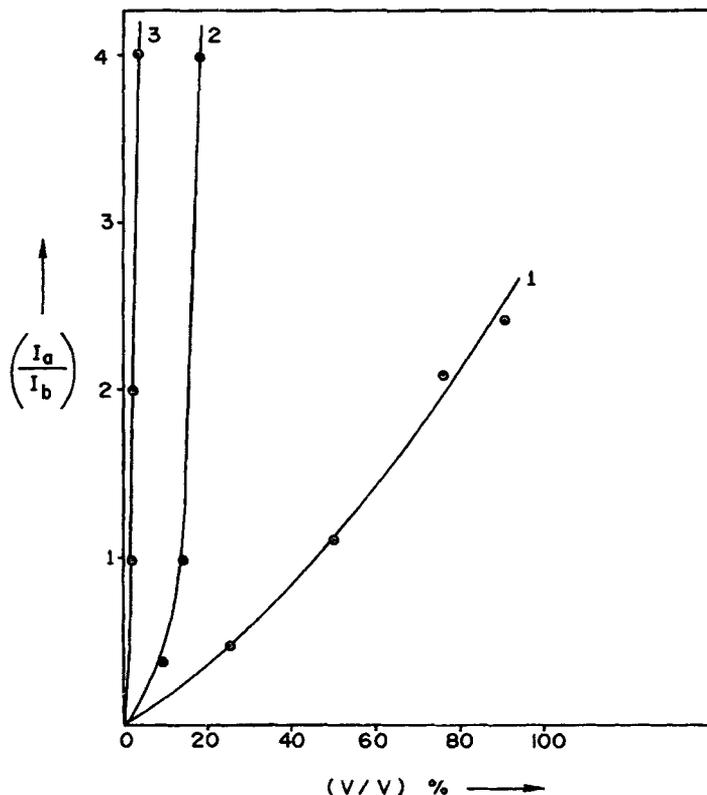


Figure 2. A plot of ASE maxima against the dielectric constant of the solvent (1 – shorter wavelength ASE and 2 – longer wavelength ASE).

Since C1 undergoes intramolecular charge transfer interactions upon excitation, its dipole moment is higher in the excited state than in the ground state (Loboda *et al* 1984). The excited dye undergoes a strong long-range interaction in aprotic polar solvents, which leads to large red shift in the fluorescence spectrum compared to non-polar solvents. It can be seen from the fluorescence maximum of C1 in various solvents (table 1) that it is red-shifted as the polarity of the solvent increases. This indicates that the species observed in all solvents using the spectrofluorimeter are the same. However, it appears that the emitting species in acetonitrile, dimethylformamide and DMSO under laser excitation are different, as their ASE appears only in the longer wavelength region though their fluorescence maxima are different.

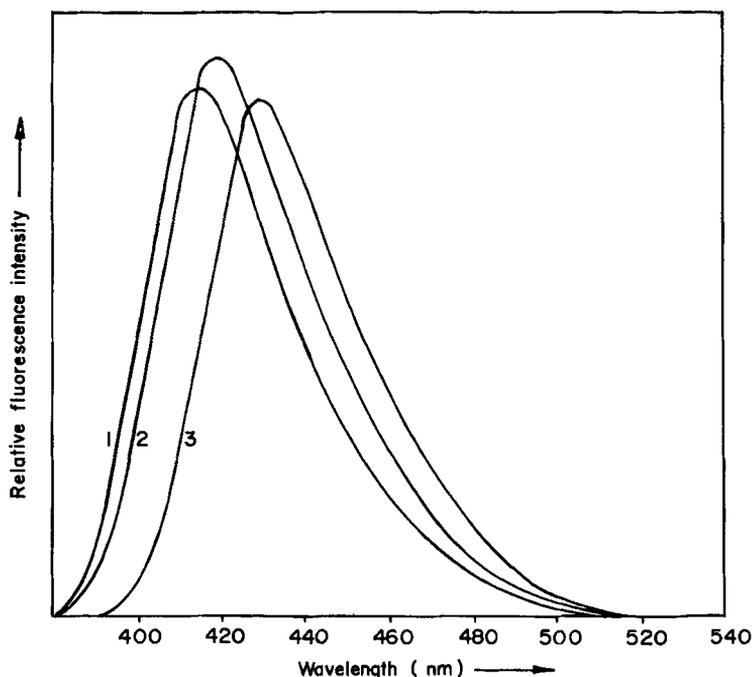
In benzene, toluene or xylene, C1 exhibits only one ASE band corresponding to the fluorescence maximum as normally expected. For instance, in benzene, the ASE band appears around 415 nm and fluorescence maximum around 414 nm. The absence of longer wavelength ASE indicates that the species emitting the longer wavelength ASE are not formed in these solvents. It is seen that increase in the dye concentration increases the formation of the species emitting the longer wavelength ASE (Sastikumar and Masilamani 1995). Therefore, the concentration of the dye solution was increased in the above solvents, However, C1 did not exhibit any ASE around 450 nm, whereas at higher concentrations even the ASE band (415 nm) started to quench. This shows that



**Figure 3.** The  $I_a/I_b$  value as a function of the addition of 1-1,2 dichloroethane, 2-acetone and 3-DMSO in benzene.

the functional groups in the solvent molecule play an important role in the formation of the species emitting longer wavelength ASE for C1.

To understand the role of solvent molecule in the formation of the species emitting longer wavelength ASE, the laser characteristics of C1 were studied in different binary solvent mixtures. When acetone, 1, 2-dichloroethane or DMSO was added to benzene (in which only one ASE band corresponding to the fluorescence maximum is observed) a new ASE started to appear in the longer wavelength ASE region and the  $(I_a/I_b)$  value increased when its concentration was increased (figure 3). For instance, when acetone (10% v/v) was added to benzene, a new ASE started to appear around 447 nm and its intensity increased with increase in the concentration of acetone. At the same time, the intensity of the shorter wavelength ASE (417 nm) was quenched. When the concentration of the acetone was about 20% v/v, only the new ASE remained. The fluorescence spectrum of this mixture was similar to that in benzene with red-shift of a few nanometers (figure 4). There is a no fluorescence peak for the new ASE. Similar behaviour was observed in other binary solvent mixtures also. It is seen in figure 3 that the change in the  $I_a/I_b$  value with the same concentration of added solvent in benzene depends upon the nature of added solvent molecule. This value increases in the order: DMSO > acetone > 1,2 dichloroethane. The dipole moments of these solvent molecules also increase in this order.



**Figure 4.** Fluorescence spectra of C1 for 8 mM concentration in 1–benzene, 2–benzene/acetone (20% v/v) and 3–acetone.

The above results indicate the occurrence of interaction between the solvent molecules (containing the functional groups) and the excited dye molecules in producing the species emitting the longer wavelength ASE. Such a formation increases with increase in the polarity of the solvent molecule. The very fact that even a small percentage of acetone molecules (as small as 10%) can produce the species emitting longer wavelength ASE of substantial strength, indicates the significance of interaction between the excited dye molecules and the functional group of the solvent molecule. It is also clear that polarity of the solvent environment is not the determining factor (since 10% addition of acetone to benzene solvent does not increase the dielectric constant of the medium much, Decroocq 1964). The dielectric constant is found to increase slightly from 2.28 (pure benzene) to around 3.4, when acetone (10% v/v) is added to benzene, but is only an aiding factor.

#### 4. Conclusion

The study of the amplified spontaneous emission characteristics of C1 in various solvents shows that a new type of emitting species is formed under laser excitation. This gives rise to longer wavelength ASE. These species are formed due to the interactions between the excited dye molecules and the solvent molecules containing the functional groups. Since benzene and toluene do not have functional groups, these solvents exhibit only one ASE band, corresponding to the fluorescence maximum as normally expected. The polar nature of the solvent environment increases the formation of these new emitting species, which leads to appearance of only one ASE band at longer

wavelengths in acetone and ethylmethylketone. However, when the polarity of the environment is not sufficiently high, the species emitting the shorter and longer wavelength ASE bands are in dynamic equilibrium which results in dual ASE.

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