Dual ASE from 7-diethylamino-4-trifluoromethylcoumarin (C35)

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MS received 3 October 1994; revised 9 March 1995

Abstract. The laser dye coumarin 35 (C35) exhibits a dual ASE band similar to coumarin 1 (C1) and does not require specific solute–solvent interaction for the formation of dual ASE.

Keywords. Coumarin 35; fluorescence; dual ASE; solute–solvent interactions.

1. Introduction

The laser dye 7-diethylamino-4-methylcoumarin (C1) exhibits dual amplified spontaneous emission (ASE) band in certain solvents, though a single ASE band is expected from its fluorescence spectrum as it contains only one fluorescence maximum (Masilamani *et al* 1986; Korol'kova *et al* 1987; Yip and Wen 1991). One ASE band appears corresponding to the fluorescence band maximum as normally expected and another ASE appears at longer wavelengths for which no fluorescence peak is observed. The dye C1, in general, shows the dependence of specific solute–solvent interaction for the formation of the longer wavelength ASE. However this ASE is attributed to different mechanisms: formation of TICT-solvent exciplex due to interaction between the dye molecule and the solvent molecule containing a functional group (Masilamani *et al* 1986), hydrogen bonding interaction between the dye and the solvent (Korol'kova *et al* 1987; Yip and Wen 1991), or solvation of the dye (Yip and Wen 1991). We report here the observation of the dual ASE phenomenon in a structurally similar laser dye C35 and its emission characteristics. These results are compared with those of C1 in view of the above proposed mechanisms.

2. Experimental

A nitrogen laser (100 kW, 10 ns) was used as an excitation source and the dye solution was pumped in a transverse configuration. A four-side polished quartz cell was used and kept canted to avoid feedback. The wavelength maximum of the ASE band was measured using a constant deviation spectrometer which was calibrated with Hg spectrum as a reference. The relative intensity of the ASE bands was measured with a photomultiplier (RCA 931)-oscilloscope combination.

The dye, 7-diethylamine-4-trifluoromethylcoumarin (C35) was purchased from Sigma Chemical Co., USA. The TLC test did not show the presence of any impurity.

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The dye was used as received. The solvents used were the spectroscopic grade. The absorption and fluorescence spectra were recorded using a Hitachi U2000 spectrophotometer and a Kontron SFM 25 spectrofluorimeter respectively.

3. Results and discussion

The dye C35 exhibits a dual ASE band (figure 1) in solvents like hexane, heptane, octane and cyclohexane (table 1). In hexane, the ASE bands appear around 432 nm (of weak intensity) and 470 nm. But the dye exhibits only one fluorescence band maximum around 431 nm (8 mM concentration) which corresponds to the shorter wavelength ASE band (i.e. 432 nm) (figure 2).

Figure 1. Spectrographic record of dual ASE band of C35 in (a) hexane, (b) heptane, (c) octane and (d) cyclohexane.

Table 1. Wavelength maxima of absorption, fluorescence and ASE bands of C35 in different solvents.

Solvents	Absorption	Fluorescence	ASE
Hexane	375	428	432 and 470
Heptane	376	430	432 and 470
Octane	375	429	431 and 471
Cyclohexane	377	432	433 and 472

(Absorption and fluorescence for 8 μ M and ASE for 8 mM concentrations) (wavelengths are in nm)

Figure 2. Absorption and fluorescence spectra of C35 in hexane for 8mM concentration.

The intensities of the longer wavelength ASE (I_a) and shorter wavelength ASE (I_b) vary with change in the concentration of the dye (figure 3). As the concentration is increased, the intensity of the longer wavelength ASE increases whereas the intensity of the shorter wavelength ASE decreases. However, the fluorescence spectrum always exhibits only one fluorescence maximum corresponding to the shorter wavelength ASE and undergoes a continuous red-shift as the concentration is increased. A similar red-shift is observed in the shorter wavelength ASE band with increase in the concentration whereas the longer wavelength ASE band remains almost the same.

The dye C1, which is similar to C35 in molecular structure with methyl group at the fourth position instead of trifluoromethyl group (figure 4), exhibits dual ASE in ethylacetate and isobutylmethylketone (table 2). The effect of concentration on the dual ASE of C1 is similar to C35 and the intensity change is more pronounced in C35 than in C1.

For C35 and C1, the I_a and I_b values also vary with a change in the temperature of the dye solution (figure 5). As the temperature is increased, the I_b value increases whereas the I_a value decreases. However, the fluorescence spectrum remains the same exhibiting only one band maximum.

The above results suggest that the longer wavelength ASE characteristics of C35 and C1 are similar and the species emitting the longer wavelength ASE are not detected using spectrofluorimeter measurements. Further the change in the ASE intensities with concentration and temperature suggests that the species emitting the longer wavelength ASE and shorter wavelength ASE are in dynamic equilibrium.

Many investigations have been carried out to understand the fluorescence characteristics of C1 and C35 (Jones *et al* 1980, 1985; Rettig and Klock 1985; Guo and Feng 1987; Yip and Wen 1990). Since C1 and C35 could undergo planar intramolecular charge transfer (ICT) and twisted intramolecular charge transfer (TICT) interactions in

Figure 3. Effect of dye concentration on I_a/I_b . C1 in *isobutylmethylketone* and in hexane.

Figure 4. Molecular structures of (1) coumarin 1 and (2) coumarin 35.

Table 2. Wavelength maxima of absorption, fluorescence and ASE bands of C1 in different solvents.

Solvents	Absorption	Fluorescence	ASE
Benzene	359	410	415
Toluene	360	410	415
Ethylacetate	362	413	417 and 450
isobutylmethylketone	365	422	425 and 450

(Absorption and fluorescence for 8 μ M and ASE for 8 mM concentrations)
(Wavelengths are in nm)

Figure 5. Plot of I_a/I_b as a function of temperature, C1 in isobutylmethylketone and C35 in cyclohexane.

the excited state (as proposed for dimethylaminobenzonitrile to explain its dual fluorescence (Grabowski *et al* 1979), the ICT-TICT model has been proposed to explain the dual ASE behaviour of C1 and C35, though these dyes exhibit only one fluorescence band maximum.

The dye C1 has been found to exhibit dual ASE in certain solvents (e.g. butyl acetate) containing functional groups or when a protic solvent (e.g. ethanol, water or butanol) or aprotic polar solvent (acetonitrile) is added to aprotic non-polar solvent (butyl acetate, dioxane or benzene). The dual ASE phenomenon observed in solvents containing functional groups is attributed to ICT planar and TICT-solvent exciplex (Masilamani *et al* 1986), and to H-bonding in the case of protic and aprotic non-polar solvent mixtures (Korol'kova *et al* 1987; Yip and Wen 1991). In aprotic polar and aprotic non-polar solvent mixture, the dual ASE phenomenon is attributed to solvation (Yip and Wen 1991).

The dye C35 exhibits dual ASE in inert solvent environments. This indicates that the species emitting the longer wavelength ASE (in the case of C35) do not require specific solute-solvent interaction for their formation.

The dye C35 is more polar than C1 due to the presence of trifluoromethyl group substitution (Loboda *et al* 1984; Guo and Feng 1987). The higher polarity of the dye molecule appears to favour the longer wavelength ASE because longer wavelength ASE is observed for C35 even in an inert solvent like hexane. In contrast, C1 which is less polar than C35, requires the assistance of a solvent having a functional group for the stabilisation of the species emitting the longer wavelength ASE.

4. Conclusion

The appearance of dual ASE in inert solvents for C35 indicates that this dye does not require specific solute-solvent interaction for the formation of the longer wavelength ASE. The polarity of the dye molecule appears to influence the dual ASE characteristics.

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