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Structural and solvent dependence of superexciplex

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Abstract

In this paper, we show that a few coumarin dye solutions exhibit dual amplified spontaneous emission (ASE) spectra under pulsed laser excitation, though all these solutions exhibit only one fluorescence band under steady-state conditions. The anomalous band, appearing only in ASE spectra, had been attributed to the superexciplex—a new molecular species. This is made of two excited molecules and is obtainable only under pulsed laser excitation. This complex is different from the well known excimer or exciplex, wherein only one atom or molecule is in the excited state. The superexciplex is possible with the two polar excited molecules coming together to form an excited state association, with the solvent acting as some sort of bridge. With very polar dye molecules, such an association is possible even with the inert benzene acting as a bridge; otherwise solvents like ethyl acetate, with an oxygen atom, is necessary for the linkage.
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1. Introduction

Dyes have proved quite useful in textiles, medicine and in laser processes [1]. In particular, dye lasers are 'pipe dreams' of the laser physicist because of their versatility in terms of tunable range in a wide spectral domain (350–1200 nm) and in time domain covering cw to femto second pulses [2]. They have also been subjects of studies to understand the intramolecular and intermolecular interactions [3].

Most dye molecules have single absorption and single fluorescence band in a solvent. Sometimes the vibrational features are resolved, particularly, in gas phase or in inert solvent environment. At other times, the bands are structureless, particularly, in polar solvents like dimethyl formamide. Whenever there is a strong solvent–solute interaction, the bands undergo marginal changes in shapes, and get shifted towards the red or violet end of the spectrum. When a molecule undergoes acid–base interaction, two or more species (neutral, anionic, zwitterionic, etc.) exist in dynamical equilibrium; hence we can get more than one band in absorption and/or fluorescence. This is true when the dye molecule is put in a mixture of inert and H-bonding, protic solvents [4]. As against these general

trends, dual band fluorescence has been observed in a few molecules like dimethyl-amino-benzo-nitrile (DMABN) in one pure, polar solvent. After a certain dose of ups and downs in interpretation, it is generally agreed that DMABN has two rotomers in the emitting state. According to [5], in the excited state DMABN has two conformations, one intramolecular charge transfer (ICT state) and the other twisted intramolecular change transfer state (TICT). Since DMABN and coumarins are similar in that, both have a flexible dialkyl-amino group as a donor, investigations were carried out to detect TICT states of coumarins by Jones II et al. [6]. According to them TICT states of coumarins, even in polar solvents are non-radiative. A comparison between the rigidized coumarins (C_{480}) and the nonrigidized one (C_{460}) has shown that the latter has reduced fluorescence quantum yield and lifetime in polar solvents [7,8]. In all these cases, when a particular dye solution is pumped hard to have laser action, we can have optical gain and amplified spontaneous emission (ASE) corresponding to the fluorescence band. Usually, there is a spectral narrowing in ASE bands ($\Delta\lambda \approx 5$ nm) for the corresponding fluorescence band ($\Delta\lambda \approx 30$ nm); the ASE is two directional, emerging out as a cone of angle of 5 mrad. In any case, there is always a fluorescence band corresponding to the ASE band since fluorescence is the seed for ASE.

In this context, Masilamani and his coworkers reported dual ASE bands from a few coumarin dye solutions under

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N_2 laser excitation. Some dyes, like C_{460} and C_{450}, exhibited dual ASE in solvents like ethyl acetate or chloroform [9–13]; some dyes like C_{480}, LD_{470} exhibited dual ASE in benzene only; [14] some other dyes like C_{485} showed the same effect in inert solvent like hexane, etc. [15–17]. The important common feature of these investigations was that, for these dye solutions there are two ASE bands though for the same solutions there is only one absorption or fluorescence band. Also, according to them, the dual ASE is strongly dependent on solvent, solute concentration and pump power for a chosen coumarin dye. Subsequently, a number of other workers confirmed the observations, though the interpretation was different [18–21]. It is commonly agreed that the long wavelength anomalous ASE band is due to exciplex of dye and solvent, and that TICT states of coumarin plays only a secondary role.

The purpose of the present paper is to get new insight into the investigations along this line. Substantial evidences are shown to enunciate the possibility of two excited dye molecules making a superexcited state complex or superexciplex giving rise to anomalous ASE.

2. Experimental

Laser grade coumarin dyes, obtained from Exciton, were used without further purification. The solvents used were all spectroscopic or analar grade and obtained from Sigma. Though Yip and Wen had considered the possibility of water vapor giving rise to anomalous ASE [18], our experimental results preclude such artifacts. For example, dual ASE has been observed in about six coumarin dyes in about 10 different solvents including hexane, benzene, etc. which are not hygroscopic [16,17].

Absorption and fluorescence spectra were obtained for concentrated (10^{-2} m) and dilute (10^{-5} m) solutions in pure solvents using Perkin-Elmer luminescence instruments. For measuring absorption of dilute solution, matched quartz cuvettes of 10 mm path lengths and of concentrated solution, 0.1 mm path length cuvettes were used. The optical densities are given only in relative units. The absorption spectra of dilute and concentrated solutions were very similar, without any new band. In a similar fashion, the fluorescence spectra for dilute and concentrated solution were taken changing the excitation wavelength from 320 to 400 nm, in 20 nm step. The spectra were similar in all the cases with no change in relative intensity. Further, these spectra were recorded before and after laser irradiation of 10,000 shots. Here again the spectral shapes were the same, indicating the absence of any fluorescing species, generated due to photochemical decomposition.

It is important to note that dual ASE could be observed in freshly prepared solution of C_{445} or C_{460} in ethyl acetate of 99.89% purity, even in first shot, if only the concentration and pump power were optimized. Further, Mohan et al. [20,21] have observed dual ASE in C_{485}, a fluorinated analogue of C_{460} in pure ethanol. Their observation strongly supports the conclusion that the dual optical gain (or ASE) is mainly dependent on concentration and laser power.

To obtain ASE spectra, the frequency tripled Nd Yag laser was used with the following specifications: $\lambda = 355$ nm, 8 ns pulse width, 1–10 Hz repetition rate and pulse energy variable from 1 to 15 mJ. The UV beam of 1 cm diameter was focused into a line image by a quartz cylindrical lens of 2 cm focal length. This was used to transversely excite the dye solution taken in a quartz cuvette which was kept canted by 20° to avoid fresnel reflection from the walls of the cuvette.

When the pump power and concentration were right, ASE came out as a cone of light on either side. This was attenuated and collected through a pinhole of 0.1 mm diameter attached to the EG&G OMA. The signals were averaged over 100 shots and processed through a computer. The whole experiment was repeated thrice to insure reproducibility.

3. Results and discussion

3.1. Dependence on laser energy

Amplified spontaneous emission in dual bands has been observed by a number of workers in different dyes [13–21], but we shall confine our results to five coumarin dyes, with closely related molecular structure as shown in Fig. 1. All are 4-methyl-7-amino-coumarins, out of which C_{460} has a diethyl-amino group; C_{450} and C_{445} have mono ethyl group and C_{440} has unsubstituted amino group in the seventh position. C_{480} has a rigidized donor at the seventh position. The position of the dual ASE bands, and their relative intensities
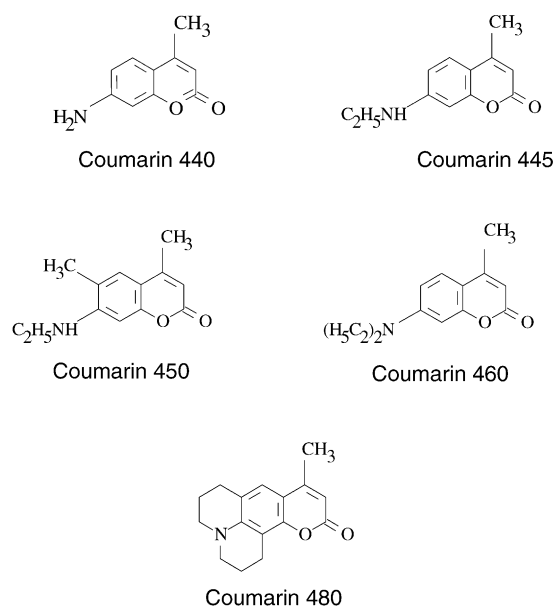

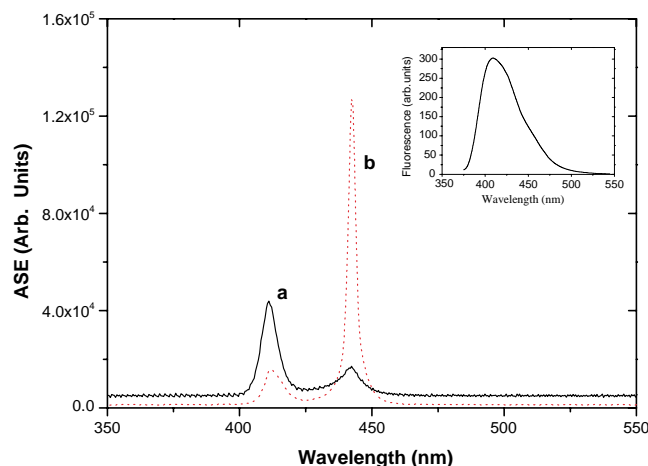Fig. 1. Molecular structure of coumarin dyes used.

Fig. 2. ASE spectra of C_{445} in ethyl acetate for two pump pulse energy. Concentration = 6 mM.

are sensitive functions of dye structure, solvent environment, temperature, concentration and pump power.

To get an insight into the dependence of dual ASE on molecular structure, four dyes, C_{440}, C_{445}, C_{450} and C_{460}, were dissolved to a concentration of 10 mM in ethyl acetate. They were subjected to identical treatment throughout, keeping the same experimental arrangement (C_{480} did not give dual ASE in ethyl acetate and hence will be taken up later).

As we can see in Fig. 2, there are two distinct bands, one around 420 nm and another around 450 nm for C_{445} in ethyl acetate. For low pump energy (Fig. 2a corresponding to 4 mJ) the band at 450 nm, henceforth called the blue band (BB), is considerably smaller than the band at 420 nm, the violet band (VB). However, BB intensity grows sharply as pump pulse energy is enhanced (Fig. 2b corresponding to 6.5 mJ). Under the conditions of non-saturation (of detector response, pump intensities and optical gain), the ASE intensity (I_{ASE}) related to the stimulated emission cross-section σ_{SE} is given as [22]:

$$I_{ASE} = k \exp(\sigma_{SE} \Delta N \ell)$$

where ΔN is the inversion density, ℓ the length of excitation region and k is an instrumental parameter, which is kept constant. Since we collect the ASE intensity through an aperture of 0.1 mm slit width, kept at a distance of 1 m, the influence of the isotropic spontaneous emission can be ignored. Here, we follow the treatment of Shank et al. [22] for measuring the optical gain in ASE for dye solution.

Since BB exhibits a nonlinear dependence, we must clarify the nature of this nonlinearity. To do this we take

$$\ln I_{DL} = \ln k + \gamma \ell$$

and

$$\gamma = \sigma \Delta N$$

For a dye laser [1]

$$\sigma = \frac{\lambda^4 E(\lambda)}{8\pi\tau\mu^2}; \qquad \int_{-\infty}^{+\infty} E(\lambda)\,d\lambda = 1.$$

Here $E(\lambda)$ is the relative fluorescence intensity at wavelength λ, τ the radiative life-time, μ the refractive index, ΔN the inversion density and σ is the stimulated emission cross-section. With reference to the fluorescence spectra given in Fig. 2 (inset), we can calculate $\sigma^{420}/\sigma^{450} = 1.20$.

If the inversion density is same for both the bands at 420 and 450 nm, which was generally expected for homogeneously broadened media such as a dye solution, the ratio of optical gain is $\gamma_{420}/\gamma_{450} = 1.20$. This would mean that optical gain at 420 and 450 nm would depend linearly upon the pump power. Under this condition, the ASE peak would occur around the fluorescence peak ($\approx$420 nm), and the ASE at 450 nm would be always less substantial. This is the general trend for thousands of dye solutions, with an important difference that only one band of ASE occurs with a gradual red shift for higher concentration.

These results indicate that ASE at 450 nm of C_{445} in ethyl acetate has a nonlinear dependence on inversion density and consequently on the pump power. For the ranges of concentration (1–10 mM) and pump pulse energy (1–5 mJ) used in this experiment, the inversion density varies from 10^{11} to 30×10^{11} molecules cc^{-1}, assuming a realistic value of $\sigma = 3 \times 10^{-17}$ cm^2.

Assuming that the ASE at 450 nm is proportional to ΔN^2, that is (pump power)^2 for a given concentration of the dye solution, above a certain critical value

$$\ln I_{DL} = \ln k + \sigma p^2 l$$

since k, the instrumental parameter as well as the length of optical gain region are the same for ASE^{420} and ASE^{450}.

$$\frac{\text{slope of ASE}^{450}}{\text{slope of ASE}^{420}} = \frac{\sigma^{450}}{\sigma^{420}} \times \frac{2}{1} = \frac{1}{1.20} \times 2 = 1.7$$

for a given pump power.

Our measurement, taken at different pump power values, but below saturation (from 2.5 to 6 mJ), gives an average of slopes of ratio 1.8 as can be found from Fig. 3. This gives a strong indication that BB is a bi-molecular process, involving two excited molecules. A plot of ln of ASE at blue and violet bands as a function of concentration (for a fixed pump power) as shown in Fig. 4 again gives a ratio of approximately 2. The trend of C_{445} is similar to that of C_{460} published recently [23].

It is important to draw attention to the fact that the bi-molecular association referred to here is not the excimer or exciplex commonly known in photo physics of organic molecules. The kinetics of excimer or exciplex have been studied for a long time [24]. These molecular species involve one excited molecule associated or loosely bonded with another ground state molecule with or without the help of a solvent. What is proposed in this paper is the formation
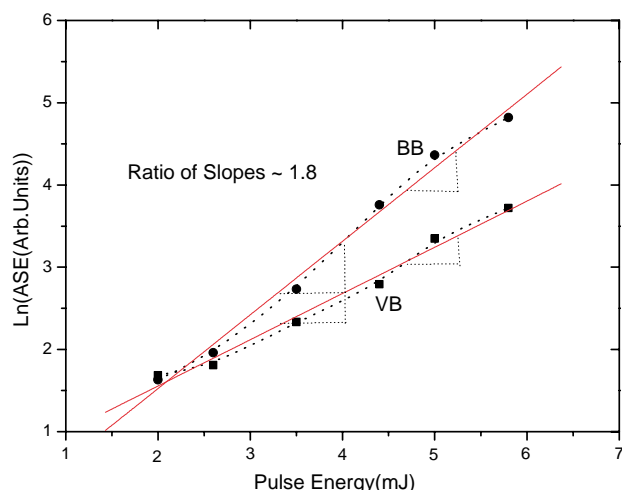
Fig. 3. ln of ASE intensity as a function of pulse energy.

Fig. 5. Ratio of ASE intensities at blue band and violet band as a function of temperature. Concentration = 5 mM and pump pulse energy = 6.5 mJ.

of superexciplex, with the solvent acting as a bridge to bring together the *two excited* coumarin molecules. From this point of view, the superexciplex proposed here is similar to the associated atoms in the excited states in an excimer (Xe_2) or exciplex (ArCl) lasers. All these excited species get dissociated after emitting a photon.

Both the conventional exciplex and superexciplex should be a sensitive function of temperature, as the thermal motion could break the bonding. Fig. 5 gives a very strong support to our model. Here (inset) one can see the violet and blue ASE bands for two temperatures, with all other parameters remaining constant (dye C_{445}, solvent ethyl acetate, pulse energy of 4 mJ and concentration of 12 mM). The rapid change of BB from a high value to a low value as temperature goes from 25 to 50 °C is a strong indication of molecular association phenomenon reminiscent of dimer, excimer, exciplex, etc. [23]. It is important to note that the intensities of both bands decrease as temperature increases due to internal conversion enhancement. The intensity of
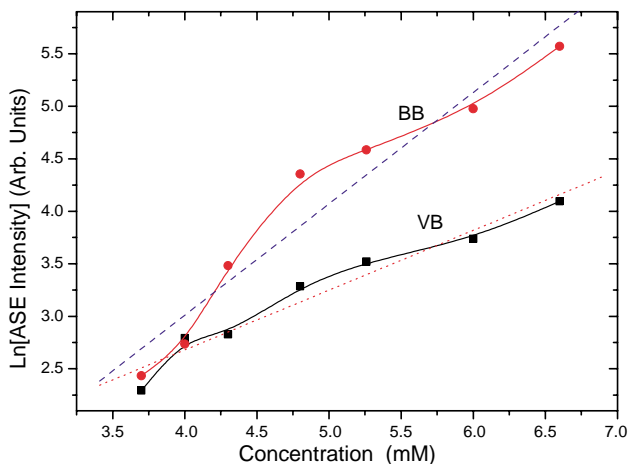

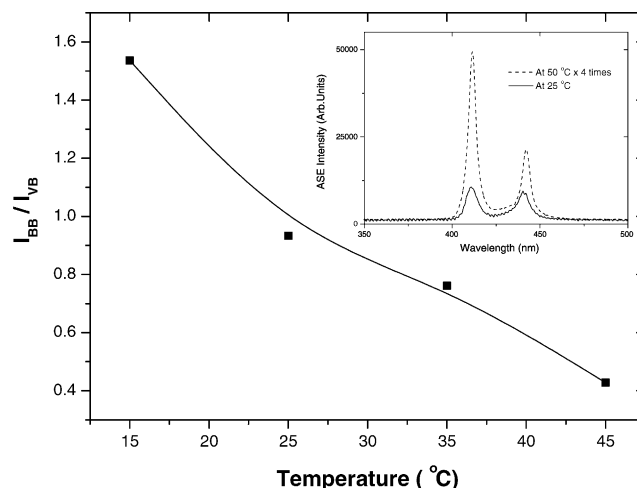Fig. 4. ln of ASE intensity as a function of concentrations. Pulse energy = 6.5 mJ.

BB decreases much faster than VB. This trend is reversed as the temperature is lowered from room temperature to 10 °C. Below this, condensation of atmospheric water vapor on the walls of cuvette makes difficult to get accurate results. Note that these results are true for all dyes studied here.

The excited state reabsorption is also strongly dependent on concentration of pump power and dye concentration (similar to superexciplex formation). If the excited state reabsorption is the cause of BB, both bands should increase or decrease in intensity as a function of temperature without any change in their intensity ratio. Our results are contrary to this and eliminates this possibility. Nor can we interpret the anomalous blue ASE due to the overlap between the ground state absorption and fluorescence bands. Because, in this case, the increase in concentration leads to a gradual red shift on the fluorescence and ASE bands (with rhodamines and fluoresceins as classic examples, wherein the overlap is stronger).

In case BB is due to the vibrational features of S_1–S_0 transition, then again, the relative intensities of the two bands should remain more or less the same, independent of concentration and the pump power. Further, this is quite unlikely since the dye solution is a homogenously broadened medium.

Yip and Wen [18] have interpreted the dual ASE in terms of exciplex of solvent–solute (1:1) complex. According to them, C_{460} makes comlexation with two ethanol molecules in the ground state, but with only one solvent in the excited state. He has shown that the lifetime of the free dye molecule is about 3.28 ns and of exciplex is 0.37 ns. His later result, employing single photon counting (apparently using low concentration and low pump power), could not be compared with ours. We worked with high power and high concentration situations. In our investigation with single photon measurement and with 5–10 mM solution of C_{460} in ethyl acetate, we were able to get only one decay time of 3.5 ns [25]. Furthermore, C_{460} has only one decay time of 3.17 ns
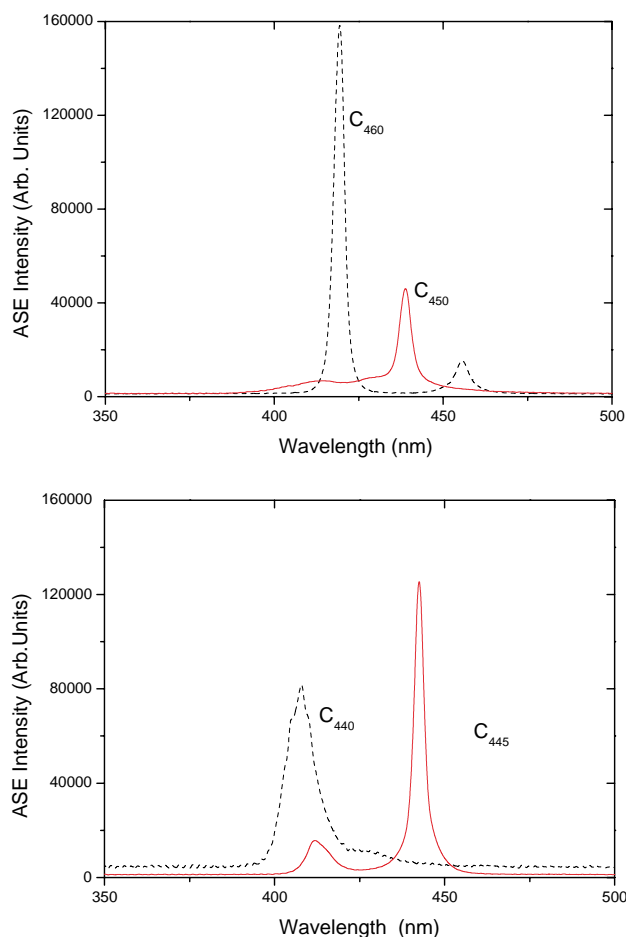
Fig. 6. Dual ASE spectra of C_{440}, C_{445}, C_{450}, and C_{460} in ethyl acetate. Concentration = 8 mM and pump pulse energy = 7.5 mJ for all.

in dichloromethane in the measurement of Yip, whereas, we get dual ASE for this solution. Similarly, C_{460} in butanol shows two decay components (0.1 and 3.75 ns), but we obtained only one ASE at 440 nm.

3.2. Dependence on molecular conformation

Shelving the nature of the proposed superexciplex for a latter discussion, we could look at the dependence of ASE on molecular structure. Fig. 6 gives the relative intensities of two bands for four coumarin dyes with same concentration, solvent, pump power, experimental set up, etc. Note that the absorption cross-section at 355 nm for C_{440}, C_{445}, C_{450} and C_{460} are in the range of 0.8–1. This is because all these dyes have a peak at around 350–370 nm in EA and we excite at 355 nm. Though all these give dual ASE, around 420 and 455 nm, the relative strengths of these bands are markedly different, indicating a strong dependence on molecular conformation.

Comparing C_{445} with C_{460}, they are very similar in their electron donor–acceptor properties, except that we have mono ethyl amino in C_{445}, and diethyl amino in C_{460}, in the seventh position as the donor. Because of these, the dual
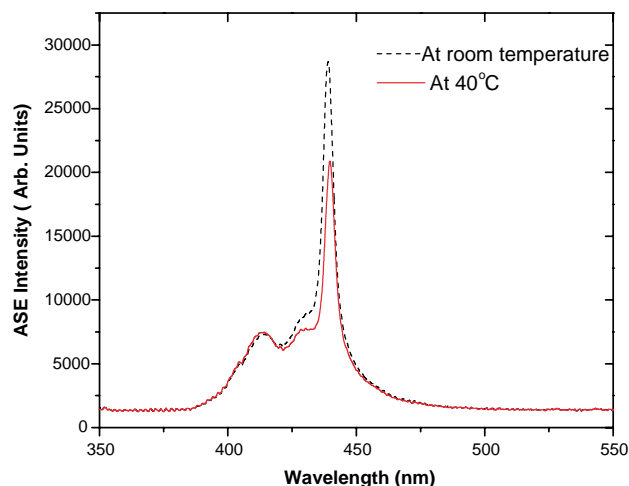

Fig. 7. ASE of C_{450} in ethyl acetate at two different temperatures. Concentration = 6 mM and pump pulse energy = 6.5 mJ.

ASE characterizations are very similar. We have tried these two dyes in different solvents and at different temperatures, pump powers, pump wavelengths ($\lambda e = 337.1$ nm from N_2 laser or $\lambda e = 355$ nm from frequency tripled Nd Yag laser); they have comparable characteristics. In contrast, C_{440} did not give a distinct BB at room temperature. The solution has to be cooled down to 5 °C to make BB prominent. In contrast, VB is quite weak in C_{450}, appearing only as a shoulder at room temperature as shown in Fig. 7. If the solution is diluted to 5 mM and heated to 40 °C, VB becomes prominent.

The difference between C_{440} and C_{460} lies in the fact that C_{440} has a poor electron donor (–NH$_2$) compared to C_{460} (with NR$_2$). This is reflected when these dyes go to the excited state. That is, C_{460} has a greater dipole moment than C_{440} in the excited state. From this point of view, molecules with considerable higher dipole moment in the excited state are potential candidates for dual ASE.

This view is supported by the behavior of C_{450}. In terms of the absorption spectra, fluorescence spectra, stokes shift as shown by Jones II et al. [6–8] as a function of solvent dipolar parameter [24], C_{450} and C_{460} are quite similar. But under optical gain conditions, BB of C_{450} is at least 10 times stronger than that in C_{460}, under identical operational parameter. The only possible reason that we could think of is that the C_{450} has a –CH$_3$ group in the sixth position, this might push the amino group at the seventh position producing twisted intramolecular charge conformation (TICT state). The TICT state is more polar than the normal intramolecular charge transfer state. Probably this might aid the superexciplex formation. However, our results are at odds with the view that TICT states are non-radiative, non-laser emissive [24].

Although the TICT state may be important for the formation of exciplex in C_{450}, it is not an essential prerequisite for superexciplex formation. What is more important is that the dye should become considerably polar in the excited state. This is confirmed by the dual ASE observed in LD$_{470}$ [24]
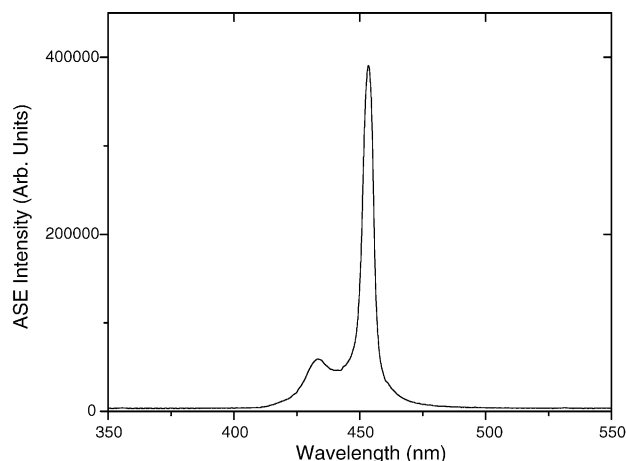
Fig. 8. ASE of C_{480} in benzene. Concentration $= 4$ mM and pulse energy $= 6.5$ mJ.

Fig. 9. ASE relative intensities $I_{\text{Blue Band}}/I_{\text{Violet Band}}$ as a function of dielectric constant of solvents.

and C_{480} in benzene, both of which are incapable of producing TICT states.

Fig. 8 shows the dual ASE of C_{480} in benzene with 4 mM concentration and under 4 mJ pulse energy. The behavior is very similar to C_{460} in propyl chloride at room temperature, or C_{450} in ethyl acetate at $40\,^\circ$C as shown in Fig. 7. Both C_{480} in benzene and C_{450} in ethyl acetate have weak VBs. But in both cases, the intensity of the long wavelength band rapidly comes down when temperature is raised to $50\,^\circ$C from the ambience. This indicates that we could get dual ASE for C_{460} and C_{480}, but at different solvent. In benzene, we get only one ASE band at around 410 nm even for a super saturated solution of C_{460}, under 25 mJ pump energy; similar to C_{480} in ethyl acetate, where only one ASE band occurs at 470 nm. This would mean that superexciplex could be formed by C_{480} even in weak non-polar solvent like benzene, but molecules like C_{450}, C_{440}, C_{445} and many others need the assistance of solvents like ethyl acetate, with the oxygen atom acting as a bridge for superexciplex formation.

Our interpretation is supported by our earlier results, where we had reported dual ASE in fluorinated alkyl-amino-coumarin [C_{35}] even in hexane, or heptane [16,17]. These are inert solvents, with negligible influence on the solute properties. Their only role is to bring a large number of excited molecules close together.

3.3. Dependence on solvent type

The "superexciplex" is quite sensitive to the solvent environment, similar to the conventional exciplex of a host of organic molecules. For coumarins like C_{460}, C_{450} and C_{445}, superexciplex could be obtained in a few moderately polar solvents, like dioxane, n-butylacetate, chloroform, ethyl acetate, diethyl ether, chlorobenzene, dichlorobenzene, tetra-hydrofuran, etc. For these dyes, we could not observe dual ASE in inert, non-polar solvents like benzene, toluene, hexane, heptane, cyclohexane, etc. There is only one band around 410 nm even for saturated solution.
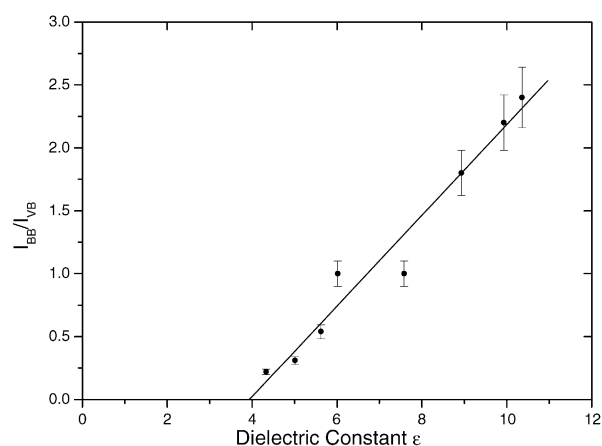
Similarly, in highly polar solvents like DMF, DMSO, ethanol, etc. there is again only one band around 450 nm.

Fig. 9 gives the relative intensity between the blue (450 nm) and violet (425 nm) ASE bands as a function of dielectric constant (ε) of the medium polar solvents. Here again, the dye concentration of 12 mM and pump energy of 4 mJ and geometry, etc. were kept constant for C_{460} and only solvent environment had been changed. The graph indicates that BB intensity increases linearly as the polarity of the solvent increases. The trend is similar for other dyes like C_{445} or C_{450}, with the major difference that one gets distinct dual ASE in C_{440}, only in ethyl methyl ketone, very much comparable to that of C_{460} in ethyl acetate. Similarly, for C_{480} we get dual ASE in inert solvent like benzene only at lower concentrations (e.g. 5 mM).

From these data, one is led to the conclusion that dual ASE comparable to C_{460} in ethyl acetate could also be obtained in other coumarin dyes also by the proper choice of the solvent, concentration, pump power and temperature. From the fact that the dual ASE has been observed under N_2 laser excitation in solvents like hexane (for C_{35}, [16,17]), one can consider that the crucial requirement for formation of superexciplex is the availability of highly polar molecules in abundance in the excited state. For 'weak' superexciplexes, solvents like ethyl acetate are required to act as a bridge (with the help of oxygen atom). For molecules like C_{480} or C_{35}, with the tendency to form excited state superexciplex, weak or inert solvents would suffice.

A suggested mechanism of superexciplex is given in Fig. 10. Following the excitation by the high power pulsed lasers, a large number of molecules go to the excited Franck Condon state, they relax to the lowest vibrational state of S_1, where they linger for a few nanoseconds. During these stages, the molecules undergo charge separation by ICT (internal change transfer *without* twisting), whereas, molecules like C_{450} may go to TICT state also. A substantial number of the excited ICT and molecules produce fluorescence and ASE in VB.
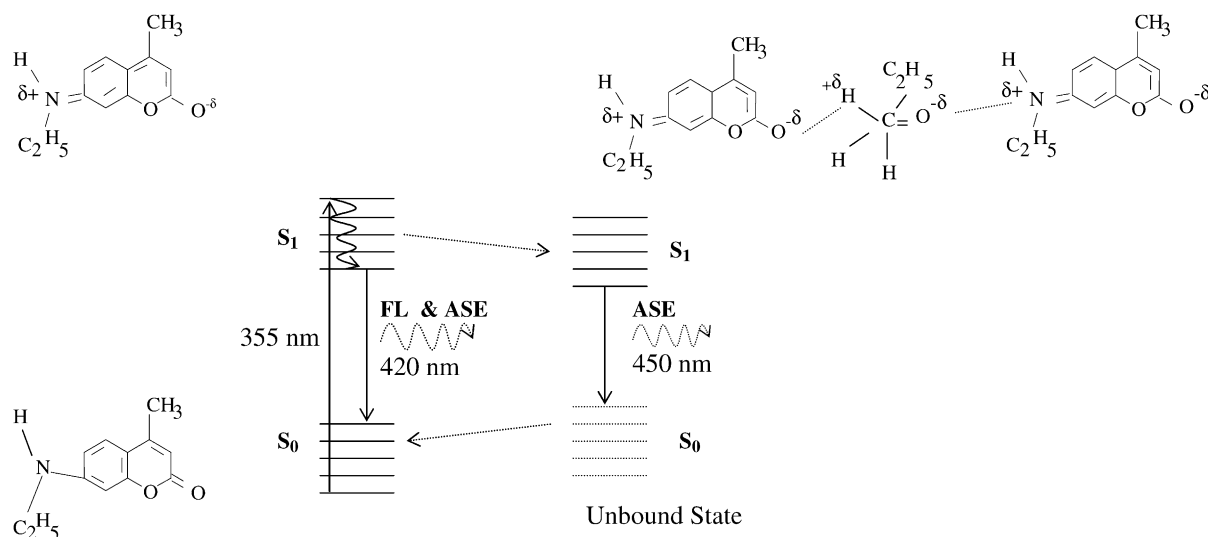
Fig. 10. A plausible scheme for supexciplex formation.

Another set of excited molecules combine together to form superexciplex, with or even without the solvent acting as a bridge. After relaxation, they produce laser-induced florescence at 450 nm; and if the inversion density is quite high they produce optical gain and ASE at 450 nm. (BB). Note that even though TICT may not be rdiative, superexciplex formed by two TICT states may be radiative. However, this is to be confirmed [26–28].

4. Conclusion

The characteristics of dual ASE observed in a few coumarin dyes under high power pulsed laser excitation show the possibility of a new molecular species called superexciplex. In this, two excited organic molecules are in association very much similar to Ar Cl excimer laser species. The superexciplex formation depends upon the nature of the dye, solvent, temperature, pump power and concentration. However, the essential requirement is the high density of excited polar molecules.

Though similar reports have appeared in the last few years, a quantitative confirmation for the involvement of excited bi-molecular process is presented only in recent times [23]. Such superexciplex need not to be confined to coumarin classes only, other polar molecules also could exhibit similar trends. These papers also bring to limelight the importance of ASE spectroscopy in elucidating excited state behavior of molecules.

Acknowledgements

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