Chapter 2

Photophysical, ASE and Lasing Properties of Coumarin 540

"If we know what we were doing it wouldn't be research".

Einstein

Abstract

The results of a detailed investigation of the various photophysical properties of Coumarin 540 laser dye in various solvent environments are reported. The effect of solvents on the quantum yield, lifetime, radiative and nonradiative decay rates, stokes' shift etc. is analyzed. Amplified spontaneous emission exhibited by the dye solution in methanol is studied in terms of excitation length and pump energy. Coumarin 540 dye solution contained in a quartz cuvette exhibits laser emission with well-resolved, equally spaced modes which originates from the subcavities formed between the walls of the cuvette. While the quantum yield remains a decisive factor, a clear correlation between the refractive indices of the medium which determines the reflectivity at the end faces of the cuvette, and the number of modes exhibited by the emission spectra of the respective samples has been demonstrated.

2.1 The Photophysics of Laser dyes

The significant properties of organic dyes which make them very attractive in the photonics world of application are the large absorption and emission cross sections which they exhibit in the visible part of the spectrum over a wide range of wavelengths. They constitute a large class of polyatomic molecules containing long
chains of conjugated double bonds. The large absorption cross section \( \sigma \) is due to the presence of large dipole moment \( \mu \) originating from the \( \pi \) electrons of carbon. These \( \pi \) electrons are free to move over a distance roughly equal to the chain length \( L \). Since the chain length \( L \) is quite large, correspondingly \( \mu \) is also large. The absorption cross section \( \sigma \) which is proportional to \( \mu^2 \) is of the order of \( 10^{-16} \text{cm}^2 \) [1]. Compounds with conjugated double bonds absorb light at wavelengths above 200 nm. The large number of conjugated double bonds present in organic dyes also increases the absorption in the visible part of the spectrum [2]. The dyes display strong broadband fluorescence spectra under excitation by visible or UV light. With different laser dyes the overall spectral range extends from 300 nm to 1.2 \( \mu \text{m} \).

2.1.1 Energy level diagram

The photophysics of laser dyes can be well explained by considering the energy level diagram. A schematic energy level diagram for laser dyes is shown in Fig.2.1. It consists of singlet states \( S_0, S_1, S_2 \) etc. with total spin zero and triplet states \( T_0, T_1, \) etc. with total spin one. Each electronic level has a manifold of vibrational states due to the many internal degrees of freedom of a complex molecule. Even more finely spaced are the rotational sublevels of each vibrational state. The total manifold of states is so dense that the absorption and emission spectra of a dye forms a continuum. Following light absorption, a sequence of different processes occurs. Optical excitation occurs in the singlet manifold. A fluorophore is usually excited to some higher vibrational levels of either \( S_1 \) or \( S_2 \). From these excited states they can relax to lower energy states through internal conversion or intersystem crossing. Internal conversion is the radiationless process by which a molecule transfers itself from one electronic state to another electronic state of the same multiplicity or within the same electronic state while in intersystem crossing the energy transfer occurs between electronic states of different multiplicity. The rate of
internal conversion between excited singlet states is extremely high, of the order of \(10^{11-10^{13}} \text{ s}^{-1}\) and consequently the lifetimes of upper excited singlet states are very short (\(10^{11-10^{13}} \text{ sec.}\)). The deactivation to the \(S_1\) state takes place before any radiative transitions or photo-reactions involving the upper state can take place. The lowest vibrational state of \(S_1\) decays to the ground state by radiative emission or by the nonradiative pathway of internal conversion and by intersystem crossing to the triplet manifold. Normally the radiative emission is between the lowest level of \(S_1\) and the various levels of the \(S_0\) state. The transition from the excited singlet state to the ground state is quantum mechanically allowed as this does not require a change of spin orientation. The lifetime of this fluorescence emission is typically a few nanoseconds. Internal conversion is generally complete before this emission.

Fig.2.1 Diagram illustrating the energy levels of a dye.
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Intersystem crossing between the singlet and triplet state is spin forbidden. Though the transition from $S_1$ to $T_1$ is radiatively forbidden, for organic dye molecules, the interaction of electron spin and orbital motion leads to inter system crossing. Radiationless transfer can also occur by external perturbations like collisions. The rate constant $k_{ST}$ of intersystem crossing usually occurs at a much lower rate ($\sim 10^7$ s$^{-1}$). Since the triplet – singlet transition is spin forbidden, the lifetime of the triplet state is large. While the molecule is in the lowest level of $T_1$, it can also absorb radiation and optically allowed $T_1$ to $T_2$ transition may occur. This absorption tends to occur in the same wavelength region where fluorescence emission occurs and this may even quench the laser emission [3].

The rates of internal conversion and intersystem crossing processes are dependent on the energy separation between lowest vibrational levels of the states involved; the larger the separation, the slower the rate. The large energy separation between the lowest vibrational levels of $S_1$ and $S_0$ states and $T_1$ and $S_0$ states reduces the decay rate of the $S_1$-$S_0$ internal conversion and $T_1$-$S_0$ intersystem crossing which is of the order of $10^6$ to $10^{12}$s$^{-1}$ and $10^{-2}$ to $10^6$ s$^{-1}$ respectively [4-5]. The decay from $T_1$ to $S_0$ state can be radiative or nonradiative and is termed as phosphorescence when it is radiative.

The process of dye fluorescence must compete with nonradiative decay of excited states by internal conversion to the ground state or by intersystem crossing to the triplet state. The long lifetime of the triplet state of the dye not only allows buildup of a species that may be chemically reactive but also provides a competitive absorber at lasing wavelengths. There is also a possibility of further excitation from the $S_1$ manifold to higher-lying singlet states. However, the cross section of the excited state absorption is 100 times smaller than that for ground state absorption [6].
2.1.2 Absorption and fluorescence spectral characteristics

The absorption spectra of organic dyes have a large spectral width which usually covers several tens of nanometers. In the general case of a dye molecule which consists of a large number of atoms, many normal vibrations of different frequencies are coupled to the electronic transition. The collisional and electrostatic perturbations caused by the surrounding solvent molecules further broaden the individual lines of such vibrational series. Every vibronic sublevel of electronic state has been further superimposed by rotationally excited sublevels. These are highly broadened by the frequent collisions with the solvent molecules and there is a quasi-continuum of states superimposed on every electronic level. Thus the absorption is practically continuous all over the absorption band. The same is true for the fluorescence emission corresponding to the transition from the electronically excited state of the molecule to the ground state. This results in a mirror image of the absorption band displaced towards higher wavelengths [3-4].

2.1.3 Solvent effect on fluorescence spectra

It has been shown that solvents play a decisive role in laser dye photophysics. The active medium of dye laser consists of typical organic dye concentration of $10^{-2} - 10^{-5}$ M dissolved in a certain solvent. For this reason the dye solvents have a major role in the design of dye lasers. Lasing wavelength and energy are very sensitive to the choice of solvents. The interaction between the solvent and the fluorophore molecules affects the energy difference between the ground state and the excited states. This energy difference is attributed to the refractive index $n$ and the dielectric constant $\varepsilon$ of the solvent and is described by the Lippert equation
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\[ \bar{\nu}_a - \bar{\nu}_f \cong \frac{2}{hc} \left( \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \left( \frac{\mu^* - \mu}{a^3} \right) + \text{const.} \]  

(2.1)

Here \( h \) is the Planck's constant, \( c \) is the speed of light, \( \mu^* - \mu \) is the change in dipole moment and \( a \) is the radius of the cavity where the fluorophore resides. The wave numbers in cm\(^{-1}\) of the absorption and emission are \( \bar{\nu}_a \) and \( \bar{\nu}_f \) respectively and the difference between them is the Stoke's shift [3].

Most laser dyes are polar ones and excitation into their low lying excited singlet state will be accompanied by an increase in the dipole moment. The solvent polarity have a decisive role in shifting the lasing wavelength. In most of the cases, increasing the solvent polarity will shift the gain curve towards the longer wavelength side which is known as the Stoke's shift. In high polar solvents the shift can be as high as 20-60 nm. Some solvents cannot be used in the longer wavelength side due to vibrational overtones of the solvents which will interfere with the lasing process. Solvents like water, methanol and ethanol which would appear optimal solvents for many dyes are not useful for the near-IR and IR dyes [2, 4].

2.1.4 Stoke's shift and solvent polarity function

The Stoke's shift is a property of the dielectric constant (\( \varepsilon \)) and refractive index (\( n \)) of the solvent. They have opposite effect on the Stoke's shift. An increase in \( n \) will decrease this shift, whereas an increase in \( \varepsilon \) results in an increase in the shift. These different effects are a result of Frank-Condor principle. An increase in \( n \) allows both the ground and excited states to be stabilized instantaneously by movements of electron within the solvent molecules. This electron redistribution results in decrease in energy difference between the ground and excited states. An increase in \( \varepsilon \) also results stabilization of the ground and excited states. However, the energy change of
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the excited state occurs only after reorientation of the solvent dipoles. The Stoke's shift is related to the orientation polarizability term $\Delta f$ which is also known as solvent polarity function which is given by

$$\Delta f = \left( \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right)$$ (2.2)

The first term accounts for the spectral shifts due to both reorientation of the solvent dipoles and to the redistribution of the electrons in the solvent molecules. The second term accounts only for the redistribution of the electrons. The difference of these two terms accounts for the spectral shifts due to reorientation of the solvent molecules. Thus only solvent reorientation is expected to result in substantial Stoke's shifts [3].

2.1.5 Fluorescence quantum yield

The fluorescence quantum yield is the ratio of the number of photons emitted to the number of photons absorbed by the sample.

$$\Phi = \frac{\text{photons}_{\text{em}}}{\text{photons}_{\text{abs}}}$$ (2.3)

The quantum yield $\Phi$ can also be described by the relative rates of the radiative and nonradiative decay pathways, which deactivate the excited state.

$$\Phi = \frac{k_r}{k_r + \sum k_{nr}}$$ (2.4)

where $k_r$ is the emissive rate of the fluorophore and $k_{nr}$ is the rate of radiationless decay. Here $\sum k_{nr}$ describes the sum of the rate constants for the various processes that compete with the emission process. These processes include photochemical and dissociative decays, where the latter includes nonradiative transitions namely
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intersystem crossing and internal conversion. The rate constants $k_r$ and $k_{nr}$ both depopulate the excited state. Quantum yield gives the probability of the excited state being deactivated by fluorescence rather than any other nonradiative mechanism. The important competition between dye fluorescence, intersystem crossing and internal conversion is reflected in quantum yields. Laser dyes show a high quantum yield for fluorescence emission. (Rhodamine 6G ~0.95)[5-6].

2.1.6 Fluorescence lifetime

The lifetime of the excited state is defined by the average time the molecule spends in the excited state prior to return to the ground state which is denoted by $\tau$. The lifetime of the fluorophore in the absence of nonradiative processes is called intrinsic lifetime or natural lifetime and is given by $\tau_0 = \frac{1}{k_r}$ (2.5)

This leads to the relationship for quantum yield

$$\Phi = \frac{\tau}{\tau_0} \quad (2.6)$$

The quantum yield is the fraction of the excited fluorophores which decay by emission ($k_r$) relative to the total decay ($k_r + k_{nr}$) and thus by the ratio in equation 2.4. The lifetime of a fluorophore is determined by the sum of the rates which depopulate the excited state. In the absence of other quenching interactions, the lifetime is given by

$$\tau = (k_r + k_{nr})^{-1} \quad (2.7)$$

The lifetime of a fluorophore is increased or decreased by the change in the value of $k_{nr}$. Almost invariably, the lifetimes and quantum yields increase or decrease together [7]. The lifetime $\tau$ alone is insufficient to distinguish changes in radiative rates from changes in non radiative rates. Measurements of fluorescence quantum yields are
needed to distinguish the two contributions. The radiative rate $k_r$ and the nonradiative rate $k_{nr}$ are calculated by the equations

$$k_r = \frac{\Phi}{\tau}$$

$$k_{nr} = \frac{(1 - \Phi)}{\tau}$$

(2.8)

Of course $k_{nr}$ represents the sum of different processes.

### 2.2 Structure of Coumarin 540 (C 540)

Coumarin derivatives with an amino group in the 7-th position are very efficient laser dyes in the blue-green regions of the spectrum. Coumarin 540 is 3-(2-Benzothiazolyl)-7-diethylaminocoumarin (C 540) whose molecular structure is given in Fig. 2.2. Substitution of coumarin with an amino group in the 7-th position generates a merocyanine chromophore characterized by the conjugation of push pull substituents (amine electron donor and carbonyl (C=O) electron acceptor groups). This pattern of substitution gives rise to an intramolecular charge transfer (ICT) transition for which there is large oscillator strength for absorption ($S_0$-$S_1$) and a high rate of fluorescence emission. A much higher dipole moment is predicted for $S_1$ [2]. The details of the investigations carried out on the photophysical properties of the laser dye C 540 along with its lasing characteristics are given in the following sections.

![Molecular Structure of Coumarin 540 (C_{20}H_{18}N_{2}O_{2}S)](image_url)
2.3 Experimental details

2.3.1 Absorption and fluorescence spectra

The photophysical properties of Coumarin 540 are investigated in detail in different solvent environments by selecting 10 different solvents which comprise of polar protic, dipolar aprotic and nonpolar solvents. Laser grade Coumarin 540 is obtained from Exciton. All the solvents used for the experiments are of spectroscopic grade. The absorption and fluorescence spectra are recorded using UV-VIS spectrophotometer (Jasco V-570) and Cary Eclipse spectrofluorimeter respectively. The typical form of absorption and fluorescence spectra of the dye Coumarin 540 in three different solvents is given in Fig.2.3 and Fig.2.4.

Fig.2.3 Absorption spectra of C 540 in dioxane, ethanol and dimethyl formamide

Fig.2.4 Fluorescence spectra of C 540 in dioxane, ethanol and dimethyl formamide
Both the absorption spectra and fluorescence spectra exhibit wavelength shift with solvent polarity and the Stoke's shift is also different correspondingly. Since absorption is a property of the ground state and fluorescence that of the excited state with greater dipole moment, both the shifts need not be the same. For a better comparison, the solvent polarity function is calculated taking dielectric constants and refractive indices of pure solvents from literature. The absorption and emission maximum in different solvents are included in Table 2.1. Fig 2.5 shows the Stokes's shift vs $\Delta f$. Three different regions are observed in the plot. Almost a linear relation is found for dipolar aprotic solvents. For polar solvents and dipolar aprotic solvents with high polarity, there is significant red shift in the fluorescence maximum. Upon excitation, the dipole moment of the dye molecule is increased and the dipole–dipole interaction between the solvent and solute molecules will result in the reduction of excited state energy. It is reported that coumarin dye may be quite polar in nature both in the ground and excited states due to the planar intramolecular charge transfer (ICT) state [8-10]. For the non-polar solvent toluene, a deviation is observed from the linear behavior and a blue shift is observed in the peak value of absorption and fluorescence compared to the observed values in other solvents. In nonpolar solvents, the dye may not exist in the polar ICT structure. It is known that the coumarin derivatives prefer to exist in nonpolar structures in nonpolar solvents. Since the dye molecule is much less polar in nature in comparison to the polar ICT structure of the dye, a less value is expected for Stoke's shift in toluene. But the plot of Stokes' shift vs $\Delta f$ shows a comparatively high value. The deviation in the Stokes's shift of the dye is attributed to a conformal change for the dye molecule at its 7-NEt$_2$ group in nonpolar solvents. It is inferred that C 540 exists in a non polar structure, when the 7-NEt$_2$ groups adopts a kind of pyramidal conformation [10-14].
2.3.2 Quantum yield measurements

The most reliable method for recording $\Phi$ is the comparative method of Williams et al. which involves the use of well characterized standard samples with known $\Phi$ values [15]. Here, the assumption made is that the samples with identical absorbance at the same wavelength can be assumed to absorb the same amount of photons. Hence a simple ratio of the integrated fluorescence intensities of the two solutions will yield the ratio of the quantum yields. Knowing the $\Phi$ of the known sample, the $\Phi$ value for test sample can be calculated. The quantum yield of the test sample is calculated from the following equation

$$\Phi_X = \Phi_{ST} \left( \frac{\text{Grad}_X}{\text{Grad}_{ST}} \right) \left( \frac{\eta_X^2}{\eta_{ST}^2} \right)$$

(2.9)
where the subscripts ST and X denote the standard and test samples respectively, $\Phi$ is the fluorescence quantum yield, Grad is the gradient from the plot of the integrated fluorescence intensity vs absorbance and $\eta$ is the refractive index of the solvent. Initially two standard compounds are cross calibrated using the above equation.

For the quantum yield measurements, the absorbance of the samples is determined by taking the samples in a quartz cuvette with 1 cm path length. While recording the absorption spectra care is taken to keep the absorbance of all the samples below 0.1 in order to minimize the effect of re-absorption.

![Fluorescence Intensity](image)

**Fig. 2.6** The fluorescence intensity for various absorbance of C540 (A<0.1 cm$^{-1}$) in DMSO used for Quantum yield calculation.

Rhodamine 6G in ethanol is taken as the reference sample for which the quantum yield is 0.95[16]. For cross calibration, Rhodamine 6G and Rhodamine B in
ethanol are taken as the standard samples. Quantum yield of each sample is calculated relative to the other and values of 0.95 ± 0.01 and 0.65 ± 0.015 are obtained which are in quite match with the literature values of 0.95 and 0.65 for Rh6G and RhB respectively [16]. For the reference sample and test samples the excitation wavelength of choice is 485 nm. For all the fluorescence measurements, the absorbance is selected as quite low (<0.1) at the excitation wavelength. The fluorescence spectra for C 540 in DMSO for different absorbance are given in Fig.2.6. Correction for the background fluorescence of the solvent is done by subtracting the emission spectrum of the solvent from the emission spectrum of the sample and the corrected emission spectrum is used for calculating the area under the curve.

![Graph](image)

**Fig.2.7** Linear plots for emission intensity of dye in two solutions  
a) Ethanol b) MEK C) Reference sample Rh6G in ethanol

The quantum yield of C 540 in different solvents are calculated by plotting the emission intensity vs absorbance which is obtained as straight lines passing through
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the origin (Fig. 2.7). Fluorescence quantum yields estimated for the dye in different solvents are listed in Table 2.1. Though there is no well-established theory to correlate $\Phi$ and $\Delta f$, a linear relationship is found between $\Phi$ and $\Delta f$ with some exceptions. The quantum yield of the dye is found to be very high in highly polar solvents which approach unity in ethanol. A clear deviation in $\Phi$ is observed for non polar solvents which are much less than the value in polar solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Polarity index</th>
<th>$\lambda_{max}$(nm)</th>
<th>$\lambda_{max}$(nm)</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.4</td>
<td>440</td>
<td>483</td>
<td>0.76±0.015</td>
</tr>
<tr>
<td>Dioxane</td>
<td>4.8</td>
<td>452</td>
<td>486</td>
<td>0.8±0.02</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>3.9</td>
<td>452</td>
<td>487</td>
<td>0.85±0.015</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>3.4</td>
<td>461</td>
<td>498</td>
<td>0.98±0.02</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>4.5</td>
<td>462</td>
<td>500</td>
<td>0.97±0.015</td>
</tr>
<tr>
<td>Dimethyl sulfoxide</td>
<td>6.5</td>
<td>469</td>
<td>509</td>
<td>0.96±0.01</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>4.5</td>
<td>458</td>
<td>497</td>
<td>0.97±0.015</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>6.4</td>
<td>464</td>
<td>505</td>
<td>0.94±0.02</td>
</tr>
<tr>
<td>Ethanol</td>
<td>5.2</td>
<td>456</td>
<td>501</td>
<td>0.99±0.015</td>
</tr>
<tr>
<td>Methanol</td>
<td>6.6</td>
<td>458</td>
<td>506</td>
<td>0.91±0.01</td>
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</table>

Table 2.1 Solvent effect on different decay parameters
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2.3.3 Lifetime measurements

Fluorescence lifetime measurements are taken using a time-correlated-single-photon-counting spectrometer (IBH-datastation-UK) with 440 nm nano LED as an excitation source. Instrument response function for the setup is \(~200\) ps at FWHM with a repetition rate of 1MHz. For all the solvents studied, the fluorescence decay curves are found to be double-exponential. For data fitting, the \(\chi^2\) values are close to unity and the distribution of the weighted residuals is quite random among the data channels.

![Fluorescence decay curves of dye in two solvents](image)

**Fig.2.8** Fluorescence decay curves of dye in two solvents a) reference b) toluene c) ethanol

The fluorescence decay values estimated for different solvents are given in Table 2.2. The lifetimes of the dye are comparatively high for solvents in which the quantum yield is high. Fig.2.8 shows the decay curves for the dye in two sample solvents.
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In order to understand more about the de-excitation process, the radiative and nonradiative rate constants for the excited state of the dye are calculated using the relations

\[ k_r = \frac{\Phi}{\tau} \]

\[ k_{nr} = \frac{1}{\tau} - \left( \frac{\Phi}{\tau} \right) \]  

(2.10)

The \( k_r \) and \( k_{nr} \) values estimated for the dye in different solvents are given in Table 2.2. The radiative rates are found to be comparatively high for the dye in solvents which exhibit high quantum yield. On the other hand, for solvents having less quantum yield, the nonradiative rates are found to be high. Usually, the radiative rates are not much different since these rates depend on the extinction coefficient of the dye.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \varepsilon )</th>
<th>( \tau ) (ns)</th>
<th>( k_r ) (ns(^{-1}))</th>
<th>( k_{nr} ) (ns(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>2.4</td>
<td>3.06</td>
<td>0.248</td>
<td>0.078</td>
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<tr>
<td>Dioxane</td>
<td>2.2</td>
<td>3.1</td>
<td>0.258</td>
<td>0.064</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>5.1</td>
<td>3.13</td>
<td>0.272</td>
<td>0.048</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>9.1</td>
<td>3.32</td>
<td>0.295</td>
<td>0.006</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>18.2</td>
<td>3.2</td>
<td>0.303</td>
<td>0.009</td>
</tr>
<tr>
<td>Dimethyl sulphoxide</td>
<td>47.2</td>
<td>3.11</td>
<td>0.308</td>
<td>0.013</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>18.5</td>
<td>3.3</td>
<td>0.294</td>
<td>0.009</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>38.3</td>
<td>3.14</td>
<td>0.299</td>
<td>0.019</td>
</tr>
<tr>
<td>Ethanol</td>
<td>24.3</td>
<td>3.41</td>
<td>0.290</td>
<td>0.0029</td>
</tr>
<tr>
<td>Methanol</td>
<td>33.1</td>
<td>3.2</td>
<td>0.284</td>
<td>0.028</td>
</tr>
</tbody>
</table>

Table 2.2 Solvent effect on different decay parameters
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Life time changes are usually caused by changes in the nonradiative rates resulting from the additional decay routes possible in the solvent environments. The nonradiative rate is found to be high for the dye in nonpolar solvent toluene whose dielectric constant is 2.4. High nonradiative decay rates are also observed for dye in dioxane and butyl acetate whose dielectric constants are low compared to other solvents (2.2 and 5.1 respectively). A higher value of $\varepsilon$ will result in stabilization of the ground and excited states of the dye molecule which may increase the quantum yield [3].

2.4 Photochemical effect

The effect of molecular structure of coumarin derivatives with an amino group in position 7 and the nature of the solvent on the solute/solvent interactions have attracted much attention. The formation of specific hydrogen bonds between coumarin dyes and protic solvents has been considered to explain the spectral shift and internal conversion process. The photochemical aspects of C 540 have been investigated by many researchers. The photochemical reactivity of C540 in halomethane solvents, owing to their physiochemical properties, is also studied upon radiation at 254 nm [17]. Here, we report the photochemical reactivity of C 540 in dichloromethane and chloroform under pulsed excitation at a wavelength of 475 nm.

C 540 dye undergoes a photochemical reaction in these two solvents. Absorbance of the dye solution in the two solvents is taken after irradiating the samples for different time durations which varied up to 30 mts. As the time of excitation increases, a decrease in absorbance is observed for both of the samples with the generation of a new band at higher wavelengths. The intensity of the new band increases with increase in the time of irradiance as shown in Fig.2.9 A and B. For the dye in chloroform, as the time of irradiation increases to 30 mts, a reduction in
absorbance of the new band is observed. This is due to the low stabilization of the excited species by the less polar CHCl₃. Fig 2.9-e shows the reduction in intensity of absorption of the new band which corresponds to an excitation time of 30 mts.

Fig.2.9 Absorption spectra of C 540 after excitation for different timings.
A) in dichloromethane B) chloroform
a) pure b) 5 mt c) 10 mt d) 20mt e) 30 mt

The photoreaction observed in the chloromethanes can be explained in terms of an intermediate exciplex formation. The excited state of aromatic carbons is expected to be involved in a charge transfer interaction with chloromethane through exciplex formation. The intensity of the new band is found to be more in dichloromethane. Due to exciplex formation, the compound exhibits different emission characteristics. The chloromethanes are strong hydrogen bond donors (HBD) and form hydrogen bonds with tertiary amines. The HBD ability of CCl₄ is less compared to CH₂Cl₂. The hydrogen bond formation becomes stronger in the excited state of CH₂Cl₂ due to increasing basicity of the excited dye [17].
The photochemical reactions in dichloromethane and chloroform are found to be reversible to some extent. We have taken the absorbance of the dye in the above two solvents two days after the excitation (Fig. 2.10 A & B). The intensity of the new bands formed by the photochemical reaction have been observed to die out strongly. It is reported that due to the photoreactivity of C 540 in chloromethanes, a C 540 radical cation along with a chloride ion is formed as the end product [17]. This photoproduct is thermodynamically less stable. When the beam of excitation is cut off, two or more C 540 radical cations will exothermally react together to form a more stable dication or dianion. The absorbance of these more stable intermediate products in the two solvents is shown in fig. 2.10 A & B. The new band with a small red shift in absorbance is found to be a stable one. The absorbance of the dye solution taken after one month does not exhibit any noticeable variation. The end product of the photochemical process exhibits a red shifted fluorescence.
2.5 Amplified spontaneous emission (ASE)

2.5.1 Introduction

Amplified spontaneous emission is a phenomenon readily observed in organic dye solution when the sample is excited by intense light pulses. The spontaneously emitted light is amplified through a single pass in the gain medium by stimulating the emission of more photons as it travels down the length. The favorable condition for strong ASE is a high gain medium combined with a long path length in the active material. This usually occurs in a gain medium with long path length either by internal multiple reflections or extended medium [18].

The shape of the medium can impose a preferred direction on the radiation it emits. As shown in Fig.2.11 the spontaneous emission along the long axis may experience a large amplification than that in the other directions producing a beam of ASE with a divergence angle depending on the length of the amplifier. This divergence is related to the length of the amplifier by the relation $L/a$ which is also refereed to as the aspect ratio. The power emitted as fluorescence increases rapidly with gain. As the pump power increases ASE becomes the dominant mechanism. At that point, an intense emission within a solid angle $\Omega$ around the axis of the active material is observed from each end of the rod where $\Omega = a/L^2$. Here $L$ and $a$ are the rod length and the cross sectional area respectively. As a result of refraction at the end faces, the geometrical aperture angle of the material will increase by $n^2\Omega$. As the length of the gain medium increases, the divergence angle decreases and the output beam becomes highly directional (Fig.2.12).
2.5.2 Features of ASE

In contrast to spontaneous emission, ASE possesses certain distinctive features of laser emission such as directionality, spectral narrowing, limited coherence, reduced pulsewidth, a soft threshold, intense beam and saturation of gain [19]. It is highly directional since ASE will build up in the direction of largest gain which is the direction of propagation. ASE accelerates the decay and shortens the output. The gain is the strongest at the wavelength where the cross section for stimulated emission is highest. This leads to narrowed spectral width. The ASE threshold behavior arises from the saturation. If the traveling wave becomes strong enough to extract all the stored energy (I_{SAT}), the output grows linearly with the pump power as observed in an ordinary laser. Since the ASE shows features of laser emission to some extent even in the absence of any external cavity, it is also known as a mirrorless lasing.

2.5.3 Experimental details to study ASE

The amplified spontaneous emission is studied in Coumarin 540 dissolved in methanol. The concentration chosen for the present study is $4 \times 10^{-4}$ M. The ASE studies of the dye solution are conducted by taking the sample solution in a quartz
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cuvette of 1 cm x 1 cm x 3 cm dimensions. The emission spectra are recorded by exciting the sample with 476 nm radiation at which the sample has good absorption. The pump beam is taken from a Quanta Ray MOPO (MOPO 700) pumped by Q-switched Nd:YAG laser which emits pulses of 7 ns duration at 355 nm and at a repetition rate of 10 Hz. A cylindrical lens is used to focus the pump beam in the shape of a stripe on the sample. Due to the high absorption cross section of the dye solution, the pump beam is fully absorbed by the front layer of the sample and it creates a stripe like excited gain medium. A vertical slit is incorporated in the path of the beam between the cylindrical lens and the sample so as to vary the stripe length on the sample. In the present case it is adjusted to a pump beam width of 7 mm. The output is collected from the edge of the front surface of the cuvette using an optical fiber in a direction normal to the pump beam. The emission spectra are recorded with Acton monochromator attached with a CCD camera (Fig.2.13). The emitted beam from the edge of the cuvette is so strong and highly directional that we could collect it even without any focusing.

![Experimental set up to study ASE from C 540 dye solution](image)
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To study the nature of emission from the dye dissolved in methanol, the emission spectra are recorded for various pump intensities starting from 45 kW/cm² keeping the excitation length of the beam as 7 mm. For a pump intensity of 45 kW/cm², the fluorescence spectrum recorded is highly broad with a spectral width of 33 nm. With the increase in pump intensity, the fluorescence emission spectra become narrow and give amplified spontaneous emission (ASE). With a pump intensity of 64 kW/cm², ASE is observed with a spectral width of 8.3 nm. Fig 2.14 shows the spectral narrowing of the emission spectra with pump intensity. The minimum spectral width obtained from the dye in methanol is 6.2 nm for a pump intensity of 95 kW/cm².

![ASE intensity vs pump intensity for C 540 dye solution in methanol in kW/cm²](image)

**Fig.2.14 ASE intensity vs pump intensity for C 540 dye solution in methanol in kW/cm²** a) 50 b) 64 c) 80 d) 95
2.6 Laser Emission from dye solution

When the pump intensity is increased beyond 95 kW/cm², a periodic modulation structure is observed in the emission spectrum. At higher pump intensities, well resolved equally spaced resonant modes are observed which could be attributed to highly directional laser emission (Fig.2.15). Occurrence of similar resonant modes was reported by Yokoyama et al. [20] in a dye medium added with dendrimers. By encapsulating the dye, the dendrimer reduced the self aggregation and molecular quenching of the dye at higher concentrations and thereby increased its gain. They had related the spacing of the modes to the penetration depth of the beam in the medium. In order to verify the validity of this explanation, in our investigations, the emission spectra are recorded for various concentrations of the dye ranging from $1 \times 10^{-4}$ to $8 \times 10^{-4}$ M which corresponds to different penetration depths. The same mode structure is repeated with more or less equal spacing and a red shift in the spectra (Fig.2.16). This confirms that the mode spacing is not directly related to penetration depth.

Fig.2.15 Lasing spectrum of C 540 solution in methanol
Resonant modes with spacing 1.62 nm
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Further investigations are done by changing the excitation length of the pump beam. For a dye solution of concentration $4 \times 10^{-4}$ M and pump intensity of 150 kW/cm², the emission spectra showed the features of ASE for an excitation length of 2 mm. The spectral width is again around 7 nm for this length but when the excitation length is further increased, the narrowed spectrum showed well resolved resonant peaks with equal spacing.

![Fig. 2.16 Lasing spectra in methanol for two concentrations. (a) $1 \times 10^{-4}$ M (b) $8 \times 10^{-4}$ M](image)

For higher excitation lengths, the modes become prominent with very high output intensity. The emission spectrum observed in the dye dissolved in methanol for an excitation length of 4 mm is exactly similar to the one observed for an excitation length of 7 mm (Fig. 2.15). An increase in pump intensity resulted in the same mode
structure with the same mode spacing. However the less prominent modes increased in their strength at higher pump intensities.

The occurrence of mode structure from dye solution was also reported by Guang S et al. where the laser emission was attributed to the Fresnel reflection feedback from the two parallel optical windows of the cuvette [21]. Considering the two surfaces of the windows and the gain medium, a multi-cavity structure can be formed between the two plane parallel walls of the cuvette. (Fig.2.17). The resonant conditions for the four subcavities formed between the two windows can be written as

\[
\begin{align*}
2[nL + n'(l_1 + l_2)] &= K_1 \lambda \\
2nL &= K_2 \lambda \\
2(nL + n'l_2) &= K_3 \lambda \\
2(nL + n'l_1) &= K_4 \lambda
\end{align*}
\]  
\tag{2.11}

Fig.2.17. Subcavities formed between the walls of the cuvette
where $L$ is the length of the dye medium, $n'$ is the refractive index of quartz, $l_1$ and $l_2$ are the thickness of the two parallel windows of the cuvette, $n$ is the refractive index of the gain medium and $K_1, K_2, K_3$ and $K_4$ are arbitrary integers [21].

The resonance condition providing the widest spectral periodicity is obtained by the subtraction of the last two equations.

$$2n' (l_2-l_1) = K \lambda$$

where

$$K = (K_3-K_4)$$

This equation is equivalent to the maximum transmission condition of a Fabry-Perot etalon. Thus the partial reflections from the windows of the cuvette produce the effect of a Fabry-Perot etalon and provide the optical feedback necessary for laser emission.

For the lasing spectrum the wavelength spacing between the different modes is given by

$$\Delta \lambda = \lambda^2 / 2n' (l_2-l_1)$$

where $\lambda$ is the average lasing wavelength. Substituting for refractive index of quartz, $n'$ as 1.46, the average lasing wavelength $\lambda$ as 515 nm and the mode spacing $\Delta \lambda$ obtained from our studies with a cuvette of 1 cm pathlength as 1.62 nm, $l_2-l_1$ is estimated as 56 $\mu$m. In order to check the validity of the above conclusion, the thickness of the windows is accurately measured using a microscope with a CCD monitor and a micrometer and the $l_2-l_1$ value is found to be around 50-60 $\mu$m at different positions of the cuvette which is in close agreement with the observed value. To confirm this result, emission spectrum of the same dye solution in a cuvette of pathlength 0.5 cm is taken. Fig.2.18 shows the mode structure observed with a different spacing of 0.92 nm. Substituting for the peak emission as 514 nm, the thickness difference $(l_2-l_1)$ of the parallel walls is obtained as 98 $\mu$m. The measured
value of \((l_2-l_1)\) for this 0.5 cm cuvette is \(\sim 100 \, \mu\text{m}\) which confirms the existence of a Fabry-Perot optical cavity effect due to the reflections from the walls of the cuvette.

The incidence angle of the pump beam is varied in order to check whether the deviation from the cavity axis could remove the mode structure. In contradiction to the previous report, we could still observe the mode structure when the cuvette is tilted to a certain angle from the direction of incidence [20, 21]. Due to the high gain of the dye medium, even a portion of the reflection from the windows along the cavity axis is sufficient enough to produce the lasing of the cavity.

![Laser emission spectrum of dye solution in a cuvette of 0.5cm. Mode spacing 0.92nm](image)

**Fig.2.18** Laser emission spectrum of dye solution in a cuvette of 0.5cm. Mode spacing 0.92nm

### 2.6.1 Solvent effect on laser emission

In the second part of the study, the features of the mode structure are employed to investigate the effect of solvents on the laser emission of the dye. Detailed investigations are done with ten solvents whose photophysical properties are already
studied in the first part of this chapter. Both polar protic and dipolar protic solvents exhibited very high quantum yield. C 540 dye in ethanol has a quantum yield of ~ 1 and toluene which is a nonpolar solvent gives the least value of 0.76. Though a direct correlation between Φ and polarity could not be observed, generally the Φ values are found to be high with solvents of high polarity.

The emission spectra are recorded for all the solvents with a fixed dye concentration of $4 \times 10^{-4}$M. All the experimental conditions remained the same throughout the investigations. Interesting results are observed and these show a correlation between the quantum yield of the dye in different solvents and the mode structure observed due to cavity lasing. With ethanol, which has a quantum yield of ~ 1, the emission spectrum has 12 modes with a total spectral width of 7 nm (Fig.2.19). With methyl ethyl ketone (MEK) having a quantum yield of 0.97, the spectral width is 5.6 nm with number of modes equal to 9 (Fig.2.20). For butyl acetate with a quantum yield of 0.85, the number of modes is reduced to 5 (Fig.2.21). In the case of toluene with a quantum yield 0.76, no mode pattern is observed. Toluene gives only an ASE spectrum with a total spectral width of 3.4 nm (Fig.2.22). The dye medium is found to be sensitive to the polarity of the solvent in its nature of laser emission. In general, the gain of the medium increases with increase in polarity. But the laser emission is observed to be high in ethanol which is less polar compared to methanol. Table 2.3 gives a comparison of solvent polarity, refractive index, quantum yield and number of modes observed in the emission spectrum.
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Fig. 2.19 Spectrum of Laser emission from C540 dye solution in ethanol. Mode spacing 1.65 nm

Fig. 2.20 Spectrum of Laser emission from C 540 dye solution in MEK. Mode spacing 1.75 nm
Fig. 2.21 Laser emission spectrum of dye solution in butyl acetate. Mode spacing 1.69 nm

Fig. 2.22 ASE spectrum of dye solution in toluene

Though Table 2.3 shows correlation between number of modes and the quantum yield of the dye in different solvents, some discrepancy is noticeable in the
Photophysics, ASE and Lasing of C 540 Dye

case of a few high polarity solvents. In the case of DMF, the number of modes is less and for DMSO, no laser emission is observed though both of them have high quantum yields. Cyclohexanone also shows the same result which is a less polar solvent. All these solvents have a comparatively high refractive index which is close to the refractive index of quartz. The reflection coefficient of the surfaces is also an important parameter in determining the lasing threshold. For a gain medium in a resonator cavity with length L and end face reflectivities R_1 and R_2, oscillations will build up when the loop gain R_1 R_2 exp(2gL) > 1 [18]. The reflectivity at the end face is given by

\[ R = \left( \frac{n_1 - n_2}{n_1 + n_2} \right)^2 \] (2.14)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Nature</th>
<th>Polarity Index</th>
<th>Ref. Index</th>
<th>Q.yield</th>
<th>No.of modes</th>
<th>Rx10^-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>pp</td>
<td>5.2</td>
<td>1.36</td>
<td>0.99</td>
<td>12</td>
<td>125.7</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>dap</td>
<td>3.4</td>
<td>1.42</td>
<td>0.98</td>
<td>10</td>
<td>19.29</td>
</tr>
<tr>
<td>Methyl ethyl ketone</td>
<td>dap</td>
<td>4.5</td>
<td>1.376</td>
<td>0.97</td>
<td>9</td>
<td>87.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>pp</td>
<td>6.6</td>
<td>1.326</td>
<td>0.91</td>
<td>7</td>
<td>231.3</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>dap</td>
<td>3.9</td>
<td>1.394</td>
<td>0.85</td>
<td>5</td>
<td>53.4</td>
</tr>
<tr>
<td>Dimethyl formamide(DMF)</td>
<td>dap</td>
<td>6.4</td>
<td>1.431</td>
<td>0.94</td>
<td>4</td>
<td>10.06</td>
</tr>
<tr>
<td>Dioxane</td>
<td>dap</td>
<td>4.8</td>
<td>1.42</td>
<td>0.8</td>
<td>3</td>
<td>19.29</td>
</tr>
<tr>
<td>Toulene</td>
<td>np</td>
<td>2.4</td>
<td>1.494</td>
<td>0.76</td>
<td>-</td>
<td>13.24</td>
</tr>
<tr>
<td>Dimethyl sulphoxide(DMSO)</td>
<td>dap</td>
<td>6.5</td>
<td>1.478</td>
<td>0.96</td>
<td>-</td>
<td>3.75</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>dap</td>
<td>4.5</td>
<td>1.45</td>
<td>0.97</td>
<td>-</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 2.3 Comparison of polarity, quantum yield, refractive index and number of modes for different solvents. pp-polar protic, dap-dipolar aprotic, np - nonpolar
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The absence of lasing modes in the above solvents can be attributed to the reduced value of the reflection coefficients. For example, cyclohexanone with a refractive index of 1.45 acts as an index matching medium yielding a negligible reflection coefficient \( R = 1.181 \times 10^{-5} \) and laser emission is not observed with such a small feedback. In the case of ethanol, where the difference in refractive indices is comparatively large giving \( R = 125.7 \times 10^{-5} \), a good lasing spectrum is obtained at a low threshold pump beam energy. It is also to be noted that dichloromethane with its rather low reflection coefficient of \( 19.29 \times 10^{-5} \) exhibits a comparatively large spectral width and a good number of modes, presumably due to its high value of \( \Phi \). For a comparison, the reflectivity at the end faces for different solvent media is also included in Table 2.3. The lasing behaviour of the gain medium is explicit from the nature of the emission spectrum observed. A correlation is explicit between the gain of the lasing medium in different solvent environments and the spectral width of emission and correspondingly the mode structure exhibited by it.

As we have seen earlier, C 540 dye in dichloromethane is photochemically reactive. Excitation for a short duration will certainly reduce its quantum yield. Naturally we could expect a change in the emission spectrum and the number of modes exhibited by it. The observed result is in confirmation with the above assumption. The emission spectrum is recorded after exciting the dye in dichloromethane for a duration of 30 minutes. The sample which exhibited a broad emission spectrum with a good number of modes before photochemical reaction could give only a narrow spectrum without any mode-structure. Fig.2.23 gives a good comparison of the relation between gain and the mode structure exhibited by the samples. Here, the red shift observed in the emission spectrum denotes the change in fluorescence of the sample due to photochemical reaction.
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The emission spectrum of rhodamine 6G, the best known of all laser dyes, is also recorded in methanol keeping the absorbance the same as that of C 540 dye in methanol. The emission spectrum exhibits only 2 modes with a total spectral width of 2.4 nm whereas the emission spectrum of coumarin has a total spectral width of 5 nm with 7-8 modes (Fig.2.24). Even though the quantum yield of C540 in methanol is slightly lower than that of Rh6G, the spectral width for C 540 is found to be greater than that of Rhodamine 6G which is the well known efficient laser dye.

Fig.2.23 Emission from C 540 dissolved in a) dichloromethane b) after photochemical reaction
2.6.2 Efficiency of the laser gain medium

The lasing efficiency is an important parameter concerned with any laser system. It marks the efficiency of the system in converting the input pump energy to useful output energy. It is defined as the ratio of the energy of the dye laser output to the energy of the pump radiation incident on the sample surfaces. We have determined the lasing efficiency of the gain medium in certain solvents. Since the absorption cross section is high for the dye solution, the pump energy is fully absorbed by the front layers of the sample itself. The input and output energy is measured using energy ratio-meter (Laser probe Inc.) with RjP 735 probes. Since light is emitted in both directions, the measured energy is multiplied by two to get the total emission. For the dye in methanol medium the efficiency observed is 32% for a pump energy of 800 µJ. This value takes into account of all losses due to reflection, scattering, diffraction etc.

Fig. 2.24 Emission spectrum in methanol (a) Coumarin 540, mode spacing 1.65 nm (b) Rhodamine 6G, mode spacing 2.01 nm
2.7. Frequency up-conversion emission

Recently, efforts are going on to design frequency up-converted laser devices which can produce a shorter- wavelength output in the visible or UV region. This can be achieved by pumping the gain medium with a longer-wavelength input using mainly IR sources. Frequency up-conversion is based on two photon absorption process. Here the excitation of the gain medium occurs by the simultaneous absorption of two photons of longer- wavelength.

Fig.2.25 Frequency up-converted emission from C 540 dye solution in methanol exciting by 790 nm radiation.

Two photon induced emission studies are carried out in C 540 dye solution in methanol. The gain medium is excited with a radiation of 790 nm from a mode-locked Ti: Sapphire femtosec laser (Spectra Physics) with pulses of 80 fs duration and average input power of 2.3 W. Emission spectrum recorded shows the peak at 515 nm with a FWHM of 44 nm.
2.8. Conclusions

The fundamental photophysical properties of C 540 are investigated in detail in different solvent environments. The quantum yield and lifetime measurements are done to compare the solvent effect in radiative and nonradiative decay mechanisms of the dye. Coumarin 540 dye exhibited significant quantum yield in certain solvents. Hence the ASE and lasing characteristics are investigated in different solvent media. Laser emission is observed from dye solution taken in a quartz cuvette. The subcavities formed between the windows of the cuvette produced the effect of a Fabry-Perot optical cavity resulting in well resolved equally spaced resonant modes. The mode spacing is related to the difference in thickness of the parallel walls of the cuvette.

The features of the mode structure in the emission spectra are employed to study the effects of solvents on laser emission of the dye. The number of modes exhibited by the emission spectra of the dye solutions is correlated to the quantum yield in the respective solvents and to their refractive indices. The observation of mode structure is a clear evidence of laser emission form C 540 dye solution.
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References

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