Chapter 6

Nonlinear characteristics of Coumarin 540

"I start where, the last man left out." Thomas Edison.

Abstract

Open aperture Z scan studies carried out to investigate the nonlinear properties of C 540 dye solution and dye doped polymer matrices are presented in this chapter. Nonlinear absorption studies are performed at a two photon resonance wavelength of 590 nm and at a near resonance wavelength of 650 nm where the absorption is comparatively less. Along with the dye solution in toluene, thin films of C 540 dye doped in PMMA, polystyrene and PVC are the samples used for the investigations. The optical limiting behaviour of the dye doped films is also discussed.

6.1 Introduction

Nonlinear optics is an important branch of science which took birth with the advent of highly intense laser systems. It is concerned with the study of the phenomena that result from highly intense light induced modifications in the optical properties of the materials. The field of nonlinear optics (NLO) explores the coherent coupling of two or more electromagnetic fields in a nonlinear medium [1-3]. The discovery of the important nonlinear effect, the second harmonic generation (SHG) introduced a new branch of experimental investigation in the area of laser-matter interaction. Later on many interesting nonlinear optical effects are discovered which have significant
applications in the field of telecommunication, optical storage, optical switching, optical power limiting etc[4-8].

The nonlinear effects are broadly classified into two categories. One is concerned with frequency conversion and the other with optical modulation. Sum and difference frequency generation comes under the frequency conversion process and Kerr effect, self phase modulation etc. are examples of optical modulation processes. New frequency generations are due to the oscillations of induced nonlinear polarization at appropriate frequencies. In optical modulation process, light modulates the properties of the medium such as the refractive index [9-10].

Study of nonlinear effects leads us to a new understanding of fundamental light-matter interaction. Implementation of the various NLO effects in the appropriate areas of technologies like optical communication, optical switching, optical data storage demands a detailed knowledge of the NLO processes and their dynamics. Nonlinear optics is observed with lasers which have high degree of spectral purity, coherence and directionality with which atoms and molecules can be irradiated with an electric field that is comparable to interatomic field. These fields are of the order of $10^{10}$ Vm$^{-1}$ corresponding to an incident light of $\sim 100$GWcm$^{-2}$. In practice it is possible to observe many nonlinear optical effects at much lower intensities due to enhancement of the nonlinear effect. If the induced dipoles in the medium oscillate coherently, the field that they radiate can add together constructively to produce a much larger intensity. This condition is called phase matching and is often used to enhance nonlinear effects. If the frequency of the light lies near the internal resonance frequency of the oscillating dipoles, there is resonance enhancement of the nonlinearity. Multiphoton process is an example of such resonance enhancement [11].

The property of optical nonlinearity can be well understood by considering the dependence of dipole moment per unit volume or polarization $P(t)$ of the material...
on the strength $E(t)$ of the applied electric field. In the case of linear optics the induced polarization has a linear dependence on the electric field strength which can be described as

$$P(t) = \chi^{(1)} E(t) \quad (6.1)$$

where the constant of proportionality $\chi$ is the linear optical susceptibility. When the electric field is significantly high, nonlinear interaction occurs and the observed nonlinear optical effects can be described by expressing the polarization $P(t)$ as a power series in the field strength $E(t)$ as

$$P(t) = \chi^{(1)} E(t) + \chi^{(2)} E^2(t) + \chi^{(3)} E^3(t) + \ldots \quad (6.2)$$

$$= P_1(t) + P_2(t) + P_3(t) + \ldots \quad (6.3)$$

where $\chi^{(1)}$, $\chi^{(2)}$ are the second and third order nonlinear optical susceptibilities respectively. The second and third order polarizations can be expressed as

$$P^2(t) = \chi^{(2)} E^2(t) \quad (6.4)$$

$$P^3(t) = \chi^{(3)} E^3(t) \quad (6.5)$$

The physical processes that occur due to second and third order polarizations are distinct from each other. Second order nonlinear effects occur only in noncentrosymmetric crystals. They are crystals which do not possess inversion symmetry. Liquids, gases, amorphous solids like glass and even many crystals display inversion symmetry and the $\chi^{(2)}$ value vanishes for such media and consequently they cannot exhibit second order nonlinear optical effects. On the other hand third order nonlinearity which is described by $\chi^{(3)}$ can occur both for centrosymmetric and noncentrosymmetric media. Third order NLO effects are particularly interesting since
they have great technological relevance and these effects are present in varying measure of strength in all materials irrespective of symmetry of materials. The third order optical susceptibility is considered to be a complex quantity having both real and imaginary components. $\chi^{(3)} = \chi_R^{(3)} + i\chi_I^{(3)}$. The real and imaginary parts are related to $\gamma$ and $\beta$ respectively where $\gamma$ is the nonlinear refractive index in $\text{cm}^2\text{W}^{-1}$ and $\beta$ is the nonlinear absorption coefficient and is defined as $\alpha(I) = \alpha_0 + \beta I$. The nonlinear refractive index $\gamma$ is one of the simplest quantities derived from $\chi^{(3)}$ and is a very complicated one in its most general form [2-4].

6.2 NLO properties of organic molecules

Since no symmetry requirement exists for the occurrence of third order nonlinear optical effects in materials, different kinds of materials like liquids, glasses, crystals and thin films exhibit these effects. Report of strong SHG in organic molecule led to intense effort to develop new organic materials for nonlinear effects. During the past two decades lots of investigations were done to develop materials with large third order nonlinearity and ultrafast response times for their potential applications in the area of science and engineering [4-7]. A variety of materials have been experimented for various NLO applications which include conjugated polymers, semiconductors, quantum dots, organic molecules, sol-gels, dye aggregates, guest-host systems, organic composites etc. During 1980s it became evident that organic materials can be a better choice for use in nonlinear optical applications. Organic chromophores generally exhibit extremely high and fast nonlinearities, much better than those exhibited by inorganic materials. Due to the versatility of organic synthesis, their nonlinear optical properties can be tailored depending on the desired applications.

In contrast to inorganic materials which consist of covalent or ionic bond of atoms, organic materials are based on independent molecules and characterized by
weak intermolecular interactions. The NLO property in these molecules is due to the virtual electron excitation occurring in the individual molecular or polymeric units. Organic dyes and polymeric materials possess lower dielectric constants and faster response time. The nature of π electron bonding sequence, the substitution of alternate atoms into the conjugate structure etc. affect the dipole moment and optical susceptibility. In organic materials large charge separation can be achieved through the easy delocalization of the π electron cloud, leading to very large and fast nonlinearity since it requires only electronic motion which could be in few femtoseconds. Moreover, these chromophores are easily amenable to structural modifications and possess tremendous applications [10]. The applications of organic molecules are related to two different nonlinear effects exhibited by the molecules. The optical limiting systems are related to the multiphoton absorption whereas signal processing applications rely upon the nonlinear refractive index change.

6.3 Nonlinear absorption (NLA)

The amount of light absorbed by any absorbing medium increases linearly with input intensity and is termed as linear absorption. But an intense monochromatic radiation from a laser can induce profound changes in the optical properties of the materials. While the linear absorption coefficient is expressed as a function of the excitation wavelength, at significantly high beam intensity, the absorption coefficient is expressed as function of wavelength and intensity as $\alpha(I,\lambda)$ and is termed as non linear absorption. At sufficiently high intensities the probability of a material absorbing more than one photon before relaxing to the ground state is greatly enhanced. Other than two or more photon absorption, many other complicated phenomena like population redistribution, complicated energy transitions in complex molecular systems and the generation of free carriers are accompanied by the intense
optical fields. The effects observed due to these phenomena are saturable absorption (SA) and reverse saturable absorption (RSA).

The nonlinear process associated with real energy level is the saturable absorption. In this process a light beam which is highly absorbed by the material when it is of low intensity, will pass through the medium without any absorption when it is highly intense. Here, the absorption cross section \( \alpha(I) \) decreases with intensity. On the other hand, when the absorption cross section increases with intensity, the system will be less transmissive when excited. This gives the opposite effect of SA and the phenomenon is termed as reverse saturable absorption\[1,12\].

The two absorptive mechanisms resulting in RSA are the two or multiphoton absorption and the excited state absorption. Two photon or multiphoton absorption involves a transition from the ground state of a system to a higher lying state by the simultaneous absorption of two or more photons from an incident radiation. This process involves different selection rules than those of single photon absorption.

When the incident intensity is well above the saturation intensity, the excited state can become significantly populated. The excited electrons can rapidly make a transition to higher excited states before it eventually makes transition back to the ground state. In organic molecules, transitions are possible to higher energy singlet and triplet manifolds. Depending on the pulse duration, pump intensity and wavelength, the excited electrons from the first excited singlet state \( S_1 \) can make transition to higher excited singlet states \( S_n \) or from the \( T_1 \) to \( T_n \) states in the triplet manifold. This is known as the excited state absorption (ESA). When the cross section for TPA or ESA is greater than that of linear absorption, reverse saturable absorption occurs. It is observable when the incident beam intensity is sufficiently high to deplete the ground state significantly \[1-3\].
6.4 Open aperture Z-Scan to Study NLA

The Z-scan technique is a simple and sensitive single beam method to measure the sign and magnitude of both real and imaginary part of third order nonlinear susceptibility $\chi^{(3)}$. The experiment uses a Gaussian beam from a laser and the transmittance of the sample is measured as the sample is moved along the propagation direction of a focused beam. In an Z-scan measurement, it is assumed that the sample is thin and the sample length is much less than the Rayleigh's range $z_0$ which is given by

$$z_0 = \frac{k\omega_0^2}{2}$$

(6.6)

where $k$ is the wave vector and $\omega_0$ is the beam waist. This is essential to make sure that the beam profile does not vary appreciably inside the sample. The refractive nonlinearity is obtained by measuring the transmittance through a finite aperture in the far field as a function of the sample position $z$ from the focal plane. This is the closed aperture Z-scan technique by which the sign and magnitude of nonlinear refractive index $n_2$ can be determined. In this method, the phase distortion suffered by the beam while propagating through the nonlinear medium is converted into corresponding amplitude variation [13-15].

The absorptive nonlinearities are determined by the open aperture Z-scan technique where the entire light is collected by removing the aperture from the experimental setup. Since Z-scan measurements are very sensitive to nonlinear refractive index effects that will spread the transmitted beam, care must be taken to collect the whole transmitted energy. Nonlinear absorption can produce thermal lensing in some cases which may also lead to strong defocusing of the beam. When the entire light is collected, the throughput is sensitive only to nonlinear absorption.
The Z-scan graphs are normalized to linear transmittance at large values of z. Thus the refractive and absorptive nonlinearities can be studied by performing the Z-scan measurements with and without an aperture [16-17]. Since the desired pump beam quality could not be achieved, we have carried out only the open aperture Z-scan measurements in the present case.

6.5 Theory of open aperture Z-scan technique

When the absorption coefficient of a medium has a nonlinear dependence on laser beam intensity, one can use the relation

$$\alpha(I) = \alpha_0 + \beta^{(2\omega)} I \quad (6.7)$$

where $\alpha_0$ is the linear absorption coefficient and $\beta^{(2\omega)}$ is the two photon absorption coefficient of the medium. In the case of three photon absorption, the dependence of the absorption coefficient on the laser radiation intensity can be represented as

$$\alpha(I) = \alpha_0 + \beta^{(2\omega)} I + \beta^{(3\omega)} I^2 = \alpha_0 + \beta_{\text{eff}} I \quad (6.8)$$

where $\beta^{(3\omega)}$ is the three photon absorption coefficient and $\beta_{\text{eff}}$ is the effective nonlinear absorption coefficient. For the measurement of nonlinear absorption coefficient, an open aperture Z-scan configuration is used. In the closed aperture Z-scan measurements, the sensitivity of the experiment to refractive nonlinearities is entirely due to the aperture. When the aperture is removed and the entire transmitted light is collected by the detector, it is sensitive only to the absorptive nonlinearities. The transmitted light is not sensitive to the phase variations. The intensity dependent nonlinear absorption coefficient $\alpha(I)$ can be written in terms of the linear absorption coefficient $\alpha$ and the effective nonlinear absorption coefficient $\beta_{\text{eff}}$ due to TPA or ESA.
\[ \alpha(I) = \alpha_0 + \beta_{\text{eff}} I \]  \hspace{1cm} (6.9)

The irradiance at the exit surface of the sample can be written as

\[ I_r(z, r, t) = \frac{I_{(z, r, t)} e^{-\alpha_0 l}}{1 + q(z, r, t)} \]  \hspace{1cm} (6.10)

where

\[ q(z, r, t) = \beta_{\text{eff}} I(z, r, t) L_{\text{eff}} \]  \hspace{1cm} (6.11)

\( L_{\text{eff}} \) is the effective length and is given in terms of sample length \( l \) and \( \alpha_0 \) by the relation

\[ L_{\text{eff}} = \frac{(1 - e^{\alpha_0 l})}{\alpha_0} \]  \hspace{1cm} (6.12)

The total power transmitted \( P(z, t) \) is obtained by integrating equation 6.10 over \( z \) and \( r \) and is given by

\[ P(z, t) = P_1(t) e^{-\alpha_0 l} \frac{\ln[1 + q_0(z, t)]}{q_0(z, t)} \]  \hspace{1cm} (6.13)

\( P_1(t) \) and \( q_0(t) \) are given by the equations

\[ P_1(t) = \frac{\pi \omega_0^2 I_0(t)}{2} \]  \hspace{1cm} (6.14)

\[ q_0(z, t) = \frac{\beta_{\text{eff}} I_0(t) L_{\text{eff}} z_0^2}{z^2 + z_0^2} \]  \hspace{1cm} (6.15)

For a pulse of Gaussian temporal profile, equation 6.13 can be integrated to give the transmission as
The nonlinear absorption coefficient is obtained by fitting the experimental data to equation 6.16.

6.6 Experimental setup

The experimental setup for the transmittance measurement as a function of incident intensity is shown in Fig.6.1. A Gaussian beam is employed for the measurements. Using a single beam in tight focus geometry, the transmittance of the nonlinear medium is collected as a function of the sample position $z$ measured with respect to the focal plane. The excitation wavelength used is 590 nm taken from a Quanta Ray MOPO (MOPO 700) pumped by Q-switched Nd:YAG laser at 355 nm that emits pulses of 7 ns duration at a repetition rate of 10 Hz. Spatially filtered input beam is focused using an achromatic lens of focal length 20 cm. The lens produces a beam waist of $1/e^2$ radius of 47 $\mu$m at 590 nm. The corresponding Rayleigh range ($z_0$) is 11.75 mm. The sample is taken in a 1 mm cuvette to ensure that the thin lens approximation is satisfied where the beam dimension does not change at the entrance and exit side of the sample. While the input energy is kept constant the medium experiences a different incident field at different positions of $z$ when it is scanned across the focus using a motorized translation stage. The ratio of the transmitted and incident energies is measured using energy ratio-meter (Laser probe Inc.) with RjP735 probes. The complete experimental setup is automated using Labview. It is assumed that the focus corresponds to sample position $z = 0$. The typical Z-scan data with fully open aperture is insensitive to nonlinear refraction; therefore the data is expected to be symmetric with respect to focus. For material with two photon absorption or ESA there is a minimum transmittance at the focus (valley) and for saturable absorption
there is a maximum transmittance at the focus (peak). The measured nonlinear transmittance is normalized with respect to the linear transmittance.

![Z-scan experimental setup](image)

**Fig. 6.1** The Z-scan experimental setup in which the ratio \( D_2/D_1 \) is recorded as a function of the sample position \( Z \)

### 6.7 Nonlinear absorption in C 540 dye solution

The nonlinear absorption studies in C 540 dye solution is performed by taking the dye solution at a concentration of \( 2 \times 10^{-4} \text{ M} \). The solution is taken in a 1 mm thick quartz cuvette. The open aperture Z-scan measurements are done to evaluate the nonlinear behavior of the dye solution. The excitation wavelengths chosen to study the nonlinear absorption in the dye doped samples are 590 nm corresponding to the two photon resonance of the absorption peak 295 nm and 650 nm which is at near resonance. At both these wavelengths the absorbance of the sample is less than 0.01(Fig.6.2). The dye in different solvents including polar, dipolar and nonpolar are tested for the nonlinear absorption but only toluene gives a good result which is a nonpolar one.
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Fig. 6.2 Absorption spectrum for C-540 dye in toluene

The open-aperture Z-scan measurements are done at various input fluences. The Z-scan plot exhibits a valley at the focal point due to the minimum transmittance which steadily increases on both sides of the focus. This behavior is typical of reverse saturable absorption. The large power density available at the focus induces nonlinear effects in the sample by which excited state absorption (ESA) occurs from $S_1$ to higher $S_n$ states or a simultaneous absorption of two (TPA) or more photons. This nonlinear absorption results in a reduced transmittance. Typical open aperture Z-scan curves of the C-540 dye solution in toluene with normalized transmittance is shown in Fig. 6.3. It shows the nonlinear absorption of the dye solution for different input fluences at a wavelength of 590 nm. The depth of the valley increases with increasing fluence level. No cross over from reverse saturable absorption to saturable absorption occurs with increase in input fluence as reported in the case of Rhodamine B dye [18-19].
Fig. 6.3 Open aperture Z-scan plots at different energy densities for C 540 dye in toluene. Excitation wavelength length 590 nm.

Z-scan experiments are repeated at a wavelength of 650 nm which is the edge of the absorption band. No significant variation in the RSA behavior is observed. Fig. 6.4 shows the plot for the dye solution at a wavelength of 650 nm. The nonlinear effects due to high power density can result in ESA or TPA. The predominance of any of these two absorption processes depends on many factors like the lifetime of various excited states of the molecule, the rate of intersystem crossing and pulse width of the laser source used.

The values of nonlinear absorption coefficient $\beta_{\text{eff}}$ for the dye solution can be extracted by fitting the experimental open-aperture Z scan data to the equation 6.16. The constant $q_0$ is obtained as the fit parameter and knowing the values of $I_0$, $z_0$ and $L_{\text{eff}}$ the nonlinear absorption coefficient can be evaluated. The experiments are done at various energy densities and the nonlinear absorption coefficient $\beta_{\text{eff}}$ is evaluated for the dye solution for the two wavelengths of excitation. The calculated values of $\beta_{\text{eff}}$ is
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given in Table. 6.1. Somewhat similar values are obtained for absorption coefficients corresponding to the two excitation wavelengths 590 nm and 650 nm. The observed RSA can be attributed to resonant two photon absorption along with some ESA effects.

![Fig. 6.4 Open aperture Z-scan plots for C 540 dye in toluene.](image)

Excitation wavelength length 650 nm

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Irradiance GW/cm²</th>
<th>$\beta_{eff}$ cm GW⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>590</td>
<td>1.5</td>
<td>0.8</td>
</tr>
<tr>
<td>590</td>
<td>2.4</td>
<td>1.6</td>
</tr>
<tr>
<td>650</td>
<td>1.25</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 6.1 Values of irradiance and $\beta_{eff}$ for C 540 dye in toluene for two wavelengths.
6.8 Nonlinear absorption in Dye doped polymer films

The nonlinear absorption and Z-scan studies are carried out in dye doped polymer films as well. PMMA, polystyrene and PVC are used as the polymer matrices. The method of preparation is described in chapter 3. The concentration for the dye doped film prepared for Z-scan studies is $2 \times 10^{-4}$ M. The thickness of the films used for the studies varied from 10 - 150 microns. Since the variation of the excitation wavelength exhibited no significant change in the absorption coefficient for the dye solution, Z-scan studies are performed only at 590 nm. The Z-scan measurements are carried out at various fluence levels for the different dye doped polymer matrices. All of them exhibit the typical RSA behavior with a transmittance minimum at the focus. Fig 6.5 and 6.6 show the nonlinear absorption plots exhibited by the dye doped in PMMA and polystyrene solid matrices. For a better comparison of the nonlinearity of the dye doped polymer matrices, the nonlinear absorption coefficients are calculated by fitting the experimental data to the equation as in the case of the dye solution. The measured values of $\beta_{\text{eff}}$ and irradiance $I_0$ for different dye doped polymer matrices are given in Table 6.2. From the table, it is clear that $\beta_{\text{eff}}$ is higher for the dye doped polystyrene films compared to the other two polymer matrices.
Fig. 6.5 Open aperture Z scan curves for C 540 doped PMMA films at three different irradiances
a) 805 MW/cm$^2$ b) 985 MW/cm$^2$ c) 1850 MW/cm$^2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness of film (μm)</th>
<th>Irradiance (MW/cm$^2$)</th>
<th>$\beta_{\text{eff}}$ (cmMW$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dye doped PMMA</td>
<td>190</td>
<td>746</td>
<td>0.05</td>
</tr>
<tr>
<td>Dye doped Polystyrene</td>
<td>30</td>
<td>400</td>
<td>6.35</td>
</tr>
<tr>
<td>Dye doped PVC</td>
<td>14</td>
<td>573</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Table 2: Values of irradiance and $\beta_{\text{eff}}$ for different dye doped polymer matrices.
Fig. 6.6 Open aperture Z scan curves for C 540 doped Polystyrene films at different irradiances
a) 322 MW/cm² b) 530 MW/cm²

6.9 Optical limiting

Optical limiters are devices which make use of the nonlinear absorption properties of materials. They are widely used for optical sensor protection including human eyes from intense beam of laser light [20-22]. They display a decrease in transmittance with increase in intensity or fluence of light. There will be a linear transmittance up to a threshold value of incident intensity. Beyond this threshold value the optical limiters exhibit an abrupt change in transmittance and the output remains a constant in spite of increase in incident intensity. This critical value of the input intensity is termed as the threshold of the device. The optical limiting results from the absorptive nonlinearity of the material which can be due to TPA or ESA.
6.10 Optical limiting in dye doped polymer films

In order to understand the optical limiting behavior of the samples and to find the threshold value of optical limiting, one has to keep the sample in a fixed position and to measure the transmittance as a function of input fluence. The optical limiting properties of a material can also be estimated from its Z-scan plots for various input fluences. For this, the nonlinear transmission has to be plotted as a function of input fluence and such plots can be generated from the Z-scan measurements. From the value of fluence at the focus, fluence level at other sample positions can be calculated using the standard equation for Gaussian beam waist given by;

\[ \omega'(z) = \omega_s' \left( 1 + \frac{z'}{z'_s} \right) \quad (6.17) \]

Fig. 6.7 shows the nonlinear transmission for the different dye doped polymer samples. Generally it is found that the threshold value of optical limiting is not sharp for material [1]. One will be able to find an exact value for threshold from the Z-scan plot for the transmission in terms of input fluence. In Fig.6.7 the arrow indicates the approximate fluence level at which the transmission deviates from its linear behaviour which is considered as the threshold value of the optical limiter. The threshold values obtained for the polystyrene, PMMA and PVC dye doped polymer films are 0.85 Jcm\(^{-2}\), 1.75 Jcm\(^{-2}\) and 4.37 Jcm\(^{-2}\) respectively. This shows that the polystyrene films exhibit a better optical limiting threshold compared to PMMA and PVC films.
Fig. 6.7 Nonlinear transmission in dye doped polymer films
a) polystyrene (b) PMMA c) PVC

6.11 Conclusion
The nonlinear absorption characteristics of C540 dye solution and dye doped polymer matrices are investigated using the open aperture Z-scan technique. The Z-scan plots are drawn for various pump fluences. For the dye solution, Z-scan plots are drawn for a two-photon resonance wavelength as well as for a near two-photon resonance wavelength and both exhibit typical reverse saturable absorption. The nonlinear absorption coefficient is determined for all the polymer matrices. The high nonlinear absorption and the observed RSA can attributed to resonant two-photon absorption along with some ESA effects. Among the different polymer matrices, dye doped polystyrene matrices exhibits better nonlinearity. The optical limiting behavior of the polymer matrices is also studied.
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References


