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Study of Third-Order Nonlinear Optical Properties of Undoped and Dye Doped 1, 7, 7-Trimethylbicyclo [2.2.1] Heptan-2-One Using Z–Scan Technique

S. Jeyaram[a], T. Geethakrishnan[b,*]

[A]*department Of Physics, School Of Engineering And Technology, Surya Group Of Institutions, Villupuram – 605652, Tamilnadu, India.*

[B]*department Of Physics, University College Of Engineering Villupuram (A Constituent College Of Anna University Chennai), Kakuppam, Villupuram – 605103, Tamilnadu, India.*

Abstract:*Third-Ordernonlinear Optical (NLO) Properties Of Undoped And Dye Doped 1, 7, 7-Trimethylbicyclo [2.2.1] Heptan-2-One Was Studied By A Single Beam Z–Scan Technique. The Experiments Were Performedusing A Continuous Wave (CW) Diode Laser Operating At 635 Nm Wavelength Witha 5 Mw Of Total Power. Both Undoped And Dye Doped Samples Exhibited A Negative Value Of Nonlinear Refraction And Nonlinear Absorption Coefficient Respectively Due To Self-Defocusing And Reverse Saturable Absorption (RSA)Behaviors.The Real And Imaginary Parts Of The Third-Order Nonlinear Susceptibility Were Found To Be The Order Of 10^{-5}esu. The Self-Diffraction Ring Pattern Of The Transmitted Beam Profile Was Also Observed At Far Field. Based On The Experimental Results The Authors Suggest That The Sample Studied Here May Be A Potential Material For Applications In Photonics And Optoelectronics.*

Keywords:*Z–Scan; 1, 7, 7-Trimethylbicyclo [2.2.1] Heptan-2-One; NLO.*

I. Introduction

Nonlinear optical (NLO) materials play an important role in photonics and optoelectronics applications uch as optical switching, optical computing, optical data storage devices, optical communications, optical limiting, etc, [1–5]. Materials with fast response time, high stability in both physical and chemical processes and large third-order NLO parameters are the significant characteristic propertiesfor NLO applications [6]. A wide range of organic and inorganic materials are applied in nonlinear optical studiesdue tolarge NLO properties [7–8]. Other than organic and inorganic materials, recently synthesis of some novel materials such as colloidal nanorods [9], quantum dots [10], reduced graphene oxides [11], carbon nano tubes [12] are also act as a perfect optical materials and exhibita large nonlinear optical properties. Study of NLO properties of organic materials is always growing interest among the researchers because they possess a delocalized π-conjugated electron system [13]. Organic dyes are the important class of organic materials consists of aromatic compounds in its structure which includes aryl rings. High level of electron donors and acceptors in the dye molecules are also made them as a potential material in photonics and optoelectronic applications. Various experimental techniques are currently available to characterize thethird-order NLO properties of materials. Of the different techniques, the single beam Z–scan technique is a simple and effective tool for measuring the third-order NLO properties of materials [14]. The direct measurement of both real and imaginary parts of the third-order nonlinear susceptibility of the sample hasalso been carried out using this single beam technique. The sign and magnitude of nonlinear refractive index n_2 and nonlinear absorption coefficient β of the samples canbe measured respectively from closed and open aperture Z–scan technique.

In the present work,third-order nonlinear optical properties of undoped and dye doped 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one have been studied using a CW diode laser with total power of 5 mW operating at 635 nm.

II. Materials

The samples 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one and organic dye (reactive blue 19) were purchased from Merck IndiaLtd and have been used for the present study without purification. Both 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-onesand reactive blue 19 dye are highly soluble in water. Reactiveblue 19 dyebelongs to the class of anthraquinone. Anthraquinone dyes are polycyclic aromatic organic compounds are also called anthracenedione or dioxoanthracene, with molecular formula of $C_{14}H_8O_2$ and mass of 208.216 g mol^{-1}. Anthraquinone dyes have gained a considerable attention in the field of nonlinear optics due to their excellent optical qualities and high thermal stabilities. These dyes have vast applications in optical switches, light emitting diodes, photovoltaic devices, organic semiconductors, reprographics, thermal printing, biology,

pharmaceutical industries, medical purposes like wound healing and photodynamic therapy, etc [15]. Anthraquinone dyes have been the subject of intensive study because of their excellent photo stability and good hues. The molecular structure of 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one and acid blue 19 dye are shown in Fig. 1 (a) and (b). The linear absorption coefficient of the sample was calculated from Beer's law, $I = I_0 e^{-\alpha L}$, where L is the length of the sample.

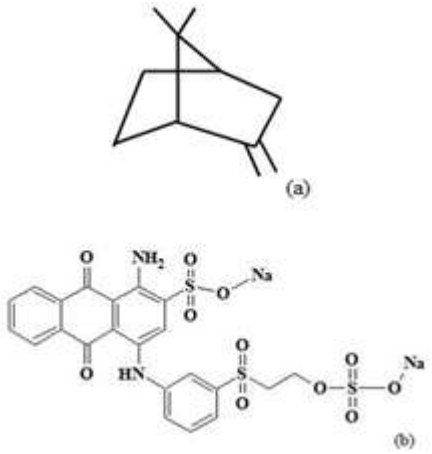

Fig.1. Molecular structure of (a) 1, 7, 7-Trimethylbicyclo [2.2.1] heptan-2-one (b) Reactive blue 19 dye.

III. Experimental

The present study is carried out the measurements of third-order NLO properties of undoped and dye doped aqueous solutions of 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one employing the single beam Z–scan method. A CW diode laser operating at 635 nm wavelength with a total power of 5 mW is used as an excitation source. The laser beam was focused by a positive lens withfocal length of 5 cm. The measured laser beam waist ω_0 at the focus and the corresponding Rayleigh length Z_R was found to be 16.84 μm and 1.4 mm respectively. A 1 mm thick cuvette containing the sample was translated along the axial direction that is the direction of the propagation of the laser beam.A photo detector fed to the digital power meter is placed at far field, which is used to measure the transmittance of laser beam through the sample. The experimental arrangement used for the present study is similar to thatof our previous work [6]. The length of the sample is less than that of Rayleigh length and therefore the thin sample estimation is completely fulfilled.

IV. Results And Discussions

The nonlinear optical properties such as nonlinear refractive index n_2 and nonlinear absorption coefficient β of the samples were respectively measured from closed and open aperture Z–scan techniques. In closed aperture case, an iris shaped aperture placed in front of the detector. On the other hand, in open aperture Z–scan technique the aperture is removed and the whole transmittance of the beam collected through a suitable lenswhich is placed before the detector. A 1 mm thick cuvette containing the solutions of the sample is mounted on a micrometer translational stage and gradually translated along the Z direction. For each Z positions, the sample experiences different intensity. When the sample is moved from negative Z in to focus (Z=0), the beam intensity is low, and a small nonlinear refraction occurs andhence the transmittance of the sample is comparatively constant. As the sample is brought closer to the focus (Z=0), the beam intensity increases, leading to self- lensing in the sample. When the sample is moved away from focus i.e., positive Z, the beam divergence causes decrease in transmittance at the aperture. The normalized transmittance curve shows a peak (maximum transmittance) followed by a valley (minimum transmittance) is the characteristic signature of negative nonlinearity or self-defocusing ($n_2 < 0$). Alternatively, an inverse effect i.e., valley followed by a peak is the characteristic signature of positive nonlinearity or self-focusing ($n_2 > 0$). Generally, the nonlinear refraction component of the sample in closed aperture Z–scan technique is affected by both nonlinear index of refraction and nonlinear absorption coefficient. For a pure nonlinear refraction, it is essential to separate the nonlinear refraction component from the nonlinear absorption coefficient component. A simple division method (closed/open) is used to extract the nonlinear refraction component from the nonlinear absorption component and this method reflects a pure nonlinear refraction of the sample. Figure.2 (a) and (b) shows the pure nonlinear refraction curve of undoped and dye doped aqueous solutions of 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one. The normalized transmittance curve shows a peak followed by the valley is the characteristic signature of self-defocusing type optical nonlinearity. The peak-valley difference of dye doped 1, 7,7-trimethylbicyclo [2.2.1]

heptan-2-one is larger than that ofundoped sample. This may be due to the presence of donor electrons in the dye molecules.In the molecular structure of reactive blue 19dye consists of nitro group which act as electron donors and oxygen of carbonyl and sulfonate group act as electron acceptors. The attractive feature of this technique is that, thesign of nonlinear index of refraction n_2 of the sample is instantly obtained from the shape of the normalization curve.The difference between the peak-valley as a function of on-axis phase shift $|\Delta\varphi_0|$ is given by,

$$\Delta T_{P-V} = 0.406(1-S)^{0.25}\,|\Delta\varphi_0| \qquad (1)$$

where S is the linear aperture transmittance and the value is S = 0.4. The sensitivity of nonlinear refraction is mainly due to the size of the aperture and the minimum size of aperture shows a better nonlinear refraction. The nonlinear refractive index n_2 of the samples in closed aperture Z–scan technique is given by,

$$n_2 = \frac{\Delta\varphi_0\lambda}{2\pi I_0 L_{eff}}\left(\frac{cm^2}{W}\right) \qquad (2)$$

where λ is the laser wavelength, I_0 is the intensity of the laser beam at focus Z = 0 and L_{eff} is the effective thickness of the sample.

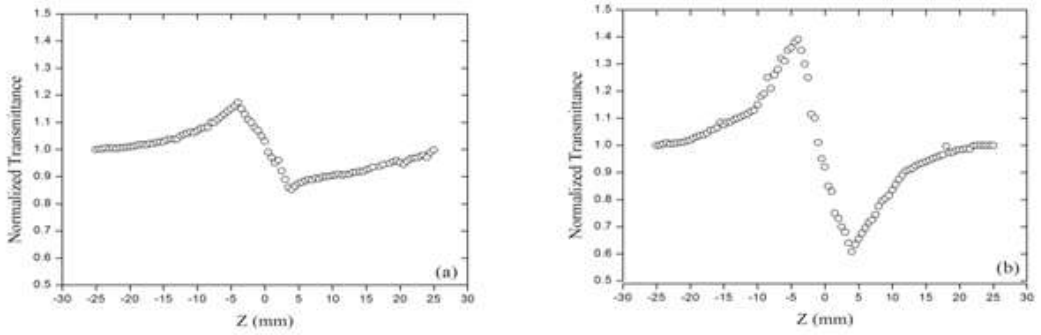

Fig.2. Pure nonlinear refraction curve for (a) undoped (b) dye doped 1, 7, 7-Trimethylbicyclo [2.2.1] heptan-2-one.

The nonlinear absorption coefficient β of samples gives the imaginary part of third order nonlinear susceptibility [Im (χ^3)]. Figure.3 (a) and (b) respectively shows the curve obtained from open aperture Z–scan technique for undoped and dye doped aqueous solutions of 7, 7-trimethylbicyclo [2.2.1] heptan-2-one. When the sample scanned from negative Z position to positive Z position, the beam intensity through the sample either increases or decreases. During the scanning process in open aperture case, the intensity of laser beam through the sample at the focus decreases and symmetric with respect to focus indicates an intensity dependent absorption effect. Both undoped and dye doped aqueous solutions of 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one exhibited a strong reverse saturable absorption (RSA) type of nonlinearity at an input intensity I_0 = 1.1 KW/cm^2. The transmittance of dye doped 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one at the focus decreases and form a deep valley position compare with undoped 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one. This may be due to the presence dye molecules (with increases in concentration) which contain strong electron donors. Nonlinear absorption (NLA) in a material can be originated by different nonlinear processes depending on the nature of the material and the excitation regime[16]. This includes, saturable absorption (SA), two-photo absorption (TPA), free carrier absorption (FCA), reverse saturable absorption (RSA). The NLA in the sample can be explained by a five level model and the energy level diagram is similar to that of our previous work [6].This model consists of singlet and triplet state. S_0, S_1 and S_2 are the singlet ground and excited states. T_1 and T_2 are triplet excited states. When two photons of same or different energy values are simultaneously absorbed from the ground state to excited state ($S_0 \rightarrow S_1$), it is known as TPA. When ESA occurs, molecules are excited from an excited state to a higher state ($S_1 \rightarrow S_2$ and/or $T_1 \rightarrow T_2$). For this to happen, the population of excited states (S_1 and/or T_1) should be high, so that the probability of photon absorption from the state is high. The ESA or RSA could be enhanced if the electrons from S_1 are transferred to T_1 via intersystem crossing (ISC), from where transitions to T_2 can occur. If the absorption cross section of the excited state is larger than that of the ground state then it is called an RSA process. The observed nonlinear absorption in the present study is due to ESA assisted RSA. The normalized transmittance in open aperture case is given by,

$$T(Z) = \sum_{m=0}^{\infty} \frac{[-q_0(z,0)]^m}{(m+1)^{3/2}} for |q_0 < 1| \qquad (3)$$

where

$q_0 = \beta I_0 L_{eff}/(1+x^2)$

where I_0 is the on-axis input intensity at Z = 0. L_{eff} is the effective thickness of the sample.

When open hole (S = 1), the transmittance takes first-order approximation of Equation (3), the normalized transmittance can be simplified to be

$$T(Z) = 1 - \frac{q_0(z,0)}{2\sqrt{2}} \quad (4)$$

or

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}}\left(\frac{cm}{W}\right) \quad (5)$$

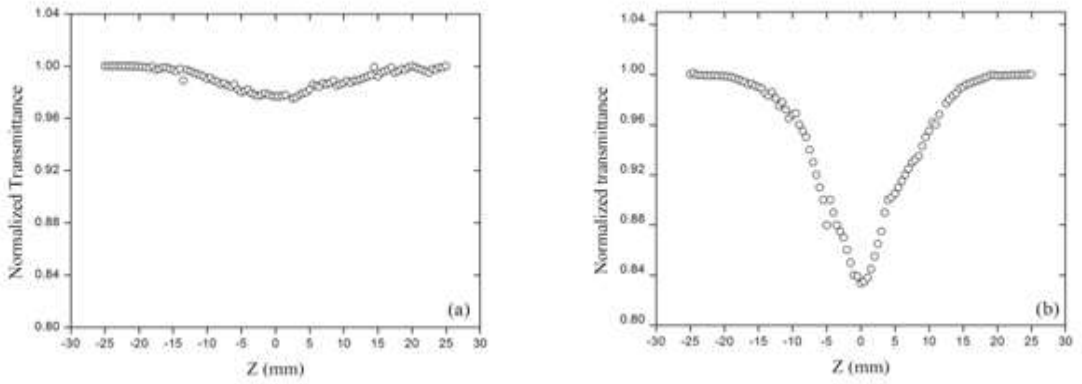

Fig.3. Open aperture Z–scan curve for (a) undoped (b) dye doped 1, 7, 7-Trimethylbicyclo [2.2.1] heptan-2-one.

The experimental measurement of nonlinear refractive index n_2 and nonlinear absorption coefficient β are directly related to the real and imaginary parts of third-order NLO susceptibility of the sample are given by the relation,

$$Re[\chi^{(3)}](esu) = 10^{-4}\frac{\varepsilon_0 c^2 n_0^2}{\pi} n_2 \left(\frac{cm^2}{W}\right) \quad (6)$$

$$Im[\chi^{(3)}](esu) = 10^{-2}\frac{\varepsilon_0 c^2 n_0^2 \lambda}{4\pi^2}\beta\left(\frac{cm}{W}\right) \quad (7)$$

whereε_0 is the vacuum permittivity and c is the velocity of light in vacuum

The value of $\chi^3$for the sample was calculated using the equation,$\chi^3 = [(Re(\chi^3))^2 + (Im(\chi^3))^2]^{1/2}$. The measured NLO properties of undoped and dye doped 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one are presented in Table.1. It is observed from the Table.1, the third-order NLO properties of dye doped 7, 7-trimethylbicyclo [2.2.1] heptan-2-one is higher than that of undoped 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one. The large value of third-order NLO properties of the sample is due to the presence of dye molecules which consists of strong donor groups.

Table 1: Measured NLO properties of undoped and dye doped 1, 7, 7-Trimethylbicyclo [2.2.1] heptan-2-one

Sample	n_2 X 10^{-7} (cm^2/W)	β X 10^{-3} (cm/W)	Re (χ^3) X 10^{-5} (esu)	Im (χ^3) X 10^{-5} (esu)	χ^3 X 10^{-5} (esu)
Undoped	0.93	0.68	0.42	0.15	0.40
Dye doped	2.70	5.75	1.21	1.30	1.22

4.1. SELF-DIFFRACTION

Self-diffraction ring pattern of dye doped 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one was studied by same experimental technique. The experimental set up for self- diffraction study is similar to that of Z–scan technique by replacing the screen with the place of photo detector.

When an intense laser beam interacts with the nonlinear medium, it produces spatial variation inside the sample. Due to change in refractive index inside the sample, a concentric diffraction ring pattern was formed at far field. This pattern consists of alternate bright and dark fringes. The self-diffraction ring pattern of the sample is due to intensity dependent refractive index and thermal lensing effect. Figure.4 shows the self-diffraction ring pattern of dye doped a 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-on.

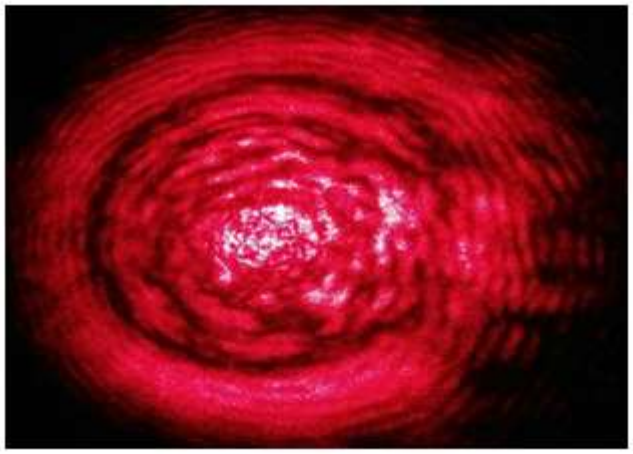

Fig.4. Self-diffraction pattern of dye doped 7, 7-trimethylbicyclo [2.2.1] heptan-2-one

V. Conclusion

Third-order NLO properties of undoped and dye doped 1, 7, 7-trimethylbicyclo [2.2.1] heptan-2-one was studied by a single beam Z–scan technique using a CW diode laser operating at 635 nm. Both undoped and dye doped samples exhibited a large negative value of nonlinear refractive index of the order of 10^{-7} cm^2/W and considerable positive nonlinear absorption coefficient of the order of 10^{-3} cm/W. Self-defocusing and reverse saturable absorption based optical nonlinearity were observed in both the samples. The third-order NLO susceptibility of the sample was found to be the order of 10^{-5} esu. All the experimental results revealed that the sample studied here may be a potential material for photonics and optoelectronics applications.

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