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Single-Beam Z-Scan Measurement of the Third-Order Optical Nonlinearities of Ethidium Bromide

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ABSTRACT

Organic dyes are very attractive optical materials for photonics and biophotonic applications. To quantitatively characterize their third-order nonlinear coefficients we have performed the experiments of Ethidium bromide dye dissolved in double distilled water using a diode laser beam at 473 nm wavelength and 4.5 mW power. The effect of nonlinearity of Ethidium bromide dye in broadening the laser beam is observed. The nonlinear absorption coefficient is calculated using the open aperture Z-scan data, while its nonlinear refractive index is measured using the closed aperture Z-scan data. The third order nonlinearity $\chi^{(3)}$ is measured using Z-scan data. Real and imaginary parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$ are changed significantly with concentration.

Keywords - Optical limiting, nonlinear refraction index , Z-scan .

I. INTRODUCTION

Nonlinear optics has received considerable attention due to their variety of applications in optoelectronic and photonic devices. Especially, nonlinear optical materials exhibiting strong two photon absorption (TPA) are in great demand, due to their applications in three-dimensional fluoresce -nce imaging and multi- photon microscopy, eye and sensor protection, frequency up conversion lasing, optical signal reshaping and stabilizing fast fluctuations of laser power [1–5]. A wide variety of materials have been investigated for third-order nonlinear optics, among which organic materials are attractive because of their optical and electronic properties which can be tuned and tailored by structural modification. The third order optical nonlinearity includes optical bleaching (i.e.,saturation) or reverse saturation in the absorption aspect, whereas self-focusing or self-defocusing occurs in the refraction aspect. Of the various techniques available, Z-scan method [6, 7] is a simple and effective tool for determining nonlinear properties and is used widely in material characterization because, it provides not only the magnitudes of the real and imaginary parts of the nonlinear susceptibility, but also the sign of the real part.

In this study, optical nonlinearity induced in dye Ethidium bromide by cw diode laser with an output power of 4.5 mWatt at 473 nm was studied using Z-scan technique, based on the sample-induced changes in beam profile at the far field. The study was made for concentrations of dye dissolved in double distilled water. The nonlinear refractive

indices n_2, and nonlinear absorption coefficients β were measured. The third-order optical nonline-arities has been studied.

II. EXPERIMENTAL

The molecular structure of the Ethidium bromide dye and the linear absorption spectrum of the dye dissolved in double distilled water at 1,2,2.5 and 3mM concentrations is shown in Fig. 1, which was acquired using a UV–VISNIR spectrophotometer (Type: CECEL 3500) .
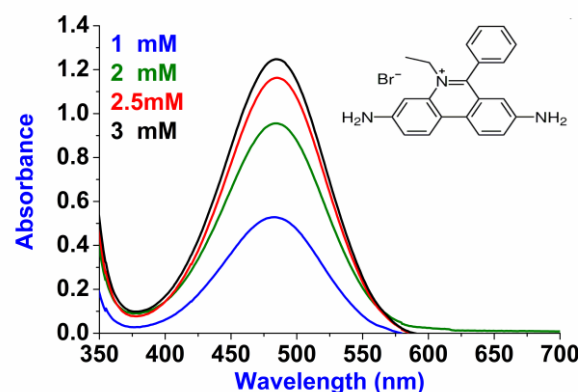

Fig. 1. Chemical structure and absorption spectra of dye with different concentration.

The schematic diagram of Z-scan technique is as shown in figure 2. By properly monitoring the transmittance change through a small aperture at the far field position (closed aperture), one is able to determine the amplitude of the phase shift. By moving the sample through the focus without placing an aperture at the detector (open aperture) one can measure the intensity dependent absorption of the

sample. When both the methods (open and closed) are used in measurements of the ratio of signals determines the nonlinear refraction of the sample.
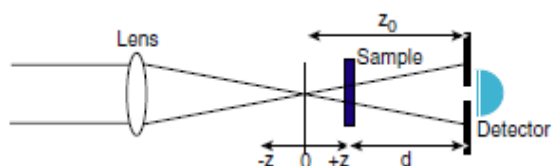

Fig.2. Z - scan experimental setup.

III. NONLINEAR OPTICAL

The nonlinear coefficients of the Ethidium bromide dye was measured by using Z-scan technique, which is a well-known technique that allows the simultaneous measurement of both nonlinear absorption coefficient β and the nonlinear refractive coefficient n_2.

A spatial distribution of the temperature in the surface is produced due to the localized absorption of tightly focused beam propagation through the absorbing sample. Hence a spatial variation of the refractive index is produced which acts as a thermal lens resulting in the phase distortion of the propagating beam. The difference between normalized peak and valley transmittance ΔT_{p-v} can be measured by Z-scan technique. The peak to valley ΔT_{p-v} is linearly related to the on- axis phase distortion $\Delta\Phi_0$ of the radiation passed through the sample [8,9]. The relation is defined as,

$$\Delta T_{P-V} = 0.406(1-S)^{0.25}\left|\Delta\Phi_0\right| \qquad \text{...... (1)}$$

and

$$\Delta\Phi_0 = kn_2I_0L_{eff} \qquad \text{....... (2)}$$

Where $S=1-\exp(-2r_a/\omega_a)$ is the aperture linear transmittance with r_a is the aperture radius and ω_a is the beam radius at the aperture in the linear region, I_0 is the intensity of the laser beam at focus z=0, $L_{eff} =(1-\exp(-\alpha_0 L))/\alpha_0$ is the effective thickness of the sample, L is the thickness of the sample, α_o is linear absorption coefficient of the Ethidium bromide dye solution and k=2π/λ is the wave number. The nonlinear refractive index n_2 can be obtained from equations 4 and 5, and the corresponding change in the refractive index $\Delta n = n_2I_0$.
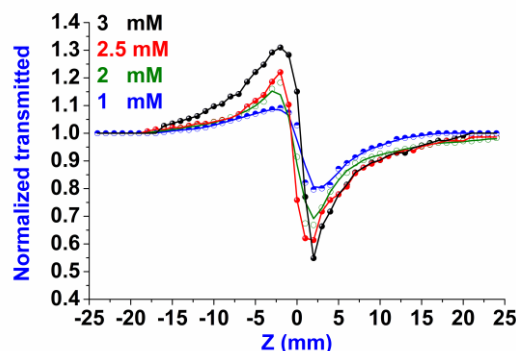

Fig.3. Closed aperture Z-scan data for Ethidium bromide with different concentration

Fig.3 shows the closed aperture (CA) Z-scan curve of Ethidium bromide dye solution. From the asymmetric curve there is obvious nonlinear absorption existing in the solution and the close transmittance is affected by the nonlinear refraction and absorption.

In the Z-scan measurement, the effective thickness of the samples are 0.058, 0.041, 0.036 and 0.034 mm, respectively. The linear transmittance of the aperture was *S*=0.61 and the optical intensity at the focus point is 5.81 *kWatt/cm²*.
The nonlinear absorption coefficient β (cm/W) can be calculated using the Eq. [10].

$$\beta = \frac{2\sqrt{2}\Delta T}{I_\circ L_{eff}} \qquad \text{...... (3)}$$

where ΔT is the normalized transmittance for the open aperture. Fig.4 shows the open aperture (S=1) Z-scan curve of sample. The enhanced transmission near the focus is indicative the for TPA process at high intensity (*z* = 0).
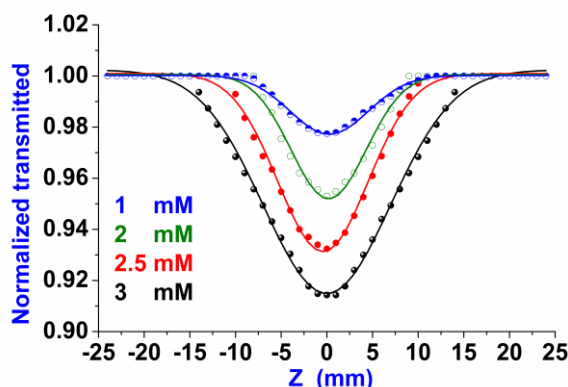

Fig.4. Open aperture Z-scan data for Ethidium bromide dye with different concentration

In order to extract the pure nonlinear refraction part, we have computed the value of the closed aperture (CA) data by the open aperture (OA)

data. Fig.5 shows the ratios of the *Z*-scan data for the dyes dissolved in double distilled water at 1, 2, 2.5 and 3 mM concentrations, respectively. A pre-focus peak followed by a post-focus valley indicates that the nonlinear property of the sample is negative and the lensing effect is defocusing. Table 1 summarizes the values of nonlinear refractive indices , nonlinear absorption coefficie- nts, and third-order susceptibilities of the dyes. The experiment was repeated for the pure solvent (double distilled water) to account for its contribution, but no significant measurable signals were produced in either the open or the closed *Z*-scan traces.
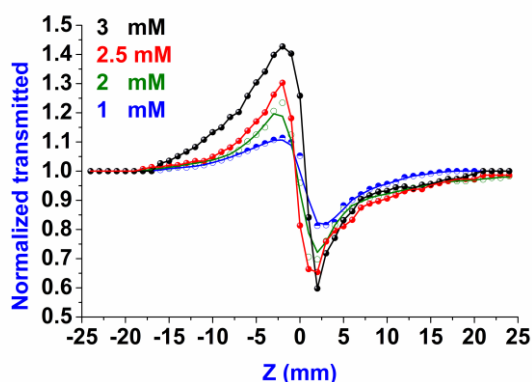

Fig.5. pure Z-scan data for Ethidium bromide dye with different concentration.

Generally the measurements of the normalised transmittance versus sample position, for the cases of closed and open aperture, allow determination of the nonlinear refractive index, n_2, and the reverse- ble saturation absorption (RSA) nonlinear coefficient, β [11]. Here, since the closed aperture transmittance is affected by the nonlinear refraction and absorption, the determination of n_2 is less straightforward from the closed aperture scans. Therefore, it is necessary to separate the effect of nonlinear refraction from that of the nonlinear absorption. A simple and approximate method to obtain purely effective n_2 is to divide the closed aperture transmittance by the corresponding open aperture scans.

The experimental measurements of n_2 , and β allow one to determine the real and imaginary parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$ according to the following relations [12-14],

$$\mathrm{Re}\ \chi^{(3)}(esu) = \frac{10^{-4}\varepsilon_0 c^2 n_0^2 n_2\ (cm^2/W)}{\pi} \quad ..(4)$$

$$\mathrm{Im}\ \chi^{(3)}(esu) = \frac{10^{-2}\varepsilon_0 c^2 n_0^2 \lambda\beta\ (cm/W)}{4\pi^2} \quad .....(5)$$

where ε_0 is the vacuum permittivity and *c* is the light velocity in vacuum.

From, Fig.6, we can see an increasing trend in values of n_2 and β as the concentration increases. This may be attributed to the fact that as the number of dye molecules increases when the concentration increases, more particles get thermally agitated resulting in an enhanced effect. According to Eqs. (4) and (5), these values of n_2 and β can be used to calculate $\chi^{(3)}$. Fig. 7 gives the plot of $\chi^{(3)}$ for these concentration. It can be seen that the trend is similar to that of n_2. The absolute value of $\chi^{(3)}$ for the Ethidium bromide dye solutions was calculated from $|\chi^{(3)}| = [(\mathrm{Re}(\chi^{(3)}))^2 + (\mathrm{Im}(\chi^{(3)}))^{\frac{1}{2}}]$, and it comes out to as shown in Table 1. It can be observed that the value of $\chi^{(3)}$ for the dye in double distilled water for different concentrations increases with concentration increases.
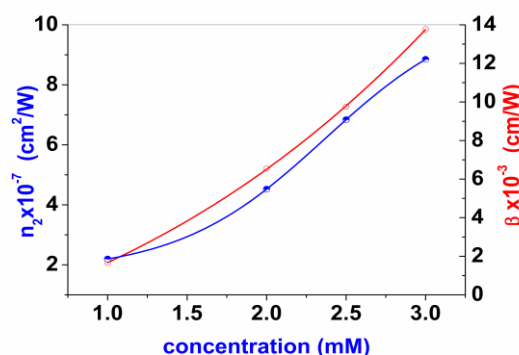

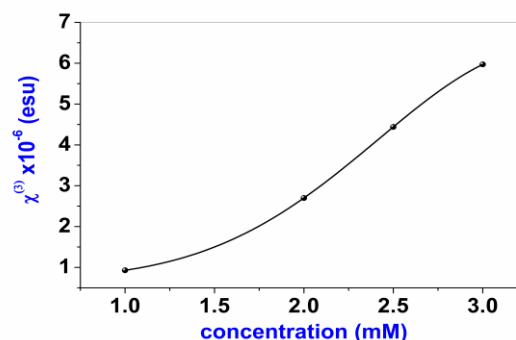Fig.6. Variation of n_2 and β of dye solutions for different concentrations.

Fig.7. Variation of |χ(3)| of dye solutions for different concentrations.

It is worth noting that the value of $\chi^{(3)}$ for the Ethidium bromide dye studied is larger than those of some representative third-order nonlinear optical materials such as organic polymers and organic metal [15–17] suggesting that the aqueous solution of Ethidium bromide may have a potential application in nonlinear optical devices.

To evaluate the suitability of a material for all-optical integrated devices, we often use two figures of merit [18]:

$$W = n_2 I / \alpha_\circ \lambda \quad \text{and} \quad T = \beta\lambda/n_2$$

Since this sample solution exhibits small one-photon absorption $\alpha_\circ$ throughout the near infrared region, the W values are ideal, i.e., W >>1 (see table 1). Due to the slight nonlinear absorption at 473 nm, the value of T is less than one for all the concentrations. Both the W and T values satisfy the requirements for the application of all-optical switching.

Table1.Nonlinear optical coefficients for aqueous dye

Dye mM	n_2 x10^{-7} cm^2/W	β x10^{-3} cm/W	Re $\chi^{(3)}$ x10^{-6}(esu)	Im $\chi^{(3)}$ x10^{-6}(esu)	$\left|\chi^{(3)}\right|$ x10^{-6}(esu)	W
1	2.07	1.86	0.26	0.89	0.93	2.1
2	5.21	5.48	0.66	2.62	2.70	3
2.5	7.27	9.08	0.92	4.34	4.44	3.5
3	9.85	12.21	1.25	5.84	5.97	4.4

IV. CONCLUSION

In summary, The nonlinear refraction index n_2 and nonlinear absorption coefficient β , of Ethidium bromide dye solution was studied using a single beam Z-scan technique under cw laser with excitation at 743 nm. Nonlinear refraction index coefficient is linear function of concentration and thickness and increased with increasing the concentration and thickness of samples. This may be attributed to the fact that, as the number of dye molecules increases when concentration increases, more particles are thermally agitated resulting in an enhanced effect. The optical nonlinearity of the dye may be due to laser heating induced nonlinear effect. A laser beam, while passing through an absorbing media, induces temperature and density gradients that change the refractive index profile. This intensity-induced localized change in the refractive index results in a lensing effect on the optical beam. It is found that the observed nonlinear absorption is caused by a reversible saturation absorption process. $\chi^{(3)}$ is calculated for different cases. These results are quite encouraging for possible applications in nonlinear optical devices.

REFERENCES

[1] J. L. Bredas , C. Adant , P. Tackx , A. Persoons and B. M.Pierce.Third-order Nonlinear Optical Response in Organic Materials : Theoretical and Experimental Aspects, *Chem. Rev.94 (1)*, 1994,243-278.

[2] V. Pandey, S. K. Tripathi A. Kumar, Optical band gap and optical constant in Se85Te15-SPbX Thin Films,*Chalcogenide Letters 2(5)*, 2005,39- 44.

[3] P. Poornesh , S. Shettigar , G. Umesh, K.B.Manjunatha , K. Prakash Kamath, B.K. Sarojini and B. Narayana, Nonlinear optical studies on 1,3-disubstituent chalcones doped polymer films, *Optical Materials* 31,2009, 854–859.

[4] K. Oe, Y. Toyoshima and H. Nagai, A reversible optical transition in SeXGe and PXSeXGe glasses, *J. Non-crystalline. Solids 20(3)* ,1976, 405-411.

[5] S. H. Wemple and M. DiDomenico, Behavior of the electronic dielectric constant in ionic materials, *Physical Reviews B3*,1971,1338-1351.

[6] M.Sheik-Bahae, A.A. Said and E.W. Van Stryland, High-sensitivity,single-beam n_2 measurements. *Opt. Lett., 14*, 1989, 955-957.

[7] M.Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan and E.W. Van Stryland, Sensitive measurement of optical nonlinearities using a single beam *IEEE. J. Quant. Elect., 26,* 1990, 760-769.

[8] S.J.,Mathews, S. Chaitanya Kumar, L. Giribabu and S. Venugopal Rao, Nonlinear optical and optical limiting properties of phthalocyanines in solution and thin films of PMMA at 633 nm studied using a cw laser. *Mater. Lett.,61*, 2007, 4426-4431.

[9] C. Gayathri and A. Ramalingam, Studies of third-order optical nonlinearities and optical limiting properties of azo dyes , *Spectrochimica Acta Part A 69* ,2008, 980-984.

[10] G. Vinitha and A.Ramalingam. Spectral characteristics and nonlinear studies of methyl violet 2B sdye in liquid and solid media. *Laser Physics, 18,* 2008, 37-42.

[11] A. Y.Al-Ahmad, Q. M. A.Hassan, H. A. Badran and K. A.Hussain. Investigating some linear and nonlinear optical properties of the azo dye (1-amino-2-hydroxy naphthalin sulfonic acid-[3-(4-azo)]-4-amino diphenyl sulfone) , *Optics & Laser Technology 44,* 2012, 1450–1455.

[12] R.K. Rekha and A. Ramalingam Non-linear characterization and optical limiting effect

of carmine dye, *Indian Journal of Science and Technology, .2(8)* 2009, 29-31.

[13] Cassano, T., R. Tommasi, M. Ferrara, F. Babudri, G.M. Farinola and F. Naso, Substituent dependence of the optical nonlinearrities in poly (2,5-dialkoxy-p-phenylenevinylene) polymers investigated by the Z-scan technique. *Chem. Phys., 272(1)*, 2001,111-118.

[14] X.B. Sun, X.Q. Wang, Q. Ren, G.H. Zhang, H.L. Yang and L. Feng, Third-order nonlinear optical properties of bis (tetrabutylammonium)bis(4,5-dithiolato-1, 3-dithiole-2-thione)copper, *Materials Research Bulletin 41*, 2006, 177–182.

[15] L. Feng , Y.lin Song , K. Yang , L. Shutian and L. Chunfei , Measurements of the triplet state nonlinearity of C_{60} in toluene using a Z-scan technique with a nanosecond laser, *Appl. Phys. Lett. 7 (15)* ,1997, 2073.

[16] G. Kumar Ravindra and F.A., Rajgara, Z-scan studies and optical limiting in a mode-locking dye ,*Appl. Phys. Lett.67 (26)* (1995) 3871.

[17] Z. Chuanlang, L. Dehua, D.qing Zhang and W. Xu, The excited-state absorption and third-order optical nonlinearity from 1-dodecaneth- iol protected gold nanoparticles: Application for optical limiting, *Optical Materials 26*, 2004, 11–15

[18] H.W. Hou, X.R. Meng, Y.L. Song, Y.T. Fan, Y. Zhu, H.J. Lu, C.X. Du and W.H. Shao, Two-Dimensional Rhombohedral Grid Coordination Polymers $[M(bbbt)_2(NCS)_2]_n$ (M = Co, Mn, or Cd; bbbt = 1,1'-(1,4- butanediyl) bis-1*H*-benzotriazole):□ Synthesis, Crystal Structures, and Third-Order Nonlinear Optical Properties,*Inorg. Chem. 41(15)* ,2002, 4068–4075.