Investigation of third order optical nonlinearity and optical limiting effect of Xylidine Ponceau dye in liquid medium by Z-Scan technique

U. MAJITHA PARVIN, M.BASHEER AHAMED*
B.S. Abdur Rahman University, Chennai-600 048, India

Third order optical nonlinearity of Xylidine Ponceau dye in ethanol solvent was studied using pulsed Nd:YAG laser operating at 532nm as the source of excitation. The nonlinear optical response and optical limiting behavior of the dye were studied using single beam Z-scan technique. The open aperture Z-scan of the dye exhibited reverse saturable absorption. The closed aperture Z-scan of the dye exhibited negative nonlinearity. The nonlinear refractive index n_2, nonlinear absorption coefficient β and third order nonlinear optical susceptibility $\chi^{(3)}$ were evaluated for different concentrations of the dye in ethanol solvent. The nonlinear refractive index and nonlinear absorption were found to vary with concentration. Optical limiting characteristics of the dye at various concentrations in solution were also studied. From the results obtained, it is found that this dye has potential application in nonlinear optics.

1. Introduction

In the recent past, rapid technological advancements in optics have placed great demand on the development of nonlinear optical (NLO) materials with prominent applications in optical limiting for sensor protection, all optical switching and optical signal processing[1-2]. Large optical nonlinearity, low optical loss, high NLO chromophore density and ultrafast response time are the essential properties that are required for organic molecules to behave as a promising class of third order NLO material [3-4].

Organic dyes are also found to have various applications in many scientific branches due to their high fluorescence quantum yield and broad gain bandwidth [5]. The wide bandwidth makes them particularly suitable for tunable ultrafast pulse generation [6].

Nonlinear optical phenomena may arise in these materials due to electronic, thermal (non-electronic) or anisotropic orientational processes. The electronic nonlinearity arises from electronic structural change due to distortion of electron clouds. Thermal nonlinearity arises as a result of generation of phonons on absorption of light. The orientational nonlinearity is due to birefringence when off resonance dichroism on resonance [7].

Z-scan technique is a simple and effective technique for determining both nonlinear refractive index and nonlinear absorption [8]. A large number of organic compounds with delocalized electron systems and a large dipole moment have been synthesized to realize the nonlinear susceptibilities far larger than the inorganic optical materials [9]

The present study aims to analyze the nonlinear optical properties of organic dye Xylidine Ponceau. This dye belongs to the family of azo dye which has good photothermal stability and dissolvability. Azo dye is chosen for study as they possess high nonlinear optical properties. Optical limiting is a nonlinear optical process in which transmittance of a material decreases with increase of incident light intensity. In this paper, the optical nonlinearity and optical limiting action of the dye in ethanol solvent for different concentrations using pulsed Nd:YAG laser at wavelength of 532 nm are studied and the third order nonlinear refractive index n_2, nonlinear absorption co-efficient β and third order nonlinear optical susceptibilits χ^3 are evaluated. The optical limiting behavior of the dye has also been discussed.

2. Experimental Procedure

2.1 Materials and Methods

Xylidine Ponceau from Azo dye family was chosen for the study. The dye sample was prepared by dissolving the dye in ethanol at different concentrations. The nonlinear optical properties of the sample was studied by using pulsed Nd:YAG laser operating at 532nm and characterized by a pulse duration of 9ns at a repetition rate of 10Hz as the excitation source. The molecular structure of the Xylidine Ponceau dye is shown in Fig. 1.

$$C_{18}H_{14}N_2O_7S_2Na_2$$
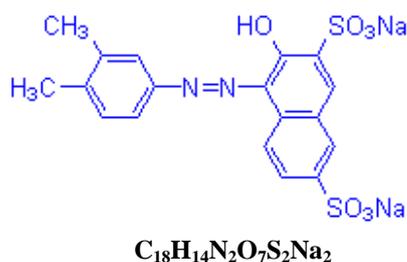
Fig. 1. Chemical structure and molecular formula of Xylidine Ponceau.

2.2 Absorption spectra

The spectral property (absorption) of the dye in liquid medium of concentration 0.01 mM was studied by recording the absorption spectra of the dye using an UV-VIS spectrophotometer (VARIAN COMPANY). The absorption spectrum of the dye is shown in Fig. 2.

The spectral parameters such as absorption peak wavelength, molar-extinction coefficient $\varepsilon(\lambda)$, oscillator strength (f), bandwidth ($v_{1/2}$) were calculated and were found to be 510 nm, $4x10^4$ $Lmol^{-1}cm^{-1}$, $0.52x10^{-24}$ $Lmol^{-1}cm^{-2}$ and $3x10^3$ cm^{-1} respectively.
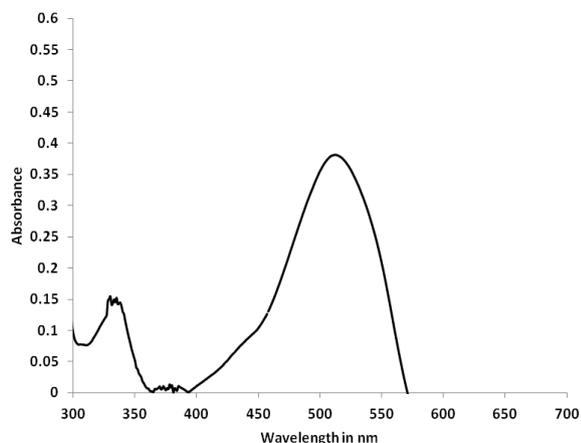
Fig. 2. UV-VIS absorption spectra of dye Xylidine Ponceau in ethanol.

2.3. Z-Scan technique

Pulsed Nd:YAG Laser (QUANTA RAY: Model Lab–170-10) of wavelength 532 nm was used as the excitation source for the Z-scan technique. The laser of Gaussian beam profile was focused by a convex lens of focal length 10 cm to produce beam waist ω_0 of 32 μm. The peak intensity of the incident laser beam, I_0 was $7.7x 10^5$ W/cm^2 and the diffraction length Z_R was found to be 6.04 mm.
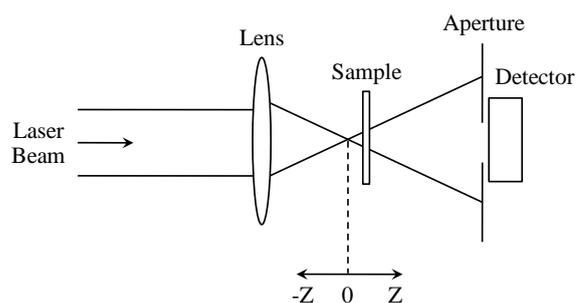
Fig. 3. Schematic diagram of the experimental arrangement for the Z-scan measurement.

The schematic diagram of the experimental set up used is shown in Fig. 3. A 1 mm wide optical cell containing the dye dissolved in solvent was translated across the focal region along the axial direction (i.e) propagation direction of laser beam. For closed aperture, the transmission of the beam through an aperture placed in the far field was measured using a photodetector and the output power was recorded by the digital power meter. For an open aperture Z-scan, the entire laser beam transmitted through the sample was measured using the photodetector on removal of the aperture. [10].

2.4 Optical limiting effect

Optical limiting effect of the dye was studied by using pulsed Nd:YAG laser at 532 nm. The experimental setup for the demonstration of optical limiting consists of a 1 mm quartz cuvette containing nonlinear material (sample solution) kept at the position where the transmitted intensity showed a valley in closed aperture Z-scan curve [11]. The input power.of the laser beam can be varied using the laser control panel.

The transmitted beam coming out from the sample was then made to fall on the photodetector. The input intensity was varied systematically and the corresponding output intensity values are measured by using photodetector [12].

3. Results and discussion

The Z-scan experiments were performed for the dye with 0.01mM concentration using ethanol as solvent employing frequency doubled Nd:YAG pulsed laser light operating at 532nm. The sample remained stable even after exposure to laser pulses for a long period of time. The nonlinearity of the dye in solvent was measured. The experiment was also repeated for pure ethanol solvent under the same conditions and no signal could be obtained. Thus the nonlinearity of solvent could be ignored under nanosecond laser beam irradiation. The experiment is repeated for 0.02mM and 0.03mM concentration of the dye.

The third order nonlinear refractive index (n_2) and the nonlinear absorption coefficient (β) of the Xyilidine Ponceau dye in ethanol solvent at various concentrations

for the incident intensity $I_0 = 7.7 \times 10^5 W/cm^2$ are evaluated by the measurements of Z-scan.

For closed aperture Z-scan, an aperture is placed in front of the detector and the measurement is sensitive to both nonlinear absorption and nonlinear refraction [4]. The closed aperture Z-scan curve was obtained by plotting the normalized transmittance as a function of the sample position.

The value of nonlinear refractive index (n_2) is calculated using the formula

$$n_2 = \Delta\phi/kL_{eff}I_0 \qquad 1)$$

where k is the wave number given by $2\pi/\lambda$ where λ is the wavelength of the light used, I_0 is the intensity of the laser beam at focus z = 0.

The effective length of the sample (L_{eff}) is measured using

$$L_{eff} = (1-e^{\alpha L})/\alpha \qquad (2)$$

where L is the length of the sample, α is the linear absorption coefficient.

The on-axis phase shift at the focus $(\Delta\phi)$ is given by

$$\Delta\phi = \Delta T_{p-v}/0.406(1-S)^{0.25} \qquad (3)$$

The measurable quantity ΔT_{p-v} can be defined as the difference between the normalized peak and valley transmittances, T_p-T_v and the linear transmittance through the aperture S is given by

$$S = 1 - \exp(-2r_a^2/\omega_a^2) \qquad (4)$$

where r_a denotes the aperture radius and ω_a denotes the radius of the laser spot before the aperture.

If we collect all the energy transmitted by the sample (open aperture Z-scan), the measurement is sensitive to nonlinear absorption only.

$$\beta = 2\sqrt{2}\Delta T / I_0 L_{eff} \qquad (5)$$

The imaginary parts of the third order nonlinear optical susceptibility (χ^3) is estimated using the value of the nonlinear absorption coefficient β obtained from the open aperture Z-scan data (Fig. 4) where ΔT is the normalized transmittance of the sample at the position of Z=0.

To get the pure nonlinear refraction contribution, we divide the closed aperture Z-scan transmittance by the one with open aperture [8] and the corresponding curves are shown in Fig.5

Experimentally determined nonlinear refractive index (n_2) and nonlinear absorption coefficient (β) can be used to find the real and imaginary part of the third order nonlinear optical susceptibility $(\chi 3)$ [13] according to the following relations,

$$Re\,\chi^{(3)}(esu) = 10^{-4}\frac{\varepsilon_o c^2 n_o^2}{\pi}n_2\left(\frac{cm^2}{W}\right) \qquad (6)$$

$$Im\,\chi^{(3)}(esu) = 10^{-2}\frac{\varepsilon_o c^2 n_o^2 \lambda}{4\pi^2}\beta\left(\frac{cm}{W}\right) \qquad (7)$$

Where ε_0 is the vacuum permittivity and c is the light velocity in vacuum.
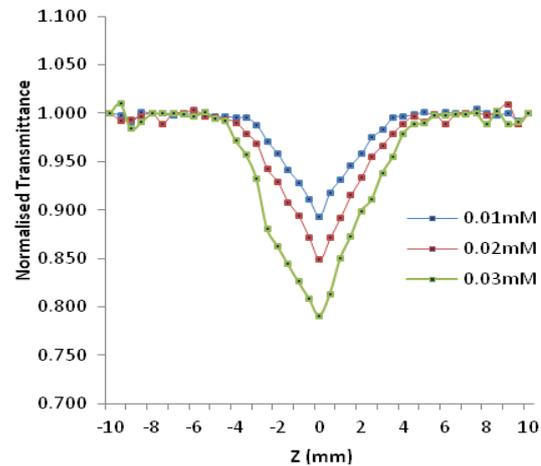
Fig.4 Open Z- scan curve for for Xyilidine Ponceau dye in ethanol at different concentrations.
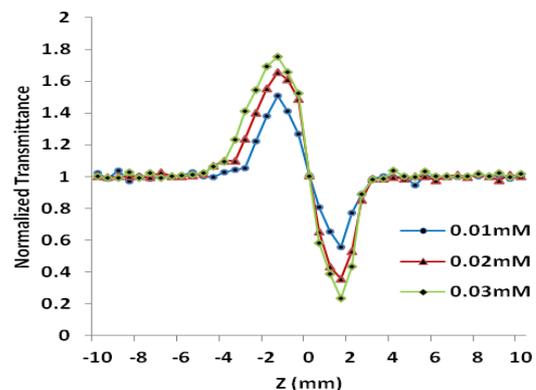
Fig.5 Ratio of Closed-to-open Z-scan curve for Xyilidine Ponceau dye in ethanol at different concentrations .

The absolute value of the third order nonlinear optical susceptibility $|\chi^3|$ is given by the relation [12].

$$|\chi^{(3)}| = [Re(\chi^{(3)})^2 + (Im(\chi^{(3)})^2]^{1/2} \qquad (8)$$

The experiment is repeated for 0.02mM and 0.03mM concentration of the dye and the corresponding nonlinear optical parameters are studied.

Experimental results for open aperture Z-scan showed that the dye possesses reverse saturable absorption and the open aperture curves for the dye in solvent for different concentrations are as shown in fig.4. Experimental results performed for closed aperture Z-scan showed peak followed by valley which suggests that the change in refractive index is negative exhibiting a self defocusing effect. The self defocusing effects of the dye in solution at various concentrations are as shown in Fig.5.

It is found that nanosecond pulse laser induces two kinds of possible contributions to nonlinear refractive index namely transient nonlinearity kerr effect and thermo-optical effect. The thermal effect of these dye molecules for a light of wavelength 532nm can be nearly neglected since the absorption due to the material is negligible or too small.

Hence, it may be concluded that the nonlinearity originated in the dye is mainly due to electronic effect and is related with strong delocalization of π-electrons [7]. Hence, the large refractive nonlinearity is mainly due to the electronic origin nonlinearity mechanism.

The experimentally determined values of ΔT_{p-v}, n_2, β and χ^3 are given in Table 1.

Table.1 Nonlinear optical parameters of Xyilidine Ponceau dye in ethanol at different concentrations

Concentration (mM)	ΔT_{p-v}	n_2 x 10^{-10} (cm^2/W)	β x 10^{-6} (cm/W)	$\lvert\chi^{(3)}\rvert$ x 10^{-9} (esu)
0.01	0.951	-2.93	3.64	0.737
0.02	1.299	-4.02	5.58	1.123
0.03	1.522	-5.19	7.73	1.554

The value of n_2, β and χ^3 increases as the concentration increases in this dye as shown in Table 1. Hence this intensity-induced localized change in the refractive index results in a lensing effect on the optical beam and is found to increase with concentration.

An optical limiter is a device which has very high transmission for weak optical signals, but becomes opaque for intense optical signals. The optical power limiting is mainly due to nonlinear absorption in the dye.

The optical power limiting behavior of the dye molecules are obtained from the open aperture Z-scan curve and the sample solution displayed a linear absorption at low input fluence and saturable absorption occurred at higher input fluence. The optical limiting threshold will determine the ability of the limiter. The lower the threshold value, better the optical limiter.
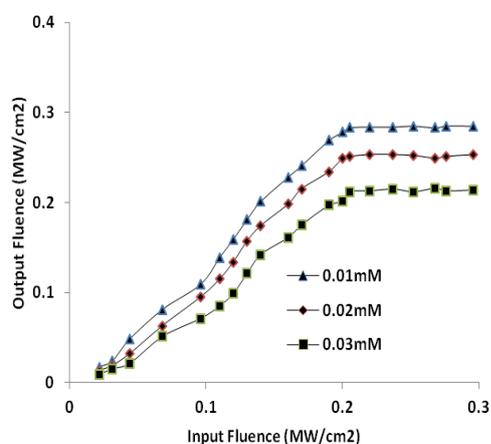
Fig.6 Optical limiting effect of Xyilidine Ponceau dye in solvent at different concentrations.

The optical limiting curve obtained with pulsed Nd:YAG laser of wavelength 532 nm for the dye in solution at different concentrations is as shown in Fig.6. The output fluence increases initially with increase in input fluence, but after a certain threshold value the sample starts defocusing the beam, resulting in a greater part of the beam cross section being cutoff by the aperture. Thus the transmittance recorded by the photodetector remains reasonably constant showing a plateau region.

At input fluence above 0.21MW/cm^2, as the nonlinear absorption coefficient starts increasing with increase in the incident irradiance, the output fluence tends to remain constant.

From Table 2, it can be seen that the optical power limiting threshold is inversely proportional to the concentration. The high concentrated dyes in solution exhibits strong optical limiting behavior when compared to low concentrated dyes as shown in fig 6. This indicates that the number density of dye molecules in the laser beam is the major factor which affects the saturated level. Hence it is found that this dye exhibited strong optical limiting behavior similar to ideal limiters.

The experimentally determined optical limiting saturated output fluence values are shown in Table 2.

Table.2 Concentration dependence of saturated output fluence of Xyilidine Ponceau dye

Concentration (mM)	Saturated Output Fluence (MW/cm^2)
0.01	0.283
0.02	0.251
0.03	0.212

From the results obtained, it is found that this dye sample possesses optical limiting effect which can be exploited in developing optoelectronic devices [14].

4. Conclusion

Third order optical nonlinear parameters like nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and nonlinear optical susceptibility (χ^3) of Xyilidine Ponceau dye have been determined using Z-scan technique. Optical limiting behavior of the dye is also studied. The Z-scan results indicate that the nonlinear absorption is caused by reverse saturation absorption process, while the nonlinear refraction leads to self defocusing in this dye.

The origin of the large refractive nonlinearity in the dye sample appears to be predominantly electronic in nature. The value of Third order nonlinear optical susceptibility evaluated for this dye is found to be several times greater than some representative third order nonlinear optical materials such as chalcone and its

derivatives[15-18].   Optical limiting studies of the dye reveal that this dye is a better optical limiter.

Hence, the dye sample investigated seems to be a promising candidate for future photonic and optoelectronic applications.

References

[1] A. Costela, I. Garcia-Moreno, J. M. Figuera, F. Amat-Guerri, J. Barroso, R. Sastre, Opt. Commun. **130**, 44 (1996).

[2] T. Huang, Z. Hao, H. Gong, Z. Liu, S. Xiao, S. Li, Chem. Phys. Lett. **451**, 213 (2008).

[3] D.S. Wu, W.D. Cheng, H. Zhang, J.T. Chen, Chem. Phys. Lett. **351,** 486 (2002).

[4] M. Sheik-Bahae, A. A. Said, T-H. Wei, D. J. Hagan, E. W. Van Stryland, Quantum Electronics, IEEE Journal **26,** 760 (1990).

[5] Zainab F. Mahdi, Iraqi J. Laser **9**,9 (2010)

[6] A.S. Hamdan, Al-Shamiri, T.H. Maram Abou Kana, I.M. Azzouz and Y.A. Badr, OPtics and Laser Technology **41**,4 (2009)

[7] C. Pradeep, S. Mathew, B. Nithyaja, P. Radhakrishnan, V.P.N. Nampoori, Applied Physics A **115**, 291 (2013)

[8] M. Sheik-Bahae, A.A. Said, E.W. Van Stryland, Opt. Lett. **14,** 955 (1989).

[9] J. L. Bredas, C. Adant, P. Tackx, A. Persoons, B.M.Pierce, Chem.Rev. **94,** 243 (2004).

[10] R. K. Rekha, A. Ramalingam, American J. of Engineering and Applied Sciences **2**, 285 (2009).

[11] K. Sendhil, C. Vijayan, M.P. Kothiyal, Opt. Laser Technol. **38**, 512 (2006).

[12] N. Venkatram, L. Giribabu, D. Narayana Rao, S. Venugopal Rao, Applied Physics B **91**, 149 (2008).

[13] T. Cassano, R. Tommasi, M. Ferrara, F. Bahaduri, G. M. Farinola, F. Naso, Chem. Phys. **272**, 111(2001).

[14] S. Kaladevi, C. Vijayan, M.P. Kothiyal, Opt. Mater. **27**, 1606 (2004).

[15] H. J. Ravindra, A. John Kiran, K. Chandrasekaran, H.D. Shashikala, S.M. Dharmaprakash, Applied Phys. B (Laser Opt.), **88**, 105 (2007).

[16] Z. Li, Z. Jin, K. Kasatani, H. Okamoto, S. Takenaka, J.Appl.Phys. **44**, 4956 (2005).

[17] Hussain A. Badran and Adil A. Al-fregi, International Journal of Physics and Research **2**, 15 (2012).

[18] A. Clementi, N. Chiodini, A. Pleari, Appl. Phys. Lett. **84**, 960 (2004)

_____

*Corresponding author: *basheerahamed@bsauniv.ac.in*