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Investigation of Optical limiting properties of Azophloxine dye using nanosecond Z- scan technique

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Abstract: In this paper, the third order nonlinear optical properties of Azophloxine dye in ethanol solution was studied by nanosecond Z-scan technique. The measurements were carried out at different input peak intensities of nanosecond Nd:YAG laser operating at 532nm. Both open and closed aperture Z-scan techniques were performed and it was found that the dye showed reverse saturable absorption and intensity-dependent positive nonlinear refraction coefficient, indicating self focusing phenomena. The nonlinear absorption and optical limiting property of the dye may be attributed to two photon absorption effect. The third-order nonlinear susceptibility and optical limiting threshold were also measured.
Keywords: Z-scan Technique, Nanosecond laser pulses, Third order nonlinear optical susceptibility, Optical limiting.

Introduction

Organic molecules with nonlinear optical process continue to attract attention because of their potential applications in a wide variety of optoelectronic and photonic devices [1,2,3]. The nonlinear response of these organic molecules results in large third order nonlinear optical susceptibilities. Extensive work has been carried out and the reports have been published for the organic molecules in liquid solutions[4,5] and for organic and biological materials doped in various solids[6]. Azo dye is an organic dye having good photo-thermal stability, dissolvability and easy preparation virtue and also found to have noticeable third order nonlinearity and good optical power limiting properties.

Out of the various techniques developed to measure the optical nonlinearities, the single beam *Z* -scan technique, developed by Sheik Bahae et al.[7,8] is a simple and effective tool. It is a method which can be used to measure both the nonlinear refraction and the nonlinear absorption and thus provides the magnitude and sign of the real part of nonlinear susceptibility and also the magnitude of imaginary part of nonlinear susceptibility.

In this paper, we have chosen Azophloxine dye which belongs to the Azo dye family for the study. We have reported the nonlinear optical response of the chosen dye sample by using Z scan technique with the help of nanosecond Nd:YAG laser pulses operated at 532nm. The study is made for different input intensities of laser light. From the open and closed aperture curves obtained, the nonlinear refractive index n_2, nonlinear absorption coefficients β and third order nonlinear susceptibilities χ^3 are measured. The optical limiting behavior of the dye has also been studied.

Experimental

The structural formula of Azophloxine dye is as shown in Fig.1. The dye is dissolved in ethanol solvent at a concentration of 3 x 10^{-5} M for experiments.

The absorption spectrum of the dye sample solution was recorded by using an UV-VIS spectrophotometer (VARIAN COMPANY) and is as shown in Fig.2. From the spectrum obtained, the spectral parameters are also evaluated. The calculated values of absorption peak wavelength, molar-extinction coefficient ε(λ), oscillator strength (f), bandwidth ($\Delta\gamma_{1/2}$) are found to be 538nm, 3.41x10^{4} $Lmol^{-1}$ cm^{-1}, 5.49x10^{-25} $Lmol^{-1}$ cm^{-2} and 3.72x10^{3} cm^{-1} respectively.

Fig.1. Chemical structure and Molecular formula of Azophloxine dye.

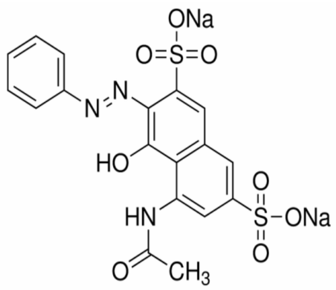
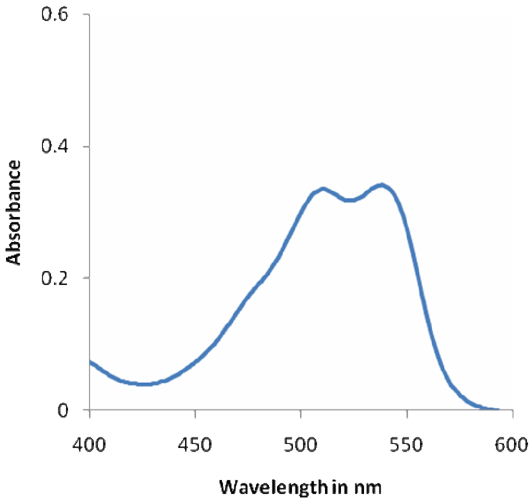


Fig.2. UV-VIS absorption spectra of Azophloxine dye in ethanol solvent.



Z-scan technique for Nonlinear optical studies

Azophloxine dye used for Nonlinear optical studies was purchased from Sigma-Aldrich, India. The solvent used was ethanol. It was supplied by Shriram Enterprises Pvt Ltd, India. Single beam Z-scan technique was employed to measure the third order optical nonlinearities of the dye sample. The schematic experimental setup for Z scan is as shown in Fig. 3. The experiment was performed on the dye by using nanosecond Nd:YAG laser pulses with a repetition rate of 10HZ operating at 532nm wavelength. In the measurements, Azophloxine dye was maintained at 0.03mM concentration in the solvent.

Initially, the nonlinearity of the solvent alone was measured and no signal was obtained indicating the nonlinearity is only due to the dye used and not of the solvent. Now the nonlinear optical studies were done for the dye in the ethanol solvent at three different input intensities. The laser beam was focused with a lens of 10cm focal length onto the sample. The beam waist was estimated to be 32μm. The Rayleigh length, $Z_R = \pi\omega_0^2/\lambda$ was calculated and was found to be 6.04mm and was much greater than the thickness of the sample cuvette (1mm), which is an essential prerequisite for Z scan measurements. Hence the thin sample approximation is valid. The experiment was performed at three input peak intensities namely 1.36, 2.33 and 3.26 MW/cm^2 respectively.

Results and Discussion

The third order nonlinear refractive index n_2 and the nonlinear absorption coefficient β of the dye in ethanol solvent at different input peak intensities were evaluated using the Z-scan measurements. Fig.4 shows the open aperture Z-scan curve of the dye at three different input peak intensities and the experimental results indicate that the dye exhibited reverse saturable absorption with a positive absorption coefficient (β). The shape of the open aperture curve suggests that the compound exhibits two-photon absorption[9]. A decrease in nonlinear absorption coefficient with increased intensity of the incident laser was observed[10] and the numbers are presented in Table 1. Normalized transmittance curve of the Azophloxine dye obtained from the closed aperture Z-scan measurements is as shown in Fig.5 and the large valley to peak configurations of the closed aperture curve obtained suggest that the change in refractive index of the dye was positive exhibiting strong self focusing effect.

Fig.3. Schematic diagram of the experimental arrangement for the Z-scan measurement.

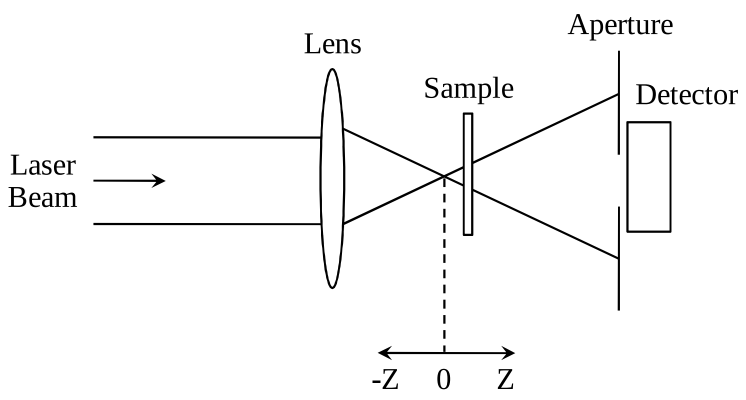


Fig.4. Open Z-scan curve for Azophloxine dye in ethanol solvent at different input intensities.

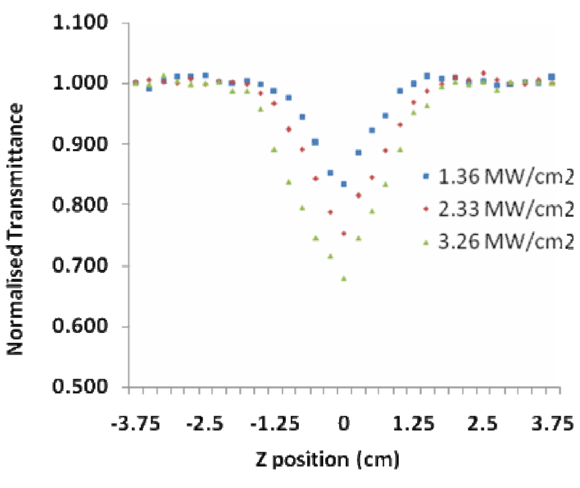
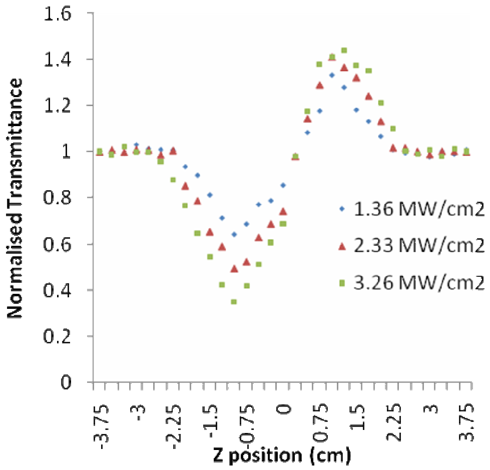


Table.1. Calculated third order nonlinear optical parameters of Azophloxine dye at different input peak intensities

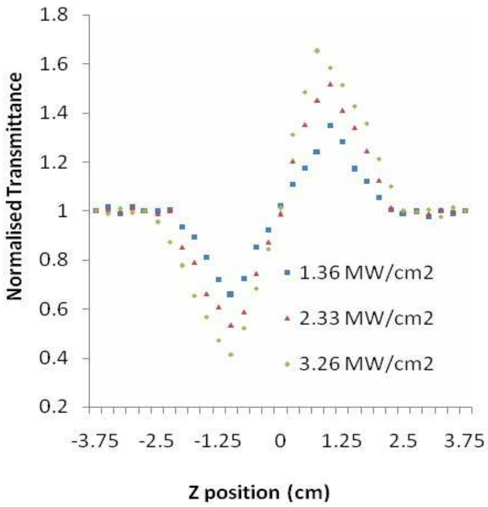
Input Peak Intensity (MW/cm^2)	ΔT_{p-v}	$n_2 \times 10^{-10}$ (cm^2/W)	$\beta \times 10^{-6}$ (cm/W)	$\lvert\chi^{(3)}\rvert \times 10^{-8}$ (esu)
1.36	0.693	1.204	3.453	6.888
2.33	0.983	0.997	3.011	6.004
3.26	1.238	0.93	2.794	5.563

Fig.5. Closed Z- scan curve for Azophloxine dye in ethanol solvent at different input intensities.



Pure nonlinear refraction curves were obtained by the division of closed aperture data by the open aperture data. Fig.6. shows the results of dividing the closed aperture data by the open aperture data at three different input incident peak intensities.

Fig.6. Closed/Open Z scan curve for Azophloxine dye in ethanol solvent at different input intensities



The value of nonlinear refractive index (n_2) is obtained from the closed/open Z- scan curve data and is calculated using the formula

$$n_2 = \frac{\Delta\Phi}{k\, L_{eff}\, I_o} \qquad (1)$$

where I_0 is the intensity of the laser beam at focus z = 0, k is the wave number given by $2\pi/\lambda$, λ is the wavelength of the light used, $L_{eff} = (1-e^{\alpha L})/\alpha$ is the effective thickness of the sample, L is the thickness of the sample and α is the linear absorption coefficient.

The value of the nonlinear absorption coefficient β is obtained from the open aperture Z-scan data and is given by

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

Experimentally determined pure nonlinear refractive index n_2 and nonlinear absorption coefficient β can be used in finding the real and imaginary parts of the third order nonlinear optical susceptibility $(\chi^{(3)})$[11] according to the following relations:

Re χ↑((3)) (*esu*) = 【10】↑(−4) $\varepsilon_1$0/(c↑2 $n_1$0↑2 n_1█(2@) (【*cm*】↑2/*W*) (3)

Im χ↑((3)) (*esu*) = 【10】↑(−2) $\varepsilon_1$0/ 【4(】↑2 c↑2 $n_1$0↑2 (β(*cm*/*W*) (4)

Where ε_0 is the vacuum permittivity and c is the light velocity in vacuum.

The absolute value of the third order nonlinear optical susceptibility $|\chi^{(3)}|$ is given by the relation.

|χ↑((3)) | = √([(*Re*(EMBED Equation.3))↑2 + (*Im*(EMBED Equation.3))↑2])

(5)

Thus we have examined the third order optical nonlinearity using pure nonlinear refraction and nonlinear absorption coefficient[8].

The calculated nonlinear absorption coefficient (β cm/W), the nonlinear refraction coefficient ($\eta_{2,}$, cm^2/W),the

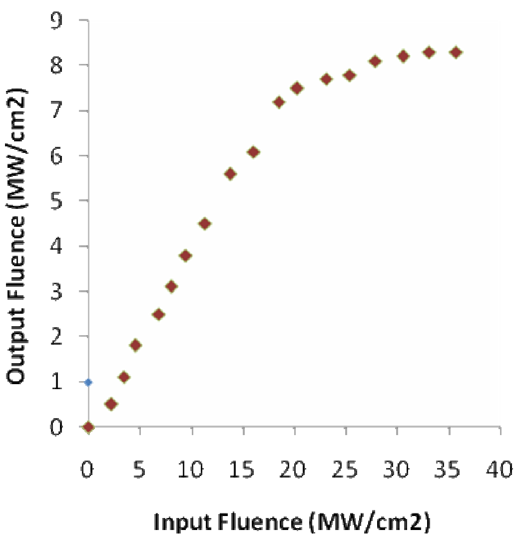
third-order nonlinear susceptibility ($\chi^{(3)}$, esu) are listed in Table 1.

From the results obtained, it is found that Azophloxine dye possess a large third-order nonlinear susceptibility with magnitude of the order of 10^{-8} esu. One of the important exploits of reverse saturable absorption in a material is its application as an optical limiter. In principle, an optical power limiter is a device which becomes opaque at high input intensities while transmitting low light intensities. An important term in optical limiting measurement is the limiting threshold. An ideal optical limiting material should have low limiting threshold.

The optical limiting response of Azophloxine dye is as shown in Fig.7. Initially as the input power is increased, the output power also starts increasing, but after a certain threshold value the sample starts defocusing the beam, resulting in a greater part of the beam cross section being cut off by the aperture. Thus the transmittance recorded by the photodetector remains reasonably constant showing a plateau region. The Optical limiting threshold value obtained for the dye sample is found to be 18.5 MW/cm^2 for 0.03mM concentration.

From the above results, it is found that the dye possess better optical limiting behavior than some representative third-order nonlinear optical materials such as organic polymers and organic metals[12].

Fig.7. Optical limiting response of Azophloxine dye



Conclusion

In conclusion, the Z-scan experiments performed on the Azophloxine dye using nanosecond Nd:YAG laser pulses operated at 532nm wavelength revealed interesting features of nonlinear optical properties of the dye. The studied dye sample exhibited self focusing effect and reverse saturable absorption. The origin of the large refractive nonlinearity in the dye sample appears to be predominantly electronic in nature. It is found that this dye have a large third-order nonlinear susceptibility, $\chi^{(3)}$ when compared to organic polymers and organic metals[13,14]. The dye also exhibits a low optical limiting threshold. These attractive properties of the dye could be exploited in developing it as an optical limiter for future photonic and optoelectronic applications.

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