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Z-scan determination of the third-order optical nonlinearities of a Schiff base compound

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The linear and nonlinear optical properties of Schiff Based compound, N-salicylidene-aniline, dissolved in organic solvents with varying dielectric constants using different concentrations are reported. Their nonlinear optical properties have been investigated by Z-scan technique with picoseconds laser pulses. The nonlinear refractive index values obtained for solutions containing 6% to 48% of N-salicylidene-aniline in toluene fall in the range -1.87 to -5.6×10^{-12} cm^2/W, while the nonlinear third order susceptibility $\chi^{(3)}$ is in the range -3.4×10^{-11} to -1.41×10^{-10}e.s.u.

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1. Introduction

In the last two decades the nonlinear properties of organic molecules are being explored with great interest because of their role in emerging technology of photonics [1-3]. The nonlinear optical properties of an organic material can severely affect the temporal and spatial behavior of light beam propagating through the medium. A variety of physical mechanisms can result in independent contributions to the refractive index. In liquids of isotropic molecules, the nonlinearities may arise from molecular redistribution or by electronic polarizability caused by distortion of electronic clouds, or by resonance effects such as saturation absorption or two-photon absorption. A large contribution to the nonlinear refractive index can also occur due to thermal effects. To measure optical nonlinearities of materials, techniques such as nonlinear interferometry, moiré deflectometry, ellipse rotation and beam distortion, are being adopted by many researchers [4-5]. The Z-scan technique is a simple, accurate and effective tool for the determining the important nonlinear properties [5-8]. It is being widely used in materials characterization because it provides not only the magnitudes of real and imaginary parts of nonlinear susceptibility, but also the sign of real part of the refractive index. Z scan can detect a light induced subtle change in the refractive index. The technique is based on the Gaussian spatial distribution of irradiance of laser light. When a Gaussian beam passes through a third order NLO material a refractive index gradient is formed in the material in response to the spatial distribution of the light irradiance.

In this communication, the results of investigation performed by using Z-scan technique to measure the sign and magnitude of the optical nonlinearity of solutions of newly discovered Schiff base material [9], N-salicylidene aniline, are reported. The experiments were performed using different concentrations in various organic solvents. The samples were found to exhibit a negative and large nonlinearity.

2. Experimental details

2.1 Theory

The phenomenon of a self-focusing (Z-scan) of an intense Gaussian beam in a nonlinear medium results in a beam distortion which can be measured and used to obtain the value of n_2 (refractive index gradient) of the medium. Analysis is quick and simple, which makes it a good technique for screening new nonlinear materials. Z scan can detect a light induced subtle change in the refractive index. The technique is based on the Gaussian spatial distribution of irradiance of laser light. When a Gaussian beam passes through a third order NLO material a refractive index gradient is formed in the material in response to the spatial distribution of the light irradiance

$$n(r) = n_o + \Delta n(r) = n_o + n_2 I(r)$$

where r is a spatial coordinate. In this technique, light enters into a material of refractive index *n* from free space with refractive index n_{fs}, its propagation direction (or the bending angle away from the surface normal to the material at the incident spot) is determined as a ratio between the refractive indices n/n_{fs} according to Snell's law. Bigger the ratio, smaller the bending angle. If a refractive index gradient is a function of spatial coordinate r then on the basis of Snell's law the exiting light must become more convergent or divergent than the incident light depending on whether $\Delta n(r)$ or n_2 is positive or negative. The refractive index gradient $\Delta n(r)$ is set-up by the interaction between the laser light and the nonlinear optical material and so Δn (r) dictates the propagation direction of the laser light in the material. Such a change in the propagation direction of the laser beam in a nonlinear optical material is called as light self bending. When $\Delta n > 0$ it is called as self-focusing and when $\Delta n < 0$ it is self defocusing. This means that a slab of self-focusing nonlinear optical material, example a quartz -cuvette filled with a solution containing nonlinear optical compounds, will respond to a Gaussian beam as a convex lens would for a linear optical material . While a slab of self defocusing nonlinear optical material will respond in the same way as a normal concave lens. It was difficult to work with the crystal sample, so powder was used in different solvents.

Fig. 1 shows the detailed schematic diagram of the experimental set-up. If the sample is moved about the focal point of the incident laser beam and the transmittance of the nonlinear medium are measured through a finite aperture located in the far field as a function of the sample position (*z*).

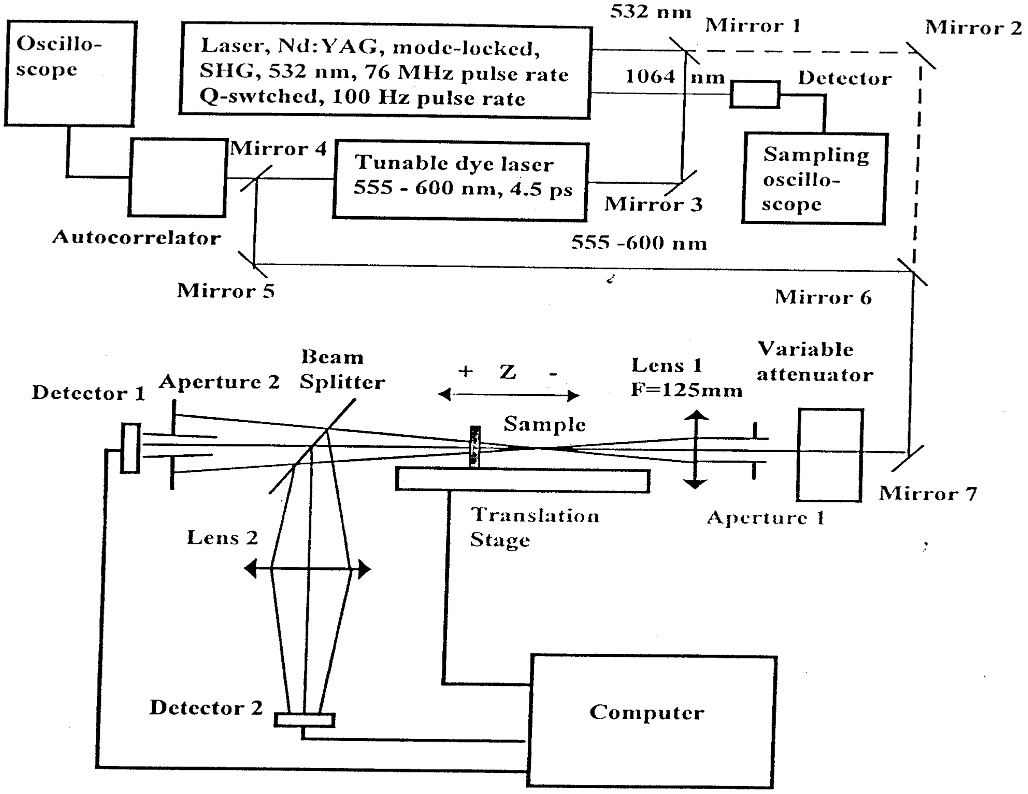

Fig. 1. Optical set-up of the Z-scan experiment with substituted salicylidene-aniline derivatives.

Then, when the sample is moved toward the focus from the negative side of the focus the radiation increases, resulting in a negative lensing effect which tends to collimate the laser beam, causing an increase in the aperture transmittance as a result the aperture transmittance is increased. When the sample is moved away from the focus (on the positive side of the focus), the negative lensing effect augments the diffraction and the transmittance reaches to the original linear value for larger + z side. This value is normalized to unity. It is observed that decreased transmittance occurs at –*z* while increased transmittance occurs at + *z* side. Therefore the sign of nonlinear refractive index n_2 is measured from the *Z*-scan. The aperture transmittance as a function of sample position depends on the magnitude and the sign of n_2. This is the basis of the Z-scan technique. The nonlinear medium impresses a phase distortion on the electric field of the transmitted light. The sign of the nonlinear refractive index (n_2) is measured from the Z-scan. The cubic optical nonlinearity expressed in terms of the nonlinear refractive index in e.s.u units is given by

$$n = n_o + \frac{n_2}{2}|E|^2 = n_0 + \Delta n \tag{1}$$

where n_o is the nonlinear refractive index and E is the electric field (13). The nonlinear refractive index and the third order susceptibility are related to each other as

$$n_2 = 5.26 \times 10^{-6}\chi^{(3)} / n_o^2 \tag{2}$$

when n_2 is in MKS units and $\chi^{(3)}$ is in e.s.u. units. $\chi^{(3)}$ is the third order NLO susceptibility being a fourth rank tensor. It is a frequency dependent quantity and its wavelength dispersion provides information about the resonance process. The objective of the z-scan method is to measure this transmittance and calculate the sign and magnitude of n_2, and its sign and also to measure the sign as well as the magnitude of χ^3.

2.2 Experiment

Fig. 1 shows the detailed schematic diagram of the experimental station. This technique is simple to set-up as it is a single beam, with no difficult alignment except to make sure that the beam is centered on the aperture. The laser source was a tunable dye laser (with laser dye Rhodamine 6G) pumped by a frequency doubled mode locked Nd:YAG laser (76-MHz pulse repetition rate, 70ps pulse width). The width of the pulses produced by the dye laser was approximately 4ps. The tuning range was 555-600 nm. The average power of the laser applied to the sample varied between 100-300mW. Special precautions were taken to maintain the laser beam Gaussian. The beam diameter was approximately 3mm. The laser peak power density in the sample placed near the focus of the 125-mm focal distance lens in the Z-scan experiment reached up to 0.088 GW/cm^2. To study the sample at higher peak power density and less pulse repetition rate a Q-switched mode-locked configuration of the Nd:YAG laser was used when the laser generated 70-ps under the envelope of a Q-switched pulse with FWHM equal to 350ns approximately. With 13.2 ns time interval between pico-second pulses, the Q switched pulse coupled is considered as a shot of a series of approximately 27 pico-second pulses, giving a power density of up to 6 GW/cm^2 at 532nm. The Q-switched pulse repetition rate was 100 Hz. A Gaussian beam from the laser is tightly focused and passed through the experimental solution in either toluene or acetone. The output power is measured by the detector after it passes through a finite aperture. The cuvette is translated along the z-axis in the positive and negative direction with respect to the focal point. This transmitted power is obtained as a function of the sample position on the z-axis measured with respect to the focal plane. The z-scan technique has been used to determine the sign of the nonlinearity of the solution.

3. Results and discussion

Using the self-focusing Z-scan method for the measurement of the nonlinear refractive index and the third harmonic generation for the crystals at 532nm a lot of scattering of the green light was observed and poor quality Z-scan was obtained using the crystals. Fig. 2 shows a typical Z-scan obtained for a solution of N-salicylidene aniline in toluene, showing the normalized spectra with open and closed aperture.

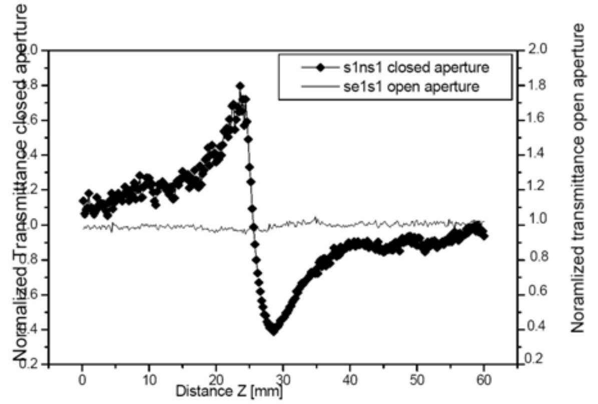

Fig. 2. A typical Z-scan of n-salicylidene aniline solution.

To get a purely refractive Z-scan transmittance curve, a closed aperture Z-scan with a partially closed aperture is obtained. The closed aperture data are divided by the open aperture data to produce a Z-scan transmittance curve which approximates a purely refractive transmittance curve. For all the Z-scan measurements S=0.5, (aperture radius r_a = 1.5mm) average power is 300mW, at a wavelength of wavelength 532nm The nonlinear refractive index, and the third order NLO susceptibility calculated from the Z-scan data n_2 are reported together with the concentration in Table 1 .

Table 1. Concentration, nonlinear refractive index and third order susceptibility of solution of N-salicylidene-aniline in toluene.

Concentration of Salicyldiene aniline (sa)	n_2 sq. cm/W	$\chi^{(3)}$ esu
0.0603g sa in 1ml	$-1.1145\text{x}10^{-12}$	$-3.4145\text{x}10^{-11}$
0.1201 g sa in 1 ml	$-1.8655\text{x}10^{-12}$	$-5.715\text{x}10^{-11}$
0.2407 g of sa in 1ml	$-4.9295\text{x}10^{-12}$	$-1.248\text{x}10^{-10}$
0.3603 g of sa in 1 ml	$-5.500\ \text{x}10^{-12}$	$-1.3925\text{x}10^{-10}$
0.4803 g of sa in 1ml	$-5.565\ \text{x}10^{-12}$	$-1.4085\text{x}10^{-10}$

The plots of concentration versus third order NLO susceptibility is plotted in Fig. 3, while the concentration against nonlinear refractive index is shown in Fig. 4 and a plot of nonlinear refractive index versus third order nonlinear susceptibility for the compound N-salicylidene aniline is given in Fig. 5.

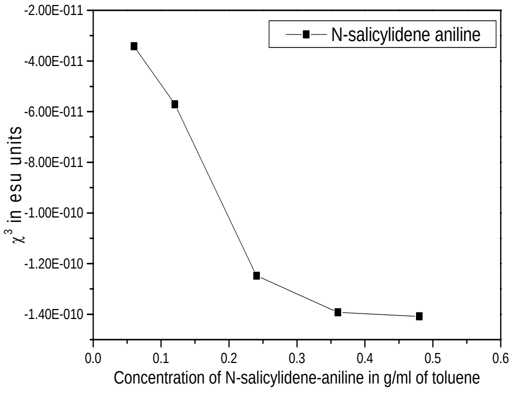

Fig. 3. Concentration of N-salicylidene aniline versus third order NLO susceptibility $\chi^{(3)}$ in esu.

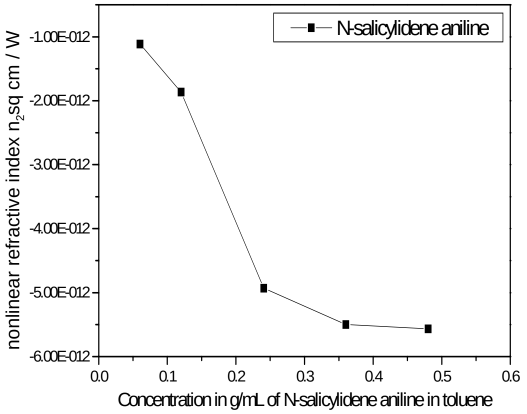

Fig. 4. Concentration of N-salicylidene aniline versus nonlinear refractive index, $n_{2,}$ in sq. cm / W.

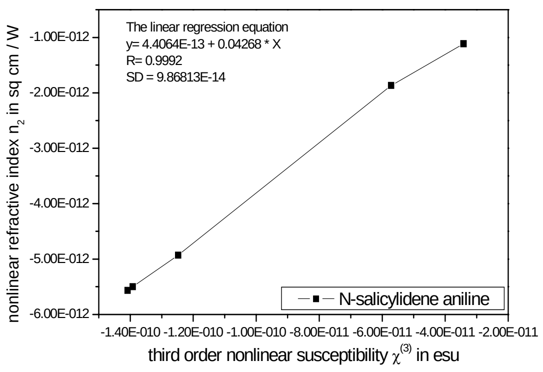

Fig. 5. Nonlinear refractive index n_2 in sq cm /W versus third order NLO susceptibility $\chi^{(3)}$ in e.s.u.

The nonlinear refractive index values obtained for N-salicylidene-aniline solution in toluene are in the range between -1.87 to -5.6 x 10^{-12} cm^2/W, while the nonlinear third order susceptibility $\chi^{(3)}$ is in the range -3.4 x 10^{-11} to -1.41 x 10^{-10} e.s.u. for a solutions containing 6% to 48% of N-salicylidene-aniline in toluene. The $\chi^{(3)}$ reported for the solvent toluene using 532nm wavelength is given as 3.8 x 10^{-14} e.s.u. as determined by the degenerate four wave mixing method. Similarly, for the solvent acetone the reported $\chi^{(3)}$ value is 1.0 x 10^{-14}e.s.u. (15). Z-scan were recorded for few substituted Schiff base derivative compounds of N-salicylidene aniline that were grown as crystals, using acetone as solvent. The nonlinear refractive indices for the compound N-salicylidene-3-chloroaniline -5.11 to -8.11 x 10^{-13} cm^2/ W while the third order susceptibility from the Z-scan experiment was obtained in the range -1.29 to -2.04 x 10^{-11}esu, in acetone containing 7% to 15% weight of N-salicylidene-3-chloroaniline. For solutions of the compound n-salicylidene-3-methyl aniline in acetone containing 9% to 16% by weight of solute, the recorded nonlinear refractive indices are – 4 x 10^{-13} to 1.07 x10^{-12} cm^2 / W and the third order NLO susceptibility is -1.03 to – 2.64 x10^{-11} e.s.u.. All the compounds show third order susceptibility in the value of 10^{-11} e.s.u. using a wavelength of 532nm. These values are comparable to those reported by Chandrashekar et al. [10] for the polymers of polydiphenyl amine at 532 nm 1.3 x10^{-10}, 1.0 x10^{-10} and 1.7 x10^{-11}e.s.u. , while for the poly (4amino biphenyl) the corresponding values are 1.4 x10^{-10}, 8x10^{-11} and 6 x10^{-11} e.s.u. for solutions containing 3.3, 6.7 and 13 g/L respectively. Kanbara et al. [11] have reported n_2 optical Kerr shutter values in the range of 6.0 x10^{-15}, 9.1 x10^{-15} and 8.3 x10^{-15} and 1.3 x10^{-14} cm^2/W measured for symmetrically substituted benzylidene aniline derivative dyes of 2.5 dichloro-terephthal-bis (4-N, N'-diethylaminoaniline) doped in PMMA.

4. Conclusions

The nonlinear refractive index and the third order susceptibility have been determined using the Z-Scan method. The linear optical properties include spectrum of propagation modes and optical extinction spectrum. The nonlinear properties include optical spectrum of nonlinear refractive index and nonlinear absorption. Light absorption of the compound is associated with the modification of the linear refractive index. The modification is a result of a process such as the heating of the compound causing its index increase where the light is passing through the nonlinear compound. Relatively high nonlinear refractive index is a result of enhancement of intrinsic third order nonlinearity of the compound by the mechanism of heat causing a circulation of the warm compound to the cooler compound. The intrinsic nonlinearity is associated primarily with an artificial lens produced in the liquid by the heat.

Acknowledgements

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