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Nonlinear Optical Measurements of R2 Dye

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Abstract: **The nonlinear refraction and nonlinear absorption of dye R2 were studied by the Z-scan technique. Continuous wave (cw) argon ion laser was employed to study the nonlinear response of this dye at several laser powers, solution concentrations and wavelengths. The results established that the R2 displayed a saturable absorption (SA) character and self-defocusing effect. Optical limiting behavior was also studied as a function of concentration and laser wavelength. The limiting threshold values were estimated for the dye solutions at different concentrations and at different laser wavelengths. Our study clearly shows that the R2 dye is excellent nonlinear material with large nonlinear response may provide the basis material for devices in optical applications.**

Keywords: **Dye; Nonlinear; Optical; Refraction; Absorption; Optical Limiting.**

I. INTRODUCTION

Nonlinear optics (NLO) is a revolutionary addition to conventional (linear) optics after the advent of lasers [1]. This area is the branch of science that deals mostly with different new optical phenomena and effects that occur from the interactions of strong coherent beam with matter to induce changed fields that are different from the incident field in frequency, amplitude or phase [1, 2].

Among many substances that exhibit the NLO properties, organic dyes have displayed significantly high third order nonlinear optical response [3]. Third order materials play a crucial role in many applications of NLO, such as optical switching, image processing, protective shields for eyes or equipment from intense laser beam [4]. To assess a material for NLO application, measurement of the NLA coefficient (β) as well as the NLR index (n_2) are essential [5].

One of the most significant methods to measure NLO properties is a single beam Z-scan. The Z-scan technique is a simple yet highly sensitive single beam method to measure NLR index (n_2) and NLA coefficient (β) [6]. The Z-scan method was developed by the Sheik- Bahae et al. in 1989 [7]. It is a well-established tool active and simple for measuring the NLO properties of a variety of materials [8].

This study studied third-order nonlinear optical properties of newly synthesized dye R2 by the z-scan technique. The investigations involve the measurement of the nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and optical limiting threshold of this material using the single beam Z-scan technique. Continuous wave (cw) tunable laser is used to study the nonlinear response of this material at several incident laser powers, solution concentrations and wavelengths.

II. EXPERIMENTAL

The dye1,3-diethyl-2-thioxo-5-(3,4,5-trimethoxybenzylidene)dihydropyrimidine-4,6(1H,5H)-dione (R2) was chosen for this study. Molecular structure of the dye is presented in Fig.1. The novel dye was synthesized by Chemistry Department of King Abdulaziz University. Their absorption and emission profiles, as well as determination of structure, characterization and stability were studied by them.

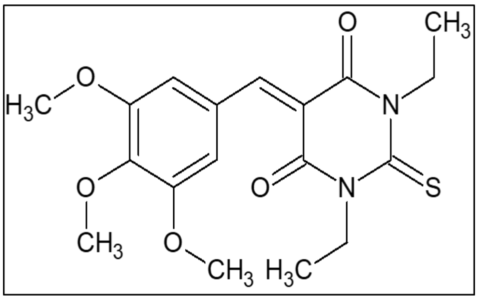


Figure 1. Chemical structure of R2 dye

Linear Absorption Spectra:

Linear absorption of the sample R2 was recorded by the UV–visible spectrophotometer. The absorption spectrum of the dye is exhibited in Fig.2. Linear absorption coefficient α_0 is obtained from these spectra.

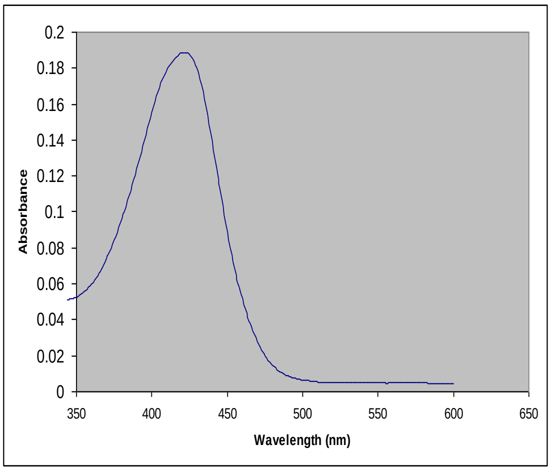


Figure 2. UV-VIS absorption spectrum of dye R2

Z-scan Technique for Determining the Nonlinear Optical Properties:

A solution of dye in chloroform solvent with concentration (C) of dye was placed in a thin cell (1 mm) for the Z-scan measurements. This experiment was performed by a argon ion laser working under experimental conditions as continuous wave (cw), certain wavelength (λ) and incident laser power (P). The laser beam was focused with a 5 cm focal length lens onto the cell sample. The sample is translated across the focal region along the axial direction that is the direction of the propagation laser beam with the help of a stepper motor controlled translation stage. The transmission of the beam through an aperture placed in the far field is detected using photomultiplier tube (McPherson). For an open aperture Z-scan, the iris aperture was kept fully opened. The Z-scans are recorded three times and an average of three scans is taken to decrease noise. Normalized transmittance of the dye was found by dividing averaged data with the solvent transmittance data measured under the same situations.

The transmittance measurements of the beam were repeated at different input laser powers, different solution concentrations and different wavelengths for both closed and open aperture Z-scans. The values of C, λ and P for each measurement are compiled in Table 1.

Table 1. Parameters for each measurement of nonlinear optical properties of Dye R2

Constant	**Change**
λ= 457.9 nm, C= 0.1 mM	Different powers (5, 6, 7, 8 and 9 mW)
λ= 457.9 nm, P= 5 mW	Different concentrations (0 .1, 0.075, 0.05, 0.025 and 0.01 mM)
C= 0.1 mM, P= 10 mW	Different wavelengths (454,457,465,477 and 488 nm)

Optical Limiting Technique:

The effect of optical limiting on the dye was obtained through a continuous wave (cw) argon ion laser. A cell sample (1-mm containing dye solution) is placed at a specific position where the transmitted intensity exhibits a valley in the transmittance curve of the closed aperture Z-scan. The input laser intensity is varied systematically using electronic control provided for in the laser power supply control unit and the corresponding transmitted intensity was recorded with the photomultiplier tube. The output power transmitted by the sample was plotted as a function of the input power in this method.

The experiments were repeated for dye at different concentrations and different wavelengths. Table 2 is presented the values of C and λ for each measurement.

Table 2. Parameter for each measurement of optical limit

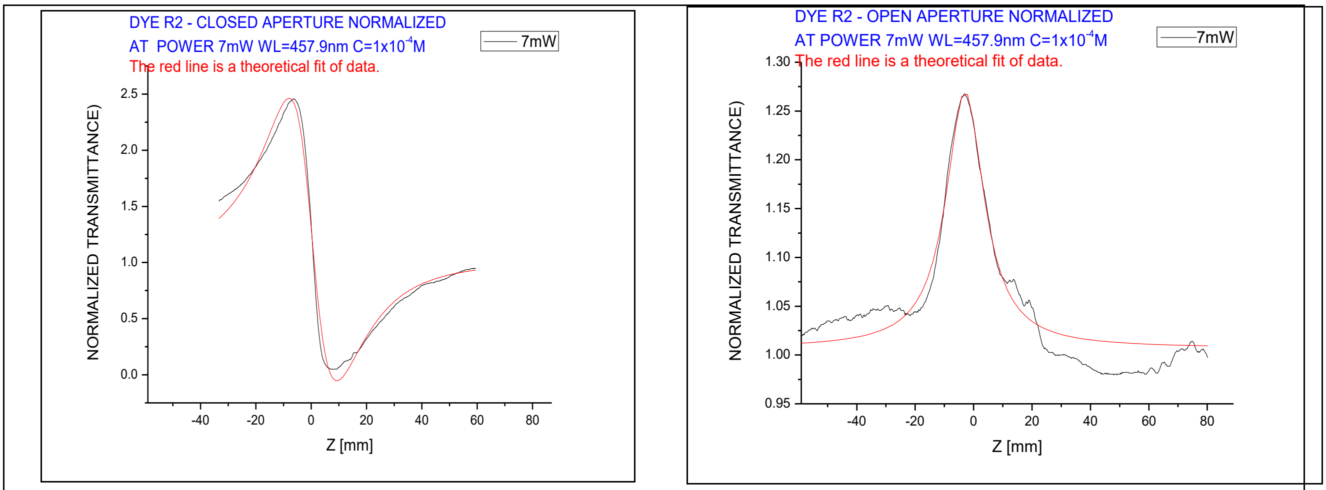
Constant	**Variable**
λ = 457.9 nm	Different concentrations (0 .1, 0.075, 0.05, 0.025 and 0.01 mM)
C= 0.1 mM	Different wavelengths (514, 502, 496, 488, 477, 472, 465, 457 and 454 nm)

III. RESULTS AND DISCUSSION

The closed aperture Z-scan results are shown in Fig. 3(a) and the open aperture scan is depicted in Fig. 3(b) recorded by moving the sample of R2 dye solution with concentration 0.1 mM (1 x 10^{-4} molarity) dissolved in chloroform. The argon ion laser wavelength used for these scan is 457.9 nm at an incident power 7 mW. The black solid line is the experimental data while the red line is a least square fit of the data. The figure shows an average of at least three repeated measurements. A simple computer program is developed in Origin Lab software to estimate the third order nonlinear refractive index n_2 and the nonlinear absorption coefficient β. The fit is very good and thus the obtained values have low uncertainties. This procedure is repeated to obtain the nonlinear parameters at various laser powers, solution concentrations and laser wavelengths.

The peak to valley configuration of normalized transmittance curve obtained from the closed aperture Z-scan data in Fig.3(a) suggest that the change in refractive index of the dye R2 was negative exhibiting strong self-defocusing effect. The self-defocusing effect is attributed to thermally induced variation in refractive index of the medium [9, 10].

Fig.3(b) shows a saturable absorption (SA) behavior from the measured Z-scan data for the open aperture set-up for solution of R2 at laser power 7 mW. This behavior indicates the nonlinear absorption (NLA) coefficient β is also negative.



(a) (b)

Figure 3. Z-scan for R2 dye at 0.1 mM with 7 mW and 457.9 nm.

The red line is a theoretical fit of data (a) Closed-aperture (b) Open-aperture

The SA in the sample enhances the peak and decreases the valley in the closed aperture Z-scan thus distorting the symmetry of the Z-scan curve about Z=0 [11].

The defocusing effect shown in Fig.3(a) is due to a thermal nonlinearity resulting from absorption of radiation at 457.9 nm. Localized absorption of a tightly focused beam propagating through an absorbing dye medium creates a spatial distribution of temperature in the dye solution and consequently, a spatial difference of the refractive index, that acts as a thermal lens resulting in phase distortion of the propagating laser beam [12].

The fitting of the measurements of the normalized transmittance versus sample position by origin program, for the case of closed and open aperture, allow determination of NLO parameters n_2 and β.

The NLR index n_2 of the dye R2 with 457.9 nm and 7 mW is calculated from closed aperture normalized transmittance in Fig.3(a) and obtained n_2 is -1.63168×10^{-6} cm^2/W. The NLA coefficient β is obtained from the open aperture Z-scan data is -0.00736 cm/W.

The n_2 and β values are used in finding the real and imaginary parts of the third-order NLO susceptibility $\chi^{(3)}$ by the relationship [13]:

$$\text{Re}\,\chi^{(3)}\,(\text{esu}) = \frac{10^{-4}\epsilon_o c^2 n_o{}^2}{\pi}\, n_2\,(\text{cm}^2/\,\text{W}) \qquad (1)$$

$$\text{Im}\chi^{(3)}\,(\text{esu}) = 10^{-2}\frac{\epsilon_o c^2 \lambda n_o{}^2}{4\pi^2}\beta\,(\text{cm}/\,\text{W}) \qquad (2)$$

The absolute value of the third-order NLO susceptibility $|\chi^{(3)}|$ is defined as

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

The absolute value $\chi^{(3)}$ of the dye R2 at 457.9 nm and 7 mW obtained is high value 8.69×10^{-5} esu.

Power Scan of Dye R2 with Wavelength 457.9 nm:

The NLO properties of the dye R2 with wavelength 457.9 nm were studied by Z-scan technique. The measurements were done at concentration 0.1 mM and different input beam power in the range from 5 to 9 mW.

Normalized transmittance curve of the R2 dye at different intensities obtained from the closed aperture Z-scan measurements is as shown in Fig.4(a) and the peak followed by a valley configuration of the closed aperture curve indicates that the change in refractive nonlinearity was negative exhibiting self- defocusing effect. The peak height of normalized transmitted of closed aperture increase with increase power while the dip of valley increase with increase power.

Fig.4(b) shows saturable absorption (SA) behavior from the open aperture Z-scan curve of the R2 dye at different input laser power. This behavior is indicative the R2 dye exhibiting negative NLA coefficient β. The peak higher (at focus) of normalized transmitted of open aperture increase with increase power.

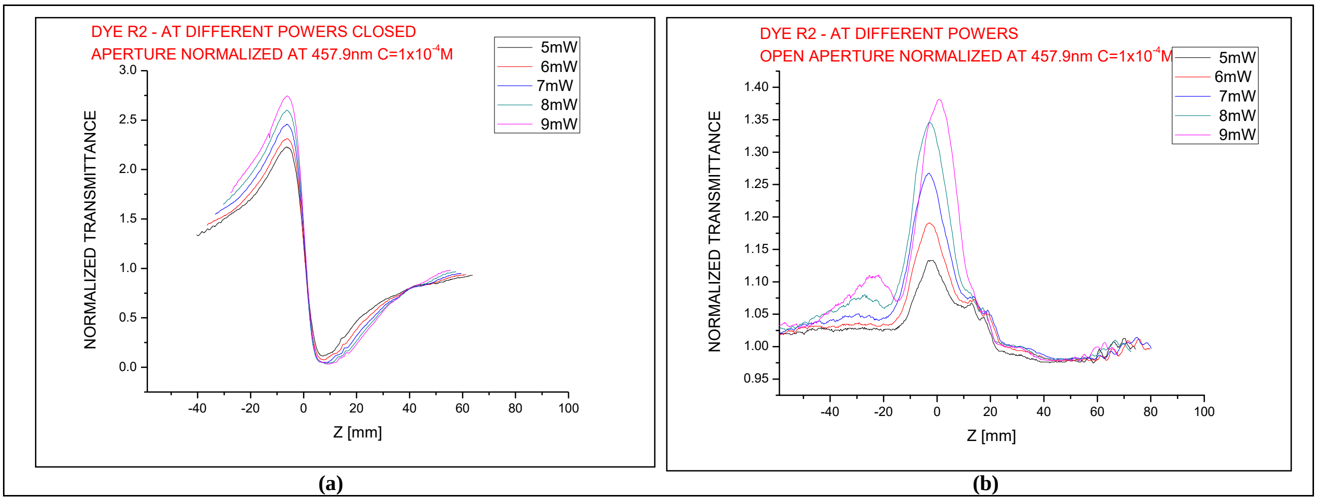


Figure 4. Z-scan for R2 dye at 0.1 mM with 457.9nm at different laser power
(a) Closed-aperture (b) Open -aperture

The values of n_2, β and $|\chi^{(3)}|$for dye R2 at 457.9 nm at different laser power are summarized in Table 3.

Table 3. Nonlinear optical parameters of the dye R2 with 457.9 nm at different laser power

LaserPower mW	$n_2 \times 10^{-6}$ cm^2/W	$\beta \times 10^{-3}$ cm/W	$\lvert\chi^{(3)}\rvert \times 10^{-5}$ esu
5	-1.74	-6.21	9.25
6	-1.66	-6.59	8.85
7	-1.63	-7.36	8.69
8	-1.61	-8.68	8.58
9	-1.60	-9.36	8.52

The variation of $\chi^{(3)}$ at different input laser power is small, Fig.5; it shows a slight decrease with increasing laser power. This indicates that nonlinearity is insensitive to laser power in the range of powers that we studied.

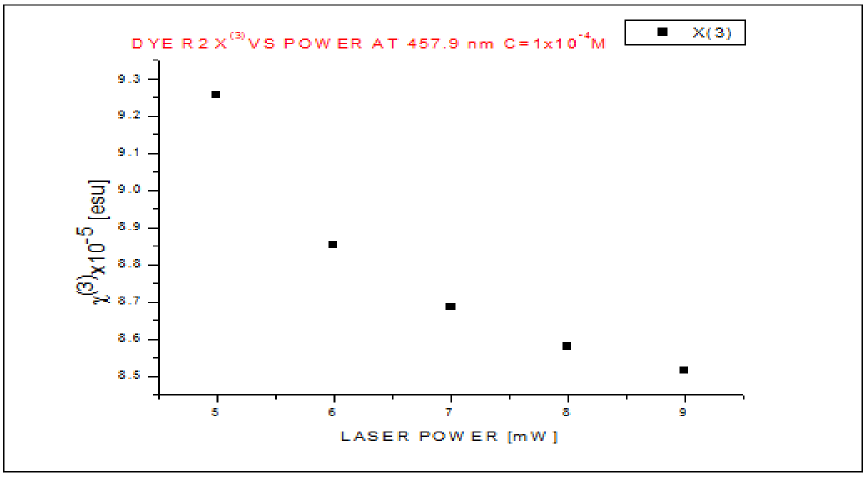


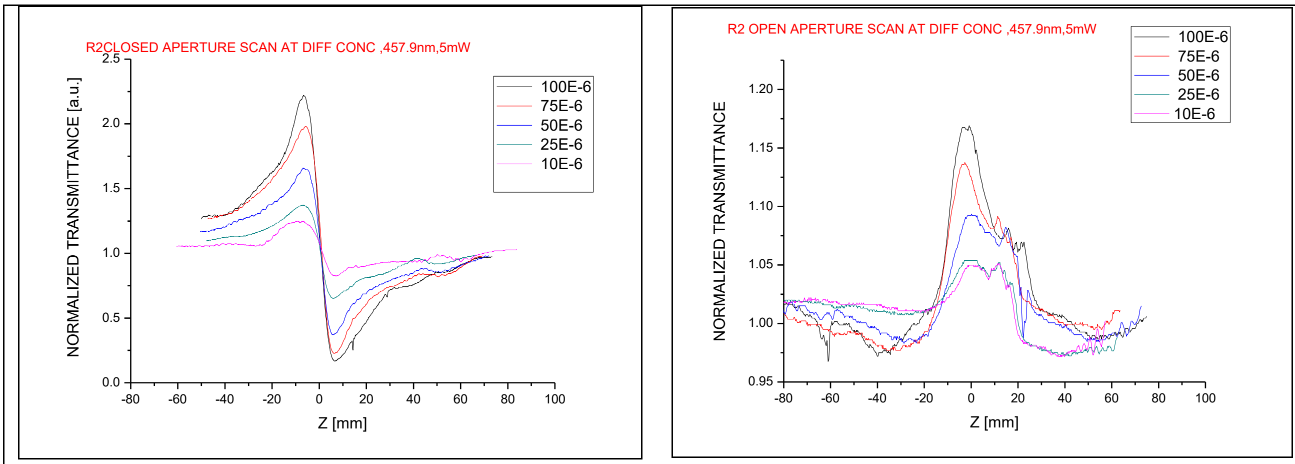
Figure 5. Variation of $\lvert\chi^{(3)}\rvert$ of R2 dye at 0.1 mM with 457.9 nm for different laser power

Concentration Scan of Dye R2 with Wavelength 457.9 nm:

The NLR index and NLA of R2 dye in different concentrations 0.1, 0.075, 0.05, 0.025 and 0.01 mM were measured by Z-scan technique.

The measurements were performed at 457.9 nm and 5 mW. A closed aperture Z-scan of the R2 is shown in Fig.6(a) for different concentrations, a prefocal peak and postfocal valley indicates the negative sign of n_2 i.e. self-defocusing for R2 at different concentrations. The open aperture Z-scan of the R2 dye in Fig.6(b) shows SA behavior indicating the NLA coefficient β is also negative for different concentrations.

Theoretical fits to the data give values of n_2 and β for R2 at different concentrations with wavelength 457.9 nm. The values of n_2, β and $\lvert\chi^{(3)}\rvert$ are reported in Table 4.



(a) **(b)**

Figure 6. Z-scan for R2 dye at 5 mW with 457.9 nm at various concentrations

(a) Closed-aperture (b) Open-aperture

Table 4. Nonlinear optical parameters of the dye R2 with 457.9 nm at different Concentrations

Concentration $\times 10^{-6}$ [M]	$n_2 \times 10^{-7}$ cm^2/W	$\beta \times 10^{-3}$ cm/W	$\lvert\chi^{(3)}\rvert \times 10^{-5}$ esu
100	-13.70	-6.94	7.29
75	-12.34	-6.54	6.57
50	-8.44	-4.44	4.49
25	-5.16	-3.14	2.75
10	-2.32	-3.12	1.24

The absolute value of $\chi^{(3)}$ (Fig.7) increase with increase concentration. This may be attributed to the fact that as the number of dye molecules increases when the concentration increases, more particles get thermally excited resulting in an enhanced third order optical nonlinearity [11, 14, 15].

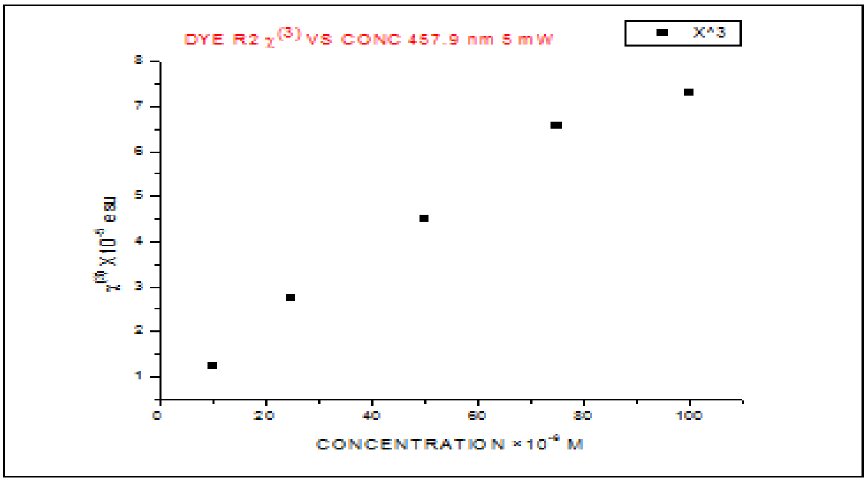


Figure 7. Variation of $\lvert\chi^{(3)}\rvert$ of R2 dye at 5 mW with 457.9 nm for different concentrations

Wave Scan of R2 Dye:

With Z-scan, the NLO properties for R2 dye in chloroform solution at concentration 0.1 mM and incident laser power 10 mW were measured using the laser of different wavelengths (454, 457, 465, 477 and 488 nm).

The peak followed by a valley normalized transmittance curve, obtained from the closed aperture Z-scan data in Fig.8(a), indicates the self-defocusing effect providing negative NLR index for R2 dye at different wavelengths.

The SA behavior of the open aperture Z–scan transmittance curve in Fig.8(b) indicates that R2 dye solution exhibits the negative NLA coefficient β at different wavelengths.

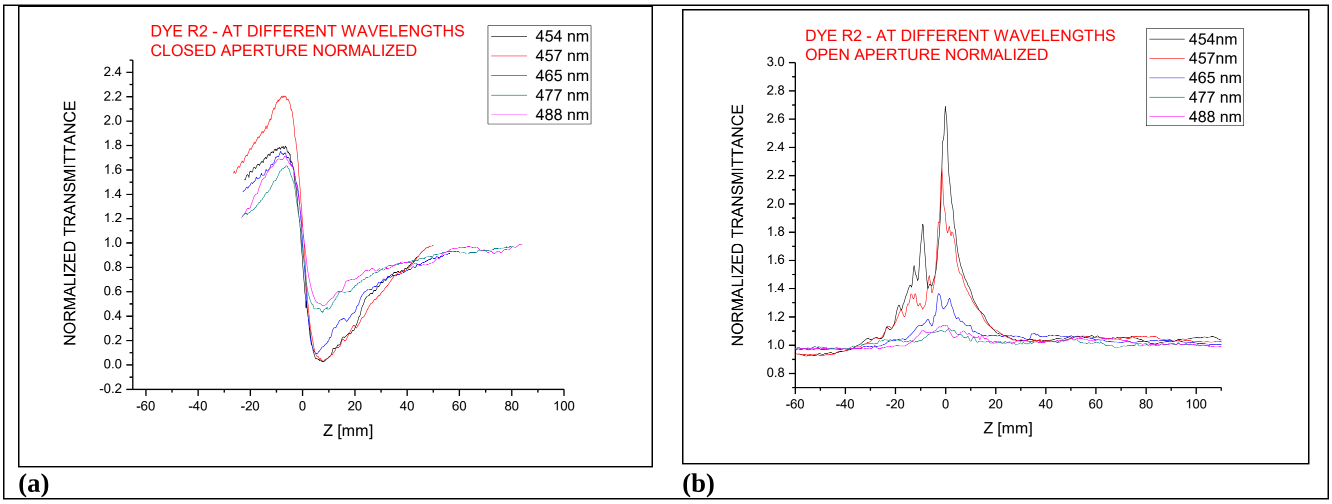


Figure 8. Z-scan for R2 dye at 0.1 mM with 10 mW at different wavelengths

(a) Closed-aperture (b) Open-aperture

The experimentally determined values of n_2, β and $|\chi^{(3)}|$for R2 dye at different wavelengths are summarized in Table 5.

Table 5. Nonlinear optical parameters of the dye R2 at different wavelengths

Wavelength Nm	**$n_2 \times 10^{-7}$ cm^2/W**	**$\beta \times 10^{-3}$ cm/W**	**$\lvert\chi^{(3)}\rvert \times 10^{-5}$ esu**
454	-11.66	-1.17	6.21
457	-12.49	-8.44	6.65
465	-7.76	-5.14	4.13
477	-3.71	-3.68	1.98
488	-3.88	-3.25	2.06

The variation of $|\chi^{(3)}|$at different laser wavelength (Fig.9) is substantially large; it shows a decrease with increasing wavelength. This indicates that nonlinearity is highly sensitive to laser wavelength in the range of wavelengths that we studied.

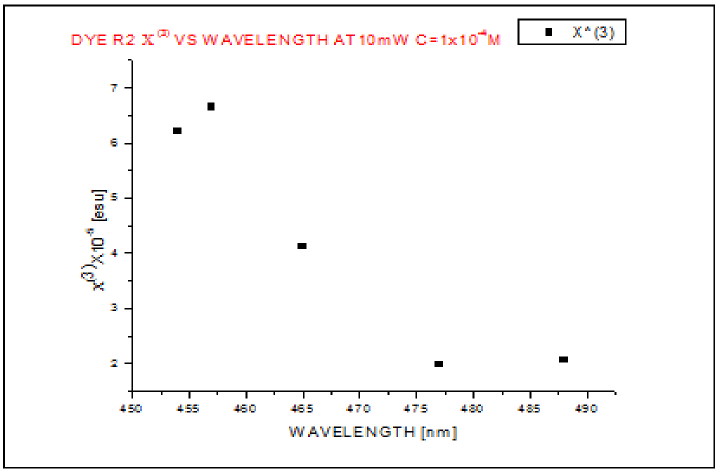


Figure 9. Variation of $|\chi^{(3)}|$of R2 dye at 0.1 mM with 10 mW at different wavelengths

Optical Limit of R2 Dye:

The optical limiting behavior of the dye R2 was studied at wavelength 457.9 nm and concentration 0.025 mM.

The optical limiting response of R2 dye is as shown in Fig.10, initially as the input power is increased, the output power also starts increasing proportionally, but after a certain value the output power start to deviate from the linear behavior and ultimately acquires a constant saturation value (the sample defocusing the beam). This value at the knee point, as indicated in the figure, is called the optical limiting threshold [10]. The optical limiting threshold value obtained for the dye sample is found to be 5.58 mW for 0.025 mM concentration. In some cases, the transmitted output power may even decrease from the saturation level by further increasing the input power.

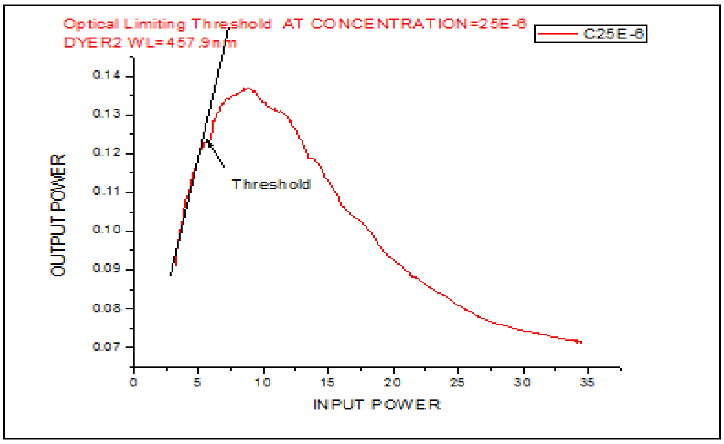


Figure 10. Optical limiting response of R2 dye at 0.025 mM concentration and 457.9 nm

Optical Limit of R2 Dye at Different Concentrations:

The optical limiting behavior of the dye R2 was studied at wavelength 457.9 nm and different concentrations.

The optical limiting behavior was observed for the R2 dye at wavelength 457.9 nm and different concentrations as shown in Fig.11.

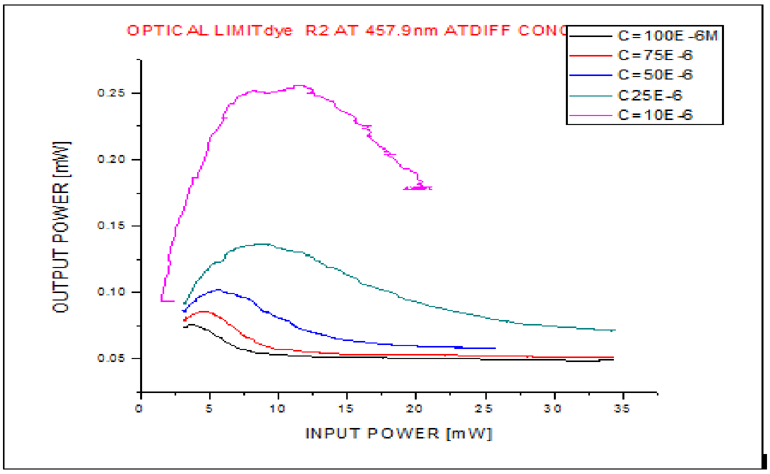


Figure 11. Optical limiting response of R2 dye with 457.9 nm for different concentrations

The optical limiting threshold value for the R2 dye at wavelength 457.9 nm and different concentrations are listed in Table 6.

Table 6. Optical limiting threshold of dye R2 with 457.9 nm at different concentrations

Concentration×10^{-6} [M]	**Optical Limiting Threshold [mW]**
100	3.79
75	4.59
50	4.764
25	5.58
10	5.82

The power limiting threshold linearly decreases with increasing the dye concentration as shown in Fig.12. This is attributed to the fact that the number of absorbing molecules increases with increasing the dye concentration which in turn lowers the limiting threshold [16].

From above results, it is found that the R2 dye at 457.9 nm possess good optical limiting behavior at different concentrations.

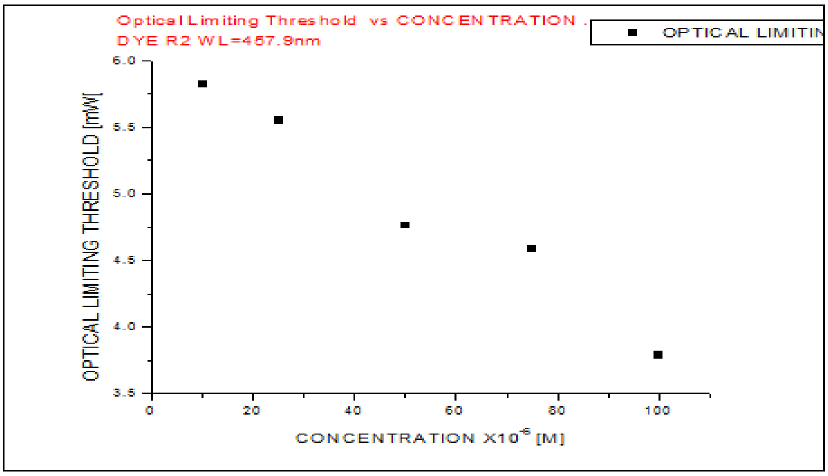
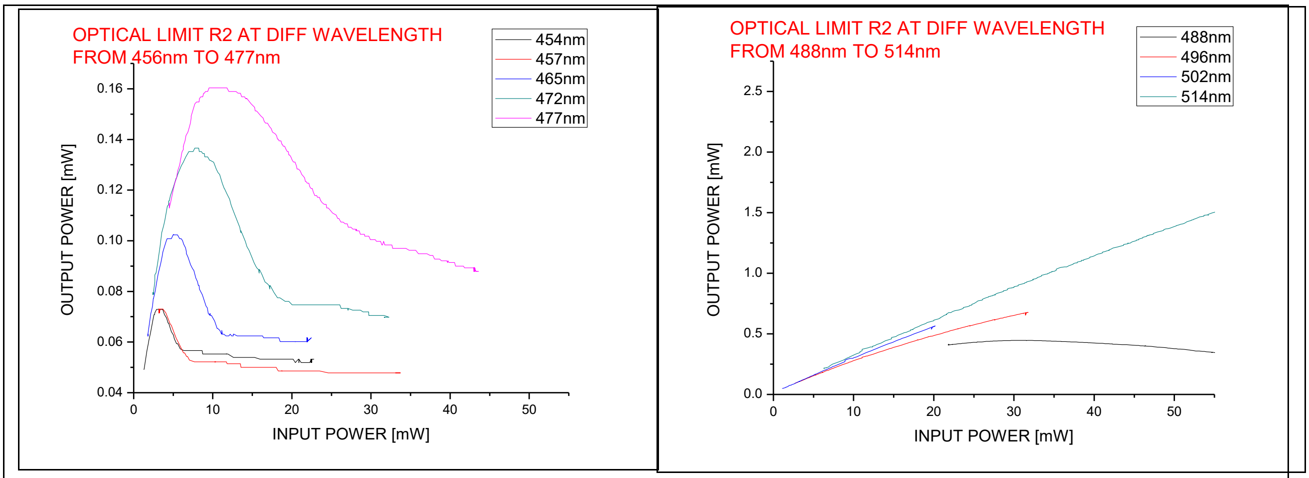


Figure 12. Optical limiting threshold of R2 dye solution as function of concentration

Optical Limit of R2 Dye at Different Wavelengths:

The optical limiting behavior was studied for 0.1 mM dye R2 in chloroform in different wavelengths (514, 502, 496, 488, 477, 472, 465, 457 and 454 nm).

From Fig.13(a and b), the dye R2 at lowers wavelengths (454, 457, 465, 472 and 477 nm) have a good optical limiting behavior.



(a) **(b)**

Figure 13. Optical limiting response of R2 dye with 0.1mM for different wavelengths in the range from (a) 454 to 477 nm (b) 488 to 514 nm

The threshold power was measured for each wavelength in the range (454, 457, 465, 472, 477 and 488 nm). Table 7 shown threshold optical limiting versus the wavelengths.

Table 7. Optical limiting threshold of dye R2 at different wavelengths

Wavelength [nm]	**Optical Limiting Threshold [mW]**
454	2.9
457	3.35
465	4.14
472	5.82
477	8.32
488	29.08

The threshold optical limiting (Fig.14) decrease with decreases wavelength.

The results of present study found that the R2 dye at 0.1 mM concentration possess good optical limiting behavior at different wavelengths.

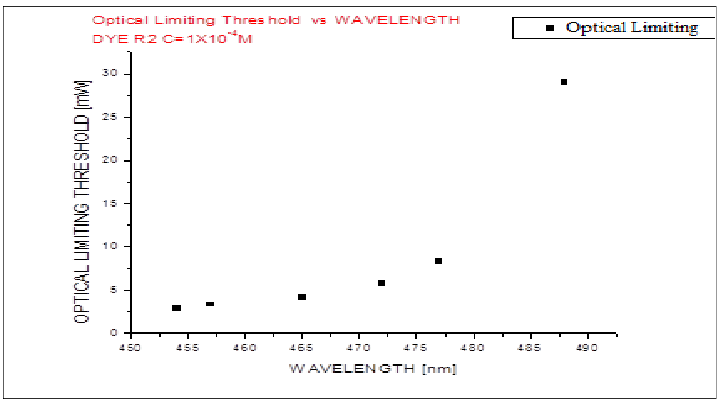


Figure 14. Optical limiting threshold of R2 dye solution as function of wavelengths

IV. CONCLUSION

The experimental results show that the studied R2 dye exhibit SA and negative nonlinear refraction at different incident intensity, concentration and wavelengths. The negative value of n_2 and β and the absolute value of $\chi^{(3)}$ of dye R2 are found to be high and increase linearly with increase in the concentration. 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. The value of n_2, β and $\chi^{(3)}$ was found to vary significantly with wavelength . Optical limiting threshold was measured for various concentrations of dye. The optical limiting threshold is inversely proportional to concentration of sample. This helps us to choose required concentration for safety of photosensitive devices at the desired intensity levels. Optical limiting threshold of R2 dye was measured for various wavelengths. The optical limiting threshold decrease with decrease wavelength. More work is needed to understand and explain this behavior by studying the molecular electronic energy level structure and the life times of the molecular states. Existence of strong third order nonlinearity with quite low limiting threshold that dye R2 have a great potential for the applications in developing photonic devices like optical limiters for eye and apparatus safety. The dye R2 shows high nonlinear properties and is therefore better candidate for applications in device development.

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