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The Effect of Dye Concentrations and Sample Thickness on The Nonlinear Optical Properties of A Soluble Rhodamine 6G Dye

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Abstract

The optical properties of Rhodamine 6G (R6G) dye in acetone solution were studied at different concentrations and thickness using Nd:YAG laser at the wavelength of 532 nm. The optical measurements were characterized by measuring the intensity of the medium using the Eclipsing Z-scan (EZ-scan) method. The samples in open aperture EZ-scan showed two-photon absorption. For the closed aperture, the dye exhibited a positive nonlinearity for all concentrations but showed negative (defocusing) nonlinearity at different thickness. The values of n_2, β and $|\chi^{(3)}|$ vary with the concentration and the thickness of the samples. Optical limiting characteristics of the dye at various concentrations and thickness in solution were studied.

Keywords: nonlinear refractive index, nonlinear absorption coefficient, third order susceptibility, Rhodamine 6G

1. INTRODUCTION

Nonlinear optical (NLO) materials were given tremendous attention due to their wide applications such as optical switching, optical communications, optical power limiting, and optoelectronic and photonic devices [1-4]. Organic compounds with delocalized electron systems and a large dipole moment have nonlinear susceptibilities larger than the inorganic compounds [5]. Laser dyes are one of the materials which can show very high nonlinear optical properties [6-9]. Rhodamine 6G (R6G) dye is one of the important dyes, which is used for its many features such as photostability, high absorption coefficients and excellent fluorescence quantum yields [10]. The dyes are very suitable in the field of nonlinear optics because of their optical properties. The Z-scan method has been accepted by the nonlinear optics community as a standard method to study nonlinear optical properties. The Z-scan has a simple set up and, under certain conditions;, it is possible to isolate the nonlinear refractive index of the nonlinear absorption coefficient. Besides that, it can also determine the magnitude and the sign of the nonlinear refractive index [11]. Recently, the focus was the interest in the outer edges of the beam, rather than the central part, and to increase the sensitivity. This can be achieved, as in the Z-scan method, by replacing the aperture with a disk, which prevents the central part of the laser beam from passing through. Since the light that seeps around the edges appears as an eclipse, thereby the name of the method is Eclipsing Z-scan, or EZ-scan [12-16].

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1.1 Materials and method

1.1.1 Materials

R6G dye has a molecular formula of $C_{28}H_{31}N_2O_3Cl$ and a molar mass of 479.02 g/mole. It is supplied by Hi Media Laboratories Pvt. Ltd. (India) and its structure is as shown in Figure 1.

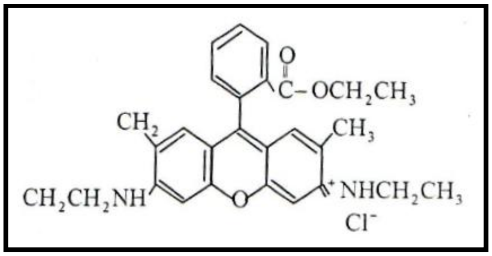


FIGURE 1. THE STRUCTURE OF RHODAMINE 6G

The acetone has the formula of CH3COCH3, refractive index of about 1.361 at temperature 17 °C, purity of 99%, and molecular weight of 58.08 g.mol^{-1}. The Spectrophotometer T60 supplied by the English company (Insrtrumrnts) was used to measure the absorption spectra of the liquid samples. This device operates within the range of the visible and ultraviolet region and the emission spectrum was taken by using Spectrofluorometer model SL174 (Elico Ltd, India). Refractive index was taken by using a refractometer (Bellingham and Stanley Ltd., Tunbridgewells, England).

1.1.2 Method: EZ-scan technique

Nd:YAG laser at the wavelength of 532 nm with 90 mW (MHHL-532-100 mW) was used as the excitation source in the EZ-scan method. The beam of laser was focused by a convex lens with focal length f = 30 cm to produce a laser beam waist at focus equal to 85 μm, diameter of a disc of about 1.5 cm, and diffraction length (or ZR) of 42 mm. Figure 2 shows the experimental setup of EZ-scan.

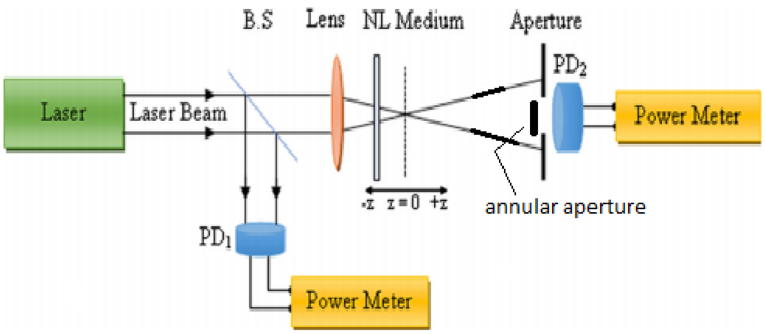


FIGURE 2. EXPERIMENTAL ARRANGEMENT FOR THE EZ-SCAN

The nonlinear absorption coefficient (β) was calculated from the experimental observations and by fitting the normalized transmittance equation T(z)[17]:

$$T(z) = \sum_{m=0}^{\infty}\left[\frac{[-q_0(z)]^m}{(m+1)^{3/2}}\right] \qquad (1)$$

where: $q_o(z) = I_o L_{eff} \beta / [1+\left(\frac{z}{z_0}\right)^2]$, and $L_{eff} = \frac{1-e^{-\alpha_0 L}}{\alpha_0}$ is the effective length of the sample, L is the sample thickness, α is a linear absorption coefficient, and I_0 is the intensity of the laser at z = 0. The β value can found by the best fitting of equation (1).

The nonlinear optical properties (n_2) can be calculated using simple expression [18]:

$$n_2 = \Delta\Phi_0 / I_0 (1-s)^{0.25} L_{eff} \mathrm{k} \qquad (2)$$

Where: $\Delta T_{pv} = 0.68(1-S)^{-0.44} |\Delta\Phi_0|$ and k, is the wavenumber

1.1.3 Transmittance spectra of R6G dye

The UV-visible linear optical transmittance of the R6G dye in acetone solvent by using Spectrophotometer T60 supplied by the English company (Insrtrumrnts) is as shown in Figure 3.

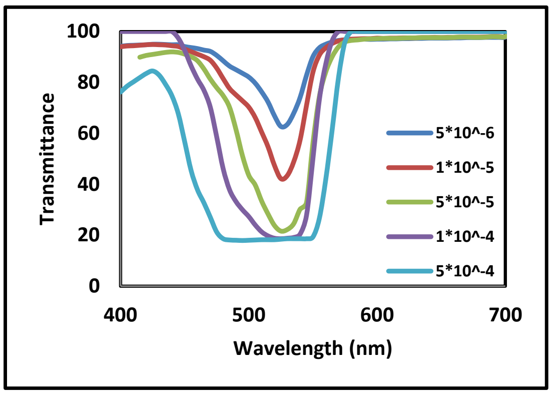


Figure 3. Transmittance spectra of R6G dye solution

2. RESULTS AND DISCUSSION

2.1 Effects of the concentration

The Rhodamine 6G dye in acetone solvent at various concentrations ($1*10^{-6}$, $5*10^{-6}$, $1* 10^{-5}$, $5*10^{-5}$ and $1*10^{-4}$ mol/l) for incident power Pin of 90 mW was studied by using EZ-scan. Figure 4 shows the transmittance of laser beam after passing through R6G dye solution which varies with the position of the sample. The R6G dye solution shows two photons absorption (TPA) for all concentrations. Also, the transmittance decreases when the sample is closer to the focus (z = 0) to form a valley in the focus, and the transmittance is symmetric about the focus (z = 0). The closed aperture EZ-scan curve is shown in Figure 5. It can be seen that the sign of the refraction nonlinearity is positive (self-focusing) for all concentrations of dye. The absolute value of the third-order nonlinear optical susceptibility $|\chi^{(3)}|$ can be calculated by using the nonlinear refractive index

(n_2) and nonlinear absorption coefficient (β). The nonlinear susceptibility value of dye solution was in the order of 10^{-9} V^2/m^2.

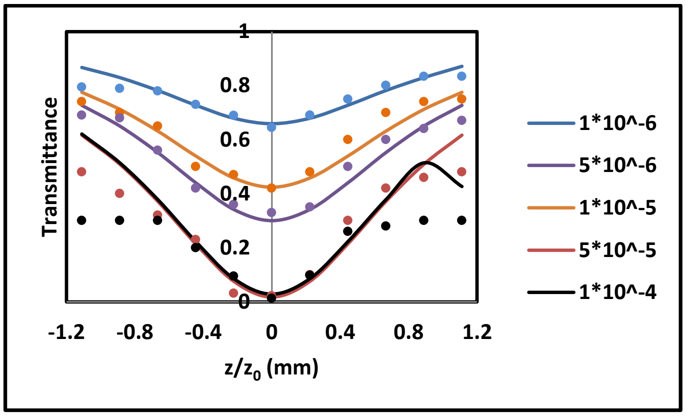


FIGURE 4. OPEN EZ-SCAN OF R6G DYE SOLUTION: APERTURE DATA (DOTTED CURVE), AND CURVE FITTING (SOLID LINE).

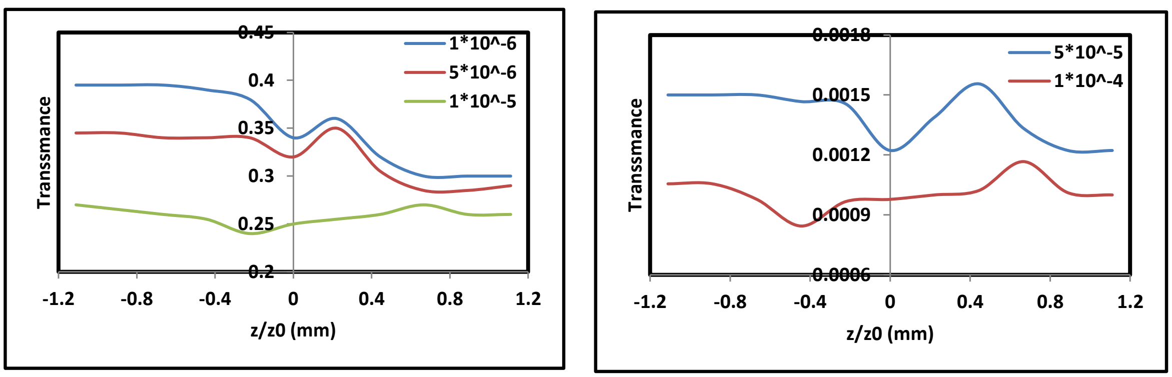


FIGURE 5. CLOSE EZ-SCAN OF THE R6G DYE SOLUTION

Table 1 shows the nonlinear absorption coefficient β, nonlinear refraction index n_2 and the absolute value of the third-order nonlinear optical susceptibility $|\chi^{(3)}|$, in which there are increases in β, n_2 and $|\chi^{(3)}|$ with increasing concentration of the dye. This may be attributed to the increase in the number of dye molecules when the concentration increased, and hence more particles were thermally agitated, resulting in an enhanced nonlinearity effect [19]. The nonlinear absorption, refraction index and susceptibility behaviors of R6G solution were in agreement with other work [20].

Table 1. Nonlinear properties of R6G dye solution at different concentration

Concentration (mol/l)	T %	A $(Cm)^{-1}$	L_{eff} (Cm)	n_2 (cm^2/W) 10^{-13}	β (Cm/W)	|χ(3)| (V^2/m^2) 10^{-9}
$1*10^{-6}$	93	0.072	0.099	0.12	0.011	0.45
$5*10^{-6}$	63.5	0.45	0.097	0.16	0.021	0.87
$1*10^{-5}$	43.4	0.83	0.095	0.198	0.026	1.08
$5*10^{-5}$	15	1.89	0.091	0.20	0.037	1.53
$1*10^{-4}$	14.2	1.95	0.090	0.202	0.038	1.57

The optical limiting curves of R6G dye are shown in Figure 6 for different concentrations with 90 mW laser and an aperture pinhole of 1.5 mm. The output power varies linearly with the input power, but after a certain value, the output stays constant (i.e. reaching threshold value), resulting in a greater part of the beam cross-section being cut off by the aperture. Table 2, shows the threshold power of optical limiting; it can be seen that the optical power limiting threshold is inversely proportional to the concentration.

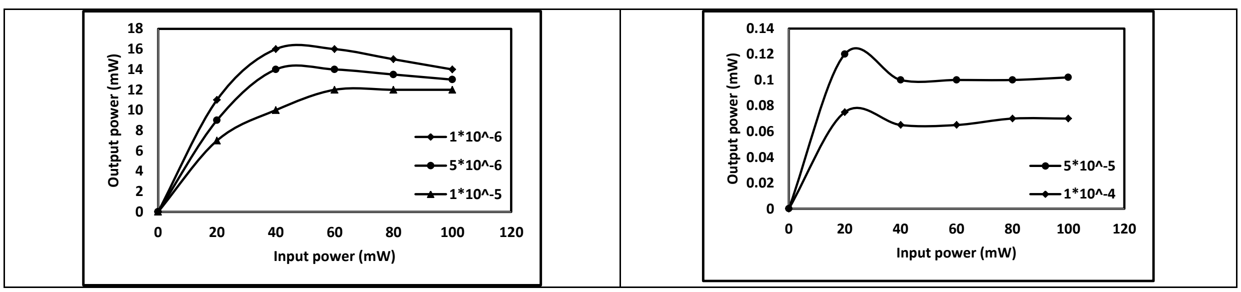


Figure 6. Optical limiter of R6G solution at different concentration

Table2. Threshold power of R6G dye solution at different concentrations

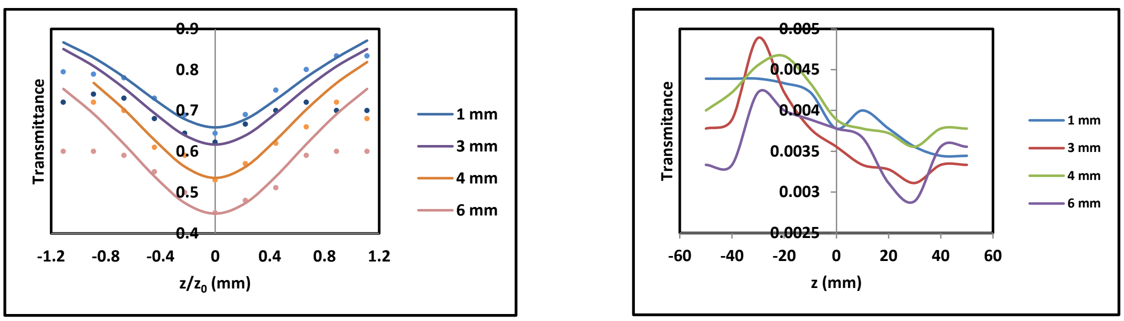
Concentration (mol/l)	Threshold power (mW)
$1*10^{-6}$	28
$5*10^{-6}$	30

1*10^{-5}	32
5*10^{-5}	15
1*10^{-4}	16

2.2 Effects of the thickness

Nonlinear optical properties of R6G dye in acetone solvent for various thickness (2, 3 and 6 mm) with incident power Pin = 90 mW was studied by using EZ-scan method. The R6G dye solution shows two photons absorption (TPA) for all thickness. Also, the transmittance decreases when the sample is closer to the focus (z = 0) to form a valley in the focus, and the transmittance is symmetric about the focus. The closed aperture EZ-scan curve is shown in Figure 7b and indicates that the sign of the nonlinear refractive index changes from positive (self-focusing) to negative (self-defocusing).

From Table 3, the values of β, n_2 and$|\chi^{(3)}|$ decrease when the concentration decreases. Since the nonlinear refractive index (n_2) is due to thermal effects [21], the reduction of nonlinearity in increase thickness can be attributed to the reduced thermal effect with increased thickness.



(a) (b)

FIGURE 7. EZ-SCAN OF R6G DYE (1 X 10-6 MOL/L) CONCENTRATION SOLUTION; A) OPEN FORM, B) CLOSE FORM

Table 3. Nonlinear properties of R6G dye solution at different sample thickness

Sample Thickness (mm)	L_{eff} (cm)	n_2 (cm2/W) 10^{-13}	B (cm/W)	$\|\chi(3)\|$ (V^2/m^2) 10^{-9}
1	0.099	0.12	0.011	0.45
3	0.29	-0.34	0.0046	0.19
4	0.39	-0.16	0.0042	0.17
6	0.58	-0.12	0.0033	0.13

Optical limiting performance of R6G solution dye in acetone solvent in different thickness (1, 3, 4 and 6 mm) with concentration of 1 * 10^{-6} mol/l and aperture pinhole of 1.5 mm is shown in Figure 8, in which the output power of laser varies with the input power. It is noted that threshold power values decrease with the increased thickness, as shown in Table 4.

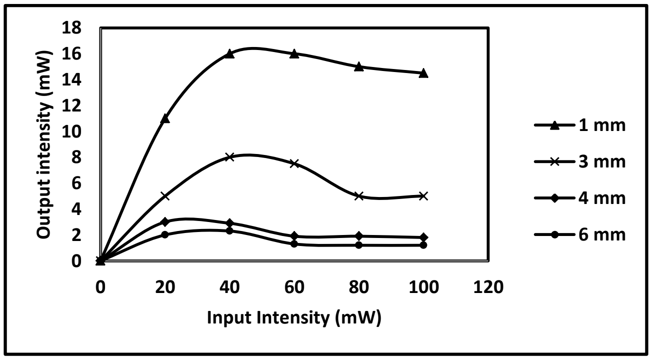


FIGURE 8. OPTICAL LIMITER OF A SOLUTION OF R6G WITH CONCENTRATION IS 1 * 10^{-6} MOL/L AT DIFFERENT THICKNESS.

Table 4. Threshold power of R6G dye solution (1 * 10^{-6} mol/l concentration) at different thickness

Sample Thickness (mm)	**Threshold Power (mW)**
1	16
3	8
4	1.9
6	1.2

3. CONCLUSION

Our aim is to study the nonlinear optical properties by using EZ-scan of Rhodamine 6G (R6G) dye solutions in acetone solvent at different concentrations and thickness, with Nd:YAG laser at wavelength 532 nm. The results showed that the β, n_2 and $|\chi^{(3)}|$ values depended of both the concentration and thickness of the samples. The experimental results showed that β, n_2 and $|\chi^{(3)}|$ increase when the concentration increases, and the results also showed decreases in n_2, β and $|\chi^{(3)}|$ with the thickness increase. The R6G dye, therefore has applications in optical limiter.

REFERENCE

1. I. Al-Deen, H. A. Al–Saidi and S. Al-Deen Abdulkareem, Optics and laser Technology,**82,**150-156(2016).
2. A. Farzana, J. Muhammad and J. J. Young, Molecular Crystals and liquid **648,** 88-113 (2017).
3. S. L. Gómez, V. M. Lenart, R. F. Turchiello, I. H. Bechtold, A. A. Vieira and H. Gallardo, J. Liquid Crystals, **43**, 2, 268-275(2016), doi: 10.1080/02678292.2015.1105313
4. K. B. Manjunatha, M. S. Vikas, R. Dileep, G. Umesh, M.N. Satyanarayan and B. B. Ramachandra, Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry,**44**,2282–290(2014). doi 10.1080/15533174.2012.750341.

5. R. K. Rekha, A. Ramalingam, Indian J Sci Technol **2**,8, 27–31(2009). doi: 10.17485/ijst/2009/v2i8/29505.
6. M. Samoc, A.Samoc, M.G. Humphrey, M. P. Cifuentes, B. L. Daves and P. A. Fleitz, Molecular Crystals and Liquid Crystals, **485**, 1, 894-902(2008), doi:10.1080/15421400801924714
7. Z. Dehghani, M. Nadafan, R. Malekfar and M. H. A. Majles, Inorganic and Nano-Metal Chemistry, **47**, 9, 1342-1347(2017). doi: 10.1080/24701556.2017.1284110.
8. R. N. Shaikh, A. Mohd, M. D. Shirsat and S. S. Hussaini, Materials Technology Advanced Performance Materials, doi,187-191(2016), doi,10.1179/1753555715Y.0000000039.
9. YING-GUEY F. ANDY and HUI-CHI LIN, Mol. Cryst. Liq. Cryst., **541,** 71–80 (2011).
10. Ali H. Al-Hamdani, A.H. Ali and M.H. Mohamed, Eng Tech J 2015; **33**,1, 273–284(2015).
11. G. Mudd, P.I. Pérez, N. Fethers, P.G. Dodd, O.R. Barbeau, et al., Methods Appl. Fluoresc **3,** 4, 1–6(2015);. doi: 10.1088/2050-6120/3/4/045002.
12. Ali H. Al-Hamdani, International journal of nanoelectronics and materials science, **6**, 139-146(2013).
13. Ali H. AL-Hamdani, M. H. Mohamed, A. H. Ali, ARPN J. Eng Appl Sci, **10**,16, 6705–6709(2015).
14. Ali H. Al-Hamadani, Z.W. Dawood, M.M. Jaber, ARPN Journal of Engineering and Applied Sciences, **12**, 2, 477-480(2017).
15. E. Shahriari, W. M. Yunus, American J. Eng Appl Sci **3**,1, 98–101(2010). doi: 10.3844/ajeassp.2010.98.101.
16. Ali H. Al-Hamdani, International Journal of ChemTech Research, **10**,6, 890-897 (2017).
17. T. Xia, D.J. Hagan, M. Sheik-Bahae, E.W. Van Stryland Optics Letters **19,**5, 317–319(1994). doi: 10.1364/OL.19.000317.
18. A.F. Jaffar, I.N. Akram, A.M.Salman and Q.R.A.Al-Taai , Int J Advance Technol Eng Sci **3**,1, 43-59(2015) .
19. A. Nag , D. Goswami, J Photochem Photobiol A Chem; **206**, 2–3, 188–197(2009). doi: 10.1016/j.jphotochem.2009.06.007.
20. M.B. Alsous, M.D. Zidan, Z. Ajji, A. Allahham , Optik – Int J Light Electron Optics 2014; **125**,18, 5160–5163(2009). doi: 10.1016/j.ijleo.2014.06.012.
21. G. Balaji, R.K. Rekha, A. Ramalingam, Acta Physica Polonica A, **119**, 359–363(2011). doi: 10.12693/APhysPolA.119.359.