Nonlinear optical characterization and optical limiting effect of Pyronin-Y dye by Z-Scan technique

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The third order nonlinear properties and optical limiting behavior Pyronin-Y dye was studied by using Z-scan technique. The pulsed Nd:YAG laser of wavelength 532 nm is used as a source of excitation. The experimental results showed that the Pyronin-Y dye exhibited saturation absorption and negative nonlinearity. The nonlinear refractive index n_2 , nonlinear absorption coefficient β and third order nonlinear optical susceptibility χ^3 were measured for different concentrations of dye in ethanol. This shows that the dye has potential application in nonlinear optics.

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1. Introduction

In recent years, the third order nonlinear optical (NLO) materials have been applied widely in many important technologies including optical recording, optical limiting for sensor protection, photonic switching, optical signal processing and optical limiting [1-5]. The Z-scan method is a simple and effective technique for determining nonlinear properties of organic dye. The present study aims to analyze the nonlinear properties of organic dye Pyronin-Y. Optical limiting is a nonlinear optical process in which the transmitted intensity of a material decreases with increased incident light intensity. It can be used for the protection of eyes and sensors from intense lasers. In this study, optical nonlinearity was induced in dye Pyronin-Y by Nd:YAG laser of wavelength 532 nm. The study was made for different concentrations of dye in ethanol.

The nonlinear refractive index n_2 , nonlinear absorption co-efficient β and third order nonlinear optical susceptibilities χ^3 are measured. The optical limiting behavior of the dye has been discussed.

2. Experimental procedure

2.1 Materials and methods

The sample was prepared by dissolving the dye in Ethanol at different concentrations. The dye Pyronin-Y was prepared in 1 mM, 1.1 mM and 1.2 mM concentration. The dye was weighed and dissolved in ethanol. The nonlinear optical properties of the sample was studied by using pulsed Nd:YAG Laser at 532 nm. The organic structure of pyronin-Y dye is as shown in Fig. 1.



Fig. 1. Chemical structure and Molecular formula of Pyronin-Y.

2.2 Absorption spectra

The spectral property of the dye Pyronin-Y in liquid medium of concentration 0.01 mM was studied by using a UV-VIS spectrophotometer (VARIAN COMPANY). The absorption was in the range of 300 to 600 nm, as shown in the Fig. 2. The spectral absorption peak wavelength (λ_a) was calculated to be 547 nm. The spectral parameters such as molar extinction co efficient $\epsilon(\lambda) 5.7 \times 10^4$ Lmol⁻¹ cm⁻¹, oscillator strength(f) 2.27×10^{-24} Lmol⁻¹ cm⁻² and band width ($\Delta \gamma_{1/2}$) 9.14×10³ cm⁻¹ were calculated at 547 nm [6].



Fig. 2. UV-VIS absorption spectra of dye Pyronin-Y in ethanol.

2.3 Z-Scan technique

A pulsed Nd:YAG Laser (QUANTA RAY: Model Lab–170-10) of wavelength 532 nm is 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 20 cm to produce beam waist (ω_0) of 488.30 μ m.



Fig. 3. Experimental setup for Z-scan Instrument.

The peak intensity of the incident laser beam was $I_0=9.77 \text{ kW/cm}^2$ and the diffraction length Z_r was found to be 2.2 mm. The schematic diagram of the experimental setup 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 which is the direction of the propagation of laser beam. The transmission of the beam was through an aperture placed in the far field was measured using detector and the output power was recorded by the digital power meter (EPM 2000, Coherent Molectron USA make). For an open aperture Z-scan, a lens was used to collect the entire laser beam transmitted through the sample with the aperture replaced [7].

2.3 Optical limiting effect

The optical limiting effect of the Pyronin-Y dye was studied by using pulsed Nd:YAG laser at 532 nm. A 1 mm quartz cuvette containing dye solution was kept at the position where the transmitted intensity showed a valley in closed aperture in Z-scan curve. An aperture of variable diameter was used to control the cross-section of the beam coming out of the sample cuvette. The beam was then made to fall on the photo detector. The input intensity was varied systematically and the corresponding output intensity values were measured by the photo detector [8].

3. Results and discussion

The third order nonlinear refractive index n_2 and the nonlinear absorption coefficient β , of the Pyronin- Y dye in ethanol at various concentrations for the incident intensity $l_0 = 9.77 \text{ kW/cm}^{-2}$ were evaluated by the measurements of Z-scan. The saturation absorption for the dye in solvent are shown by the open Z-scan curve (S=1)

in (Fig. 4). S is the aperture linear transmittance is given by

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

With r_{a} , ω_{a} indicates the aperture radius and the radius of the laser spot before the aperture. The open aperture Zscan curves for the Pyronin Y dye as shown in Fig. 4. The open aperture transmittance curve is symmetric with respect to the focus and the transmittance is calculated at the focus point indicating intensity dependent absorption effect. The Z-scan curve closed aperture as shown in Fig. 5. The peak to valley configuration of the curve suggests that the refractive index change is negative exhibiting a self defocusing effect. This shows that the dye has a large negative nonlinear refraction [9].



Fig. 4. Open Z-Scan curve for dye in solvent at various concentrations.



Fig. 5. Closed Z scan curve for dye in solvent at various concentrations.

The measurable quantity $\Delta T_{(p-v)}$ can be defined as the difference between the normalized peak and valley transmittances, Tp-Tv. The variation of this quantity [10] as a function of $|\Delta \varphi_0|$ is given by

$$\Delta T_{p-\nu} = 0.406(1-S)^{0.25} \left| \Delta \phi_0 \right|$$
 (2)

Where, $\Delta \phi o$ is the on-axis phase shift at the focus. The onaxis phase shift is related to the third order nonlinear refractive index (n₂) by,

$$\left| \Delta \phi_0 \right| = kn_2 L_{\text{eff}} I_0 \tag{3}$$

Where l_0 is the intensity of the laser beam at focus Z= 0, k is the wave number (k = $2\pi / \lambda$), λ is the wavelength of the light used, $L_{eff} = (1-e^{-\alpha L})$ is the effective thickness of the sample, L is the sample length, α is the linear absorption coefficient. If we collect all the energy transmitted by the sample (open aperture Z-scan), the measurement is sensitive to nonlinear absorption only. If an aperture is placed in front of the detector (closed aperture Z-scan), the measurement is sensitive to both nonlinear absorption and nonlinear refraction [11].

$$\beta = 2 \sqrt{2\Delta T} / I_o L_{eff}$$
(4)

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 when at the position of Z.

Experimentally determined nonlinear refractive index n_2 and nonlinear absorption coefficient β can be used in find the real and imaginary part of the third-order nonlinear optical susceptibility (χ^3) [12] according to the following relations,

$$\operatorname{Re} \chi^{3}(\operatorname{esu}) = 10^{-4} \frac{\varepsilon_{o} c^{2} n_{o}^{2}}{\pi} n_{2} \left(\frac{\operatorname{cm}^{2}}{W}\right)$$
$$I_{m} \chi^{3}(\operatorname{esu}) = 10^{-2} \frac{\varepsilon_{o} c^{2} n_{o}^{2} \lambda}{4\pi^{2}} \beta(\frac{\operatorname{cm}}{W})$$

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 (χ^3) is given by the relation.

$$\chi^{3} = \left[(R_{e}(\chi^{3}))^{2} + (I_{m}(\chi^{3}))^{2} \right]^{1/2}$$

The experiment was repeated for various concentrations of the dye Pyronin-Y to obtain the nonlinear parameters. The experimentally determined values of ΔT_{p-v} , $n_{2,\beta}$, Δn and χ^3 are given in Table 1.

Table 1. Nonlinear parameters of Pyronin-Y dye in solvent.

Concentration	$\Delta T_{(P-V)}$	$n_2 \times 10^{-8}$ cm ² /w	$eta imes 10^{-3}$ cm/w	$\Delta n \times 10^{-4}$	$\left \chi^{3}\right \times 10^{-6}$ (esu)
1 mM	13	-4.0	- 2.56	-3.8	26.6
1.1 mM	14	- 4.25	-2.87	-4.12	29.8
1.2 mM	15	- 4.50	-2.96	-4.36	30.8

The value of $n_{2,\beta}$ and $\chi 3$ increases as the concentration increases in this dye. As the number of dye molecules increases when concentration increases more particles are thermally agitated resulting in an enhance effect. A pulsed Nd:YAG laser beam passing through an absorbing media induces temperature and density gradient that change the refractive index profile. This intensity induced localized change in the refractive index results in a lensing effect on the optical beam [6, 10].



Fig. 6. Optical limiting effect of the dye in solvent.

The optical limiting curve obtained with an Nd:YAG laser of wavelength 532 nm for the dye in solution at 1 mM concentration is shown in Fig. 6. The output power increases initially with increase in input power, but after a certain threshold value the sample start 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 photo detector remained reasonably constant showing a plateau region. The UV-VIS absorption spectrum of the sample before and after the laser irradiation shows that the pattern and intensity of the spectrum does not show any change, indicating that the sample possess good photo stability [13-20].

4. Conclusion

In summary, the third order nonlinear parameters like nonlinear refractive index (n_2) , nonlinear absorption coefficient (β) and nonlinear susceptibility (χ^3) of Pyronin-Y dye have been determined using z-scan technique. The z-scan results indicated that the nonlinear absorption is saturation absorption, while the non linear refraction leads to self defocusing in this dye. This shows that the dye has a large third order nonlinear susceptibility other than some representative third order optical materials. These results are quite encouraging for possible applications in nonlinear optical devices.

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