

Non-linear characterization and optical limiting effect of carmine dye

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Abstract: Thermally induced optical nonlinearity of carmine dye in methanol is studied using a CW Nd-YAG laser at 532 nm as the source of excitation, both in solution and solid film (Methylmethacrylate- MMA), respectively. The optical response is characterized by measuring the intensity dependent refractive index (n_2) of the medium using the Z-scan technique. The dye exhibited a negative (defocusing) nonlinearity and large nonlinear refractive index of the order of 10^{-7} cm²/W. The nonlinear refractive index was found to vary with concentration. The third-order nonlinearity of the dye was dominated by nonlinear refraction, which leads to strong optical limiting of laser. The result reveals that carmine dye can be a promising material for optical limiting applications.

Keywords: Z-scan, carmine dye, NLO properties, optical limiting

Introduction

In the recent past, rapid technological advancements in optics have placed great demand on the development of nonlinear optical (NLO) materials with prominent applications in optical limiting and all optical switching (Venkatram *et al.*, 2008; Ting Huang *et al.*, 2008). A large number of organic compounds with delocalized electron systems and a large dipole moment have been synthesized to realize the non linear susceptibilities far larger than the inorganic optical materials (Tapati Mallik & Tanusree Kar, 2005). Carmine dye from natural family with delocalized electrons is attractive material for optical limiting applications for a wide variety of CW laser sources whose wavelengths lie in the visible region. Z-scan technique (Sheik-Bahae *et al.*, 1989; 1990), based on the spatial distortion of a laser beam passed through a nonlinear optical material, is widely used in material characterization because of their simplicity and high sensitivity.

Optical limiting is a nonlinear optical process in which the transmitted intensity of a material decreases with increased incident light intensity. An ideal optical limiter has a linear transmitted intensity at low input intensities, but above the threshold intensity, its transmitted intensity becomes constant. Nonlinear optical effects can be employed for the design and performance of optical limiter. It has been demonstrated that optical limiting can be used for

the protection of eyes and sensors from intense lasers (Li *et al.*, 2008). In this paper, the optical nonlinearity and optical limiting action of dye in methanol solvent at 50 mw CW Nd-YAG laser power at the wavelength of 532 nm was studied.

Experiment

Synthesis of Dye Doped Polymer Film

Carmine dye from natural family was chosen for the study. The molecular structure of the dye is shown in Fig.1. Thin layer chromatography (TLC) test confirms the absence of any impurities in the dye. Methylmethacrylate (MMA) was chosen as a monomer for synthesizing dye doped polymer film. Spectroscopic grade methanol was chosen as additive; because it combines better solubility for the dye and enhances the laser damage threshold. Benzoyl peroxide was used as the initiator. The dye doped polymer film (DDP) is synthesized using thermal bulk free radical polymerization method (Costela *et al.*, 1996; Sindhu Sukumaran & Ramalingam, 2006). The DDP film of concentration 0.050 mM and thickness of 0.93 mm was synthesized. The optical quality of this film is checked by passing He-Ne laser beam of power of 5mW. Film which shows no distortion or dispersion of the laser beam alone is taken for further studies.

Absorption Spectra

The UV-VIS absorption spectrum of the dye in methanol solvent was obtained using a (PERKIN-EIMER LAMDA 35) spectrophotometer and is shown in Fig.2. The spectral parameters such as absorption-peak wavelength, molar-extinction coefficient ϵ (λ), oscillator strength (f), bandwidth ($\Delta\nu_{1/2}$), were calculated to be 515 nm, 10.48×10^4 L mol⁻¹cm⁻¹, 2.72×10^{-24} Lmol⁻¹cm⁻² and 6.0×10^3 cm⁻¹ respectively.

Nonlinear Studies

The Z-scan technique developed by Sheik-Bahae *et al.* is used to characterize the nonlinear optical properties of natural dyes. It is based on the intensity dependent refractive index and includes the variation of the refractive index as a function of the incident beam irradiance on the sample,

$$n = n_0 + n_2 I \quad (2.1)$$

where n is the index of refraction, n_0 is the linear index, I is the intensity and n_2 is the nonlinear index of refraction. It is associated with the real part of

Fig.1. Chemical structure & molecular formula of carmine dye

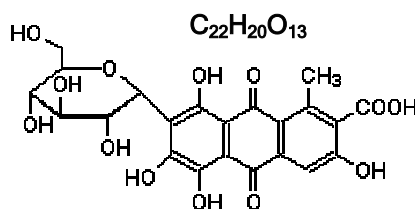
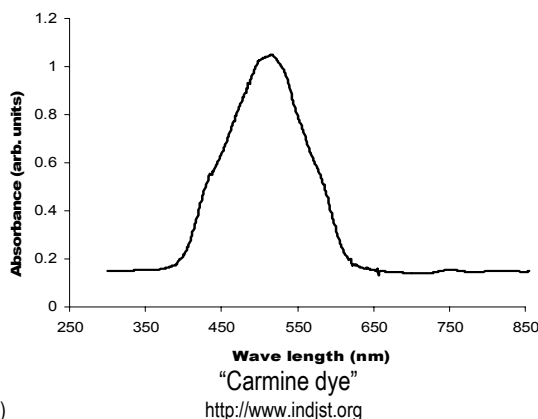


Fig. 2. UV-Vis. absorption spectrum of carmine dye



[χ^3] in the Taylor expansion of the material's polarizability.

Z-Scan Technique for Determining the Nonlinear Refractive Index:

The nonlinear refractive index of the dye was studied by Z-scan technique, where a Gaussian beam from a Nd-YAG laser of wavelength 532 nm is focused by a convex lens of focal length 35 mm and passed through the sample. The sample is scanned through the beam, the far field profile shows intensity variation across the beam profile, which is recorded through an aperture using photo detector fed to the digital power meter (Field master Gs- coherent) as shown in Fig.3. The peak intensity of the incident laser beam is $I_0 = 3.78 \text{ kW/cm}^2$ and the beam waist ω_0 of $18.82 \mu\text{m}$. The diffraction length, Z_R was found to be 2.09mm. Since the sample length was less than the diffraction length of the focused beam, thin sample approximation was used to analyze the data. For an open aperture Z-scan, a lens was used to collect the entire laser beam transmitted through the sample with the aperture replaced. The experiment was performed for, different concentrations of the sample (solvent) and polymer film.

Optical Limiting Technique: The limiting effect of the dye was studied by using a 50mW Nd: YAG CW laser at 532 nm. The experimental set-up for the demonstration of optical limiting is shown in Fig.4. A 1-mm quartz cuvette

containing dye solution is kept at the position where the transmitted intensity shows a valley in closed aperture Z-scan curve (Sendhil et al., 2006). A Variable Beam Splitter (VBS) was used to vary the input power. An aperture A of variable diameter is used to control the cross-section of the beam coming out of the sample cuvette. This beam is then made to fall on the photo detector (PD). The input laser intensity is varied systematically and the corresponding output intensity values are measured by the photo detector.

Results and discussion

The third-order nonlinear refractive index n_2 and the nonlinear absorption coefficient β , of the carmine dye in methanol at various concentrations and the polymer film for the incident intensity $I_0 = 3.78 \text{ kW/cm}^2$ were evaluated by the measurements of Z-scan. The saturation absorption for the dye in solvent and polymer film are shown by the open Z-scan curve ($S=1$) in

Fig.3. Experimental setup for Z-scan

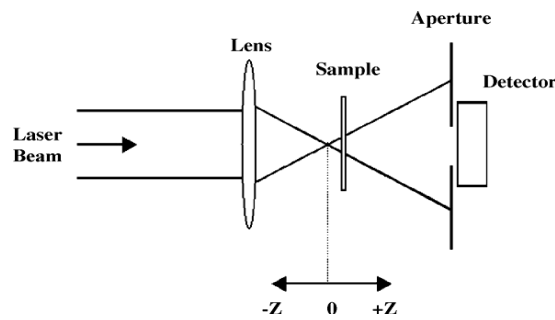


Fig.5 (i & ii). S the aperture linear transmittance is given by $S = 1 - \exp(-2 r_a^2 / \omega_a^2)$ (3.1)

with r_a denoting the aperture radius and ω_a denoting the radius of the laser spot before the aperture. The typical Z-scan data with fully open aperture is insensitive to nonlinear refraction, therefore, the data is expected to be symmetric with

respect to the focus, but saturation absorption in the sample enhances the peak and decreases the valley in the closed aperture Z-scan curve and results in distortions in the symmetry of the Z-scan curve about $Z=0$.

The peak followed by a valley-normalized transmittance curve obtained from the closed aperture Z-

Fig. 4. Experimental setup for measuring limiting effect

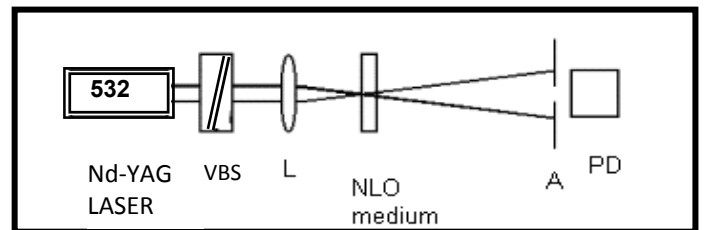
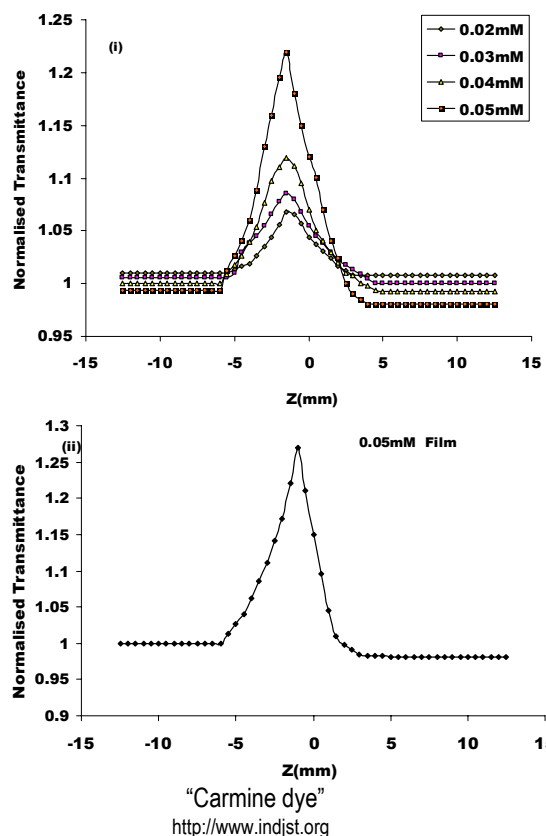


Fig.5. Open Z scan curve - (i) Dye in solvent at various concentration (ii) Polymer film



scan data, indicates that the sign of the refraction nonlinearity is negative, i.e. self-defocusing. The self-defocusing effect is due to the local variation of the refractive index with temperature. The defocusing effect for the dye in solvent and polymer film is shown in Fig.6 (i & ii), is attributed to a thermal nonlinearity resulting from the absorption of radiation at 532 nm.

Localized absorption of a tightly focused beam propagating through an absorbing-dye medium produces a spatial distribution of temperature in the dye solution and, consequently, a spatial variation of the refractive index that acts as a thermal lens resulting in the phase distortion of the propagating beam. The measurable quantity ΔT_{p-v} can be defined as the difference between the normalized peak

and valley transmittances, $T_p - T_v$. The variation of this quantity (Mathews *et al.*, 2007) as a function of $|\Delta\phi_0|$ is given by

$$\Delta T_{p-v} = 0.406 (1 - S)^{0.25} |\Delta\phi_0| \quad (3.2)$$

where $\Delta\phi_0$ is the on-axis phase shift at the focus. The on-axis phase shift is related to the third order nonlinear refractive index (n_2) by,

$$|\Delta\phi_0| = kn_2 L_{eff} I_0 \quad (3.3)$$

where I_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, $L_{eff} = (1 - e^{-\alpha L}) / \alpha$ is the effective thickness of the sample, L is the of the sample thickness 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. The pure nonlinear refractive index n_2 is obtained by dividing the closed aperture data by the open aperture data (Sheik-Bahae *et al.*, 1990). The pure nonlinear refraction Z-scan curves are shown in Fig.7 (i & ii) for the dye in solvent and polymer film. 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.

$$\beta = 2\sqrt{2} \Delta T / I_0 L_{eff} \quad (3.4)$$

where ΔT is the normalized transmittance of the sample when at position Z.

Experimentally determined 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 [χ^3] (Cassano *et al.*, 2001) according to the following relations,

$$\text{Re } \chi^3 (\text{esu}) = 10^{-4} \frac{\epsilon_0 c^2 n_0^2}{\pi} n_2 \left(\frac{\text{cm}^2}{\text{W}}\right) \quad (3.5)$$

$$\text{Im } \chi^3 (\text{esu}) = 10^{-2} \frac{\epsilon_0 c^2 n_0^2 \lambda}{4\pi^2} \beta \left(\frac{\text{cm}}{\text{W}}\right) \quad (3.6)$$

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 is given by the relation

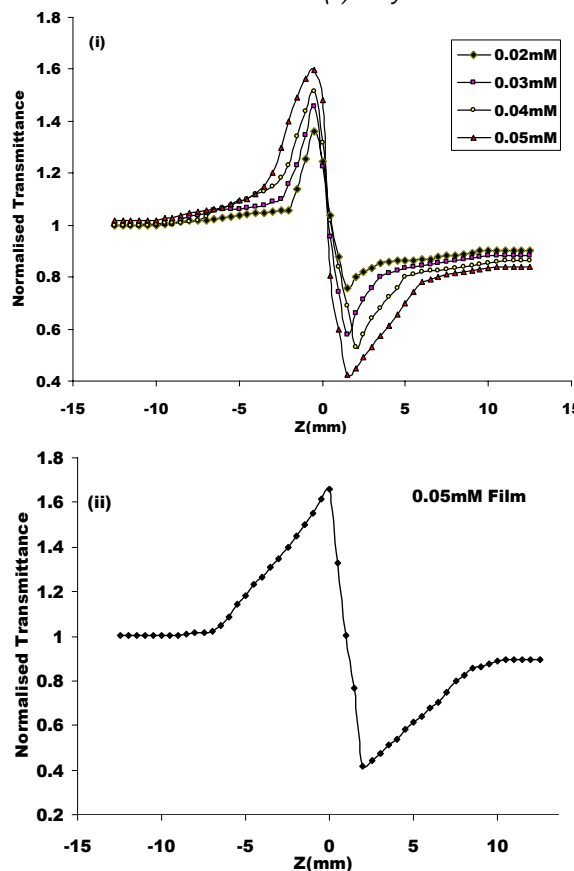
$$|\chi^3| = \left[(\text{Re } (\chi^3))^2 + (\text{Im } (\chi^3))^2 \right]^{1/2} \quad (3.7)$$

In order to know the contribution from the solvent to the observed nonlinear response, the Z-scan was performed on pure solvent. Neither nonlinear absorption nor nonlinear refraction was observed. The experimentally determined values of ΔT_{p-v} , n_2 , β , Δn and χ^3 are given in Table 1. The value of ΔT_{p-v} has increased for the dye doped polymer film when compared to the dye in methanol. This may be due to the heat

dissipation being faster in liquids as compared to that in a solid medium. The large value of n_2 in solid form of the dye, may be due to greater concentration of dye molecules in solid film compared with the solution. Pure PMMA matrix showed no Z-scan signal. From Fig.8 (a & b), there is an increasing trend for the values of n_2 and β as the concentration increases. This may be attributed to the fact that, the number of dye molecules increases as the concentration increases, more particles are thermally agitated resulting in an enhanced effect. The source used to probe the nonlinear material is a continuous wave laser; the optical nonlinearity of the dye, observed here is likely to be of thermal origin, arising from the temperature dependence of refractive index.

The optical limiting curves obtained with an Nd: YAG laser of wavelength 532 nm for the dye in solution at different concentrations and dye doped polymer film are shown in Fig.9. All the samples show a similar optical limiting behavior. The output power rises initially with increase in input power, but after a certain threshold value the samples 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.

Fig.6. Closed Z scan curve - (i) Dye in solvent at various concentration (ii) Polymer film



Separate optical limiting experiment was performed on pure methanol and it is found to have no contribution to optical limiting in the power range of the laser used. The UV-VIS absorption spectrum of the samples before and after the laser irradiation shows that the pattern and intensity of the spectrum does not show any change, indicating that the samples possess good photo stability. The dye investigated here are very weakly fluorescent and is non fluorescent at the wavelength studied, optimizing the conversion of the absorption energy into heat (Rashidian *et al.*, 2008). The optical limiting effect shows an increase with increasing the concentration of the dye solution. The results were comparable to some of the reports of low power optical limiting (Kaladevi Sendhil *et al.*, 2004). Hence, the sample possesses limiting effect for the light of 532 nm.

Conclusion

The third order nonlinear optical properties and optical limiting behavior of carmine dye have been studied. Both NLA and NLR contribute to the large third-order nonlinearity of the dye. It is worth noting that the value of χ^3 for the dye studied is larger than those of some representative third-order nonlinear optical materials such as chalcone and its derivatives and organic dyes like Croconium (Ravindra *et al.*, 2007; Zhongyu Li *et al.*, 2005). The origin of optical nonlinearity observed in the CW regime is attributed to the thermal variation of refractive index in the medium. The aperture limited designs based on thermo-optic nonlinearity such as the one studied here can be used as efficient limiters in the CW regime.

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Research article

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Fig.7. Pure Nonlinear Refraction Curve (i) Dye in solvent at various concentration (ii) Polymer Film

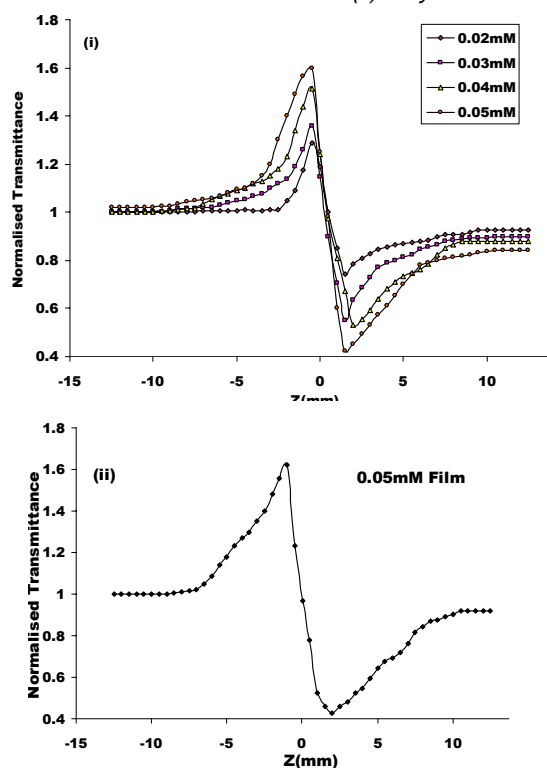
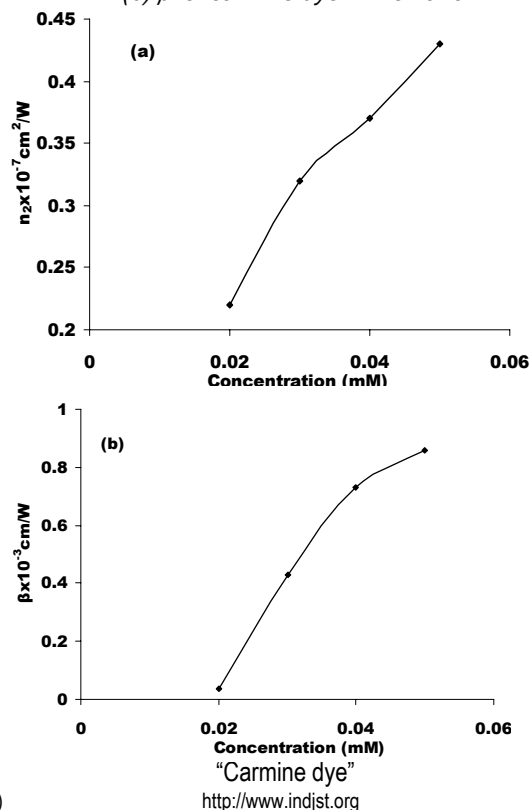


Fig.8. Concentration dependence (a) n_2 (b) β of carmine dye in methanol



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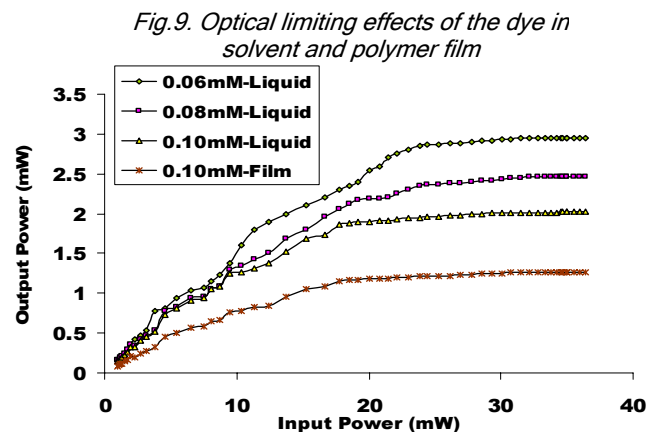


Table 1. Nonlinear parameters of carmine dye in methanol

Concentration		ΔT_{p-v}	$n_2 \times 10^{-7}$ cm^2/W	$\beta \times 10^{-3}$ cm/W	$\Delta n \times 10^{-4}$	$ \chi^{(3)} \times 10^{-6}$ (e.s.u)
Liquid Medium	0.02mM	0.61	0.22	0.36	1.48	0.97
	0.03mM	0.88	0.32	0.43	2.16	1.41
	0.04mM	1.00	0.37	0.73	2.48	1.62
	0.05mM	1.18	0.43	0.86	2.88	1.92
Polymer film (0.05 mM)		1.22	0.46	0.95	3.12	2.03