Study of third-order NLO properties of organic dye for optoelectronics applications

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Third-order nonlinear optical properties of aqueous solutions of methylene blue dye with different concentrations were studied by Z─scan technique. The magnitude of nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and third-order nonlinear optical susceptibility ($\chi^{(3)}$) were found to be the order of 10^{-7} cm^2/W, 10^{-2} cm/W and 10^{-5} esu, respectively. The dye sample possesses a large negative nonlinear index of refraction due to self-defocusing phenomena and saturable absorption behavior with significant nonlinear absorption coefficient. The experimental results revealed that the dye sample studied here may be a potential material for future photonics and optoelectronics applications.

(Received September 5, 2018; accepted February 12, 2021)

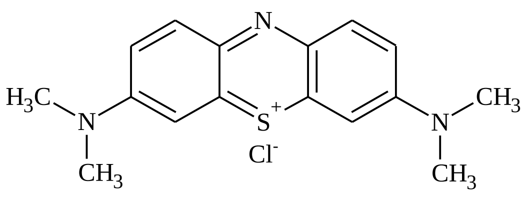
Keywords: NLO, Organic dye, Z–scan method

1. Introduction

Novel nonlinear optical (NLO) materials have attracted many research groups in the recent past due to its numerous potential applications in photonics and optoelectronics [1, 2]. A wide variety of materials [3─7] have been extensively studied to determine the NLO properties under pulsed and continuous wave regime. Among the availability of materials, organic molecules have gained a considerable attention in NLO study due to highly delocalized π-conjugated electron system and quick response time. Such functional materials have received a special attention in the field of optical communications, optical data storage, optical computing, optical switching and optical limiting [8─13]. Several experimental techniques currently available to measure the third-order NLO parameters of materials such as, nonlinear interferometry, degenerate four-wave mixing, nearly degenerate three-wave mixing, ellipse rotation and beam distortion measurements. The first three methods are potentially sensitive, but all of them required relatively complex experimental arrangements. Beam distortion measurements on the other hand, are potentially insensitive and required detailed wave propagation [14─15]. The single beam Z─scan technique, developed by Mansoor Sheik-Bahae et.al [16─17] is a popular and powerful tool for measuring the optical nonlinearity of wide class of materials. This technique has several advantages such as high sensitivity, simplicity, and ability to determine the sign and magnitude of the nonlinear medium simultaneously over the other methods. The principle of this technique is that, the spatial distortion of the Gaussian laser beam, arising from an optically induced nonlinear self-phase modulation (SPM), when the laser beam propagates inside the sample [18]. The extremely useful features of the Z─scan method is that, the sign of nonlinear index of refraction and absorption is immediately obvious from the data and the magnitude can also be easily estimated using a simple analysis for a thin medium [16]. In this paper, we report the third-order NLO properties of aqueous solutions of methylene blue dye using low power laser operating at 635 nm.

2. Materials

The dye chosen for our study is methylene blue (or) methylthionium chloride (Color Index: 52015; Molecular weight: 319.85 g mol^{-1}). This dye has immense applications in the field of biology, chemistry and optical technology [19]. The dye was purchased from Sigma Aldrich and has been used for the study without any further purification. Methylene blue dye is in the form of bright greenish blue powder and highly soluble in water. The molecular structure and formula of the dye are shown in Fig. 1. The optical characterization of the dye was studied by recording electronic spectra in the wavelength range of 400–700 nm using UV-1601 PC Shimadzu spectrophotometer and is shown in Fig. 2.



Molecular Formula: $C_{16}H_{18}ClN_3S$

Fig. 1. Molecular structure and formula of methylene blue dye

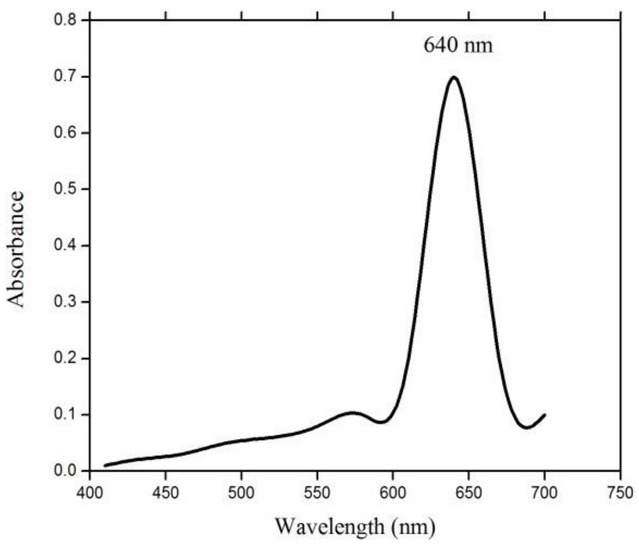


Fig. 2. UV-Vis absorption spectra of methylene blue dye

3. Experimental

The experimental setup used in the present study is similar to that of our previous work [4]. The Z─scan experiments were performed using a CW diode laser operating at 635 nm wavelength with total power of 5 mW. A convex lens of 5 cm focal length was used to focus the beam. By assuming that the sample thickness of ~ 1 mm is less than the Rayleigh length, it can be treated as a thin medium and hence ensuring the validity of the Z─scan investigations. A cuvette containing the aqueous solution of methylene blue dye is translated across the focal region along the axial direction i.e., is the direction of propagation of the laser beam. The transmittance of the beam through a sample with and without aperture in the far field was measured using an optical power meter.

4. Results and discussion

The closed aperture Z─scan experiments were performed to determine the sign and magnitude of the nonlinear refractive index n_2 of the dye solution. Usually the closed aperture data obtained from Z–scan technique include both nonlinear refraction and nonlinear absorption. It is necessary to separate the nonlinear absorption components from the nonlinear refraction so as to extract pure nonlinear refraction part, a simple and accurate division method was used. The pure nonlinear refraction curve for methylene blue dye at different concentrations is shown in Fig. 3. The observed normalized transmittance curve exhibits pre-focal transmittance maximum followed by a post-focal transmittance minimum, indicating self-defocusing nonlinearity. Hence, the sample possesses a negative nonlinear index of refraction. A peak – valley separation of the sample is more than 1.7 times the Rayleigh range (Z_R) is the clear indication of thermal nonlinearity and indicates that the observed nonlinear effect is a third-order process [15].

The quantity ΔT_{p-v} is defined as the difference between the normalized peak and valley transmittances, i.e., $T_P - T_V$. The variation of this quantity as a function of $\Delta\varphi_0$ is given by,

$$\Delta T_{P-V} = 0.406(1-S)^{0.25} \left|\Delta\varphi_0\right| \quad (1)$$

where $\left|\Delta\varphi_0\right|$ is the on-axis phase shift at the focus, $S = 1 - \exp(-2r_0^2/\omega_0^2)$ is the aperture linear transmittance, here r_0 denotes the aperture radius and ω_0 denotes the beam radius at the aperture in the linear regime. The nonlinear refractive index of the sample is given by,

$$n_2 = \frac{\Delta\varphi_0\lambda}{2\pi I_0 L_{eff}} \quad (2)$$

where λ is the laser wavelength, I_0 is the intensity of the laser beam at focus Z = 0, L_{eff} is the effective thickness of the sample, α is the linear absorption coefficient and L is the thickness of the sample.

Fig. 4 shows the typical open aperture (S=1) Z─scan data for aqueous solutions of methylene blue dye at different concentrations of 0.03 mM, 0.04 mM and 0.05 mM. The enhanced transmission near the focus indicates that the saturation of absorption (SA) takes place at higher value of light intensity. 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.

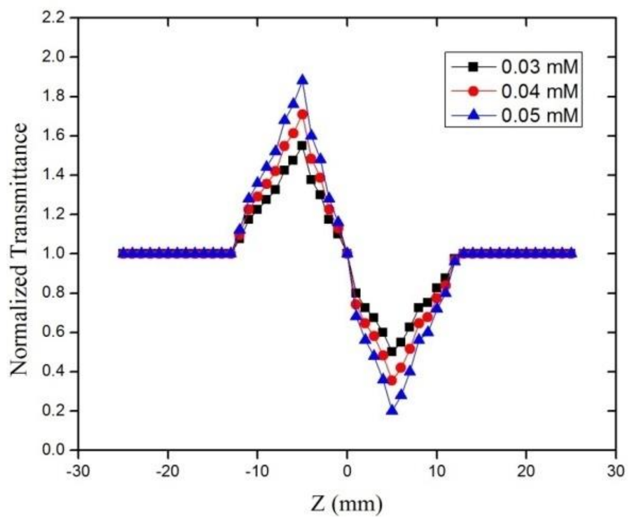


Fig. 3. Pure nonlinear refraction Z─scan curve

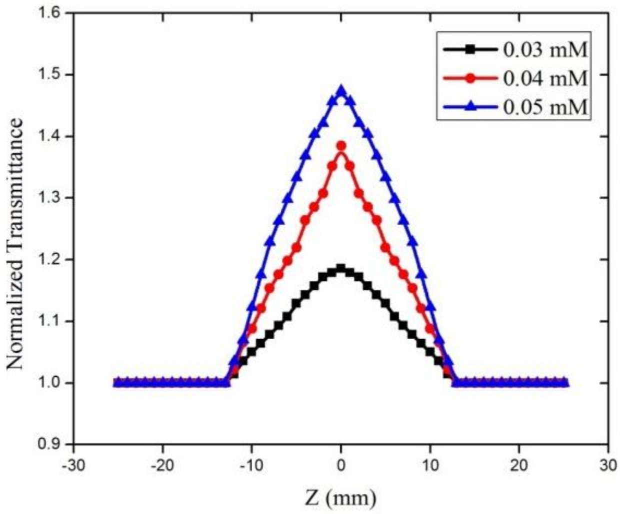


Fig. 4. Open aperture Z–scan curve

The nonlinear absorption coefficient β can be estimated from the open aperture Z–scan data using the relation,

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \tag{3}$$

The experimental measurements of nonlinear refractive index n_2 and nonlinear absorption coefficient β allowing the evaluation of the real and imaginary parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$ are given by the relation,

$$Re[\chi^{(3)}](esu) = 10^{-4}\frac{\varepsilon_0 c^2 n_0^2}{\pi} n_2 \left(\frac{cm^2}{W}\right) \tag{4}$$

$$Im[\chi^{(3)}](esu) = 10^{-2}\frac{\varepsilon_0 c^2 n_o^2 \lambda}{4\pi^2} \beta \left(\frac{cm}{W}\right) \tag{5}$$

where ε_0 is the vacuum permittivity and c is the light velocity in vacuum. The absolute value of $\chi^{(3)}$ for the sample was calculated using the equation, $\chi^{(3)} = [(Re(\chi^{(3)}))^2 + (Im(\chi^{(3)}))^2]^{1/2}$.

Systematic studies have been carried out in order to examine the concentration dependence of the nonlinear refractive index and absorption coefficient. From Fig. 5 and 6 it is very clear that the values of n_2 and β increases as the concentration of the dye increases. This may be attributed to the fact that as the number of dye molecules increases with increase in concentration and more number of particles get thermally agitated resulting in an enhanced effect. The increase in n_2 and β with dye concentration indicates that the contribution to nonlinear refraction and absorption arises mainly from the chromophores of methylene blue dye. The nonlinear optical properties of materials are closely related to its structure. In the molecular structure of methylene blue dye, the methyl group in 1-, 5- positions acts as electron donors. On the other hand the quinine moiety and amino group in 6-position act as electron acceptors. The present dye possesses four methyl groups, so it acts as strong electron donors. By the introduction of electron donor groups, the electron density gets enhanced [20]. As a result, an efficient charge transfer (CT) takes place within the dye molecules (from dopants to the benzene rings), which in turn increase the dipole moment. With increase in dipole moment, the electron delocalization increases and this in turn increase the optical nonlinearity of the sample. The second order hyperpolarizability of the dye sample is related to the nonlinear susceptibility by the following relation [21],

$$\gamma = \chi^3 / (L^4 N) \tag{6}$$

where N is the number density of the molecules in cm^{-3} and L is the local field correction factor given by $[(n^2+2)/3]$, where n is the linear refractive index. The third-order nonlinear optical parameters obtained for aqueous solution of methylene blue dye are tabulated in Table 1. As it evident from Table 1 that the contribution of real part of third-order susceptibility is relatively higher than that of imaginary part of third-order susceptibility indicating that the nonlinear refraction is dominating as compared to nonlinear absorption. Further, the obtained value is higher than that of some recently reported materials [22-23].

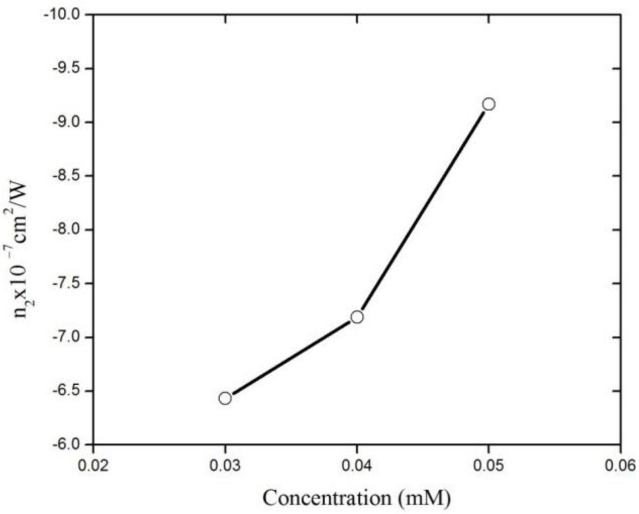


Fig. 5. Concentration dependence on n_2 of methylene blue dye

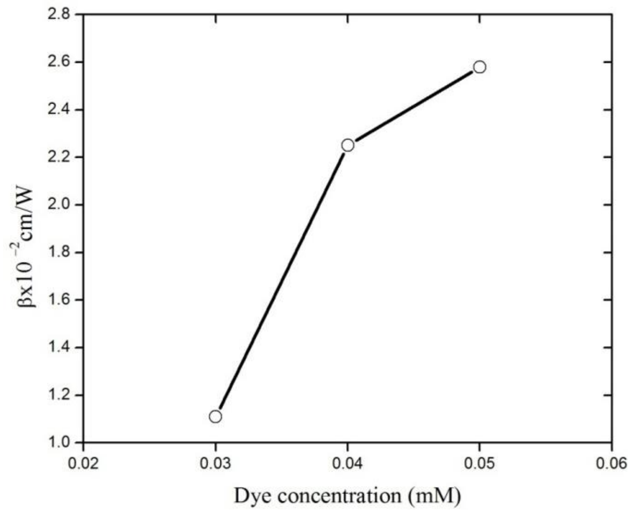


Fig. 6. Concentration dependence on β of methylene blue dye

Fig. 7. Self-diffraction ring pattern of methylene blue dye (color online)

When a Gaussian laser beam passes through a dye sample, it tends to form a far-field intensity distribution ring pattern. The change in refractive index of a dye sample is proportional to intensity of light given by $\Delta n = n_2 I$, where n_2 is the nonlinear refractive index. The observed self-diffraction ring pattern in the dye sample is attributed to the thermally induced spatial refractive index variation. Fig. 7 shows the photograph of the self-diffraction ring pattern image observed in the far field for aqueous solutions of methylene blue dye at 0.03 mM concentration.

5. Conclusion

The nonlinear optical properties of methylene blue dye solution at different concentrations were studied using a single beam Z─scan technique with a CW diode laser operating at 635 nm with total power of 5 mW. The dye sample possesses a large negative nonlinear refraction and saturable absorption process. The magnitude of third-order nonlinear susceptibility was found to be of the order of 10^{-5} esu and observed increases with increases in dye concentration. The second order hyperpolarizability of the dye sample was also studied and the value is found to be the order of 10^{-29} esu. The self-diffraction ring pattern was observed in the far-field due to thermal lensing effect. The experimental results confirm that methylene blue dye is a potential material for NLO applications.

Table 1. Third-order NLO parameters of aqueous solution of methylene blue dye

Dye concentration (mM)	$n_2 \times 10^{-7}$ (cm^2/W)	$\beta \times 10^{-2}$ (cm/W)	Re $\chi^{(3)} \times 10^{-5}$ (esu)	Im $\chi^{(3)} \times 10^{-6}$ (esu)	$\chi^{(3)} \times 10^{-5}$ (esu)	$\gamma \times 10^{-29}$ (esu)
0.03	– 6.43	–1.11	– 2.89	–2.51	2.90	1.93
0.04	– 7.19	–2.25	– 3.22	–5.10	3.26	2.17
0.05	– 9.17	–2.58	– 4.11	–5.85	4.12	2.74

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