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Nonlinear refraction characteristics of disperse blue 1/Dioxane solutions under He-Ne laser irradiation via Z-scan method

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The evolution of nonlinear refractive index coefficient with concentration of disperse blue 1 (DB1) dye in dioxane solution was investigated. Solutions were pumped with He-Ne laser. The values of the nonlinear refractive index coefficient increased exponentially from -5.69×10^{-8} to -3.4×10^{-8} cm^2/W as the dye concentration increased from 3.7×10^{-5} to 74.6×10^{-5} M, and were negative; indicating that the studied solutions acted as a negative lens. Kwak's formalism was employed in order to characterize the transmission changes and calculate the nonlinear refractive index coefficient values.

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1. Introduction

In the past few years, we have witnessed extensive quest for materials possessing fast and large optical nonlinearities [1-7]. A vast number of organic materials with large 3rd-order nonlinear optical (NLO) characteristics have been found to own laser-induced refractive index and nonlinear transmission, which are both intensity-dependent [5-7]. Such materials form future candidates for numerous photonic and bio-photonic applications. As some examples of the research published recently, Rashidian *et al.* [4] investigated the solution of Basic Violet 16 dye in water, which showed that upon irradiating with 100 mW CW frequency-doubled Nd-YAG laser beam at 532 nm (using the Z-scan technique), the NL refractive index coefficient, γ, decreased from -2.8120×10^{-8} to -14.2305×10^{-8} cm^2/W as the sample concentration increased from 15×10^{-5} to 6×10^{-4} M, and the observed negative lensing effect was credited to thermal nonlinearity [4]. Jamshidi-Ghaleh *et al.* [5] investigated the NLO properties of fast green FCF (Acid Blue 3) dye under 35 mW CW He–Ne laser pumping using the Z-scan technique, at three different concentrations (1×10^{-5}, 1×10^{-4}, and 2×10^{-4} M). They showed that the power limiting threshold at 2×10^{-4} M was measured as 7 mW. The values of linear absorption coefficient, α, increased from 0.41 to 4.18 mm^{-1}, NL absorption coefficient, β, increased from 0.65×10^{-5} to 6.5×10^{-5} cm/W, and γ increased from 0.1×10^{-8} to 3.2×10^{-8} cm^2/W. Pramodini and Poornesh [6] investigated the optical limiting (OL) and 3rd-order NLO of aniline copolymers using the Z-scan technique and He–Ne laser (633 nm) as a pumping source. It was found that the copolymer samples demonstrated reverse saturable absorption (RSA) process and self-defocusing property. Also, the calculated values of β, γ, and $\chi^{(3)}$ were of the order of 10^{-2} cm/W, 10^{-5} esu and 10^{-7} esu, respectively. Zidan *et al.* [7] investigated 1-(carboxymethyl)-8-hydroxyquinolin-1-ium chloride and 1-(carboxymethyl)quinolin-1-ium chloride salts via the Z-scan technique with a 26 mW diode laser (635 nm). They showed that β values were estimated to be 5.89×10^{-4} and 8.37×10^{-4} cm/W for 1-(carboxymethyl)-8-hydroxyquinolin-1-ium chloride and 1-(carboxymethyl)quinolin-1-ium chloride, respectively; and that γ values were estimated to be -3.81×10^{-8} and -4.66×10^{-8} cm^2/W for these dyes, respectively. These examples of literature and other vast published literature illustrates the importance and the potency of organic substances as feasible candidates for photonic device applications.

Since Sheik-Bahae *et al.* [1] first introduced the Z-scan method as a simple and accurate mean to characterize NLO materials, it was widely employed as a standard routine for investigating γ and β [2]. In this technique, the sample was moved longitudinally along the propagation direction of a focused beam of Gaussian nature. Because of optical nonlinearity, the incident Gaussian beam induces changes in the absorption coefficient and the refractive index of the sample. Consequently, changes in the beam intensity distribution in a plane located after the sample were detected as the sample was moving across the beam's focal plane.

As for this work, 1,4,5,8-Tetraamino-9,10-anthracenedione, or otherwise known as disperse blue 1, is an aminoanthraquinone-based dye stuff used in hair colour formulations and in colouring fabrics and plastics. We have shown in a previously published work [8] that the solutions of this dye in dioxane have optical limiting characteristics at 632.8nm owing to the distinct locus of this wavelength in the UV-visible absorption spectrum of this dye. Extensive work was carried out on the solutions of this dye, especially on its nonlinear characteristics of absorption and refractive index. However, the present work emphasizes on the exploration of the NL refractive index properties of DB1/dioxane samples at different concentrations, under the influence of 632.8 nm CW laser irradiation. Nevertheless, the nonlinear absorption characteristics and optical limiting effects of DB1 dye were represented and discussed thoroughly in another paper, which is currently under publication elsewhere [9]. To our knowledge, this dye has never been studied before and is a prospective candidate material for nonlinear optics applications.

2. Experimental

2.1. Sample preparation

Fig. 1 shows the chemical structure of DB1 dye ($C_{14}H_{12}N_4O_2$, molecular weight: 268.28 g/mol), which was acquired from Acros Organics. Solutions of DB1 in dioxane were prepared by solving the 0.1 g of DB1 in 20 ml of 1,4-dioxane ($C_4H_8O_2$), and mechanically stirred for four hours in a closed flask at room temperature. A series of different concentrations (3.70×10^{-5}, 7.46×10^{-5}, 11.2×10^{-5}, 14.9×10^{-5}, 18.6×10^{-5}, 37.3×10^{-5}, and 74.6×10^{-5} M) were prepared from this solution using a precise digital micropipette (Transferpette Electronic, from Brand). These concentrations were chosen to start from the lowest concentration that could be prepared precisely to the highest concentration where the saturation in the absorption spectra at 632.8 nm appeared clearly. A quartz cell (1 mm thick) was used as a test cell.

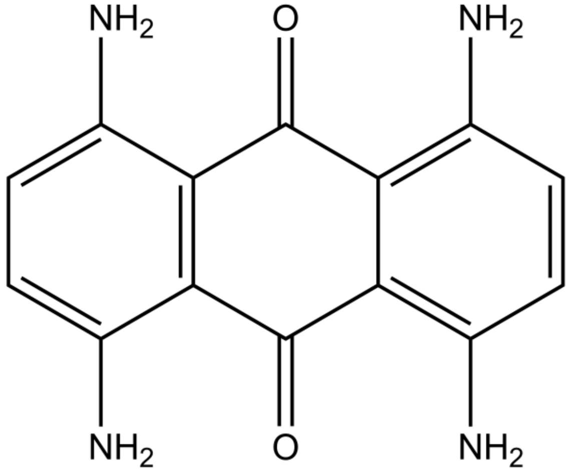

Fig. 1. The chemical structure of disperse blue 1 dye

2.2. Experimental setup and instrumentation

A 632.8 nm CW (35 mW, 1.24 mm spot diameter) linearly polarized TEM_{00} Gaussian beam He-Ne laser (31-2140-000, from Coherent) was used in this work. Fig. 2 displays the optical setup used for Z-scan measurements. A small portion of the laser beam was reflected by a microscope slide and directed towards the photodiode PD1, whose signal was used as a reference for normalizing the gathered data throughout the experiments (by dividing the signal of PD2 by that of PD1). The laser beam was focused to about 31 μm of waist radius with a 150 mm focal length lens, at which the Rayleigh length Z_R was 0.46 cm. Hence, the calculated power density was ~2.4 kW/cm^2 at the focus. Needless to say that since the thickness of the sample was smaller than the Rayleigh length of the focused beam, the sample was considered as a thin medium, which can be viewed as a thin lens with variable focal length [10]. The introduction of the 150 mm focal length lens in the setup helped us to increase easily the beam irradiance of the sample as it moved toward the focal point or to decrease this irradiance as the sample moved away from the focal point. The sample was mounted on a home-made Z-scan mechanical assembly, which was controlled by the software via a stepper motor controller. A 4.4 mm diameter aperture was used to block the transmitted beam (whose diameter was 16.85 mm at the aperture location), so that only the central part of this beam was allowed to reach the photodiode PD2. The intensity of the reference beam (through the photodiode PD1) was collected and recorded via the auxiliary input of the DSP lock-in amplifier (SR-850, from Stanford Research Systems), whereas the intensity of the sample beam (through photodiode PD2) was collected and recorded via a current preamplifier (SR-570, from Stanford Research Systems), which was connected to the DSP lock-in amplifier. A laser beam chopper (SR-540, from Stanford Research Systems) was connected to the lock-in amplifier for the signal detection. An IEEE 488.2 GPIB (National Instruments) card was used to control and gather the experimental data. A Borland C++ program was written in order to automate the setup.

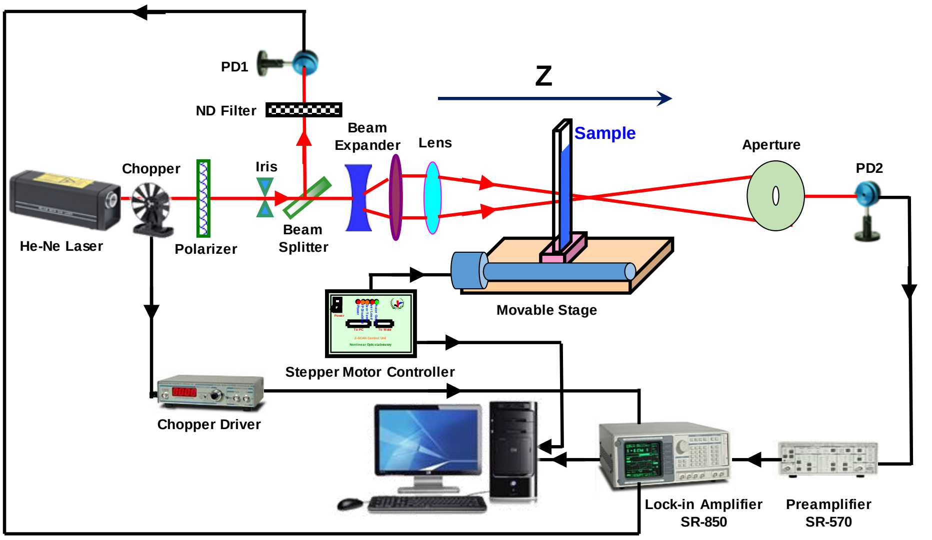

Fig. 2. Schematic drawing of the automated Z-scan system (closed aperture configuration) for measuring the nonlinear refractive index coefficient

3. Results and discussions

3.1. Effective path length calculations

A Photodiode Array Photospectrometer (PDA) Specord S100, from Analytik Jena, was used to acquire the UV-visible absorption spectra of DB1 liquid samples (fig. 3). The absorption increased with increasing the dye concentration and a saturation effect started to appear at the maximum concentration used. This figure showed as well position of the irradiation laser wavelength, relative to the absorption maxima.

The Beer-Lambert’s law was used to estimate the linear absorption coefficients of the samples [11],

$$\alpha = \frac{\ln\left(\frac{1}{T}\right)}{L} \tag{1}$$

where T is the sample’s transmission at 632.8 nm, and L is the sample thickness. The effective path length of the laser beam within the sample was deduced from the results of the linear absorption coefficient values, using the formula [10],

$$L_{effective} = \frac{1-e^{-\alpha L}}{\alpha} \tag{2}$$

The estimated values of the linear absorption coefficients and the effective path lengths for all concentrations used are listed in Table 1.

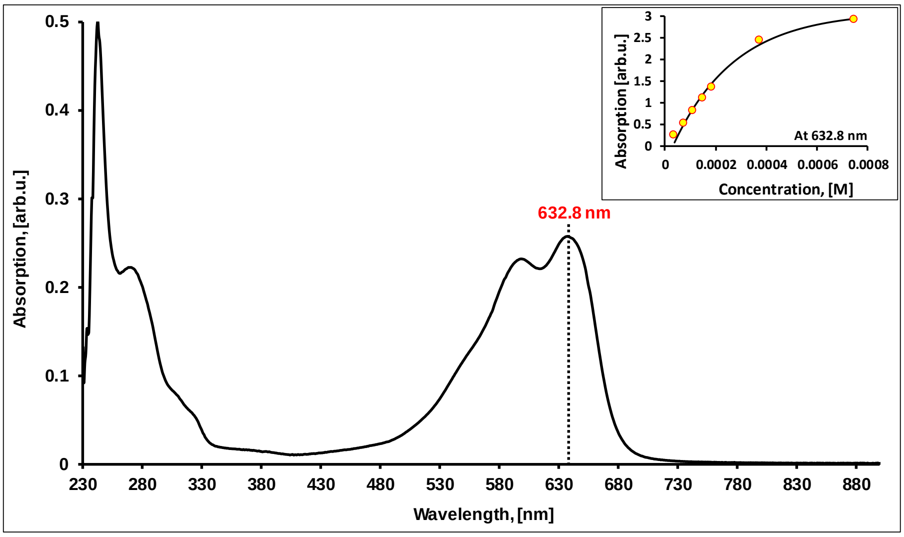

Fig. 3. UV-vis absorption spectrum of DB1/dioxane, at the concentration of 3.70×10-5 M. The inset shows the absorption variations at 632.8 nm for the studied concentrations

3.2. Closed aperture Z-scan measurements

In this closed-aperture setup [1], the Z-scan curve is acquired by plotting the far-field on-axis intensity against the sample's position. Then, fitting the measured Z-scan data with theoretical ones, the NL refractive coefficient, γ, is then determined [3]. Therefore, this technique counts on the intensity variation fact along the axis of the convex lens, which has its maximum at the focus. Subsequently, moving the sample in incremental steps across the focus, and observing the variation of the spot size at the plane of finite aperture/detector combination, the NL refraction can then be measured. The transmission for the sample was measured with the aperture in the lens's far-field, while the sample was being shifted across the focus. The transmittance curves for all samples were described by a pre-focal peak followed by a post-focal valley. The apparent peak-valley configuration implies that the NL refractive index coefficients of the solutions were negative ($\gamma < 0$), which is known as a self-defocusing case. Furthermore, a Z-scan experiment was also applied to the dioxane alone, whose contribution to the observed nonlinearity was found to be negligible. Therefore, any involvement from the solvent to the observed nonlinearity was insignificant at the laser input intensity used. The recorded peak-valley Z-scan measurements were asymmetric with regard to the focus (Z=0). The laser light used in the investigation was a quasi-CW because of using a mechanical beam chopper in the acquisition of the experimental data. We have fitted the Z-scan data to the Sheik-Bahae (Eq. (3)) [1], Cuppo's thermal model (Eq. (4)) [12], and Kwak's (Eq. (5) [13] formalisms:

$$T(z) \approx 1+\Delta\phi_0 \frac{4x}{\left(1+x^2\right)\left(9+x^2\right)} \tag{3}$$

$$T(z) = \frac{1}{1+\frac{2x}{1+x^2}\Delta\phi_0+\frac{1}{1+x^2}\Delta\phi_0^2} \tag{4}$$

$$T(z) = \frac{1}{1-\frac{4x}{\left(1+x^2\right)^2}\Delta\phi_0+\frac{4}{\left(1+x^2\right)^3}\Delta\phi_0^2} \tag{5}$$

where $T(z)$ is the normalized transmittance, $\Delta\phi_0 = k\gamma L_{eff} I_0$ the on-axis nonlinear phase shift experienced by the laser beam as passing a thin sample of thickness L, $x = \frac{Z}{Z_R}$ is the sample position, $Z_R = \frac{k\omega_0^2}{2}$ is the beam's diffraction length, ω_0 is the waist radius of the beam at the focal point, $I_0 = \frac{2P_0}{\pi\omega_0^2}$ is the laser beam intensity at the focus, P_0 is the laser input power, and $k = \frac{2\pi}{\lambda}$ is the wavevector.

Hence, the values of the nonlinear ref. index coefficient, γ, that were taken into account were those that led to having the best theoretical fit to the experimental data according to Eqs. (3), (4) and (5).

Fig. 4 represents a comparison between the Sheik-Bahae, Cuppo's thermal model, and Kwak formalisms. This comparison illustrated that Eq. 5 described well the asymmetric shape of the recorded curve, while Sheik-Bahae's model under-estimated the experimental data and did not fit well the peak-valley asymmetric behaviour. On the other hand, despite that Cuppo's model took into account the peak-valley asymmetry, it over-estimated the experimental data, especially in the peak section.

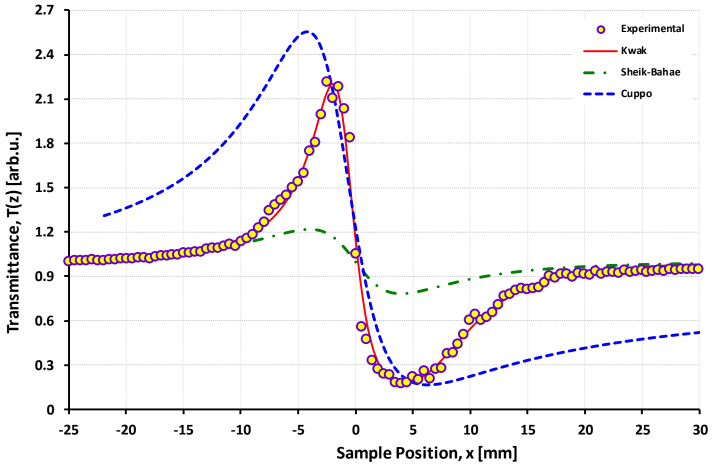

Fig. 4. A comparison between the Sheik-Bahae, Cuppo's thermal model, and Kwak formalisms, for a DB1/dioxane sample at the concentration of 3.7×10-5 M

Fig. 5 (the dotted curves) shows the normalized transmissions for our samples, in terms of the samples' positions. At larger on-axis nonlinear phase shift (Table 1), the valley has greatly been suppressed (nearly to zero) and broadened, while the peak has greatly been enhanced. As the sample concentration increased, the on-axis nonlinear phase shift became smaller, the valley suppression lessened and became less broadened, and the peak enhancement became less obvious. Moreover, at high concentration, the peak-valley became more symmetric. The nonlinear refractive index coefficient value at each concentration was calculated by fitting the measured Z-scan data with Eq. 5. The achieved results of the calculations revealed that the value of this coefficient increased with increasing the concentration of the DB1/dioxane solutions (Table 1). The asymmetric Z-scan transmittance depicted in Fig. 5 and the calculated change in γ result almost entirely from the large nonlinear phase distortions. Fig. 6 shows that the nonlinear refractive index coefficient increased with increasing the dye concentration. The final stabilization at the last two points in Fig. 6 indicated that a saturation case had been reached.

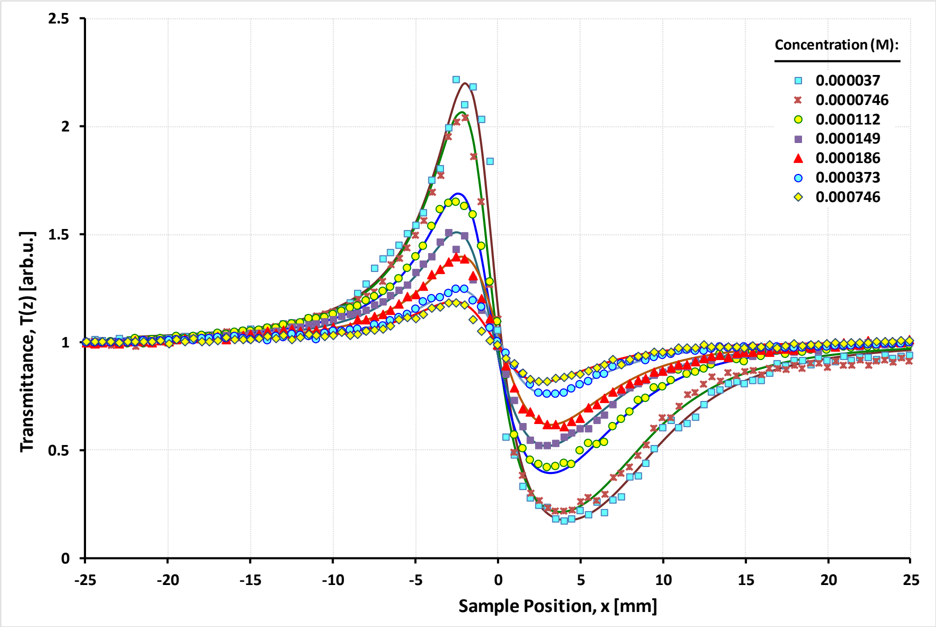

Fig. 5. Normalized transmittance curves of closed aperture Z-scan of DB1/dioxane solutions at different concentrations. The solid lines represent the fitting according to Eq. 5

Table 1. Summary of the calculated parameters for DB1/dioxane solutions as a function of concentration.

Concentration $\times 10^{-5}$ (M)	α (cm^{-1})	$L_{effective}$ $\times 10^{-2}$ (cm)	$\lvert\Delta\phi_0\rvert$ (Rad)	$\gamma \times 10^{-8}$ (cm^2/W)
3.7	5.04	7.86	1.1	-5.69
7.46	7.6	7.01	0.93	-5.56
11.2	17.83	4.67	0.54	-4.86
14.9	21.3	4.14	0.41	-4.18
18.6	25.83	3.58	0.34	-3.70
37.3	43.53	2.27	0.19	-3.53
74.6	53.46	1.86	0.15	-3.40

This is consistent with the values of the absorption variations shown in the inset of Fig. 3 at these concentrations. However, at the rest of the concentrations used, a linear increase in γ with increasing concentration could be observed. This increase followed an exponential manner that could be expressed by a logistic equation of the form,

$$\gamma = \gamma_f + \frac{\gamma_i - \gamma_f}{1+\left(\frac{C}{C_0}\right)^p} \tag{6}$$

where γ_i and γ_f are the final and initial values of the NL refractive index, respectively, at which C (the concentration) becomes asymptotic; C_0 is the concentration at which C acquires a value equal to half of the amplitude of the curve, i.e., the point midway between γ_i and γ_f (the inflection point); and p is the power of this function which controls the steepness of the curve; *i.e.*, it is the parameter that affects the slope of the area about the inflection point.

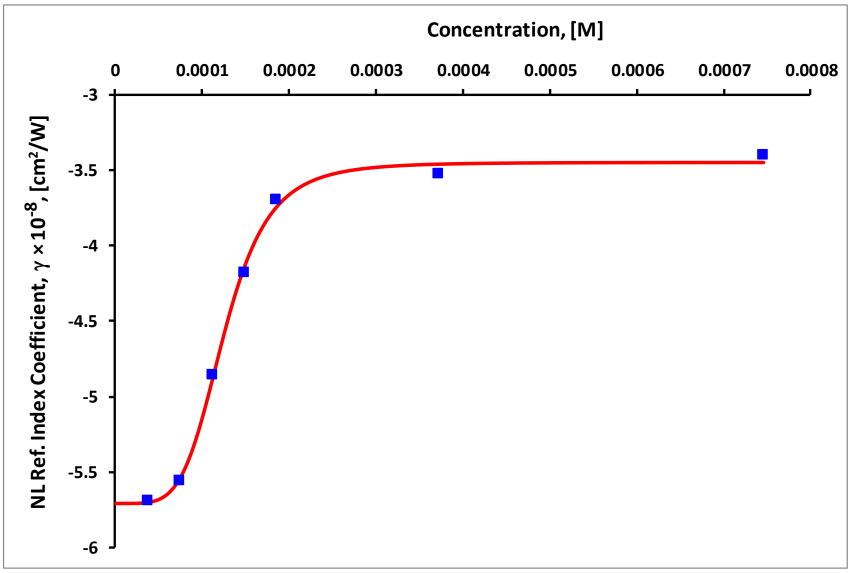

Fig. 6. Fitting procedure of the nonlinear refractive index coefficient as a function of DB1/dioxane concentrations

4. Conclusion

In summary, we have studied the evolution of the nonlinear optical refraction of disperse blue 1 in dioxane under He–Ne laser illumination at several concentrations. The dye solutions were characterized with negative nonlinear refraction property. It was observed that the nonlinear refraction increased with increasing the dye concentration. Also, in comparison with Sheik-Bahae's and Cuppo's thermal lens models, we found that Kwak's model was more appropriate for describing the behaviour of the observed changes in the transmission characteristics of the dye samples along the z-scanning range. Furthermore, the increase in the nonlinear refractive index was exponential, as the dye solution concentration increased. Hence, we concluded that DB1 organic dye investigated here appears as a possible candidate for future nonlinear optical applications.

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