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RESEARCH ARTICLE

NONLINEAR ABSORPTION AND PHOTOLUMINESCENCE EMISSION BEHAVIOUR OF ERIOCHROME CYANINE R DYE CHROMOPHORE

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ABSTRACT

The linear and nonlinear optical absorption as well as photoluminescence emission behaviour of the organic dye, Eriochrome Cyanine R in aqueous solution were investigated. The samples exhibited intense photoluminescence emission when excited with 518 nm radiation. An investigation into the absorptive nonlinearity exhibited by the Eriochrome Cyanine R dye in aqueous solution under low power continuous wave (cw) laser light illumination at 442 nm, performed using the Z-Scan technique is presented. The samples exhibited Reverse Saturable absorption under the experimental conditions.

INTRODUCTION

Nonlinear optical materials have been evoking world wide interest in researchers owing to their vast potential for applications in optoelectronic devices, high speed optical communication network and the recent significant applications in biological and medical sciences. In the recent past, rapid technological advancements in optics have placed great demand on the development of nonlinear optical (NLO) materials suitable for photonic devices[1,2].

Numerous Organic chromophores exhibit extremely large and fast nonlinearities, much better than those observed in inorganic crystals. In addition , due to the versatility of organic synthesis, their NLO properties can be custom-tailored for a specific application and are therefore, a much better choice for uses in NLO applications [3,4]. NLO organic molecules possess a strong donar-acceptor intermolecular interaction due to the presence of easily polarizable delocalized π -electrons in the system.

The nature of the π bonding sequence and the conjugation length govern the Optical nonlinearities of organic materials. Among these materials, those exhibiting large and fast nonlinear absorption, especially reverse saturable absorption (RSA), have emerged as media of considerable research interest, because RSA is the basis of optical limiting action in resonant nonlinear absorbers [5,6]. Materials showing RSA become more opaque as the incident optical intensity is increased, due to enhanced absorption from the excited state or a multiphoton absorption of both [7]. Such materials can be used for the protection of eyes and sensitive devices from intense radiation, apart from their applications in passive mode locking, and optical pulse shaping and processing [8].

Dye chromophores are a class of organic molecules with multiple π-conjugated bonds, which can exhibit large optical nonlinearities and fast response time, as a result of the ease of polarization of the extended mobile π- electron clouds over large molecular distances [9].

The organic dye Eriochrome Cyanine R (ECR; LobaChemie, Mumbai, India) , belonging to triaryl methane family, is an important histological and bacterial stain and used for colouring textiles and leather. In this paper, we report on the nonlinear absorption, linear absorption and Photoluminescence(PL) properties of the organic dye , ECR (molecular structure shown in Fig.1) in aqueous solution under irradiation with 442 nm CW He-Cd laser light for three different dopant concentrations.

Open aperture (OA) Z-scan study performed with 442 nm, He-Cd laser light pulses allowed the determination of the NLO properties of the sample. RSA is usually observed with high peak power, short pulsed laser light excitation; however, recently, there have been reports of RSA occurring in certain

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organometallic phthalocyanines and fast green FCF dye on excitation with CW laser light [10].

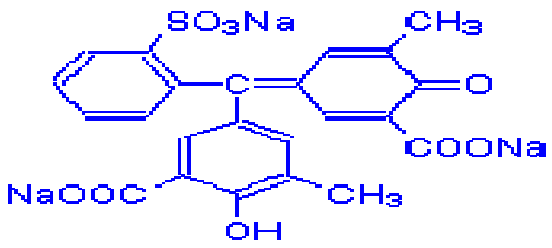


Fig.1 Molecular structure of Eriochrome Cyanine R dye molecule

Experimental

The linear absorption spectra of ECR, aqueous solution of the dye were recorded using a ultra-violet (UV-Vis) Spectrophotometer (Shimadzu UV-2450). The Photoluminescence (PL) emission spectra of the samples were recorded using a Horiba YobinYvonFluorolog-III Spectroflurometer. The nonlinear absorption behaviour of ECR dye,in aqueous solution were investigated using the open aperture(OA) mode of the Z-scan technique[11]. The standard Z-scan set up, showm in Fig:2 was used for the measurement of NLO coefficients.

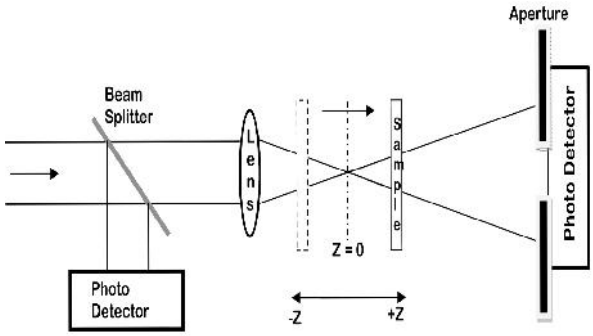


Fig 2 Schematic diagram of Z-scan experimental arrangement

This technique, which has sensitivity comparable to that of the interferometric methods, makes use of the distortions induced in the spatial and temporal profiles of the input beam passing through the sample to give a qualitative as well as a quantitative measure of the nonlinearities occurring in the material medium. Using a lens of focal length 18.5 cm, the Gaussian beam was focused to a spot size of 18 μm. This yielded a Rayleigh range of 19.1 mm, which was greater than the sample thickness, satisfying the thin sample approximation condition required for the Z-scan theory[12].The beam, after transmission through the samle was collected and monitored to yield the OA Z-scans , which provide accurate information about the nonlinear optical absorption behaviour of the sample.

RESULTS AND DISCUSSION

The linear absorption spectra of ECR dye in aqueous solution for various dye concentrations are shown in Fig:3. The standard value of absorption maxima for ECR dye is 518nm. The observed values of absorption maxima for the samples for different concentrations are 517 nm. This shift in peak absorption wavelength is accounted for the structural and enviourmental changes occurring in the dye in polar solutions.

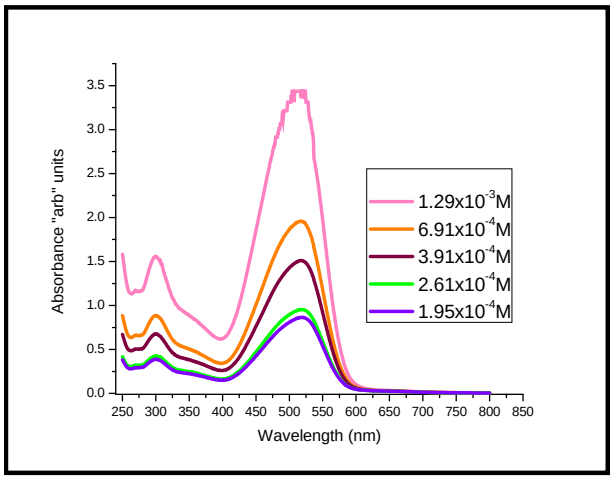


Fig 3 UV- Visible Absorption Spectra of Eriochrome Cyanine R in Solution

Figure 4 depicts the PL emission spectra of EC R in aqueous solution at room temperature. The solution exhibit red emission at room temperature. The main emission maximum appear in the range (560-600 nm) when excited (at wavelength 518 nm) in the vicinity of their absorption maxima, λ_{max}.When molecules are excited to a singlet state, they eventually de-excite to the ground state either by fluorescence emission or by internal conversion process.From the Figure it is clear that as the concentration of the samples increases the intensity of emission also increases.

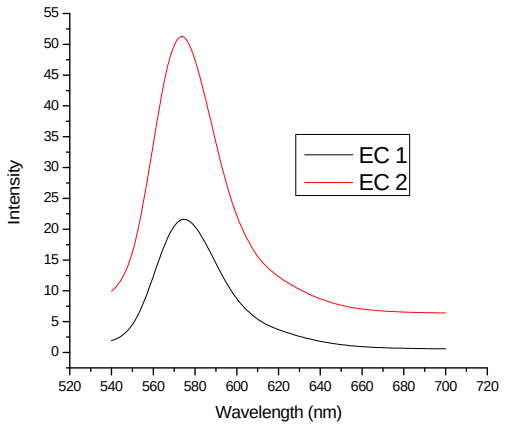


Fig 4 PL emission spectra of E C R

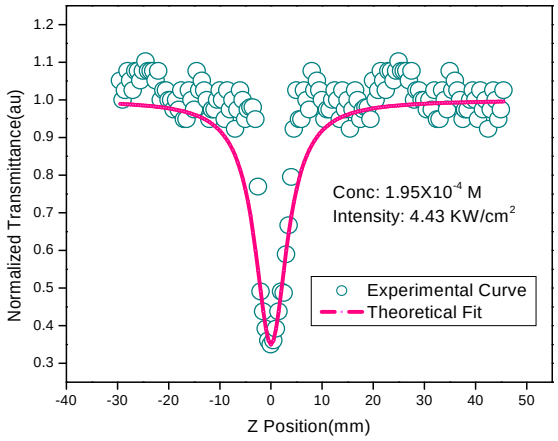
In the open aperture scheme of the Z-scan experiment , where all the transmitted light is detected ,the z-scan traces contain information as regards absorptive nonlinearity such as saturable absorption(negative nonlinear absorption), reverse saturable absorption (positive nonlinear absorption) or a flip of one to the other. Fig(5-7) displays the open aperture Z-scan data for ECR dye in aqueous solution, for three different concentrations: (a) 1.95×10^{-4} M, (b) 2.61×10^{-4} M and (c) 3.95×10^{-4} M, at a peak incident intensities, I_0= (4.43 and 3.25)KW/cm^2 at the focus. When the sample is at closer diastances from the focus of the lens, the transmission suddenly decreases forming a well

defined sharp normalized valley (dip) at Z=0, indicating the occurrence of an enhanced absorption process like RSA. It may be noted that the dip transmission at the focus decreases further when the incident focal point intensity, I_0 is increased. Moreover , the width of the OA Z-scan profiles also increases steadily, with increase in I_0 ; and , as the sample is translated from left to right, the commencement of RSA (the fall in transmitted intensity) starts at an earlier Z-position with increase in either the intensity or the concentration of the dye content in the sample. An initial enhancement in both intensity and concentration can cause promotion of an increasing number of molecules of the higher state, thus facilitating the onset of RSA. The normalized transmittance for the standard Open aperture Z-scan is expressed by the relation [13]

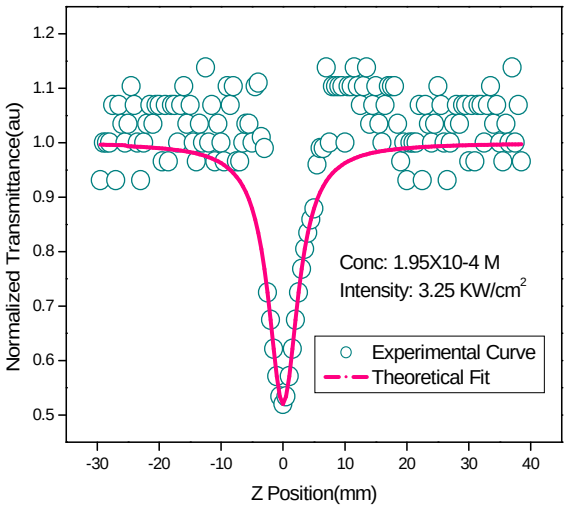
$$T(z,s=1) = \sum_{m=0}^{\alpha} \frac{[-q_0(z,0)]^m}{[m+1]^{\frac{3}{2}}} \qquad \ldots\ldots\ldots\ldots(1)$$

Where $q_0 = \frac{\beta I_0 L_{eff}}{1+\frac{z^2}{z_0^2}}$ Here, L_{eff} is the effective length of the sample which is equal to $L_{eff} = (1 - e^{-\alpha L})/\alpha$ With L sample length and α linear absorption coefficient; I_0 is the on axis intensity at the focus, $z_0 = \frac{kw_0^2}{2}$ is the diffraction length of the beam, $k = \frac{2\pi}{\lambda}$ is the wave vector and λ is the laser wave length . The theoretical curves generated with eq(1) were fitted with our experimental data for RSA and the effective nonlinear absorption coefficients β , for the different concentrations of the dye under the excitation conditions ,were obtained from a best fit, as had been done in references [14,15](See Table 1).

RSA has been found to occur in many organic materials especially in π- electron conjugated molecules and those with a centrosymmetric structure. RSA type (positive nonlinear absorption) behaviour can be caused by any of the NLO mechanisms such as two photon absorption (TPA) Excited state absorption (ESA), Free carrier absorption (FCA), Nonlinear scattering or a combination of these processes

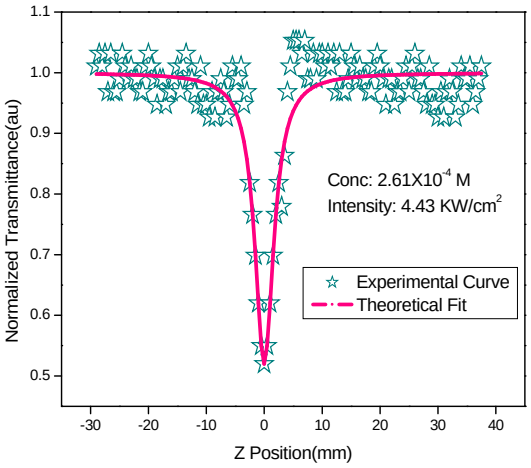


A



B

Fig. 5 OA Z-Scan profiles of EC R in aqueous solution with Concentration $1.95X10^{-4}$ M at I_0= (4.43 and 3.25) KW/cm^2 .



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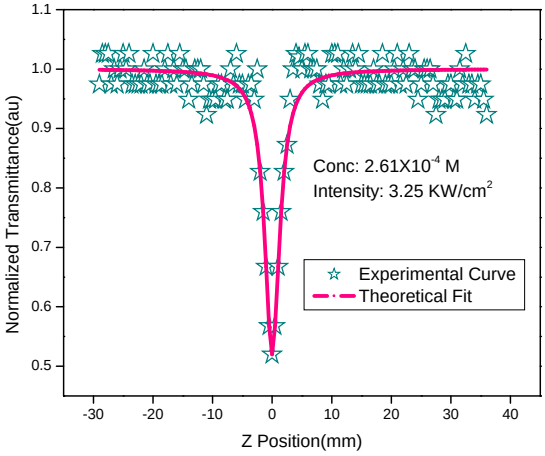
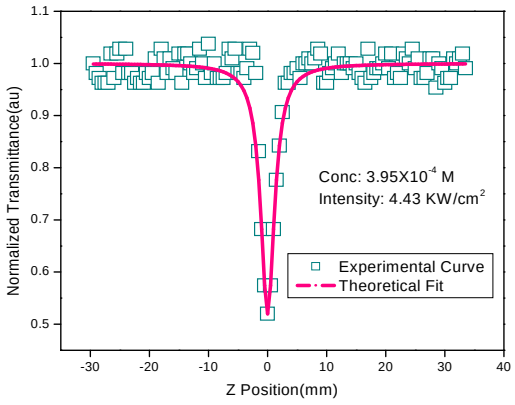
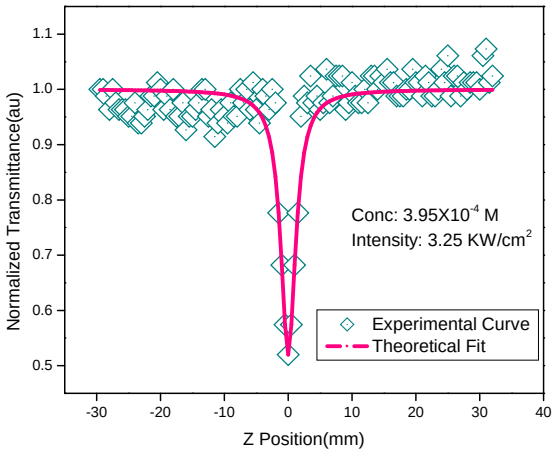


D

Fig. 6 OA Z-Scan profiles of EC R in aqueous solution with Concentration$2.61X10^{-4}$ M at I_0= (4.43 and 3.25) KW/cm^2 .



E



F

Fig. 7 OA Z-Scan profiles of EC R in aqueous solution with Concentration3.95X10^{-4} M at I_0= (4.43 and 3.25) KW/cm^2 .

Table 1 The values of [illegible] three different concentrations of EC [illegible] queous solution

Concentration ($\times 10^{-4}$ M)	**I_0 (KW/cm^2)**	**ΔT_{p-v}**	**β ($\times 10^{-5}$) (m/W)**	**esu (m^3/W) $\times 10^{-7}$**
1.95	4.43	.4815	3.72	5.886
	3.25	.692	7.29	11.53
2.61	4.43	.41812	1.565	2.476
	3.25	.42304	2.1611	3.422
3.95	4.43	.409	.857	1.35
	3.25	.5157	2.03	3.201

CONCLUSION

In summary, aqueous solutions of the organic dye EC R, were prepared for three different concentrations and its low-threshold NLO properties were investigated.

The effect of dye concentration on the absorption spectra was studied using UV-Visible spectrophotometer and found to be in well agreement with the Beer-Lambert law.PL emission spectra was also studied.

The third order nonlinear absorption behaviour was studied using the single beam Z-scan technique, employing the 442 nm cw He-Cd laser as excitation source. The dye samples exhibit positive nonlinear absorption. It may be noted that the dip transmission at the focus decreases when the incident focal intensity I_0 is increased .The occurrence of nonlinear processes in this dye, signifies the possibility of utilizing it in photonic device applications.

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