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Nonlinear optical properties of certain colored, free-flowing, dye-based fountain pen inks

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The paper is dedicated to Prof D V G L N Rao

In this work, we investigate the nonlinear optical absorption behaviour of a set of thirteen dye-based fountain pen inks, employing the open-aperture Z-scan technique. 532 nm, 5 ns laser pulses obtained from a frequency-doubled Nd:YAG laser are used for exciting the samples. The inks show reverse saturable absorption (RSA) of varying strengths at high laser fluences, which arises primarily from excited state absorption (ESA). The nonlinear absorption coefficient for each ink is determined by numerically fitting the measured data to the nonlinear propagation equation. Because of strong RSA the inks exhibit an excellent optical limiting property. These inks can have potential applications in the design and fabrication of optical limiter devices for the protection of human eyes and sensitive optical detectors from hazardous laser beams.

Keywords: Z-scan, dye-based ink, Reverse saturable absorption, Optical limiting, Pulsed laser.

1 Introduction

Nonlinear optics is the study of the interaction of intense optical radiation with matter [1]. The study of the nonlinear optical properties of organic and polymer systems has enjoyed rapid and sustained growth in the past few decades. Because of their large optical nonlinearities, organic materials are potential media for fabricating optoelectronic devices. From several works in literature, it is evident that organic dyes exhibit a wide range of nonlinear optical behavior [2-5].

Inks are colloidal systems of fine pigment particles dispersed in a solvent. The pigment may or may not be colored, and the solvent may be aqueous or organic [6]. Researchers have shown that commercial fountain pen inks can be used in efficient dye-sensitized solar cells [7]. In the present work, we have investigated the absorptive optical nonlinearity of a few low-cost, free-flowing dye-based fountain pen inks, using the technique of open aperture Z-scan. 532 nm, 5 ns laser pulses obtained from a frequency-doubled Nd:YAG laser are used for the measurements. Some of the inks are found to show excellent optical limiting property because of the occurrence of strong reverse saturable absorption (RSA) in them at the excitation wavelength. The nonlinear absorption coefficient has been determined and tabulated for each ink sample. As our primary interest is the nonlinear absorption behavior, we did not employ the closed aperture Z-scan experiment to measure the nonlinear refraction of the samples.

2 Materials and Methods

Thirteen color variants of the Daytone brand ink (manufactured by Daylight Industries, India) were used for the investigations. The absorption spectra of the samples were recorded using a UV-Vis-NIR

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spectrometer (Perkin Elmer, Lambda 750). Samples were diluted in water and taken in a 1 mm path length cuvette for performing the Z-scan measurements.

Fig 1. The ink samples and their color codes.

As we are making a comparative study of the nonlinear absorption strength of the samples, it is necessary that the linear absorptions of the samples are made equal before the measurements. To achieve this, the linear transmissions of all the samples at 532 nm were adjusted to be 70%, when taken in the 1 mm cuvette, by appropriate dilution. The relatively high linear transmission ensures that the samples are sufficiently transparent at low light levels, which is a pre-requisite for practical optical limiting devices.

Open aperture Z-scan is a popular technique which can be employed for measuring the nonlinear absorption coefficient of a variety of materials [8]. In this experiment, a laser beam is first focused using a lens, for making the optical intensity different along the beam propagation axis. The light intensity will be maximum at the focal point, and will decrease uniformly towards either side of the focus. The sample to be studied is placed at different positions with respect to the focus, and the corresponding transmissions are measured (Fig 2). In this way, the transmittance of the sample for different input intensities can be found out.

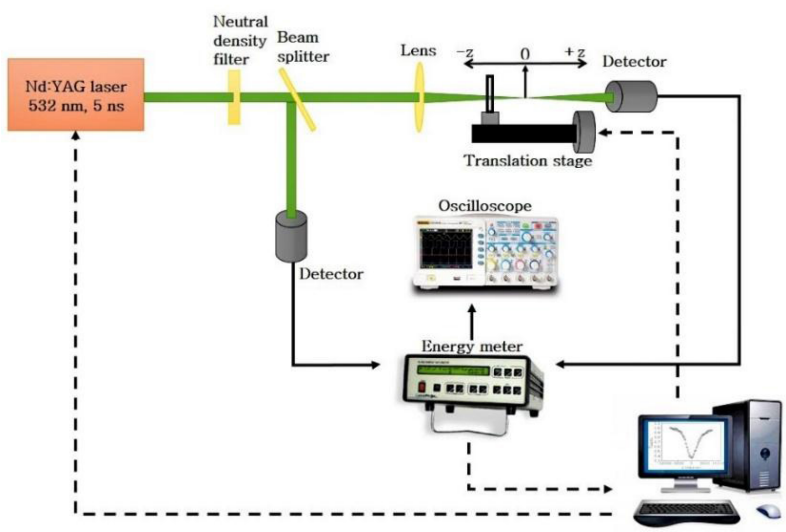

Fig 2. Schematic of the experimental setup used for open aperture Z-Scan measurements.

In our experimental set up the beam is split into two using a beam splitter, and the reflected beam (which is less intense) is used as a reference beam (to normalize for pulse-to-pulse variations in the laser energy), the energy of which is detected by detector A. The transmitted beam is focused using a planoconvex lens of focal length 10 cm. The beam waist radius at the focus (ω_0) is found to be 15 µm, and the corresponding Rayleigh length, given by

$$z_0 = \pi\omega_0^2/\lambda$$

is calculated to be 1.32 mm (this is larger than the sample thickness, which is a requirement for Z-scan measurements). The focused beam is allowed to pass through the sample in the cuvette, and the energy of the beam transmitted through the sample is measured by detector B. A translation stage is used for moving the sample from one side of the focal point to the other side. The beam's propagation direction is taken as the z-axis and the focal point is taken as $z = 0$. The measurement is automated by using a computer program. The graph plotted between the sample position z and the sample transmittance is called the open aperture Z-scan curve. The maximum transmittance of the sample is normalized to the value of 1 while plotting the Z-scan curve.

It is possible to plot the sample transmission as a function of the input laser fluence as well, by using the Z-scan data. For this, we note that for a spatially Gaussian beam, the light fluence $F_{in}(z)$ at any position z can be calculated from the corresponding beam radius $\omega(z)$ and the input laser pulse energy E_{in}. The beam radius is given by

$$\omega(z) = \omega(0)\left[1 + \left(\frac{z}{z_0}\right)^2\right]^{1/2} \tag{2}$$

and the position-dependent fluence can be calculated from the expression, $F_{in}(z)$

$$F_{in}(z) = \frac{4(\log 2)^{1/2} E_{in}}{\pi^{3/2}\,\omega(z)^{1/2}} \tag{3}$$

The position-dependent intensity is given by $I(z) = F(z)/\tau$, where τ is the laser pulse width.

$$F_{out}(z)/F_{in}(z) = \exp(-(\alpha + \beta I_{in}(z))l) \tag{4}$$

where $F_{in}(z)$ is the incident fluence (J/cm^2), $F_{out}(z)$ is the transmitted fluence (J/cm^2), α is the linear absorption coefficient (cm^{-1}), β is the third order nonlinear absorption coefficient (cm/W), and l is the sample path length (cm).

As mentioned, all samples we used were adjusted to have a linear transmittance ($F_{out}(z)/F_{in}(z)$) of 0.7 at the excitation wavelength, when taken in a cuvette of 1 mm pathlength. This translates to an α value of 3.57 cm^{-1}. The curve drawn between $F(z)$ and the normalized transmittance is known as the nonlinear transmission curve. The β values can then be obtained by numerically fitting the nonlinear transmission curves to Eq (4). The values thus obtained for the thirteen samples studied are given in Table 1.

3 Results and Discussion

The photographs of four of the sample solutions are shown in Fig 3, and the UV-Vis absorption spectra measured for these samples are shown in Fig 4.

Fig 3. Photographs of some of the sample solutions (emerald green, yellow ochre, crimson and turquoise blue).

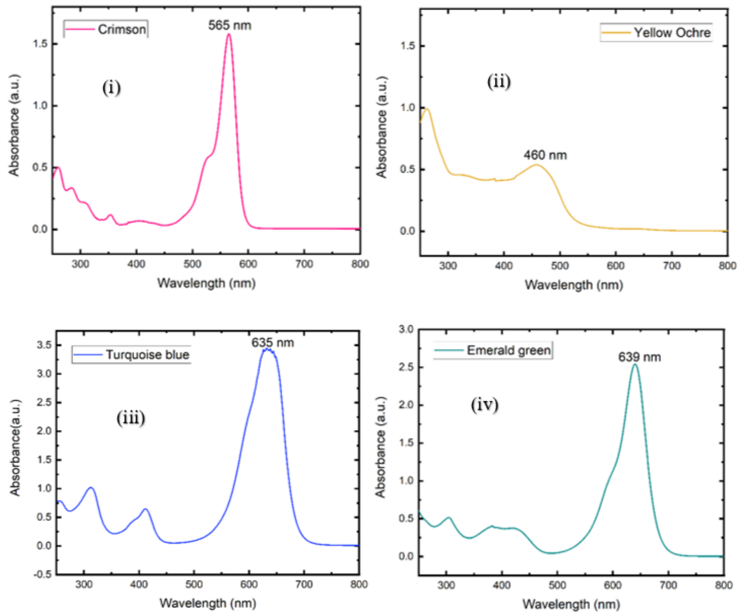

Fig 4. UV-VIS absorption spectra measured for the samples shown in Fig 3. (i) crimson, (ii) yellow ochre, (iii) turquoise blue, and (iv) emerald green.

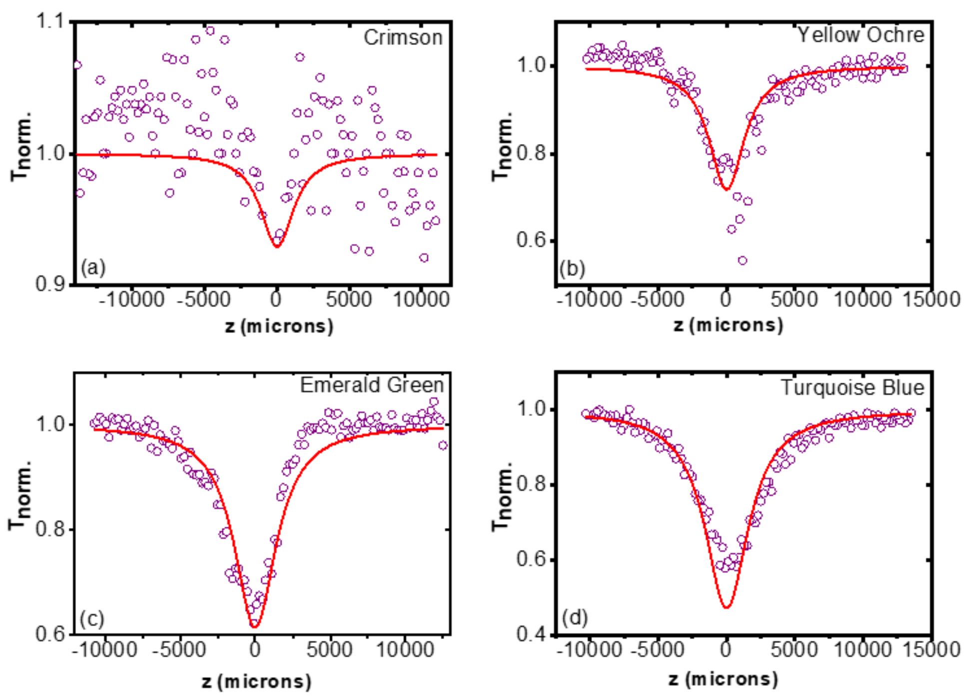

Fig 5. Open aperture Z-scan curves measured for the ink samples shown in Fig 3. All samples have a linear transmission of 70% at the excitation wavelength of 532 nm. The laser pulse energy used is 50 μJ. Circles are data points while solid curves are numerical fits according to Eq (4).

All samples exhibit absorption bands in the UV and visible spectral regions. Crimson has an absorption band in the range 450-600 nm, with a peak at 565 nm. Yellow ochre shows absorption in the range 400-500 nm, with peak at 460 nm. Turquoise blue and emerald green show absorption bands in the 500-700 nm region, with peaks at 635 and 639 nm, respectively.

Figure 5 shows the open aperture Z-scans measured for the samples. The curves show valleys at the beam focus, indicating the occurrence of reverse saturable absorption (RSA). In Fig 6, the normalized transmittance of the samples is plotted as a function of the input laser fluence. Considering the fact that the inks are organic molecules and the excitation is by nanosecond pulses, the RSA behavior should arise primarily from strong excited state absorption (ESA), involving the sequential absorption of two photons. Such sequential absorption is distinctly different from genuine two-photon absorption (2PA) which is relatively weak for nanosecond laser excitation, compared to ultrafast (ps and fs) excitation [9-11]. RSA will be prominent for molecules in which the ESA cross-section is larger than the ground state absorption (GSA) cross-section (this is the case with all the ink samples investigated). On the other hand, if the ESA cross-section is lower than the GSA cross-section, saturable absorption (SA) will occur. This critical dependence of RSA and SA on the value of the ESA cross-section can be demonstrated by considering a three-level or five-level model for the electronic energy states of the molecule, and solving the state population rate equations simultaneously with the nonlinear propagation equation [12,13].

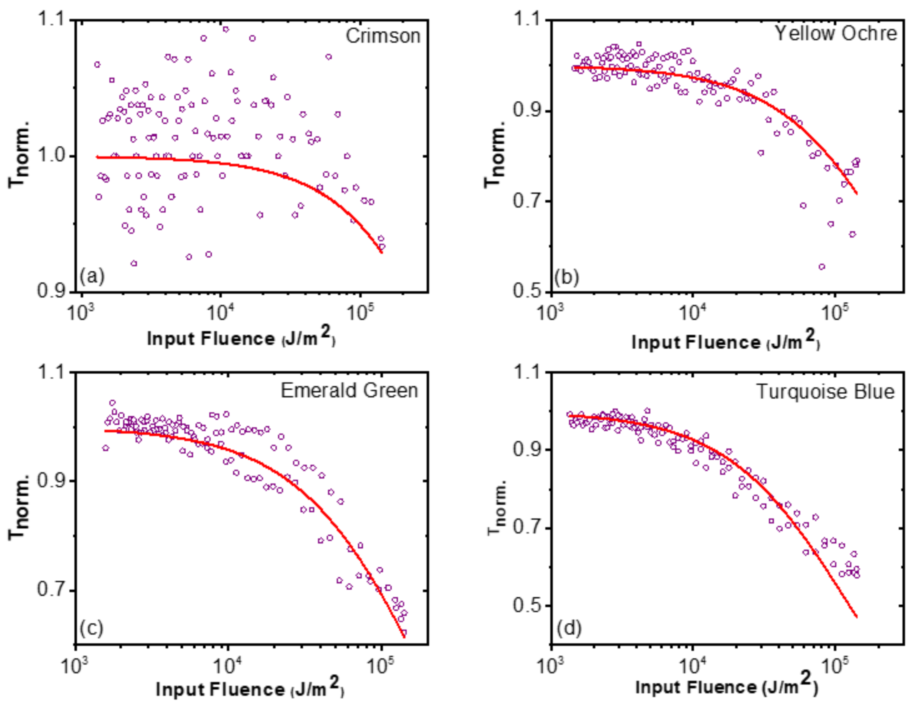

Fig 6. The nonlinear transmission curves calculated using the Z-scan curves, for the samples given in Fig 5. Circles are data points while solid curves are numerical fits according to Eq (4).

It is found that the β value is minimum for the ink sample called Crimson (3×10^{-10} cm/W) and maximum for the ink sample called Turquoise Blue (4.29×10^{-9} cm/W), showing that ESA is most prominent in the latter. These values are close to those reported for some good dye-based optical limiters in literature [5,14,15], showing that the samples we studied are potential optical limiters that can be used for the protection of human eyes and sensitive detectors from powerful laser radiation.

Table 1. Nonlinear absorption coefficient (β) values calculated for the ink samples from open aperture Z-scan measurements

Ink	β (× 10^{-9} cm/W)
Crimson	0.30
Brilliant Red	0.45
Deep Black	0.60
Blue Black	0.70
Dark Grey	0.79
Rose Red	0.85
Mauve	1.00
Olive Brown	1.02
Dark Brown	1.20
Havana Brown	1.30
Yellow Ochre	1.70
Emerald Green	2.70
Turquoise Blue	4.29

4 Conclusion

The nonlinear optical transmission of thirteen differently coloured free-flowing dye-based inks have been investigated using 532 nm, 5 ns laser pulses employing the open aperture Z-scan technique, using a frequency-doubled Q-switched Nd:YAG laser. The samples show prominent reverse saturable absorption behavior, because of which they show excellent optical limiting property. A comparative measurement of the RSA coefficients has been carried out for fixed concentrations of the studied inks at identical experimental conditions. The comparison shows that the color Turquoise Blue has maximum RSA coefficient compared to the other color variants, making it the most suitable sample among the studied group for optical limiting applications.

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