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Influence of solvent contribution on nonlinearities of near infra-red absorbing croconate and squaraine dyes with ultrafast laser excitation

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Third order optical nonlinearities of various solvents such as Dimethylformamide (DMF), ethanol, chloroform, CCl₄, acetone, toluene, Tetrahydrofuran (THF), and CS₂ are studied in picosecond (ps) and femtosecond (fs) time scales using Z-scan technique. All the solvents show reverse saturable absorption behavior which is attributed to significant two-photon absorption and three-photon absorption processes in ps and fs time scale regimes, respectively. Nonlinear refraction studies reveal the positive signature of nonlinearity of solvents in both pulse regimes. We have investigated the effect of solvents on observed nonlinearities of near infra-red absorbing squaraine and croconate dye samples. Interestingly, a change in the sign of nonlinearity of molecules (phe cro, ptbu cro, phe squ, and ptbu squ) is observed in the ps regime when the solvent contribution is removed. Further, we also observed a change in magnitude of the nonlinearity for all the molecules under both pulse regimes. This gives clear evidence on the role of the solvents in the measurement of optical nonlinearities and that the true nonlinearities of the solute in fs/ps time domain can only be obtained when the measurements account for the solvent. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4823817>]

I. INTRODUCTION

Third order optical nonlinearities of several materials were measured during the past two decades for various photonic and optoelectronic applications.^{1–16} Z-scan is one of the simplest techniques for the measurement of the third order nonlinear optical susceptibility, and it is also helps in understanding the nonlinear absorption (NLA) and nonlinear refraction (NLR) phenomena of the materials. The NLA and NLR processes have been investigated on materials including inorganic semiconductors, organic compounds, fullerenes, inorganic metal clusters, and graphene-porphyrin composites.^{17–43} The NLA could either follow saturable absorption (SA), in which the nonlinear absorption coefficient value is negative in general, or reverse saturable absorption (RSA), in which the nonlinear absorption coefficient value is positive. RSA can occur when the excited state absorption cross section is larger than the ground state absorption cross section, with large nonlinear scattering or by two photon absorption (TPA) and multi-photon absorption. SA is seen when the excited state becomes saturated at higher intensities of the pump laser. From the NLR process, one can evaluate the sign and magnitude of the nonlinearity of the material. In comparison with nanosecond and picosecond pulses, the femtosecond pulse is of same order as that of the lifetimes of higher excited states, which plays an important role in the NLA phenomena. Pure nonlinearities of the material should be computed by eliminating the solvent contribution, which is very important for materials with weak third order nonlinearities in the ultrafast regime. In this

work, we have presented fs and ps optical nonlinearities of several solvents such as Dimethylformamide (DMF), ethanol, CCl₄, chloroform, acetone, toluene, Tetrahydrofuran (THF), and CS₂. CS₂ is one of the ideal reference materials for nonlinear optics, because it shows a large nonlinearity and is a widely studied material.^{44–46} Very few reports are available on solvent effect on optical limiting, nonlinear absorption, two-photon absorption, and fluorescence,^{47–52} where they have shown a difference in nonlinear optical behavior when a material was measured in different solvents. Here, we have studied the solvent contribution on nonlinearities of croconate and squaraine dye molecules in DMF. The NLR behavior of some dyes dramatically changed their signature of nonlinearity from positive to negative when the solvent contribution is removed and further magnitude of nonlinear refractive index coefficient (n_2) is reduced by one order for all dye molecules.

II. EXPERIMENTAL DETAILS

The third order nonlinear optical studies are carried out by the Z-scan method.⁵³ The ultra-short laser pulses used are obtained from a conventional chirped pulse amplification system comprising of an oscillator (Maitai, Spectra-Physics Inc.) that delivers a ~80 fs, 82 MHz pulse train with pulse energy of 1 nJ at 800 nm and a regenerative amplifier (Spitfire, Spectra Physics Inc.), pumped by a 150 ns, 1 kHz, Q-switched Nd:YLF laser. After regenerative amplification, we obtained amplified pulses of pulse width ~100 fs, determined by second order intensity autocorrelation, with output energy of up to 1 mJ at 1 kHz repetition rate. The ps laser source is a frequency doubled Nd:YAG laser (EKSPLA PL 2143A) delivering 532 nm, 30 ps, 10 Hz laser pulses. Croconate and squaraine dyes are taken as solutions in DMF

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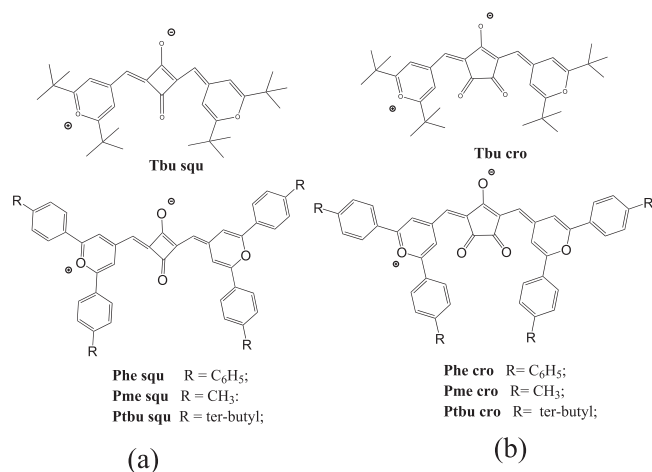


FIG. 1. Chemical structures of (a) squaraine dye molecules and (b) croconate dye molecules.

for the experimental studies. Measurements are taken in a 1 mm cuvette for Z-scan studies. Open and closed aperture Z-scan studies are carried out by focusing the input beam on the sample using a 120 mm focal length lens, forming a

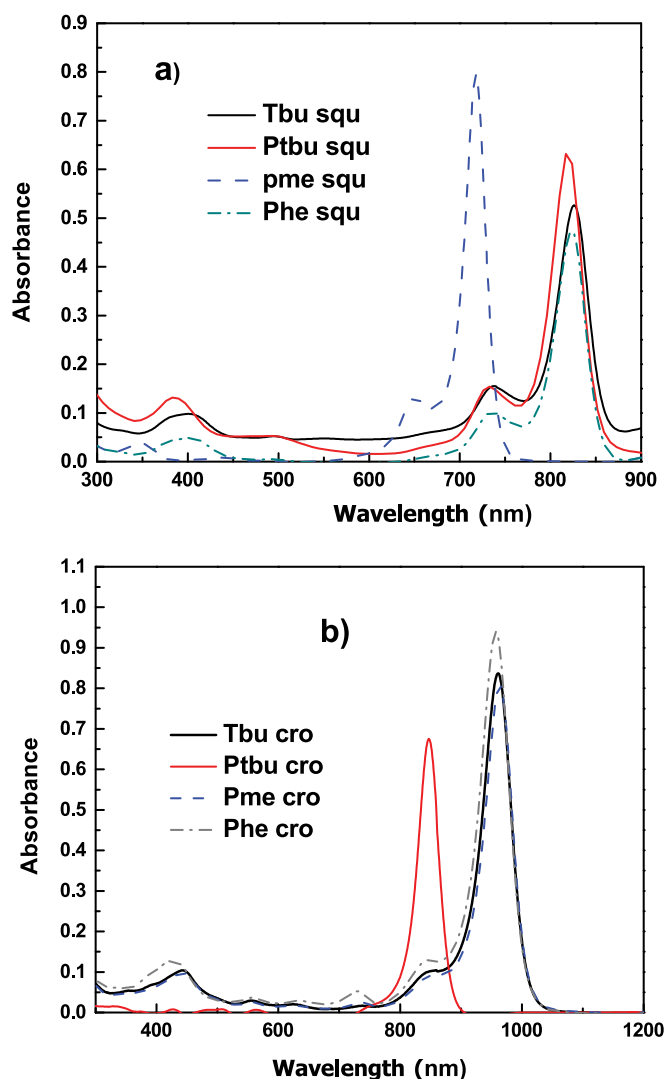


FIG. 2. UV-VIS absorption spectra of (a) squaraine and (b) croconate dyes in DMF at 1×10^{-6} M.

27 μm (40 μm) spot size at focus for the ps (fs) regime. The transmitted light is collected with a fast photodiode. The peak intensity used in the Z-scan experiments is 25 GW/cm^2 in ps and 550 GW/cm^2 in fs time scales.

III. RESULTS AND DISCUSSION

Chemical structures of squaraine and croconate dye molecules are shown in Figs. 1(a) and 1(b), respectively, with corresponding names for each dye molecule in the figure. These names are used throughout the manuscript. The

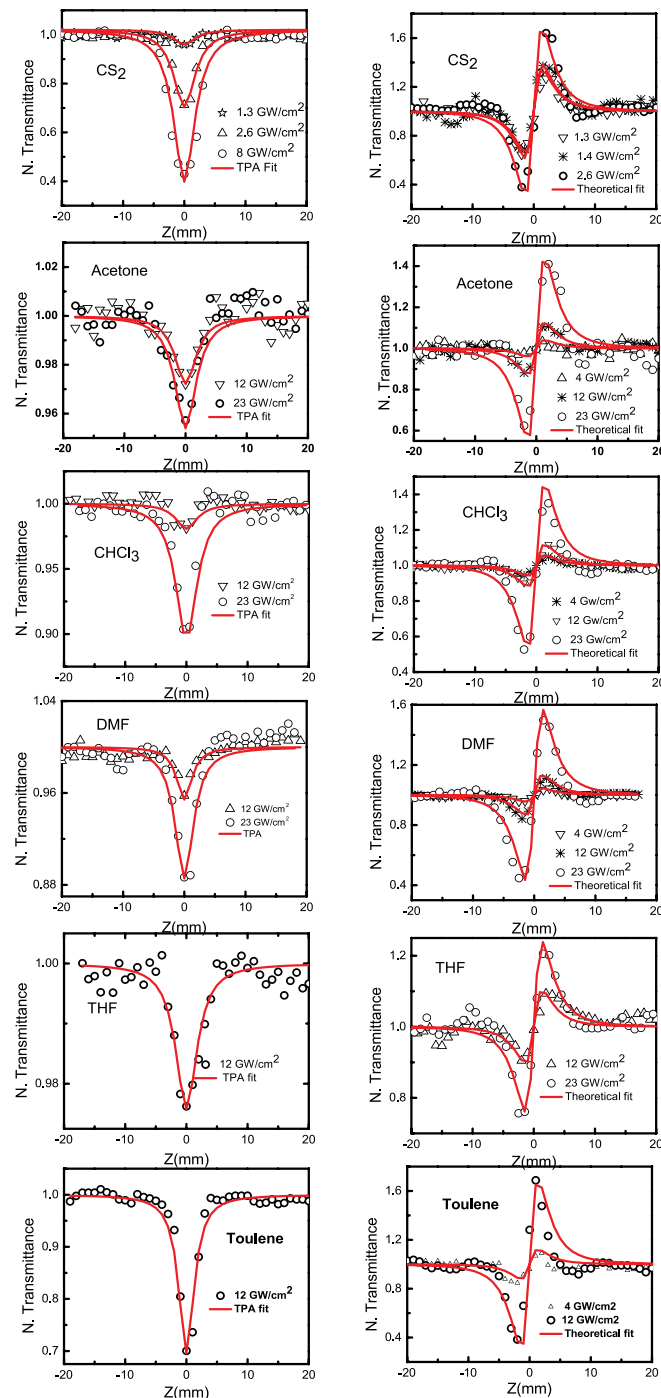


FIG. 3. Open and closed aperture Z-scan curves for CS₂ and several solvents with 532 nm, 30 ps, and 10 Hz repetition rate laser pulse excitation. Symbols represent experimental data and solid lines represent theoretical fits.

TABLE I. Third order nonlinear optical parameters of solvents in ps regime with 532 nm, 10 Hz, and 30 ps laser pulses.

Solvent	$n_2 \times 10^{-15}$ (cm ² /W)	$\beta \times 10^{-10}$ (cm/W)	$\text{Im } \chi^{(3)} \times 10^{-14}$ esu	$\text{Re } \chi^{(3)} \times 10^{-13}$ esu	$\chi^{(3)} \times 10^{-13}$ esu
Acetone	4.37	0.60	1.19	2.04	2.05
Chloroform	5.19	1.25	2.81	2.75	2.76
DMF	4.70	1.22	2.68	2.43	2.45
THF	4.01	0.57	1.21	2.01	2.01
Toluene	4.27	3.2	7.70	2.42	2.54
CS ₂	113	20	57.10	76.00	76.21

dyes have an absorption maximum in near infra-red (NIR) region as shown in Fig. 2. For UV-VIS absorption recordings 1×10^{-6} M of dye molecules are taken in DMF. One can find from Fig. 2 that the wavelength maxima for Tbu squ, Phe squ, Pme squ, and Ptbu squ are at 718, 819, 823, and 826 nm, respectively, for Tbu cro, Phe cro, Pme cro, and Ptbu cro the absorption peaks are at 847, 958, 961, and 963 nm. These dye molecules have a large optical transmission window from the ultra-violet (UV) to visible and in the far IR.

Picosecond optical nonlinearities of solvents are measured at 532 nm using Z-scan technique. Fig. 3 shows open and closed aperture Z-scan curves for solvents, revealing the nonlinear absorption and nonlinear refraction behavior. In this regime, all of the solvents exhibited RSA kind of nonlinear absorption behavior due to two-photon absorption process and also shows the valley-peak configuration in closed aperture curves due to the positive nonlinearity of solvents. Theoretical fittings of these curves will give the nonlinear absorption and nonlinear refraction coefficients such as two-photon absorption coefficient (β) and n_2 . In order to estimate the dominant nonlinear absorption whether it is from TPA or three photon absorption (3PA) is confirmed by fitting the experimental data using theoretical formalism developed by Sheik Bahae *et al.*⁵³ Here, the transmittance of open aperture Z-scan curve for n-photon absorption is

$$T_{OA(nPA)} = 1 - \frac{\alpha_n I_0^{n-1} L_{eff}^{(n)}}{n^{3/2} (1 + z^2/z_0^2)^{n-1}}. \quad (1)$$

Transmittance for two-photon ($n=2$) and three-photon ($n=3$) absorption were deduced from Eq. (1)

$$T_{OA(2PA)} = 1 - \frac{\alpha_2 I_0 L_{eff}}{2^{3/2} (1 + z^2/z_0^2)}, \quad (2)$$

$$T_{OA(3PA)} = 1 - \frac{\alpha_3 I_0^2 L_{eff}^2}{3^{3/2} (1 + z^2/z_0^2)^2}, \quad (3)$$

where I_0 is the peak intensity, z is the sample position, $z_0 = \pi \omega_0^2 / \lambda$ is Rayleigh range, ω_0 is the beam waist at the focal point ($z=0$), and λ is the laser wavelength. Effective path lengths in the sample of length, $L_{eff}^{(n)}$, for TPA and 3PA is given as $L_{eff} = [1 - \exp(-\alpha_0 L)] / \alpha_0$, and $= [1 - \exp(-2\alpha_0 L)] / 2\alpha_0$, respectively. α_2 (β) and α_3 represent nonlinear absorption coefficients for TPA and 3PA, respectively. Z-scan traces are fitted using Eqs. (2) and (3). The red line represents TPA and the blue line 3PA process. The nonlinear refraction coefficient (n_2) is obtained by fitting the nonlinear transmission expression of the closed aperture Z scan⁵³ data using Eq. (4)

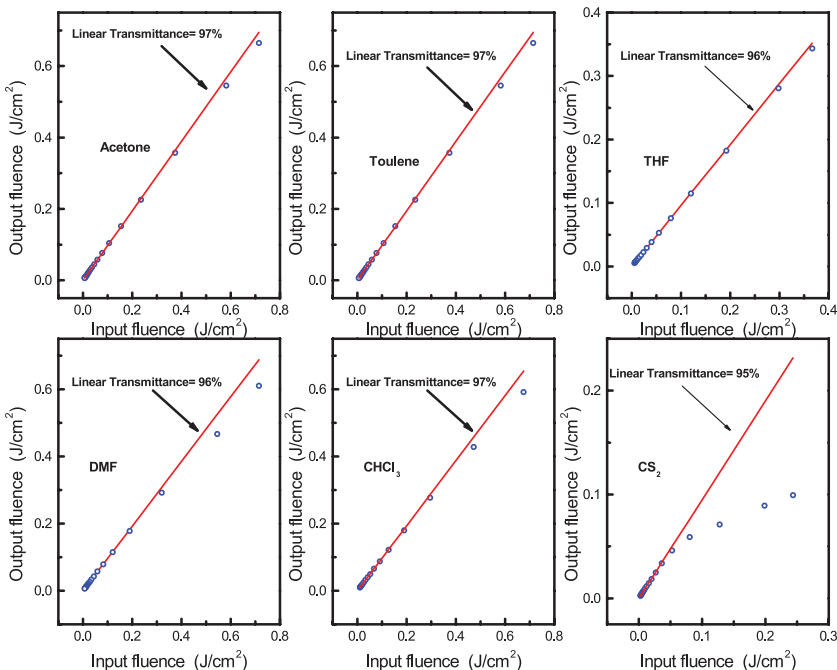


FIG. 4. Transmittance curves for various solvents with 532 nm, 30 ps pulse duration of 10 Hz laser pulses.

$$T_{CA} = \frac{4\Delta\Phi_0(z/z_0)}{[1 + (z/z_0)^2][9 + (z/z_0)^2]}, \quad (4)$$

where $\Delta\phi_0$ is the phase change of the laser beam due to the nonlinear refraction. The value of $\Delta\phi_0$ is estimated from a theoretical fit to the experimental data. Third order nonlinear refractive index(n_2) is calculated from

$$n_2(\text{cm}^2\text{W}^{-1}) = \frac{|\Delta\Phi_0|\lambda}{2\pi I_{00}L_{eff}}. \quad (5)$$

The nonlinear refractive index of each solvent is in the order of $10^{-15} \text{ cm}^2/\text{W}$ while β is of the order of $10^{-10} \text{ cm}/\text{W}$. We have estimated $\text{Im} \chi^{(3)}$ from β and $\text{Re} \chi^{(3)}$ from n_2 . $\chi^{(3)}$ will then be $\sqrt{(\text{Im} \chi^{(3)})^2 + (\text{Re} \chi^{(3)})^2}$, and is in the order of 10^{-13} esu. All these parameters for the individual solvents are summarized in Table I.

CS_2 has large optical nonlinearities in ps regime due to strong nonlinear absorption and refraction. The values of n_2 and β are found to be $1.13 \times 10^{-13} \text{ cm}^2/\text{W}$ and $2 \text{ cm}/\text{GW}$, respectively. Due to these large nonlinear optical coefficients, CS_2 acts as an ideal reference material for third order nonlinear optical materials. Transmittance curves for various solvents in ps regime are shown in Fig. 4. Solvents have large transmittance (L.T) over 95% at 532nm wavelength. CS_2 alone has shown deviation from the linear transmittance compared to other solvents at input fluence of $0.1 \text{ J}/\text{cm}^2$. This could be due to strong multi-photon absorption in CS_2 .

Fig. 5 shows open and closed aperture Z-scan curves of solvents recorded at 800nm, 1 kHz repetition rate, and 110 fs pulse duration of laser excitation. In this regime, all the solvents have shown RSA kind of nonlinear optical absorption behavior due to 3PA.

From the open aperture Z-scan curves of solvents shown in Fig. 5, the three-photon absorption fit (solid blue line)

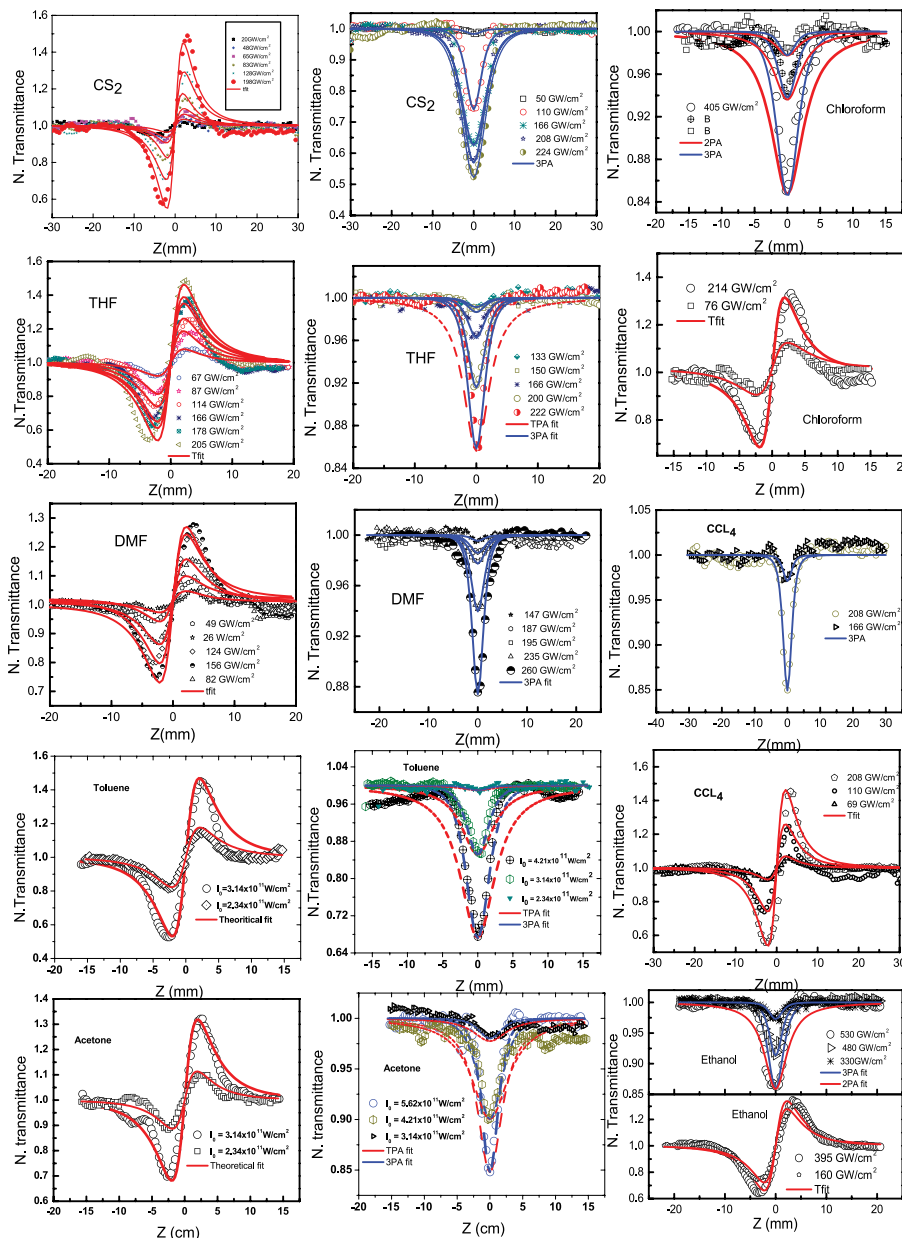


FIG. 5. Closed and open aperture Z-scan curves for CS_2 and several solvents with 800nm, 110 fs, and 1kHz repetition rate laser pulse excitation.

TABLE II. Third order nonlinear optical parameters of solvents in fs regime with 800 nm, 1 kHz, and 110 fs laser pulses.

Solvent	n_2 (cm ² /W) $\times 10^{-16}$	α_3 (cm ³ /W ²) $\times 10^{-23}$	Re $\chi^{(3)}$ esu $\times 10^{-14}$
Acetone	9.34	7.8	4.37
Chloroform	9.37	5.2	4.96
DMF	10.36	9.7	5.37
THF	12.88	15.0	6.46
Toluene	14.00	20.5	7.95
Ethanol	10.90	21.0	5.11
Ccl ₄	11.68	18.2	6.31
CS ₂	17.75	74.7	12.00

matches well with experimental data while the two-photon absorption fitting (dashed red line) does not fit. Closed aperture Z-scan curves of solvents in Fig. 5 show valley-peak configuration indicating a signature of positive nonlinearity. We have studied intensity dependent observations for some of the solvents such as CS₂, THF, and DMF in closed aperture configuration and CS₂, THF, DMF, Toluene, Acetone, Chloroform, and Ethanol in open aperture configuration. Nonlinear absorption and nonlinear refraction coefficients remain unchanged from the nonlinear transmission curves. Nonlinear refractive index of solvents is in the order of 10^{-16} cm²/W and three-photon absorption coefficient (α_3) is in the order of 10^{-23} cm³/W². The estimated value of Re $\chi^{(3)}$ is in the order of 10^{-14} esu. All these parameters of individual solvents are tabulated in Table II. Nonlinear thermal

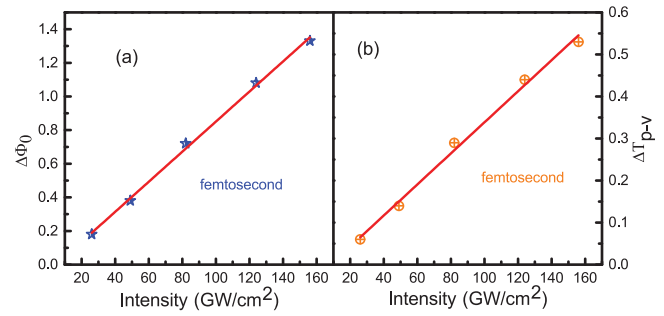


FIG. 6. (a) Phase shift, $\Delta\Phi_0$, versus incident laser intensity and (b) difference between normalized peak and valley transmittance, ΔT_{p-v} , versus incident laser intensity for DMF at 800 nm with 110 fs and 1 kHz repetition rate laser pulse excitation. Symbols represent experimental data and solid lines represent theoretical fits.

effects were shows a difference in normalized transmission when compare its prefocal and postfocal in closed aperture Z-scan technique.⁵⁴ In our case, we did not see such a difference is an evident that observed nonlinearities are due to pure electronic in ps and fs time scales. CS₂ has shown the highest nonlinearity compared to the other solvents and its n_2 and α_3 are 1.77×10^{-15} cm²/W and 7.5×10^{-22} cm³/W², respectively.

Fig. 6(a) represents the dependence of $\Delta\Phi_0$ with incident laser intensity for DMF. As can be seen, no saturation of the nonlinear refraction is present since $\Delta\Phi_0$ increases linearly with input intensity for our experimental conditions. A plot

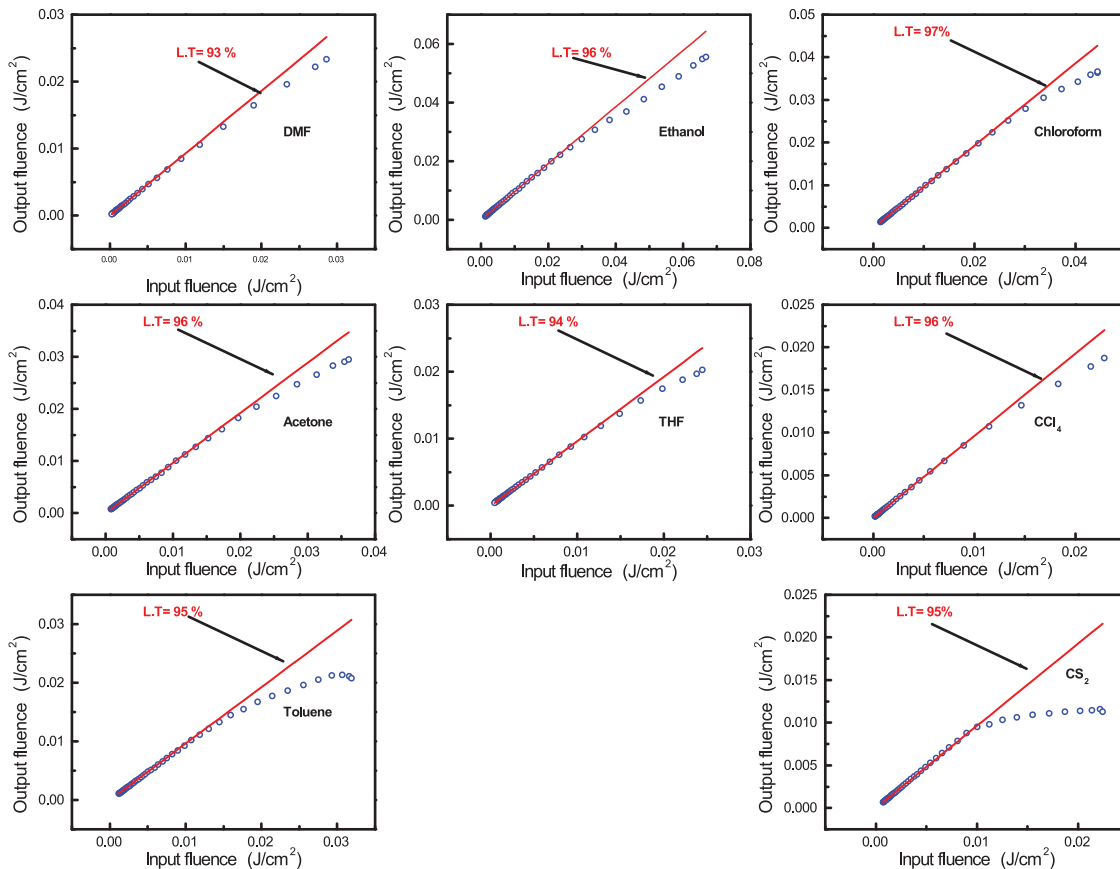


FIG. 7. Transmittance curves for DMF, Ethanol, Chloroform, Acetone, THF, CCl₄, CS₂, and Toluene with 800 nm, 110 fs pulse duration, and 1 kHz repetition rate laser pulses.

of ΔT_{p-v} versus incident laser irradiance, which is measured from various Z-scan curves on the same DMF sample is shown in Figure 6(b). The linear behavior of this plot demonstrates that sample nonlinearities are from pure cubic nonlinearities.⁵³ Output versus input fluence curves for all the solvents in the fs regime is shown in Fig. 7. Each of the solvents has shown a deviation from the linear transmittance due to 3PA. Compared to all other solvents CS₂ shows an optical limiting behavior with a limiting threshold 22 mJ/cm² in the fs regime.

Closed aperture Z-scan curves of squaraines and croconates with 532 nm, 30 ps laser excitation are shown in Figure 8. We estimated the n_2 values of these samples through a theoretical fit using Eqs. (4) and (5). As the solvents show comparable nonlinearities, solvent contribution needs to be subtracted from the sample solution data. A systematic study is undertaken to take out the solvent contribution on the

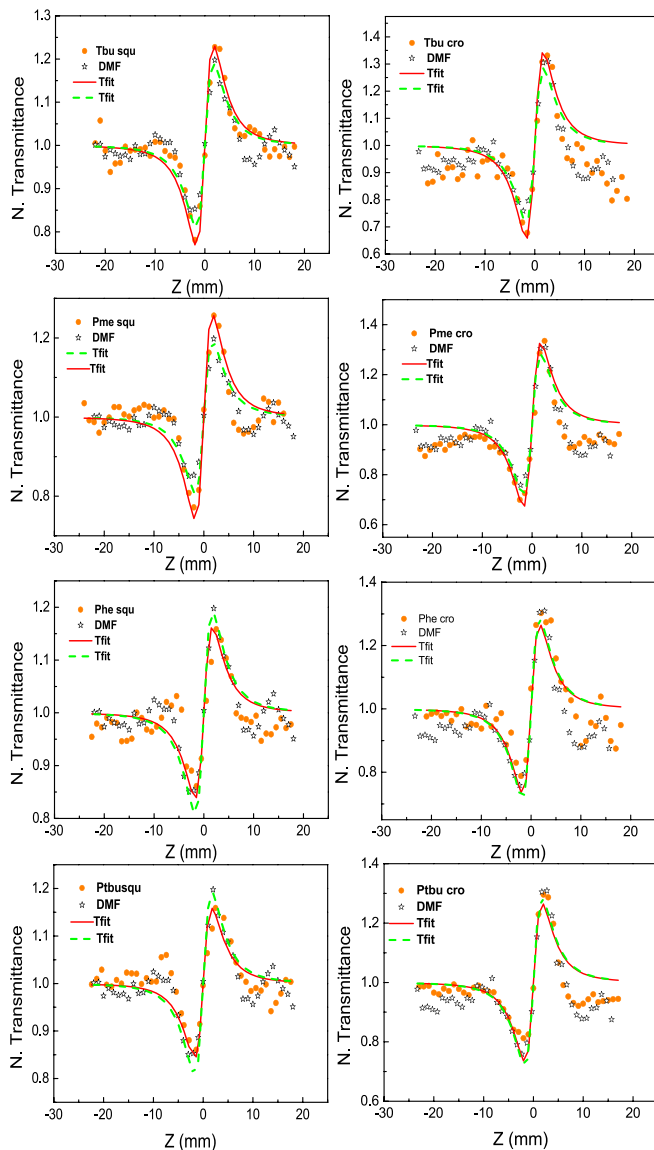


FIG. 8. Closed aperture Z-scan curves for squaraines and croconates with 532 nm, 30 ps, and 10 Hz repetition rate laser pulse excitation with intensity 25 GW/cm². Symbols represent experimental data and lines represent theoretical fits.

measured nonlinearities. First, we measured the nonlinear refractive index of the sample along with the solvent contribution, and then measured pure solvent nonlinear refractive index. Solvent contribution is now subtracted from the sample solution to obtain solute contribution to the nonlinear refractive index. DMF is the solvent and it has n_2 value of 4.7×10^{-15} cm²/W.

After removal of solvent nonlinearities from the solution of the samples, we observe a reduction in the magnitude of nonlinearity. We also observed a change in the sign of the nonlinearity in Phe squ, Ptbu squ, Phe cro, and Ptbu cro from positive to negative and a change in the magnitude from 4.51, 4.52, 4.53, and 4.57×10^{-15} cm²/W to -1.90 , -1.80 , -1.70 , and -1.30×10^{-16} cm²/W, respectively. Other samples Pme squ, Tbu squ, Pme cro, and Tbu cro have shown a change in magnitude only with the sign remaining constant after removal of the solvent contribution. n_2 and $\text{Re } \chi^{(3)}$ values of these dye molecules with and without the contribution of the solvent is tabulated in Table III.

Closed aperture Z-scan curves of squaraines and croconates with 800 nm, 110 fs laser excitations are shown in Fig. 9. We found that n_2 values of these compounds are in the order of 10^{-15} cm²/W before removing the solvent contribution. Removal of the solvent contribution leads to a reduction in the nonlinear refractive index, which is in the order of 10^{-16} cm²/W. In the fs regime, samples do not show any change in sign of the nonlinearity but a change in magnitude is observed after removal of solvent contribution. Measurements for all these dye molecules are recorded at the input peak intensity of 120 GW/cm² in the Z-scan studies. Measured n_2 and $\text{Re } \chi^{(3)}$ values are presented in Table IV.

Nonlinear absorption behavior of croconates and squaraines are measured at 532 nm with 10 Hz and 30 ps laser pulses. All the dye molecules show RSA kind of behavior due to TPA process. Nonlinear absorption of the solvent is removed from the solution data and pure nonlinear absorption behavior of the molecules is shown in Fig. 10. Removal of solvent contribution is done by adopting our earlier work⁴³ on graphene-porphyrin composites. Phe cro and Ptbu cro have shown large nonlinear absorption compared to other dye molecules. TPA coefficient, β , values are 1.45, 2.49, 0.34, 2.46, 1.20, 0.37, 0.37, and 0.37 cm/GW for Pme cro, Phe cro, Tbu cro, Ptbu cro, Pme squ, Phe squ, Tbu squ, and

TABLE III. Third order nonlinear optical coefficients of croconate and squaraine dyes in ps regime with 532 nm, 10 Hz repetition rate, and 30 ps laser pulses.

Sample	n_2 (cm ² /W) $\times 10^{-15}$	n_2 (cm ² /W) $\times 10^{-16}$	$\text{Re } \chi^{(3)}$ esu $\times 10^{-14}$
	With solvent contribution	After removal of solvent contribution	After removal of solvent contribution
<i>Pme cro</i>	5.01	3.10	1.61
<i>Phe cro</i>	4.53	-1.70	-0.88
<i>Tbu cro</i>	5.02	3.20	1.66
<i>Ptbu cro</i>	4.57	-1.30	-0.67
<i>Pme squ</i>	5.04	3.40	1.76
<i>Phe squ</i>	4.51	-1.90	-0.98
<i>Tbu squ</i>	5.04	3.40	1.76
<i>Ptbu squ</i>	4.52	-1.80	-0.93

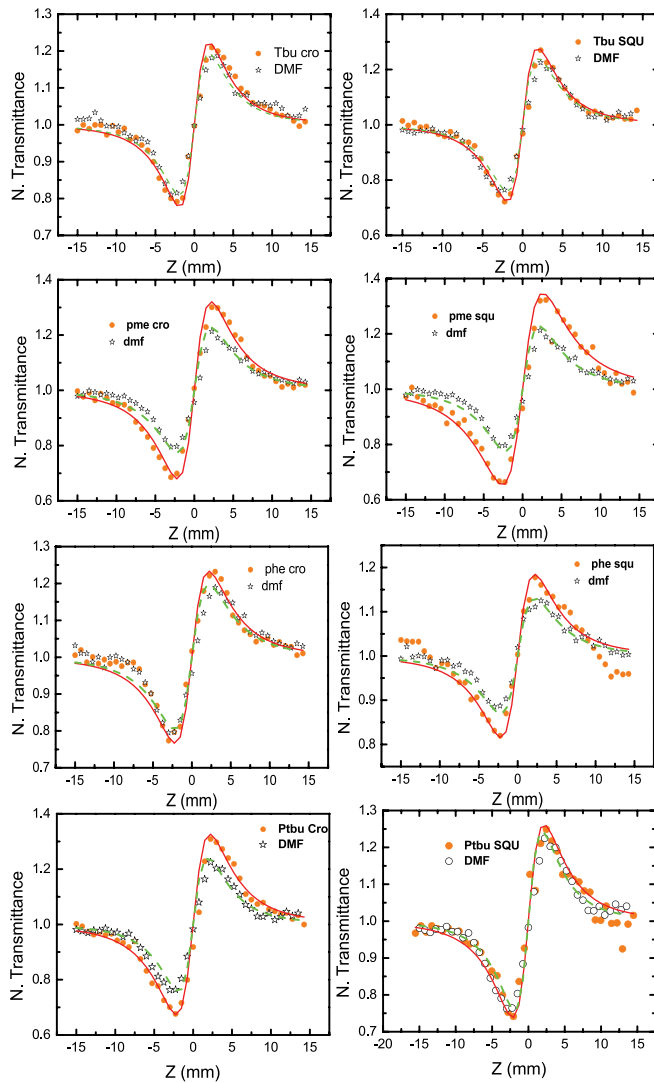


FIG. 9. Closed aperture Z-scan curves for squarainates and croconates with 800 nm, 110 fs, and 1 kHz repetition rate laser pulse excitation with intensity 120 GW/cm². Symbols represent experimental data and lines represent theoretical fits.

Ptbu squ, respectively. Pure solvents show that n_2 is in the order of 10^{-15} and 10^{-16} cm²/W in the ps and fs time scales, respectively. These nonlinearities play a major role in deciding the sign of the nonlinearities of moderate and low

TABLE IV. Third order nonlinear optical coefficients of croconate and squaraine dyes in fs regime with 800 nm, 1 kHz repetition rate, and 110 fs laser pulses.

Sample	n_2 (cm ² /W) × 10 ⁻¹⁵	n_2 (cm ² /W) × 10 ⁻¹⁶	$\text{Re } \chi^{(3)}_{\text{esu}}$ × 10 ⁻¹⁴
	With solvent contribution	After removal of solvent contribution	After removal of solvent contribution
<i>Pme cro</i>	1.77	7.33	3.80
<i>Phe cro</i>	1.35	3.16	1.63
<i>Tbu cro</i>	1.39	3.54	1.83
<i>Ptbu cro</i>	1.78	7.47	3.87
<i>Pme squ</i>	2.37	13.35	6.91
<i>Phe squ</i>	1.39	3.56	1.84
<i>Tbu squ</i>	1.48	4.40	2.28
<i>Ptbu squ</i>	1.80	7.68	3.98

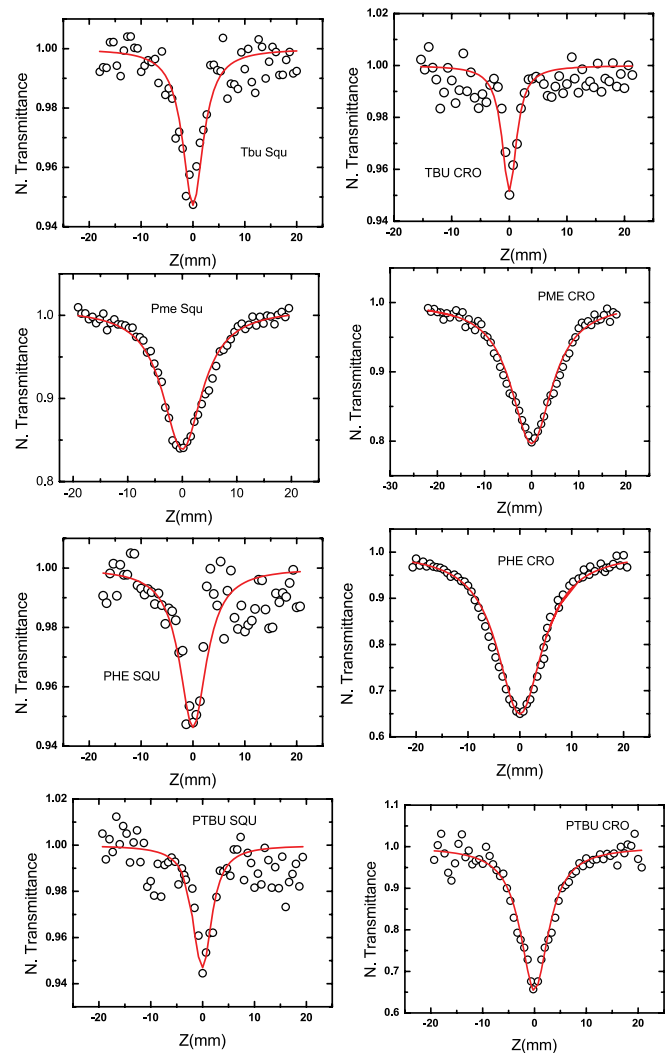


FIG. 10. Open aperture Z-scan curves for squarainates and croconates with 532 nm, 30 ps, and 10 Hz repetition rate laser pulse excitation with intensity 32 GW/cm².

nonlinear optical materials. In our case, phe and ptbu molecules have shown a change in sign of n_2 after removing the solvent contribution. Squaraine and croconate dye molecules have shown good nonlinear absorption behavior, which is due to strong two-photon absorption.

IV. CONCLUSIONS

The systematic study of nonlinear absorption and nonlinear refraction of solvents in ps and fs time scale regimes gives an approach to estimate the solvent contribution to third order optical nonlinearity of croconate and squarinate dye molecules. All the solvents have shown RSA kind of nonlinear absorption behavior and positive nonlinearity in both pulse regimes. Solvents show n_2 values are in the order of 10^{-15} and 10^{-16} cm²/W in the ps and fs time scales and are due to pure electronic nonlinearities. Phe cro, ptbu cro, phe squ, and ptbu squ dye molecules exhibit a change in the sign of the nonlinearity from positive to negative after removing the solvent contribution. Other dye molecules do not show the change in sign but a change in magnitude of

nonlinearity is observed. All the dye molecules show strong TPA in the ps regime.

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