

# Wavelength dependent studies of nonlinear absorption in zinc *meso*-tetra(*p*-methoxyphenyl)tetrabenzoporphyrin (Znmp TBP) using Z-scan technique

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**ABSTRACT:** We report here, our experimental results and theoretical analysis of the dispersion data of nonlinear absorption in zinc *meso*-tetra(*p*-methoxyphenyl)tetrabenzoporphyrin (ZnmpTBP). Using a ns optical parametric oscillator (OPO) we obtain the open aperture Z-scan data over the visible region starting from 480 nm to 600 nm. We use a more general five-level model for evaluating the excited state parameters like excited state absorption coefficients, two-photon absorption coefficient, etc. Due to its large excited state absorption cross-sections this material acts as a very good candidate for a broadband optical limiter in the visible region. Copyright © 2001 John Wiley & Sons, Ltd.

**KEYWORDS:** Z-scan technique; porphyrins; excited state absorption; two-photon absorption; optical limiting

## INTRODUCTION

With the advent of high power ps and fs lasers the necessity for protection of the sensors and the eye from intense laser fields has increased enormously over the last few years. Various mechanisms have been proposed for optical limiting which include scattering 1, thermal/nonlinear refractive beam spreading 2, excited state absorption (ESA)/reverse saturable absorption (RSA) 3, two-photon absorption/multi-photon absorption (TPA) 4, photorefractive 5, free carrier absorption in semiconductors 6, polarization changes 7, 8, etc. Different materials investigated, in the solid and liquid forms, are fullerenes 9, porphyrins/metalloporphyrins 10, phthalocyanines 11, inorganic clusters 12, organometallics 13, organic dyes 14, particle suspensions 15, liquid crystals 16, bacteriorhodopsin 17, photonic band gap materials 18, christiansen filter 19, nanosols 20, and chinese tea 21. Several reviews have been published on mechanisms for optical limiting, material requirement, optimization and realization 22–25. The minimum criteria identified for a material to act as an effective optical limiter are: (1) low limiting threshold and large dynamic range (over a wide range of input fluences); (2) longer excited state lifetime to accumulate the popula-

tion; (3) high optical damage threshold; (4) broadband response; (5) fast response time; and (6) high linear transmittance, optical clarity, and robustness. Among the above-mentioned materials fullerenes, porphyrins, and phthalocyanines have been found to satisfy the majority of the criteria with a few exceptions, e.g. the damage threshold. Since the mechanism of limiting in these materials depends on absorption of excited molecules it is important to characterize the excited state dynamics and evaluate

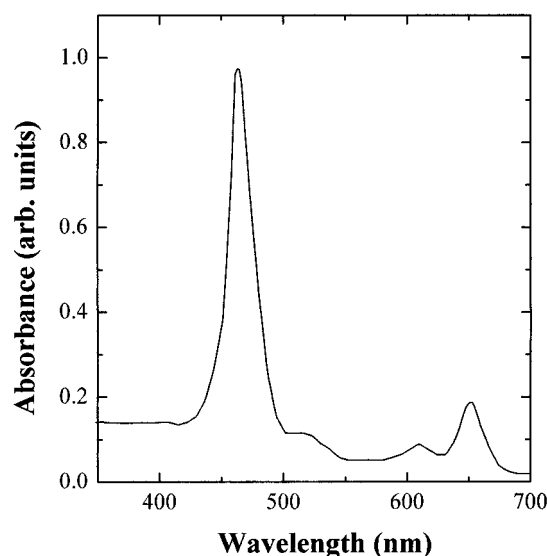
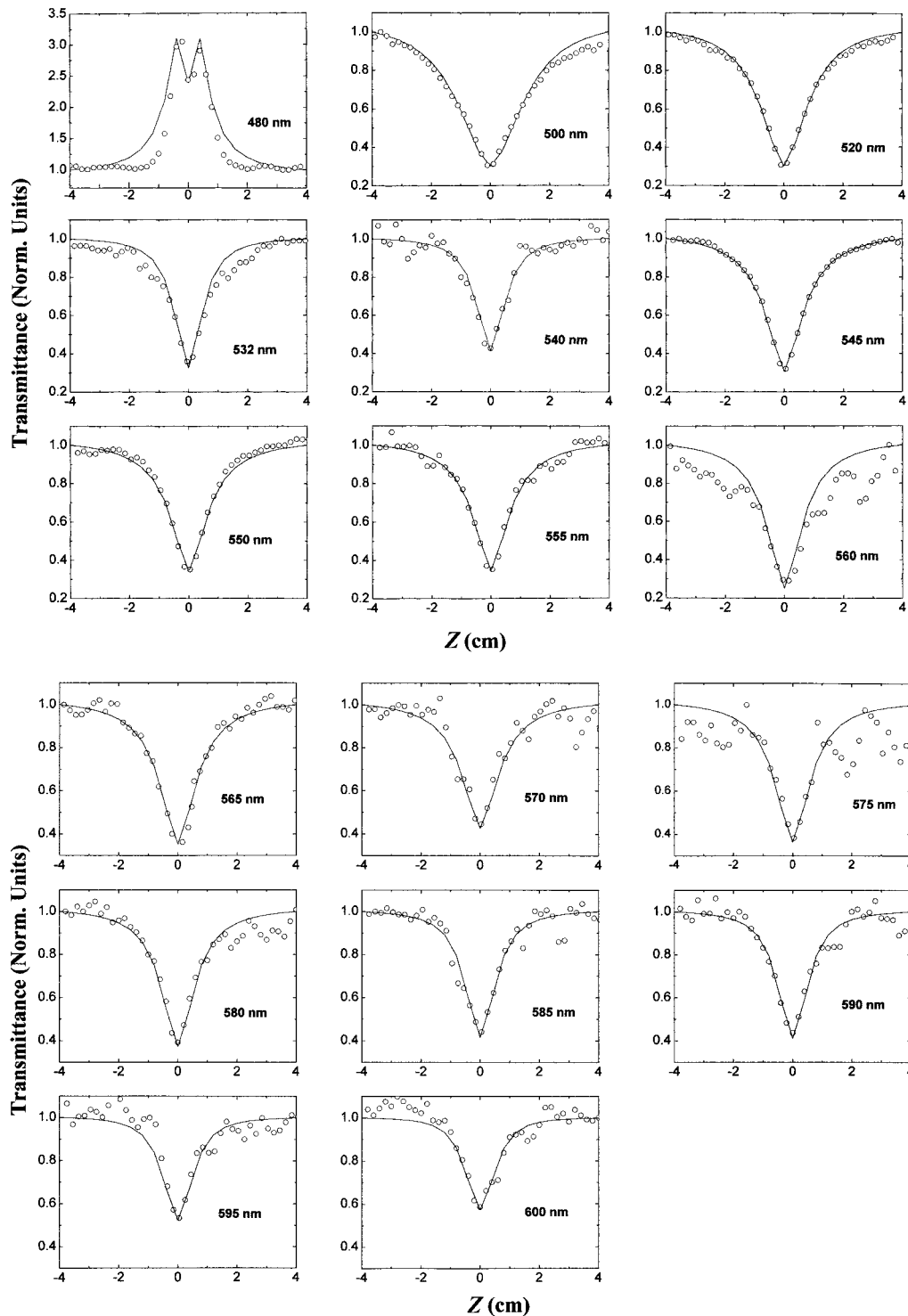


Fig. 1. Absorption spectrum of the sample (in THF).

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**Fig. 2.** Open aperture Z-scan data (scattered points) and the theoretical fits (solid lines) obtained using the five-level model for wavelengths ranging from 480 nm to 600 nm.

parameters like absorption cross-sections, lifetimes, etc. to optimize them in the making of a realistic device. A recent paper, where a RSA material (a phthalocyanine) is used along with  $\text{CS}_2$ , reports a high figure of merit (defined as the ratio of linear transmittance to minimum transmittance at high energy) within the measured dynamic range of the limiter, as  $\sim 7500$ , the largest reported to date 26. With such a goal in mind we attempted a comparative study of  $\text{C}_{60}$ , Zinc *meso*-tetra-(*p*-methoxyphenyl)tetrabenzoporphyrin

(ZnmpTBP), and a copper phthalocyanine (CuPC) for optical limiting over a broad spectrum (440 nm to 680 nm) using the Z-scan technique 27.

Here, we report on the dispersion studies of nonlinear absorption in a tetrabenzoporphyrin (ZnmpTBP). RSA and optical limiting in porphyrins are well-established concepts 28, 29. However, most of the earlier studies are at a single wavelength. For fs and ps pulse excitation, triplet level contribution to the nonlinear absorption can be neglected

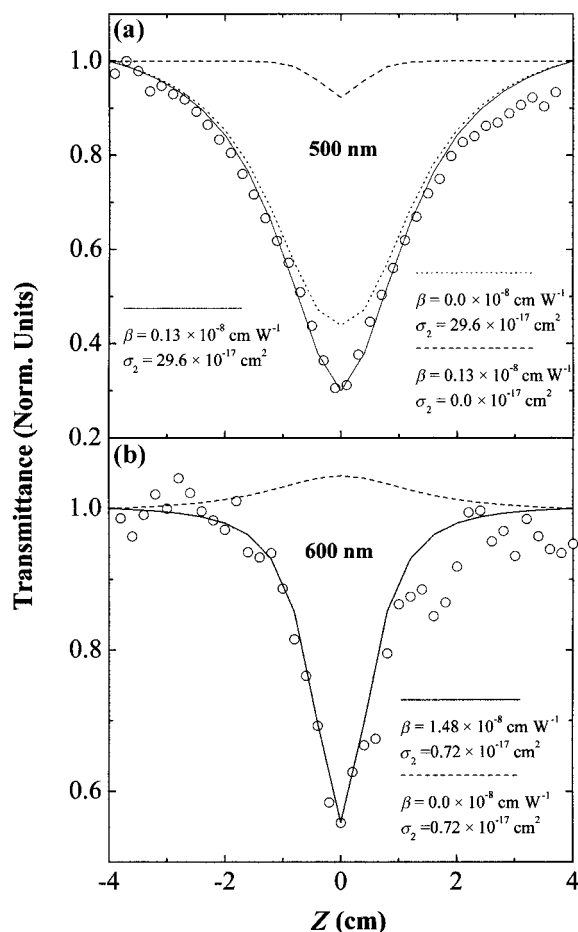


Fig. 3. Effect of  $\beta$  and  $\sigma_2$  on the open aperture Z-scan curves at (a) 500 nm and (b) 600 nm.

due to the slower intersystem crossing rate whereas with ns pulses the triplet levels do play an important role. Depending on the pump intensity, temporal duration and wavelength, absorption could be: (1) from the ground state  $S_0$  to the first excited singlet state  $S_1$  and then to the  $T_1$  state through inter-system crossing; (2) directly from  $S_0$  to  $S_n$  states (two-photon absorption); (3) from the first excited singlet state  $S_1$  to higher excited states  $S_n$  (ESA/RSA); or (4) from  $T_1$  to  $T_n$  states (ESA/RSA). We consider here, a more general five-level model and fit our open aperture Z-scan data to the above model, while incorporating all the above nonlinear absorption mechanisms.

## EXPERIMENT

We employed a commercial optical parametric oscillator (OPO) (MOPO, laser by Spectra Physics) pumped by the third harmonic (355 nm) of a Quanta Ray Nd:YAG laser with a repetition rate of 10 Hz and tunable in the range of 380–1000 nm. The pulse duration of the laser was 6 ns and an aperture of 1.4 mm was used at the output of the MOPO laser to obtain a smooth profile in the far field. The energy after the aperture was varied from 0.2 mJ/pulse to 2 mJ/pulse depending on the wavelength. The input beam was focused using a lens of focal length  $\sim 50$  mm into a 1-mm quartz cell containing the sample dissolved in spectroscopic grade tetrahydrofuran (THF). The input energy was

monitored using a fast photo-diode and the output was measured using a similar photo-diode. ZnmpTBP (>99% pure) solutions with concentration in the range  $\sim 10^{-4}$ – $10^{-3}$  M were freshly prepared and used for the study. Open aperture Z-scans were obtained in the wavelength region covering 480 nm to 600 nm. The values of beam waist at focus were  $\sim 20$ – $30 \mu\text{m}$  and the corresponding peak intensities were  $\sim 10^8$  to  $10^9 \text{ W cm}^{-2}$ . The Rayleigh ranges were calculated to be  $\sim 3$  mm to 6 mm depending on the wavelength. Rate equations for the five-level model ( $S_0$ ,  $S_1$ ,  $S_n$ ,  $T_1$ , and  $T_n$  states) are:

$$\frac{dN_0}{dt} = -\frac{\sigma_0 I N_0}{\hbar\omega} - \frac{\beta I^2}{2\hbar\omega} + \frac{N_1}{\tau_1} + \frac{N_3}{\tau_4} \quad (1)$$

$$\frac{dN_1}{dt} = -\frac{\sigma_1 I N_1}{\hbar\omega} + \frac{\sigma_0 I N_0}{\hbar\omega} - \frac{N_1}{\tau_1} - \frac{N_1}{\tau_{ISC}} + \frac{N_2}{\tau_2} \quad (2)$$

$$\frac{dN_2}{dt} = \frac{\sigma_1 I N_1}{\hbar\omega} + \frac{\beta I^2}{2\hbar\omega} - \frac{N_2}{\tau_2} \quad (3)$$

$$\frac{dN_3}{dt} = -\frac{\sigma_2 I N_3}{\hbar\omega} - \frac{N_3}{\tau_4} + \frac{N_1}{\tau_{ISC}} + \frac{N_4}{\tau_3} \quad (4)$$

$$\frac{dN_4}{dt} = \frac{\sigma_2 I N_3}{\hbar\omega} - \frac{N_4}{\tau_3} \quad (5)$$

and the intensity transmitted through the sample is given by:

$$\frac{dI}{dz} = -\sigma_0 I N_0 - \sigma_1 I N_1 - \sigma_2 I N_3 - \beta I^2 \quad (6)$$

with:

$$I = I_{00} \times \left( \frac{\omega_0^2}{\omega^2(z)} \right) \times \exp\left(-\frac{t^2}{\tau_p^2}\right) \times \exp\left(-\frac{2 \times r^2}{\omega^2(z)}\right) \quad (7)$$

and:

$$\omega(z) = \omega_0 \left[ 1 + \left( \frac{z}{z_0} \right)^2 \right]^{1/2}; z_0 = \frac{\pi \times \omega_0^2}{\lambda}$$

where  $\sigma_0$  is the ground state absorption cross-section,  $\sigma_1$  and  $\sigma_2$  are the excited state absorption cross-sections from  $S_1$  and  $T_1$  states, respectively,  $N_i$ 's are the corresponding populations in the different states,  $\tau_i$ 's are the lifetimes of the excited states,  $z_0$  is the Rayleigh range,  $\omega_0$  is the beam waist at focus,  $I$  is intensity as a function of  $r$ ,  $t$ , and  $z$ ,  $I_{00}$  is peak intensity at the focus of the gaussian beam,  $\tau_p$  is the input pulse width used,  $\beta$  is the two-photon absorption cross-section, and  $\tau_{ISC}$  is the intersystem crossing rate. The differential equations are solved numerically using the Runge–Kutta fourth-order method. The differential equations are first de-coupled and then integrated over time, length, and along the radial direction. Assuming the input beam to be a Gaussian, the limits of integration for  $r$ ,  $t$ , and  $z$  are varied from 0 to  $\infty$ ,  $-\infty$  to  $\infty$ , and 0 to  $L$  (length of the sample), respectively. Typical number of slices used for  $r$ ,  $t$ , and  $z$  are 60, 30, and 5, respectively.  $\sigma_1$ ,  $\sigma_2$ , and  $\beta$  are then estimated through a least square fit of the experimental data.

## RESULTS AND DISCUSSION

Figure 1 shows the UV-vis absorption spectrum of the

**Table 1.** Calculated values of different excited state parameters using a five-level model and comparison with those reported in the literature

$\sigma_0$ ( $10^{-17}$ cm <sup>2</sup> )	$\sigma_1$ ( $10^{-17}$ cm <sup>2</sup> )	$\sigma_2$ ( $10^{-17}$ cm <sup>2</sup> )	$\beta \times 10^{-8}$ (cm W <sup>-1</sup> )	Ref.
				Our study
0.298	1.00	0.1	0.18	480 nm
1.478	3.00	29.6	0.13	500 nm
0.826	1.00	33.4	0.25	510 nm
0.739	1.00	27.5	0.27	520 nm
0.739	3.00	11.9	0.57	532 nm
0.910	3.00	11.0	0.60	540 nm
0.956	3.00	10.8	0.61	545 nm
1.000	3.00	10.7	0.60	550 nm
1.043	3.00	10.7	0.70	555 nm
1.000	6.00	10.5	0.70	560 nm
1.130	6.00	10.3	0.77	565 nm
1.261	6.00	9.00	0.82	570 nm
1.478	6.00	8.50	1.26	575 nm
1.696	6.00	4.90	1.28	580 nm
1.867	6.00	0.93	1.28	585 nm
2.130	6.00	0.78	1.30	590 nm
2.610	6.00	0.72	1.45	595 nm
3.174	6.00	0.72	1.48	600 nm
–	1.7	7.2	–	Chen <i>et al.</i> 28 ZnTPP 532 nm (35 ps)
$\sigma_g$		$\sigma^a$	$(\beta_{\text{eff}})$	Henari <i>et al.</i> 33 ZntaP
0.35	–	1.2	1.48	532 nm (35 ps)
19.0		2.5	0.64	450 nm (500 ps)
		$\sigma^a$	$(\beta_{\text{eff}})$	Mishra <i>et al.</i> 28 ZnTPP
2.7	–	10.8	–	527 nm (20 ns)
				Guha <i>et al.</i> 10 ZnmpTBP
2.4 cm <sup>-1b</sup>	–	3.0 ± 0.25	2.5 ± 0.2	21 ps and 6 ns, 532 nm ZnmpTBP
3.8 cm <sup>-1b</sup>	–	3.0 ± 0.25	≤0.5	532 nm

<sup>a</sup> Effective excited state cross-section.<sup>b</sup> Linear absorbance.

sample recorded by a Shimadzu UV-160 A. The absorption spectrum of the ZnmpTBP sample matches very well with that reported in the literature 31. The Q-band is centered around 460 nm and the B-bands are around 610 nm and 650 nm. Figure 2 shows the open aperture Z-scan data (scattered points) and the theoretical fits (solid lines) obtained using the five-level model for wavelengths ranging from 480 nm to 600 nm. The ground state absorption cross-sections for different wavelengths are calculated using  $\sigma_0 = \alpha/N$ , where  $\alpha$  is the linear absorption and  $N$  is the density of molecules per cm<sup>3</sup>. Depending on the wavelength,  $I_{00}$  is taken as  $\sim 10^8$ – $10^9$  W cm<sup>-2</sup>,  $\omega_0 \sim 20$ – $30$   $\mu$ m, and  $z_0 \sim 3$ – $6$  mm. The relaxation time of the first excited state  $\tau_{S1}$ , intersystem crossing time  $\tau_{ISC}$ , and the lifetime of the first excited triplet state  $\tau_{T1}$  are taken as 40 ps, 2 ns, and 200  $\mu$ s,

respectively. Our earlier studies, performed using degenerate four-wave mixing (DFWM) with incoherent light, indicate an excited state lifetime of  $\sim 40$  ps for the S<sub>1</sub> 32. The relaxation times of the S<sub>n</sub> and T<sub>n</sub> states are taken as 100 fs. Excitation wavelengths are indicated for each Z-scan curve.

Figure 3 shows the effect of  $\sigma_2$  and  $\beta$  at both 500 nm and 600 nm. Fig. 3(a) shows theoretical curves generated at 500 nm. The dotted line represents the curve with  $\sigma_2 = 29.6 \times 10^{-17}$  cm<sup>2</sup> and  $\beta = 0.0$  cm W<sup>-1</sup>, whereas the solid line is generated with  $\sigma_2 = 29.6 \times 10^{-17}$  cm<sup>2</sup> and  $\beta = 0.13 \times 10^{-8}$  cm W<sup>-1</sup>. We have also generated a dashed curve with  $\sigma_2 = 0.0 \times 10^{-17}$  cm<sup>2</sup> and  $\beta = 0.13 \times 10^{-8}$  cm W<sup>-1</sup> to show the contribution of  $\sigma_2$  at this wavelength. All these curves are generated without varying other parameters ( $\sigma_0 = 1.478 \times 10^{-17}$  cm<sup>2</sup>,  $\sigma_1 = 3.00 \times 10^{-17}$  cm<sup>2</sup>). Figure

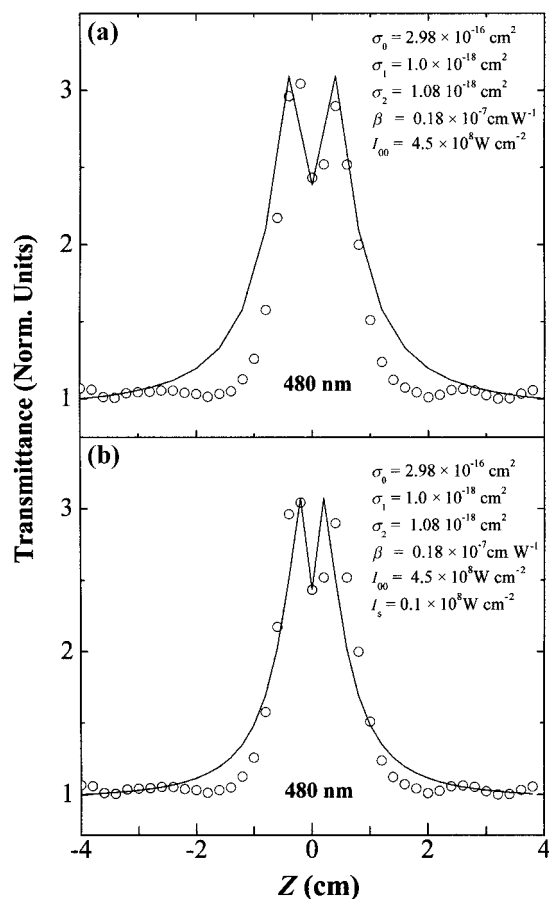


Fig. 4. Experimental (open circles) and theoretical open aperture Z-scan curves (solid lines) at 480 nm.

3(b) shows theoretical curves generated at 600 nm for  $\sigma_0 = 3.174 \times 10^{-17} \text{ cm}^2$ ,  $\sigma_1 = 6.00 \times 10^{-17} \text{ cm}^2$ ,  $\sigma_2 = 0.72 \times 10^{-17} \text{ cm}^2$ ,  $\beta = 0.0 \text{ cm W}^{-1}$  (dashed line) and  $\beta = 1.48 \times 10^{-8} \text{ cm W}^{-1}$  (solid line) while keeping all other parameters the same. We can clearly see from Fig. 3(a) that variation in  $\sigma_2$  shows significant effect on the curve at 500 nm. At 500 nm,  $\sigma_2$  domination is evident as without  $\sigma_2$ , the half width as well as the absorption at the focus (dotted lines in Fig. 3(a)) become too shallow compared to the experimental values. Therefore, at shorter wavelengths, both  $\sigma$  and  $\beta$  contribute to RSA behavior. Variation with  $\beta$  is found to be much more dramatic at 600 nm compared to the variation with  $\sigma_2$ , indicating a dominance of  $\beta$  at longer wavelengths. Energy localization is dominant at this wavelength leading to a two-photon absorption process. Since the pulses used are of ns duration the intersystem crossing rate being 2 ns duration, and the lifetime of the triplet state is very high compared to the singlet, a variation in  $\sigma_1$  has very little effect on the shape of the curves generated at 500 nm and 600 nm. Table 1 summarizes the  $\sigma_1$ ,  $\sigma_2$ , and  $\beta$  values obtained from our measurements along with those reported in the literature for similar compounds.

In the wavelength region close to absorption peaks an increase in transmission with increased intensity was observed (SA). This is evident in the Z-scan curves at 480 nm, where there is an absorption band. Henari *et al.* 33 reported saturation of absorption at 450 nm with a similar porphyrin, again the excitation wavelength having

strong absorption, supporting our arguments. At these wavelengths the absorption from the ground state dominates in comparison to the excited state absorption coefficient.

In order to see the effects of linear absorption and the saturation effect, we generated the curves shown in Fig. 4 with and without saturation of the first excited state  $S_1$ . Figure 4(a) shows the curve (solid line) generated with linear absorption for  $\sigma_0 = 2.98 \times 10^{-16} \text{ cm}^2$ ,  $\sigma_1 = 1.0 \times 10^{-17} \text{ cm}^2$ ,  $\sigma_2 = 1.08 \times 10^{-18} \text{ cm}^2$ , and  $\beta = 0.18 \times 10^{-7} \text{ cm W}^{-1}$  along with the experimental data (circles). Figure 4(b) shows the curve generated (solid line) saturation intensity  $I_s = 0.1 \times 10^8 \text{ W cm}^{-2}$ , with  $\alpha_0$  being replaced by  $\alpha_0/(1 + I/I_s)$  34. We observe better fit for the experimental data taking saturation effects for the  $S_1$  level. This is understandable as the input intensities exceed that of the linear absorption. These large intensities lead to RSA behavior at the focal point with  $\sigma_1 = 1.0 \times 10^{-17} \text{ cm}^2$ ,  $\sigma_2 = 1.08 \times 10^{-18} \text{ cm}^2$ , and  $\beta = 0.18 \times 10^{-7} \text{ cm W}^{-1}$ . Previous reports 35, 36 suggest saturation of the higher singlet states where they observe RSA and SA around the focal region (quite the opposite is observed here). In our studies we have employed a ns laser where the intensities cannot saturate the higher excited  $S_n$  states. At lower intensities all the population could get trapped in the first excited triplet states ( $T_1$ ) thereby saturating the absorption. With still higher intensities the population is excited into the higher excited states ( $T_n$ ) thereby giving rise to the small amount of RSA. Since the lifetime of the  $S_1$  state is very small we do not expect saturation in that state.

Thus porphyrins show RSA behavior even around 480 nm at higher intensities, which has not been reported earlier. Porphyrins can therefore be used as RSA material over a much wider wavelength region than the transmission window (500–600 nm). The added advantage of porphyrins over other materials is that they can be cast into thin films by doping them in a suitable host (polymer, sol-gel, or glass) 29, 37. From these studies the strong contribution of the  $\sigma_2$  is evident over the entire visible region studied. Efforts are being made to reduce the inter-system crossing rate thereby enhancing the role of triplets for RSA.

## CONCLUSIONS

In conclusion we have studied the dispersion of nonlinear absorption in ZnmpTBP using open aperture Z-scan data obtained with an OPO. We evaluated the excited state absorption coefficients ( $\sigma_1$  and  $\sigma_2$ ) and two-photon absorption coefficient ( $\beta$ ) using a five-level model. Our results indicate that TPA dominates at longer wavelength and ESA dominates at shorter wavelengths. When the excitation is into the absorption band we see saturation type of behavior. At higher intensities we observe RSA behavior even at these wavelengths. With strong RSA shown over a wide region ZnmpTBP is an attractive broadband optical limiter.

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