Spectral dependence of third order nonlinear optical susceptibility of zinc phthalocyanine

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Wavelength dependence of saturable absorption (SA) and reverse saturable absorption (RSA) of zinc phthalocyanine was studied using 10 Hz, 8 ns pulses from a tunable laser, in the wavelength range of 520–686 nm, which includes the rising edge of the Q band in the electronic absorption spectrum. The nonlinear response is wavelength dependent and switching from RSA to SA has been observed as the excitation wavelength changes from the low absorption window region to higher absorption regime near the Q band. The SA again changes back to RSA when we further move over to the infrared region. Values of the imaginary part of third order susceptibility are calculated for various wavelengths in this range. This study is important in identifying the spectral range over which the nonlinear material acts as RSA based optical limiter. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2338135]

I. INTRODUCTION

We report the wavelength dependence of nonlinear (NL) absorption of zinc phthalocyanine (ZnPc) dissolved in dimethyl formamide (DMF) under nanosecond excitation. The studies of nonlinear processes in photonic materials are significant in the context of their technological applications, especially in areas such as passive optical power limiting, optical switching, and the design of logic gates. Optical limiting occurs when the absolute transmittance of a material decreases with increase in input fluence. Metallophthalocyanine (MPc) molecules are widely researched because their planar π-conjugated electron systems are expected to cause strong reverse saturable absorption (RSA) effect and also because they exhibit remarkable thermal stability and chemical resistance. One mechanism for optical limiting (OL) is provided by RSA, in which the excited state absorption cross section is higher than the ground state absorption cross section. It is also known that the substitution of heavy metal dopants significantly improve the limiting performance of Pc's at 532 nm.

II. EXPERIMENT

When a high irradiance laser beam propagates through any nonlinear material, photoinduced refractive index variations may lead to self-focusing of the beam. The propagation of laser beam inside such a material and the ensuing self-refraction can be studied using the z scan technique. The details of this technique are well documented in literature.[1,2] It enables one to determine the nonlinear properties of solids, ordinary liquids, and liquid crystals. In this method the intensity dependence of refractive index and absorption are manifested as a position dependent transmission variation of the material which in turn can be made use of in extracting various nonlinear optical parameters such as real and imaginary parts of susceptibility, cross sections of nonlinear absorption and nonlinear refraction, etc. However, we are mainly focusing on the wavelength dependence of nonlinear absorption studies in a 0.5 mM solution of ZnPc in DMF with particular emphasis on the RSA and saturable absorption (SA) properties.

The experimental setup for nonlinear absorption measurements consists of a wavelength tunable laser (Quanta Ray MOPO) emitting pulses of 8 ns full width at half maximum (FWHM) duration at a repetition rate of 10 Hz. A few percent of the output of this laser was collected, spatially filtered, and made to pass through an achromatic convex lens before entering the sample. We measured the intensity dependent transmission of the sample for a number of wavelengths in the range of 520–686 nm. For this we need to move the sample through the beam waist of the laser which was done using a motorized translation stage. The lens which we used to produce this beam waist gives $1/e^2$ beam radius in the range of 35–45 μm. The corresponding Rayleigh range is 7.59–9.25 mm and hence we used a cuvette of path length of 1 mm to satisfy thin lens approximation. The transmitted and incident energies were measured using energy ratiometer (Laser probe Inc.) with RjP 735 probes. For OL studies, the sample was placed slightly away from the focus and the input and output fluences were measured from the ratio arm and the transmittance arm using the same energy meter.

III. RESULTS AND DISCUSSION

Chemical structure of ZnPc is given in Fig. 1. Its electronic absorption characteristics given in Fig. 2 show a B band around 350 nm and a Q band around 730 nm. A somewhat wide optical window is formed between these two bands. Most Pc's have been described with a five-level energy diagram consisting of three singlets and two triplets as in Fig. 3.[3] Here S stands for singlet states with the suffix 0 for ground state and 1 and 2 for first and second electronic

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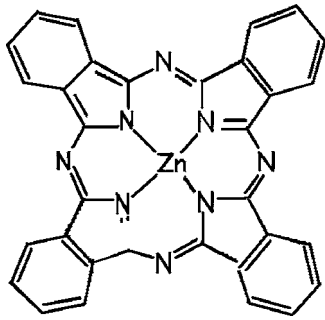[b]Present address: International University of Bremen, 28759 Bremen, Germany.

FIG. 1. Structure of the ZnPc.

FIG. 3. Schematic energy level diagram of ZnPc.

excited states. σ's are the absorption cross sections. If the molecules at S_1 are excited to S_2 (with cross-section σ_{12}), and then relaxes to the state S_0, losing energy by radiation and/or by some radiationless process, it is characterized by a constant $k_{10} = 1/t_{10}$. If it suffers intersystem crossing to the triplet state $T_1(k_{ISC} = 1/t_{ISC})$, then it is possible for the molecule to go to T_2 with the corresponding triplet absorption cross section, σ_T. The efficiency of the T_1 formation is called quantum yield ϕ. Porphyrins have rather high quantum yield of the triplet formation.[4]

Saturable absorption is characterized by transmittance increase with the increase of the energy input, whereas the opposite happens in RSA. Here, we have to consider the transmittance of the sample under two situations: (1) in the presence of RSA and (2) in the presence of SA. RSA is also referred to as induced absorption and there are various mechanisms leading to this process. In the presence of RSA the optical nonlinearity is described by the equation[5]

$$\alpha(I) = \alpha_0 + \beta I, \tag{1}$$

where α_0 is the linear absorption coefficient (cm^{-1}) corresponding to transition from S_0 to S_1 and β is the nonlinear absorption cross section ($m\,W^{-1}$). β is related to the imaginary part of susceptibility by the relation
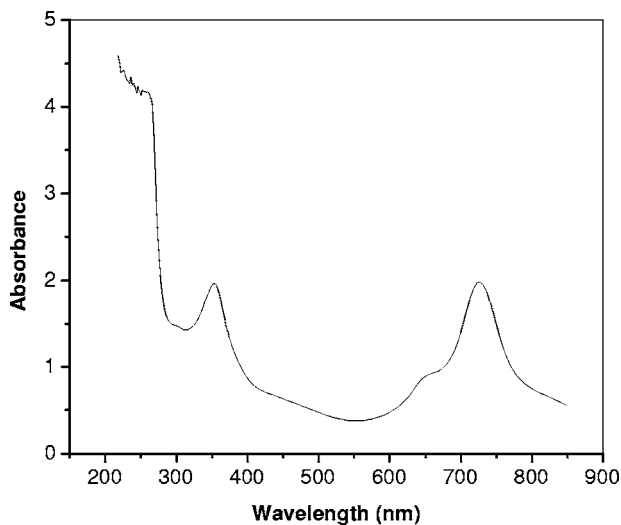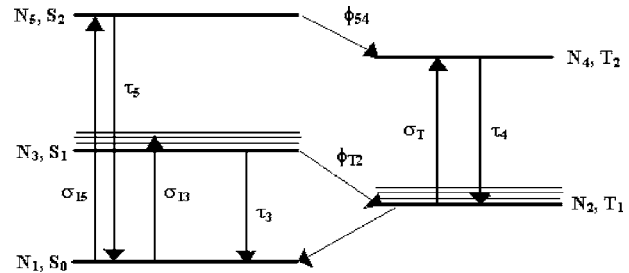

FIG. 2. Absorption spectrum of ZnPc dissolved in DMF.

$$Im(\chi^3) = \frac{\lambda \epsilon_0 n_0^2 c \beta}{4\pi}, \tag{2}$$

where λ is the excitation wavelength, ϵ_0 is the permitivity (F/m or C/V m), n_0 is the linear refractive index of the sample, and c is the speed of light. For obtaining a convenient unit for $Im[\chi^{(3)}]$ it is useful to remember that V=J/C. This expression gives $\chi^{(3)}$ in units of $m^2\,V^{-2}$. However, most of the reported values of nonlinear optical constants are in esu (cgs esu unit). We can convert $Im\,\chi^{(3)}$ in $m^2\,V^{-2}$ using the conversion formula (express lengths in cm and 1 V $= (10^8/c)$ esu, where c is speed of light in cgs units). Hence we will get

$$1\ m^2\ V^{-2} = 9 \times 10^8\ \text{esu.} \tag{3}$$

The propagation through the sample is given by the relation

$$\frac{dI}{dz} = -\alpha(I)I. \tag{4}$$

Solving Eq. (4) by integrating between limits I_0 to I, and putting transmission $T = I/I_0$, we get

$$T = \frac{e^{-\alpha_0 L}}{1 + \beta I_0 L_{\text{eff}}}, \tag{5}$$

where

$$L_{\text{eff}} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}. \tag{6}$$

This equation can be used to fit the experimental data of the open aperture z scan trace (the nonlinear absorption measurements), treating I_0 as the position dependent intensity. The position dependence in intensity should be incorporated into the expression by considering the variation of beam size on either side of the focus $[\omega(z)]$. The equation is $\omega(z)^2 = \omega_0^2[1 + (z^2/z_0^2)]$, where $z = 0$ is the focus and $z_0 = \pi\omega^2/\lambda$ is referred to as the Rayleigh range or diffraction length of the beam. β can be treated as an adjustable parameter. From the value of β we can calculate $Im\,\chi^{(3)}$.

When SA is present, Eq. (1) modifies to[6]

$$\alpha(I) = \frac{\alpha_0}{1 + (I/I_s)}. \tag{7}$$

Substituting this in Eq. (4) and integrating between the limits I_0 to I_L gives
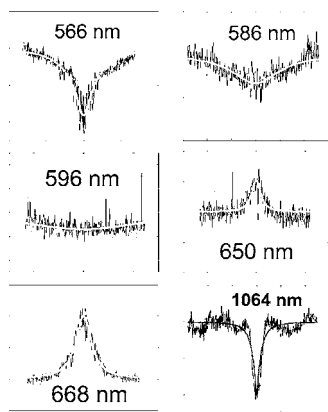
FIG. 4. Open aperture traces for various wavelengths of excitation and its theoretical fit. All plots are in the same scale. On the Y axis, the normalized transmittance, and on the X axis, the value z, the distance of the sample are given. $z=0$ at the peak/valley position and is negative towards left and positive towards right.

FIG. 5. Calculated values of Im $\chi^{(3)}$ for various wavelengths.

$$\ln \frac{I_L}{I_0} = -\alpha_0 L - \left(\frac{I_L - I_0}{I_0}\right). \quad (8)$$

This can be solved numerically to get the transmission of the sample, I_L. If excitation intensity I_0 is less than I_s, we can consider SA as a third order process and in such cases $-\alpha_0/I_s$ is equivalent to nonlinear absorption coefficient β which will then give Im $\chi^{(3)}$.

We have observed that the nature of NL absorption in ZnPc is dependent on the wavelength of the excitation beam. It was seen that the material exhibits RSA for wavelengths within 527–576 nm after which the NL response decreases and stops completely at 596 nm. This means that the material does not exhibit any sign of absorptive nonlinearity at this wavelength. As we move farther from 596 nm the behavior gradually changes to SA and reaches a maximum at 668 nm which is close to the resonance peak of 724 nm. This interesting feature is illustrated in Fig. 4. At 650 nm also the material has a small peak in the absorption spectrum. We were not able to explore the regions from 670 to 1064 nm due to the limitations of frequency mixing in MOPO. However, it can be concluded that the nonlinear absorption changes from RSA to SA when the excitation wavelength changes from off resonant to near resonant regions. At 1064 nm also the material exhibits RSA behavior.

In general, induced absorption can occur due to a variety of processes. However, which of them dominates is decided by factors such as duration of the excitation pulse, lifetimes of excited singlet and triplet states and intersystem crossing time, crossing yield, etc. Nonlinear absorption can occur through the transitions $S_n \leftarrow S_0$ by instantaneous two photon absorption (TPA) or through $S_n \leftarrow S_1 \leftarrow S_0$ which is sequential TPA. This is an irradiance dependent process.[8] If the molecules undergo vibrational relaxation in S_1 and then reaches S_n by further absorption, it is referred to as the singlet excited state absorption (ESA). Unlike TPA, ESA is a fluence dependent process. This means that the same fluence for two different pulse widths will give the same nonlinear absorption if the mechanism is ESA. Singlet ESA is more likely to happen
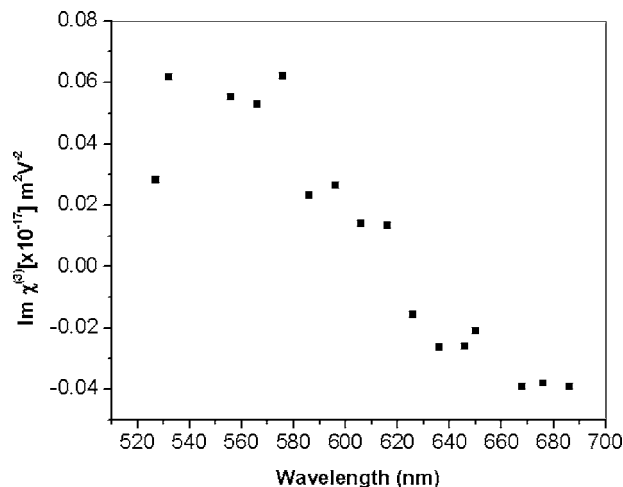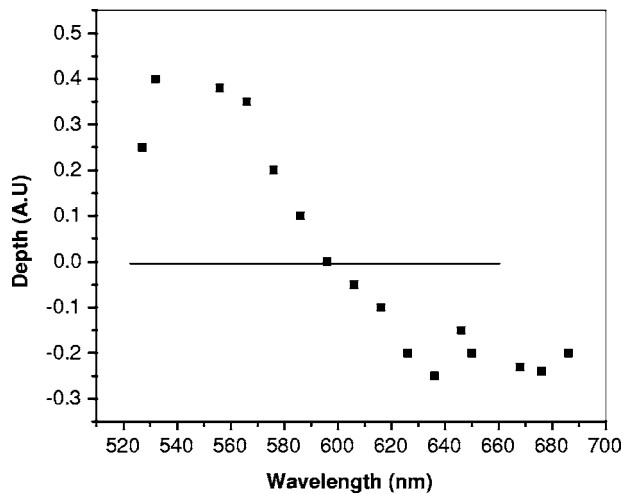
when the excitation pulse duration is picoseconds or shorter. For longer pulses, usually triplet ESA, $T_2 \leftarrow T_1$ dominates.

Moreover, in MPc's, the S_n lifetimes are of the order of a few picoseconds and the triplet crossover time is a few hundred picoseconds. For ZnPc the singlet excited state S_n have a lifetime of 9 ps and the triplet states are longer lived.[9] The vibrational relaxation in singlet states takes place very fast, in picosecond time scales. Joseph *et al.* reported that the reverse saturable absorption and the optical limiting of metal phthalocyanines can be enhanced by use of the heavy-atom effect. They demonstrated this with Pc's containing heavy metal atoms, such as In, Sn, and Pb. The enhancement in the ratio of effective excited state to ground state absorption cross sections compared with those containing lighter atoms, such as aluminum and silicon, was nearly two times.[10] The fluorescence quantum yield for ZnPc is small, approximately 0.16–0.28.[11] Considering all these factors and also that we used nanosecond excitation pulses, it is reasonable to assume that triplet ESA is one important factor contributing to induced absorption in our sample. It is possible to confirm whether ESA or TPA dominates in contributing to induced absorption, by measuring the nonlinear absorption for various pulse durations. As a rule, transmittance change ΔT at a fixed pulse energy will be independent of pulse width if the mechanism is ESA but will depend on pulse width if it is TPA. All RSA materials possess a higher absorption cross section of excited states (σ_e) compared to that of the ground state (σ_g) at the excitation radiation wavelength.[12] Interestingly they will also give a positive value for the imaginary part of susceptibility Im$[\chi^{(3)}]$ which is actually a measure of the induced absorption. On the other hand, a saturable absorber has a negative value for Im$[\chi^{(3)}]$.

The calculated values of Im $\chi^{(3)}$ as a function of wavelength is shown in Fig. 5. This is the bulk third order susceptibility. $\chi^{(2)}$ and $\chi^{(4)}$ vanish in liquids and higher order odd terms such as $\chi^{(5)}$ will be very small compared to $\chi^{(3)}$. These values are within an error of 17% contributed mainly by the uncertainty in intensity measurements in the sample and the fitting error. One should be very careful while comparing the susceptibility values available in literature. These values vary to a great extent depending on the excitation

FIG. 6. Depth of the *z* scan trace as a function of wavelength.

TABLE I. The linear and nonlinear absorption coefficients, and saturation intensity of ZnPc in DMF, for various wavelengths. The material acts as saturable absorber for wavelengths at which I_s is given. β_{eff} is mentioned only for the case of RSA.

λ (nm)	α_0(cm^{-1})	β_{eff}(cm GW^{-1})	I_s(GW cm^{-2})
527	0.405	22.09	⋯
532	0.394	47.74	⋯
556	0.376	40.92	⋯
566	0.384	38.43	⋯
576	0.400	44.22	⋯
586	0.426	16.21	⋯
596	0.461	18.27	⋯
606	0.506	9.5	⋯
616	0.568	9.03	⋯
626	0.653	⋯	0.0637
636	0.766	⋯	0.0454
646	0.867	⋯	0.0523
650	0.892	⋯	0.0672
668	0.950	⋯	0.0469
676	0.998	⋯	0.0431
686	1.106	⋯	0.0397

wavelength, pulse duration, experimental technique, concentration of the molecular species in the sample, etc. Unnikrishnan has reported Im $\chi^{(3)}$ values of $Sm(Pc)_2$ and $Eu(Pc)_2$ dissolved in DMF at various wavelengths using the same technique.[13] These molecules have a different structure compared to ZnPc. However, in the SA regions, their reported values are in the range from -3.2 to -0.07×10^{-18} m^2 V^{-2} for $Eu(Pc)_2$ and from -4.0 to -0.14×10^{-18} m^2 V^{-2} for $Sm(Pc)_2$ which are of the same order of magnitude as we obtained. de la Torre *et al.* give an extensive review of nonlinear optical studies in porphyrins and phthalocyanines and list the values of $\chi^{(2)}$, $\chi^{(3)}$, and also the molecular hyperpolarizability values obtained using various techniques.[3] However, the value of Im $\chi^{(3)}$ of ZnPc is not mentioned. Diaz-Garcia reported the magnitude of $\chi^{(3)}$ of Langmuir-Blodgett films of octasubstituted MPc's using third harmonic generation (THG) experiments at 1064 nm. These values are in the range of $(3.4–5.7) \times 10^{-13}$ esu.[14]

From the graph it can be seen that the value of nonlinear absorption is positive (RSA), when the linear absorption for the corresponding excitation wavelength is very small. The magnitude of NL absorption gradually decreases and becomes negative (SA) as the excitation shifts to near resonant wavelengths. The absolute value of this absorption increases as the excitation gets closer to the resonant peaks. When we used 1064 nm excitation wavelength from Nd:YAG (yttrium aluminum garnet), we observed RSA with a large nonlinear absorption of 0.3313×10^{-17} m^2 V^{-2} which is an order of magnitude higher than what we obtained at other wavelengths. The depth of the normalized *z* scan trace varies, as shown in Fig. 6. The measured values of β_{eff} for those wavelengths at which the material shows induced absorption are given in Table I. Considering the possibility of sequential and/or pure TPA and triplet ESA, we feel that it is more appropriate to assume that an effective nonlinear absorption coefficient is what we can measure from the *z* scan data, which we denote as β_{eff} instead of β. When it is a saturable absorber, a more useful parameter to extract from the transmission measurements is the saturation intensity I_s, which is also given in the table. The corresponding linear absorptions are also shown. It can also be assumed that for a saturable

absorber $-\alpha_0/I_s$ is equivalent to β_{eff} of a RSA material. Henari *et al.* used the same technique to find out the these nonlinear optical parameters of certain group IV metal phthalocyanines using 665 nm, picosecond laser.[7] The absolute values of β_{eff} they obtained are nearly of the same order of magnitude as we calculated. However, they report I_s values that are at least two orders of magnitude higher than what we observed. We attribute these differences to the type of laser excitation and to differences in sample properties.

As the wavelength of excitation approaches the wavelength of resonant absorption, α_0 increases and the nonlinear absorption gradually changes to SA. It will be useful to define a figure of merit *F* for this type of materials as the ratio $|\text{Im}\chi^{(3)}|/\alpha_0$, which specifies the magnitude of nonlinear absorption for unit value of linear absorption loss (Fig. 7). *F* is larger by a small amount in the valley region between 500 and 600 nm in the absorption spectrum. It helps in comparing the absorptive nonlinearities at various excitation wavelengths.
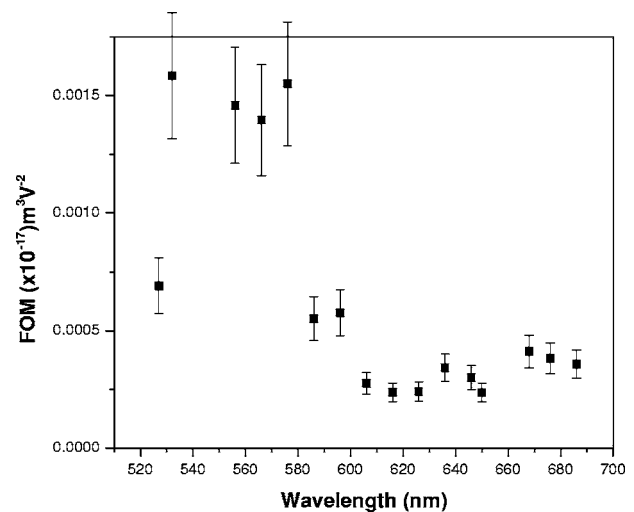

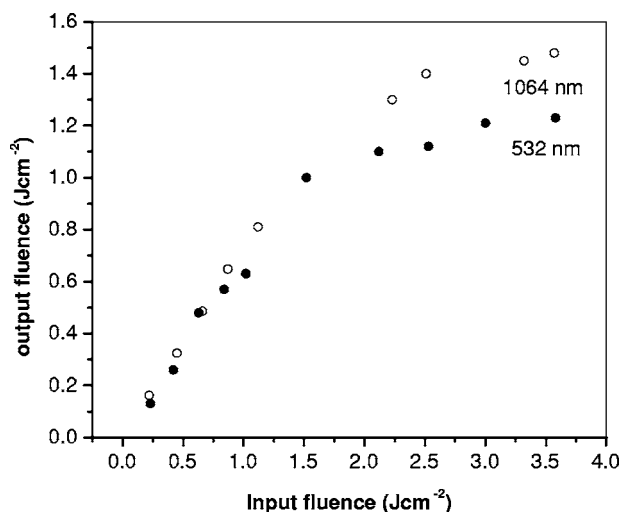FIG. 7. Figure of merit as a function of wavelength.

FIG. 8. Optical limiting performance of ZnPc at 532 and 1064 nm.

Since in our case the intersystem crossing is very fast compared to the duration of the pulse, T_1 state gets populated. Therefore the observed nonlinear absorption is directly related to the product $(\phi\sigma_T)/\sigma_0$, where ϕ is the triplet yield. Certain metal ions can influence the intersystem crossing rate and thus increase ϕ significantly. Zinc being a transition metal with partially filled d states, it enhances the intersystem crossing efficiency through spin orbit coupling leading to enhanced RSA behavior than other light metal phthalocyanines.

The most important application of these materials is in optical limiting and to be used as a saturable absorber. Since these properties are spectral dependent, it is more common to use another figure of merit, σ_{exe}/σ_g, which is the ratio of excited to ground state absorption cross section. The value of σ_g can be obtained from the linear absorption spectrum using Beer's law. To evaluate σ_{exe} we need to analyze the z scan signal in a different manner, for example, as followed by Wei *et al.*[8] These features are under investigation and will be communicated later.

We have also performed the optical limiting studies using 532 and 1064 nm of the Nd:YAG laser (Fig. 8). The material can act as a RSA based optical limiter over all the wavelength regions we mentioned in the previous sections. It is highly desired that optical limiters possess broadband response. Since SA behavior begins to dominate at resonant wavelengths, it will be very attractive if the B band and the Q band are well separated in wavelength. Sun *et al.* had demonstrated that this can be achieved by modifying the side chains in porphyrinlike complexes.[15]

The low intensity transmission for ZnPc at 532 and 1064 nm are 67% and 81%, respectively. The limiting threshold, which is the input intensity at which the absorption in the material increases to two times its low absorption value, is approximately $2.5~\text{J cm}^{-2}$ for 532 nm and $2.2~\text{J cm}^{-2}$ for 1064 nm excitation. The limiting throughput is 1.44 and $1.2~\text{J cm}^{-2}$, respectively, at 1064 and 532 nm wavelengths. There are observations that heavy metal substitution results in enhanced optical limiting the Pc's. Shirk

et al. reported OL studies in lead phthalocyanine at 532 nm which showed limiting behavior for input energies as low as 10 nJ. They obtained a threshold for limiting of 8 nJ for a linear transmission of 68%. They also demonstrated that the limiting threshold and throughput depends on the f number of the collection optics.[16] OL results are also available for derivatized fullerenes in Reference 17. The throughput value they obtained at 532 nm are nearly $2.55~\text{J cm}^{-2}$ for 50% linear transmission.

IV. CONCLUSION

We have studied the nonlinear optical properties if ZnPc dissolved in DMF over a wide wavelength range. It has been observed that the nonlinear response shifts from RSA to SA when the excitation wavelength changes from off resonant to near resonant regions. The wavelength dependence of nonlinear absorption coefficient, imaginary part of the third order nonlinear susceptibility, and also the figure of merit are calculated. We conclude that the RSA behavior is due to the combined effect of TPA and triplet ESA. The material can act as a RSA based optical limiter in the wavelength range of 527–576 nm and also at 1064 nm. When the excitation wavelength approaches the Q band, the nonlinear mechanism changes to SA. In the SA region we observed approximately 50% enhancement in Im $\chi^{(3)}$ for a wavelength change from 656 to 686 nm towards the resonant peak.

[1] M. Sheik-Bahae, A. A. Said, and E. W. Van Stryland, Opt. Lett. **14**, 955 (1989).
[2] A. Santhi and V. N. Vinu, Proc. SPIE **5710**, 91 (2005).
[3] G. de la Torre, P. Vazquez, F. Agullo-Lopez, and T. Torres, Chem. Rev. (Washington, D.C.) **104**, 3723 (2004).
[4] M. Pineiro, A. L. Carvalho, M. M. Pereira, A. M. Rocha Gonsalves, L. G. Arnaut, and S. J. Formosinho, Chem.-Eur. J. **4**, 2299 (1998).
[5] M. Sheik-Bahae, IEEE J. Quantum Electron. **26**, 760 (1990).
[6] R. Rojo, S. Yamada, and H. Matsuda, J. Opt. Soc. Am. B **15**, 2937 (1998).
[7] F. Z. Henari, J. Callaghan, W. J. Blau, P. Haisch, and M. Hanack, Pure Appl. Opt. **6**, 741 (1997).
[8] T. H. Wei, D. J. Hagan, M. J. Sence, E. W. Stryland, J. W. Perry, and D. R. Coulter, Appl. Phys. B: Photophys. Laser Chem. **54**, 46 (1992).
[9] I. Rckmann, A. Zeug, R. Herter, and B. Rder, Photochem. Photobiol. **66**, 576 (1997).
[10] J. W. Perry, K. Mansour, S. R. Marder, K. J. Perry, D. Alvarez, and I. Choong, Opt. Lett. **19**, 625 (1994).
[11] I. Scalise and E. N. Durantini, Proceedings of the Seventh International Electronic Conference on Synthetic Organic Chemistry (ECSOC-7), 2003, C002.
[12] P. J. Gonalves, I. E. Borissevitch, L. de Boni, N. M. Barbosa Neto, J. J. Rodrigues, Jr., and S. C. Zlio, XXVI Encontro Nacional de Física da Matétia Condensada, 2003 Caxambu. XXVI ENFMC-Annals of Optics, Vol. V5 (2003).
[13] K. P. Unnikrishnan, Opt. Commun. **217**, 269 (2003).
[14] M. A. Diaz Garcia, Appl. Phys. Lett. **69**, 293 (1996).
[15] W. Sun, C. Byeon, M. McKerns, and C. Lawson, Appl. Phys. Lett. **73**, 1167 (1998).
[16] J. S. Shirk, R. G. S. Pong, F. J. Bartoli, and A. W. Snow, Appl. Phys. Lett. **63**, 1880 (1993).
[17] L. Smilowitz, D. McBranch, V. Klimov, J. M. Robinson, A. Koskelo, M. Grigorova, B. R. Mattes, and H. Wang, Opt. Lett. **21**, 922 (1996).