Chapter 3

Excited State Absorption Spectrum Using Z-scan

"What we have to learn to do, we learn by doing." - Aristotle

ABSTRACT

Wavelength dependence of saturable and reverse saturable absorption (SA and RSA) of zinc phthalocyanine (ZnPc) is studied using 10 Hz, 8 ns pulses from an OPO in the wavelength range from 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, Im $\chi^{(3)}$, 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. A five level energy diagram is used to account for the spectral dependence of nonlinear absorption.

3.1 Introduction

In the previous chapter the nonlinear absorption and refraction measurements of four metal phthalocyanines were discussed. It was seen that the material ZnPc behaves slightly different from the rest of the MPc's and also has very prominent peaks in the absorption spectrum compared to other materials. Therefore its nonlinear absorption studies were conducted in little more detail and has been presented in this chapter. The wavelength dependence of nonlinear (NL) absorption of ZnPc dissolved in dimethyl formamide (DMF) under nanosecond
excitation, has been studied and made use of in recording the excited state absorption spectrum. The studies of nonlinear processes in photonic materials are significant in the context of their technological applications, especially in areas like passive optical power limiting, in optical switching and in the design of logic gates. Optical limiting occurs when the absolute transmittance of a material decreases with increase in input fluence.

Metallophthalocyanine (MPC's) molecules are widely researched because of their strong reverse saturable absorption (RSA). 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.

3.2 Nonlinear Absorption

As discussed in the previous chapter, nonlinear absorption can be studied using the open aperture z-scan technique. Two important situations are encountered here, namely, saturable and reverse saturable absorption (SA and RSA).

3.2.1 Reverse Saturable Absorption (RSA)

Reverse saturable absorption is defined as the situation when absorption by suitable photons excite molecules into a higher-lying energy state, whereby the excited-state species absorb photons at a rate that is greater than the ground-state species. It is this situation that leads to strong optical limiting. In the open aperture z-scan experiment, this will be manifested as a dip at the z=0 position. In the literature RSA dyes are defined as those materials having a larger excited-state absorption cross section $\sigma_e$ than the ground-state absorption cross section $\sigma_g$ [1, 4]. It has therefore been common to define the critical condition for the achievement of RSA to be $R > 1$, where $R = \sigma_e/\sigma_g$. This criterion originates from taking a steady-state model for the classic RSA five-level energy scheme which will be discussed later in this chapter. One can see that the RSA medium will become opaque for high intense optical radiation.

3.2.2 Saturable Absorption (SA)

A saturable absorber exhibits reduced absorption coefficient at high input intensities. In the open aperture z-scan, this will result in a peak at the z=0 position. SA can occur in a medium with absorbing species, when a strong
optical intensity leads to depletion of the ground state of these ions. Similar effects can occur in semiconductors. These materials find application in passive Q switching or mode locking of lasers. Particularly for passive mode locking, semiconductor saturable absorber mirrors (also called SESAMs) are often used. Other saturable absorbers for mode locking are based on quantum dots (e.g. lead sulfide (PbS) suspended in glasses). For passive Q switching of solid state lasers, Cr4+:YAG crystals are most popular. They are also used as gain media.

3.3 Measurement of Nonlinear Absorption in the Presence of RSA and SA

Z-scan method is widely used for studying self refraction in nonlinear materials [15, 6]. As discussed earlier, it enables the determination of nonlinear properties of solids, ordinary liquids, and liquid crystals. In the z-scan experiment, the intensity dependence of refractive index and absorption are reflected as a position dependent transmission variation of the material which in turn can be made use of in extracting various nonlinear optical parameters like real and imaginary part of susceptibility, cross sections of nonlinear absorption and nonlinear refraction etc. However, we are mainly focussing on the wavelength dependence of nonlinear absorption studies in a 0.5 mM solution of ZnPc in DMF with particular emphasize on the RSA and SA properties.

The experimental set up for nonlinear absorption measurements consists of a wavelength tunable OPO (Quanta Ray) emitting pulses of 8 ns (FWHM) duration at a repetition rate of 10 Hz. A portion of the output of this laser was made to pass through an achromatic convex lens before entering the sample. An aperture was placed before the convex lens to obtain required beam size. The intensity dependent transmission of the sample for a number of wavelengths in the range from 520-680 nm was measured. For this, it is necessary to move the sample through the beam waist of the laser which was done using a motorized translation stage. Apart from the excitation source, other details of the experimental arrangement is more or less similar to that discussed in the previous chapter. However, some of the important optical parameters in this configuration is as follows. The focussing lens produces a beam waist of $1/e^2$ radius in the range 35-45 $\mu$m for these wavelengths. The corresponding Rayleigh range is 7.59 - 9.25 mm in this configuration. The transmitted and incident energies were measured using energy ratio-meter (Laser probe Inc.) with RjP 735 probes.

Chemical structure of ZnPc was given in the previous chapter. Its electronic
absorption characteristics (Figure 3.1) shows 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 5-level energy diagram consisting of three singlets and two triplets as in Figure 3.2 [7].

![Figure 3.1: Absorption spectrum of ZnPc dissolved in DMF. The bands at 350 and 730 nm are designated as B band and Q band respectively.](image)

In this diagram, S stands for singlet states with the suffix 0 for ground state and 1 and 2 for first and second electronic excited states. $\sigma$ are the absorption cross sections. If the molecules at $S_1$ are excited to $S_2$ (with cross-section $\sigma_{12}$), and then relaxes to the state $S_0$, losing energy by radiation and/or by some radiationless process, it is characterized by a constant $k_{10} = 1/\tau_3$. 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, $\sigma_T$. The efficiency of the $T_1$ formation is called triplet quantum yield $\phi$. Porphyrins have rather high quantum yield for the triplet formation [8].

3.3.1 Theory

Saturable absorption is characterized by transmittance increase with the increase of the energy input, whereas the opposite happens in RSA. Here, we
Figure 3.2: Schematic energy level diagram of ZnPc. The various symbols are, N - number density of molecules in each level, S- singlet states, T- triplet states, $\sigma$-absorption cross sections between the corresponding levels, $\tau$ - the life times of the decaying levels, $\phi$ - quantum yield for triplet formation.

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, [9]

$$\alpha(I) = \alpha_0 + \beta I$$  \hspace{1cm} (3.1)

$\alpha_0$ is the linear absorption coefficient (in $cm^{-1}$) corresponding to transition from $S_0$ to $S_1$ and $\beta$ is the nonlinear absorption cross section ($mW^{-1}$). The parameter $\beta$ is related to the imaginary part of susceptibility by the relation,

$$Im(\chi^3) = \frac{\lambda \varepsilon_0 n_0^2 c \beta}{4\pi}$$  \hspace{1cm} (3.2)

where $\lambda$ is the excitation wavelength, $\varepsilon_0$ permittivity (Farad/m or coulomb/Vm), $n_0$ is the linear refractive index of the sample, and $c$ is speed of light. For obtaining a convenient unit for $Im(\chi^{(3)})$ it is useful to remember that $volt = joule/coulomb$. This expression gives $\chi^{(3)}$ in units of $m^2V^{-2}$. However, most of the reported values of nonlinear optical constants are in the electro static units (CGS esu unit).

$$1m^2V^{-2} = 9 \times 10^8 esu$$  \hspace{1cm} (3.3)
The spatial variation of the intensity of the laser beam as it propagates through the sample is given by the relation,

$$\frac{dI}{dz} = -\alpha(I)I$$  \hspace{1cm} (3.4)

Solving Equation 3.4 by integrating between limits \(I_0\) to \(I\), (the intensities at the entrance and exit surface of the sample, respectively) and putting transmission, \(T = I/I_0\), we get,

$$T = \frac{e^{-\alpha_0 L}}{1 + \beta I_0 L_{eff}}$$  \hspace{1cm} (3.5)

where

$$L_{eff} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}$$  \hspace{1cm} (3.6)

This equation can be used to fit the experimental data of the open aperture z-scan trace, treating \(I_0\) as the position dependent intensity. This is because of the presence of the focussing lens before the sample. 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 \(\omega(z)^2 = \omega_0^2(1 + \frac{z^2}{z_0^2})\) where \(z = 0\) is the focus and \(z_0 = \pi \omega^2/\lambda\) is referred to as Rayleigh range or diffraction length of the beam. \(\beta\) can be treated as an adjustable parameter. From the value of \(\beta\) we can calculate \(Im\chi^{(3)}\) using Equation 3.2 in SI units.

In the presence of SA, Equation 3.1 modifies to [10]

$$\alpha(I) = \frac{\alpha_0}{1 + \frac{I}{I_s}}$$  \hspace{1cm} (3.7)

Substituting this in Equation 3.4 and integrating between the limits \(I_0\) to \(I\) gives

$$ln\frac{I}{I_0} = -\alpha_0 L - \left(\frac{I - I_0}{I_0}\right)$$  \hspace{1cm} (3.8)

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

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 nm to 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 Figure 3.3. At 650 nm 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 OPO. 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. 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 1064 nm excitation wavelength from Nd:YAG was used, RSA was observed, with a large nonlinear susceptibility of $0.3313 \times 10^{-17} \text{m}^2 \text{V}^{-2}$ which is an order of magnitude higher than what we obtained at other wavelengths.

3.4.1 Explanations for the RSA Behavior in ZnPc

In general, induced absorption or RSA, can occur due to a variety of processes. However, which of them dominates is decided by factors like duration of the excitation pulse, life times 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 [11]. If the molecules undergo vibrational relaxation in $S_1$ and then reaches $S_n$ by further absorption, it is referred to as singlet excited state absorption (SESA). 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 pico seconds or shorter. For longer pulses usually triplet excited state absorption (TESA), $T_2 \leftarrow T_1$ dominates.
Figure 3.3: Open aperture trace of ZnPc for various wavelengths of excitation and its theoretical fit. All plots are in the same scale. On Y axis, the normalized transmittance and on X axis, the value of z, distance of the sample are given.
Moreover, in MPc's, the $S_n$ life times are of the order of a few picoseconds and the triplet cross over time is a few hundred pico seconds. For ZnPc the singlet excited state $S_n$ have a life time of 9 ps and the triplet states are longer lived [12]. The vibrational relaxation in singlet states takes place very fast, (in ps 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 [19]. 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 Al and Si was nearly two times. The fluorescence quantum yield for ZnPc is small, approximately 0.16 - 0.28 [14]. Considering all these factors and also that we used ns excitation pulses, it is reasonable to assume that TESA is one important factor contributing to induced absorption in our sample. It is possible to confirm whether TESA or TPA dominates in contributing to induced absorption, by measuring the nonlinear absorption for various pulse durations. As a rule, transmittance change $\Delta T$ at a fixed pulse energy will be independent of pulse width if the mechanism is TESA but will depend on pulse width if it is TPA. Since in our case the inter system 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 $\phi$ is the triplet yield. Certain metal ions can influence the inter system crossing rate to increase $\phi$ 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.

3.4.2 Figure of Merit for RSA materials, $\sigma_e/\sigma_g$

All RSA materials possess a higher absorption cross-section of excited states($\sigma_e$) compared to that of the ground state ($\sigma_g$) at the excitation radiation wavelength [15]. Interestingly they will also give a positive value for the imaginary part of susceptibility $\text{Im}(\chi^{(3)})$ which is actually a measure of the induced absorption. On the other hand a saturable absorber has a negative value for $\text{Im}(\chi^{(3)})$. The most important application of these materials is in optical limiting. However, they also act as saturable absorbers at certain excitation wavelengths. Since these properties are spectral dependent, it is more common to use a figure of merit, $\frac{\sigma_e}{\sigma_g}$ which is the ratio of excited to ground state absorption cross-section. The value of $\sigma_g$ can be obtained from the linear absorption spectrum using the
Beer's law. To evaluate $\sigma_e$ we need to analyze the z-scan signal in a different manner, for example as followed by Wei et al [11].

### 3.4.3 Calculation of Exited State Absorption Cross-section

In analyzing the ESA spectrum from the z-scan trace, we neglected all excitations to singlet states higher than the first singlet excitation and assumed that the inter system crossing rate is fast compared with the pulse duration, (it is actually of the order of hundreds of pico seconds, [16]) and that all of the initially excited molecules are in the lowest triplet state. Excitation from the first triplet state then leads to ESA. The equations governing the spatial variation of absorption through the medium are[17],

$$\frac{dI}{dz} = -\alpha I - \sigma_e N(t)I$$  \hspace{1cm} (3.9)

$$\frac{dN}{dt} = \frac{\alpha I}{\hbar \omega}$$  \hspace{1cm} (3.10)

where $I$ is the intensity, $\sigma_{es}$ is the excited-state absorption cross section, $N$ is the number density of species in the excited state, and $\omega$ is the angular frequency of the laser pump beam. Equations 3.9 and 3.10 can be combined to yield

$$\frac{dI}{dz} = -\alpha I - \frac{\sigma_{es} \alpha I}{\hbar \omega} \int_{-\infty}^{t} I(t')dt'$$  \hspace{1cm} (3.11)

Solving this equation for the fluence and integrating over the spatial extent of the beam, we may write the normalized energy transmission $T$ as

$$T = \ln(1 + \frac{q_0}{1 + x^2})/\left(\frac{q_0}{1 + x^2}\right)$$  \hspace{1cm} (3.12)

where $q_0 = \frac{\sigma_{es} F_0 (r = 0)L_{eff}}{2\hbar \omega}$, $x = z/z_0$ and $L_{eff} = \frac{(1-e^{-\alpha z_0})}{\alpha}$. The experiment was performed as explained previously and the ratio of the transmitted intensity and the incident intensity was recorded for each pulse, using the energy ratio meter, and averaged to obtain the open aperture z-scan trace. Equation 3.12 was used to fit this experimental trace and this yields the value of $q_0$. The value of $q_0$ will then give the excited state absorption cross section, $\sigma_{es}$. The ground state absorption cross section can be calculated from the linear absorption spectrum, using Beer's law. This is plotted in Figure 3.4(a).
Figure 3.4: (a) Comparison of excited state and ground state absorption cross sections (b) Figure of merit for $\text{Im} \chi^{(3)}$

3.5 Spectrum of Third Order Susceptibility

The calculated values of $\text{Im} \chi^{(3)}$ (this is the bulk third order susceptibility) as a function of wavelength is shown in Figure 3.5(a). The depth of the normalized $z$ scan trace varies as shown in Figure 3.5(b). These values are within an error of 17% contributed mainly by the uncertainty in intensity measurements in the sample and the fitting error. $\chi^{(2)}$ and $\chi^{(4)}$ vanish in liquids and higher order odd terms such as $\chi^{(5)}$ will be very small compared to $\chi^{(3)}$. One should be very careful while comparing the susceptibility values available in literature. These values vary to a great extent depending on the excitation wavelength, pulse duration, experimental technique, concentration of the molecular species in the sample etc. K.P.Unnikrishnan et al have reported $\text{Im} \chi^{(3)}$ values of $\text{Sm}(Pc)_2$ and $\text{Eu}(Pc)_2$ dissolved in DMF at various wavelengths using the same technique [18]. $\text{Sm}(Pc)_2$ and $\text{Eu}(Pc)_2$ have a different structure compared to ZnPc. However, in the SA regions, their reported values are in the range from $(-3.2 \text{ to } -0.07) \times 10^{-18} m^2 V^{-2}$ for $\text{Eu}(Pc)_2$ and from $(-4.0 \text{ to } -0.14) \times 10^{-18} m^2 V^{-2}$ for $\text{Sm}(Pc)_2$ which are of the same order of magnitude as we obtained. Gema et al gives an extensive review of nonlinear optical studies in porphyrins and phthalocyanines and lists the values of $\chi^{(2)}$, $\chi^{(3)}$ and also the molecular hyperpolarizability values obtained using various techniques [7]. However, the value of $\text{Im} \chi^{(3)}$ of ZnPc is not mentioned. Diaz-Garcia reported the magnitude of $\chi^{(3)}$ of Langmuir–Blodgett films of octasubstituted MPc's using THG experiments,
at 1064 nm. These values are in the range $3.4 \text{ to } 5.7 \times 10^{-13}$ esu [19].

### 3.5.1 Effective Nonlinear Absorption Coefficient

The measured values of $\beta_{\text{eff}}$ for those wavelengths at which the material shows induced absorption are given in Table 3.1. Considering the possibility of sequential and/or pure TPA and TESA, 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 $\beta_{\text{eff}}$ instead of $\beta$. 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 $\frac{\alpha_{\text{sat}}}{I_s}$ is equivalent to $\beta_{\text{eff}}$ of an RSA material. Henari et al used the same technique to find out the nonlinear optical parameters of certain group IV metal phthalocyanines using 665 nm, picosecond laser [20]. The absolute values of $\beta_{\text{eff}}$ 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 the differences in sample properties.
### Table 3.1: The linear ($\alpha_0$) and nonlinear ($\beta_{eff}$) absorption coefficients, and saturation intensity ($I_s$) of ZnPc in DMF, for various wavelengths of excitation. The material acts as saturable absorber for wavelengths at which $I_s$ is given. $\beta_{eff}$ is mentioned only for the case of RSA.

<table>
<thead>
<tr>
<th>$\lambda$(nm)</th>
<th>$\alpha_0$(cm$^{-1}$)</th>
<th>$\beta_{eff}$(cmGW$^{-1}$)</th>
<th>$I_s$(GWcm$^{-2}$)</th>
</tr>
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<tbody>
<tr>
<td>527</td>
<td>0.405</td>
<td>22.09</td>
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<tr>
<td>532</td>
<td>0.394</td>
<td>47.74</td>
<td>-</td>
</tr>
<tr>
<td>556</td>
<td>0.376</td>
<td>40.92</td>
<td>-</td>
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<td>566</td>
<td>0.384</td>
<td>38.43</td>
<td>-</td>
</tr>
<tr>
<td>576</td>
<td>0.400</td>
<td>44.22</td>
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<td>586</td>
<td>0.426</td>
<td>16.21</td>
<td>-</td>
</tr>
<tr>
<td>596</td>
<td>0.461</td>
<td>18.27</td>
<td>-</td>
</tr>
<tr>
<td>606</td>
<td>0.506</td>
<td>9.5</td>
<td>-</td>
</tr>
<tr>
<td>616</td>
<td>0.568</td>
<td>9.03</td>
<td>-</td>
</tr>
<tr>
<td>626</td>
<td>0.653</td>
<td>-</td>
<td>0.0637</td>
</tr>
<tr>
<td>636</td>
<td>0.766</td>
<td>-</td>
<td>0.0454</td>
</tr>
<tr>
<td>646</td>
<td>0.867</td>
<td>-</td>
<td>0.0523</td>
</tr>
<tr>
<td>650</td>
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<td>-</td>
<td>0.0672</td>
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<td>-</td>
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<td>686</td>
<td>1.106</td>
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<td>0.0397</td>
</tr>
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</table>

### 3.5.2 Figure of Merit for $\text{Im}\chi^{(3)}$

As the wavelength of excitation approaches the wavelength of resonant absorption, $\alpha_0$ increases and the nonlinear absorption gradually changes to SA. It will be useful to define a figure of merit 'FOM' for this type of materials as the ratio $\frac{\text{Im}\chi^{(3)}}{\alpha_0}$, which specifies the magnitude of nonlinear absorption for unit value of linear absorption loss (Figure 3.4(b)). FOM is larger by a small amount in the valley region between 500 nm and 600 nm in the absorption spectrum. The value FOM helps in comparing the absorptive nonlinearities at various excitation wavelengths.

### 3.6 Five-level Model for $\text{Im}\chi^{(3)}$

To account for the spectral dependence of $\text{Im}(\chi^{(3)})$ we have developed a theoretical formalism, using a 5 level model for energy transfer mechanism in the ZnPc molecules. It is depicted in Figure 3.2 and the notations are explained earlier. The resulting rate equations should be properly solved to get the population dynamics and the expressions for susceptibility. The details are given below.
3.6.1 Rate Equations for Five-level Model

To clearly understand the mechanisms for RSA, we need to solve the coupled rate equations for non steady state (time dependent) in Pc's, assuming a 5 level model for the energy levels. This gives a picture of the population transients in various levels[16]. This should be compared with the duration of the pump beam, and we will get a clear idea of various possible transitions that can take place while the pulse lasts inside the sample. The result of this simulation is shown in Figure 3.6(a) where two-photon absorption (TPA) is not taken into account.

Figure 3.6: (a) Calculated population densities of $S_0$, $S_1$ and $T_1$ when TPA is absent (b) Calculated population densities of $S_0$, $S_1$ and $T_2$ when TPA is present

This means that when the excitation wavelength does not favor multiphoton processes, the triplet to triplet excited state absorption is the dominant mechanism for RSA. However, if we consider the possibility of two photon absorption, the rate equation should be modified, taking into account, the variation of population of ground state as proportional to $p^2$ ($p$ being the fluence) and the TPA cross section obtained from the theoretical fit to OA z-scan trace. Then the first term on the right hand side of equation 3.13(c) can be neglected, which is due to one photon absorption, and the first term in the Equation 3.13(e) will be modified as, $(N_1 - N_5)\beta p^2$. The modified plot of time dependent population is given in Figure 3.6. The pulse duration of the laser used for this study is 8 ns. It can be assumed that within this time, most of the molecules were excited through TPA, and hence the population in $S_1$ and $T_1$ will be very negligible [21, 13]. The coupled rate equations implied by the energy level diagram given
in Figure 3.2 (considering only the relevant terms) are as follows,

\[ N_1 + N_2 + N_3 + N_4 + N_5 = N_0 \]  
(3.13a)

\[ \frac{dN_2}{dt} = \frac{N_3 \phi_{32}}{\tau_3} + \frac{N_4}{\tau_4} \]  
(3.13b)

\[ \frac{dN_3}{dt} = (N_1 - N_3)\sigma_{13}p - \frac{N_3 \phi_{32}}{\tau_3} - \frac{N_3(1 - \phi_{32})}{\tau_3} \]  
(3.13c)

\[ \frac{dN_4}{dt} = (N_2 - N_4)\sigma_{T}p - \frac{N_4}{\tau_4} + \frac{N_5 \phi_{54}}{\tau_5} \]  
(3.13d)

\[ \frac{dN_5}{dt} = (N_1 - N_5)\sigma_{15}p - \frac{N_5(1 - \phi_{54})}{\tau_5} - \frac{N_5 \phi_{54}}{\tau_5} + (N_3 - N_5)\sigma_{35}p \]  
(3.13e)

where \( \phi \) are the intersystem crossing yields, \( \sigma \) are the absorption coefficients, and \( \tau \) are the life time of the energy levels. \( \beta \) can be obtained from the OA signal as described in the previous chapter.

### 3.6.2 Rate Equations in the Transient Regime - Excited State Dynamics

It can be assumed that during the rising part of the excitation pulse, the population in various levels undergo a change due to all possible excitation and de-excitation processes in the molecular system. The solution of the governing rate equations as given by the above set of Equations 3.13, keeping the time dependent terms, will therefore give the excited state dynamics of the system. This is what is plotted in Figure 3.6, under two conditions, viz, with and without the presence of two photon absorption. Such calculations will help in determining the exact nature of the induced absorption processes. For example in the system under our investigation, it is the triplet to triplet absorption that leads to RSA [14, 27].

### 3.6.3 Rate Equations in the Steady state Regime - Evaluation of \( \chi^{(3)} \)

When the system attains steady state, one can equate the \( dN/dt \) terms in the rate equations to zero, and solve them and by a proper rearrangement of the terms it will finally lead to expressions for the real and imaginary part of susceptibility. Since only the nonlinear absorption studies were carried out, the focus is mainly on the derivation for \( \text{Im}\chi^{(3)} \) as a function of wavelength of excitation
Vibrational relaxation  $10^{-12} - 10^{-10}$ s
Fluorescence $10^{-9} - 10^{-5}$ s
External conversion $10^{-12} - 10^{-7}$ s
Electronic excitation $10^{-10} - 10^{-14}$ s
Phosphorescence $10^{-4} - 10^{-6}$ s
Internal conversion $10^{-12} - 10^{-7}$ s
Intersystem crossing $10^{-12} - 10^{-7}$ s

Table 3.2: Time scales for various excitation and relaxation processes in metal phthalocyanines

and the linear absorption coefficient. This will give a theoretical model for the excited state absorption spectrum.

To develop this model, the following steps are taken:

1. Identify the various processes that can take place in a time of $\sim 10$ ns, which is the pulse duration of the laser used.

2. Write down the rate equations for a 5 level system, incorporating all these possible transitions.

3. Solve for steady state, neglecting processes that take more than 10 ns to take place.

4. Substitute the results into the expression for susceptibility obtained from the density matrix formalism and simplify.

5. Compare the results with the experimentally obtained values given in the previous sections.

In the case of ZnPc, and other common metal Pc's the time scales of various electronic excitation and de-excitation processes are given in Table 3.2. From these data it is reasonable to assume that, the system attains steady state during the time in which one pulse lasts in the medium, provided we neglect fluorescence and phosphorescence.

To derive a general expression for susceptibility, we can use the density matrix formalism adopted in reference [28]. For example, considering a simple two level system, the corresponding density matrix is written as

$$
\begin{pmatrix}
\rho_{11} & \rho_{12} \\
\rho_{21} & \rho_{22}
\end{pmatrix}
$$
When light interacts with this system (Electric field \( E \)), it is represented by the interaction Hamiltonian,

\[
H'(t) = -\mu E(t) \tag{3.14}
\]

where \( \mu \) is the component of the dipole operator along the direction of the field, and the diagonal elements of \( H'(t) \) are taken as zeroes. As appropriate to the transitions between states of definite parity, one can also put

\[
\mu_{11} = \mu_{22} = 0 \tag{3.15a}
\]

\[
\mu_{21} = \mu_{12} = \mu \tag{3.15b}
\]

and the total Hamiltonian is

\[
H = H_0 + H' \tag{3.16}
\]

and

\[
E = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}
\]

The ensemble average of the dipole moment is \( \langle \mu \rangle \) and we should solve for \( \langle \mu \rangle \) of the atom that is induced by field \( E(t) \).

\[
\langle \mu \rangle = \text{trace}(\rho \mu) = tr \begin{pmatrix} \rho_{11} & \rho_{12} \\ \rho_{21} & \rho_{22} \end{pmatrix} \begin{pmatrix} 0 & \mu \\ \mu & 0 \end{pmatrix} = \mu(\rho_{12} + \rho_{21}) \tag{3.17}
\]

Using the relations

\[
\frac{d\rho_{21}}{dt} = -\frac{i}{\hbar} (H \rho)_{21}
\]

and using the equation 3.16, one gets the sets of equations,

\[
\frac{d\rho_{21}}{dt} = -\frac{i}{\hbar} \left[ H'_{21} (\rho_{11} - \rho_{22}) + (E_2 - E_1) \rho_{21} \right] \\
= \frac{i\mu}{\hbar} E(t) (\rho_{11} - \rho_{22}) - i\omega_0 \rho_{21} \tag{3.18}
\]

and

\[
\frac{d\rho_{22}}{dt} = -\frac{i\mu}{\hbar} E(t) (\rho_{12} - \rho_{21}) \\
= -\frac{i\mu}{\hbar} E(t) (\rho_{21} - \rho_{21}^*) \tag{3.19}
\]
The normalization condition is

\[ \rho_{11} + \rho_{22} = 1 \]

and therefore we get,

\[ \frac{d}{dt} (\rho_{11} - \rho_{22}) = \frac{2i\mu}{\hbar} E(t) (\rho_{21} - \rho_{21}^*) \quad (3.20) \]

Equation 3.18 can be modified to include the collision terms as

\[ \frac{d\rho_{21}}{dt} = \frac{i\mu}{\hbar} E(t) (\rho_{11} - \rho_{22}) - i\omega_0\rho_{21} - \frac{\rho_{21}}{T_2} \quad (3.21) \]

Here \( \rho_{ii} \) is the probability of finding the atom in the \( i^{th} \) state. If \( N \) is the density of atoms, \( N(\rho_{11} - \rho_{22}) \equiv \Delta N \) is the average density of the population difference between the two levels. Let the equilibrium value of (ie at \( E(t) = 0 \)), \( \rho_{11} - \rho_{22} \) is \( (\rho_{11} - \rho_{22})_0 \) and when \( E(t) \) is turned off, \( \Delta N \) relaxes towards its equilibrium value \( N(\rho_{11} - \rho_{22})_0 \) with a time constant \( \tau \). Therefore Equations 3.18 and 3.19 becomes,

\[ \frac{d}{dt} (\rho_{11} - \rho_{22}) = \frac{2i\mu E(t)}{\hbar} (\rho_{21} - \rho_{21}^*) - \frac{\rho_{11} - \rho_{22}}{\tau} - (\rho_{11} - \rho_{22})_0 \quad (3.22) \]

The perturbing field can be written as

\[ E(t) = E_0 \cos \omega t \quad (3.23) \]

and when it is zero, Equation 3.21 becomes

\[ \frac{d\rho_{21}}{dt} = -i\omega_0\rho_{21} - \frac{\rho_{21}}{T_2} \]

so that when \( \omega \approx \omega_0 \) we can define a quantity \( \sigma_{21} \) as

\[ \rho_{21}(t) = \sigma_{21}(t)e^{-i\omega t} \quad (3.24a) \]

\[ \rho_{12}(t) = \sigma_{12}(t)e^{-i\omega t} = \rho_{21}^* \quad (3.24b) \]
Using Equations 3.23 and 3.24 in Equations 3.21 and 3.20 we get

\[ \frac{d\sigma_{21}}{dt} = \frac{d}{dt} \left( \rho_{21} e^{i\omega t} \right) = i(\omega - \omega_0)\sigma_{21} + \frac{i\mu E_0}{2\hbar}(\rho_{11} - \rho_{22}) - \frac{\sigma_{21}}{T_2} \]  (3.25)

and

\[ \frac{d}{dt}(\rho_{11} - \rho_{22}) = \frac{i\mu E_0}{2\hbar}(\sigma_{21} - \sigma_{21}^*) - \frac{(\rho_{11} - \rho_{22}) - (\rho_{11} - \rho_{22})_0}{\tau} \]  (3.26)

using these Equations 3.17 leads to the expectation value of the density matrix as

\[ \langle \mu \rangle = 2\mu [\text{Re}\sigma_{21}(t)\cos\omega t + \text{Im}\sigma_{21}(t)\sin\omega t] \]  (3.27)

To obtain steady state solutions, equate the Equations 3.25 and 3.26 to zero. Thus we get the absolute value of \( \sigma_{21} \) as a complex number. Its real and imaginary parts are,

\[ \text{Im}\sigma_{21} = \frac{\Omega T_2(\rho_{11} - \rho_{22})_0}{1 + (\omega - \omega_0)^2 T_2^2 + 4\Omega^2 T_2^2} \]  (3.28a)

\[ \text{Re}\sigma_{21} = \frac{(\omega_0 - \omega)\Omega T_2^2(\rho_{11} - \rho_{22})_0}{1 + (\omega - \omega_0)^2 T_2^2 + 4\Omega^2 T_2^2} \]  (3.28b)

where \( \Omega = \mu E_0 / 2\hbar \) is the precession frequency. To obtain the expression for \( \chi^{(3)} \), we need to use the relation \( P = N\langle \mu \rangle \). Here P is the macroscopic polarization and use the Equation 3.27 to obtain P and then compare it with the standard relation

\[ P(t) = E_0 \left( \epsilon_0 \text{Re}(\chi^{(3)})\cos\omega t + \epsilon_0 \text{Im}(\chi^{(3)})\sin\omega t \right). \]  (3.29)

This leads to

\[ \text{Re}\chi^{(3)}(\omega) = \frac{\mu^2(\omega_0 - \omega)T_2}{2\epsilon_0\hbar} \Delta N g(\nu) \]  (3.30a)

\[ \text{Im}\chi^{(3)}(\omega) = \frac{\mu^2}{2\epsilon_0\hbar} \Delta N g(\nu) \]  (3.30b)

where the normalized line shape function is

\[ g(\nu) = \frac{\Delta \nu / 2\pi}{(\nu - \nu_0)^2 + (\Delta \nu / 2)^2} \]  (3.31)

and \( \Delta \nu \) is the full width at half maximum is also the inverse of the dephasing time \( T_2 \).
This is extended to 5 level model to obtain the nonlinear susceptibility. To reduce the complexity in calculations, the rate equations given earlier are reformulated as follows, considering only the important and relevant terms.}

\[
N_5 R_{52} + N_3 R_{32} + \frac{N_4}{\tau_{42}} = 0 \tag{3.32a}
\]

\[
(N_1 - N_3)\sigma_{13}p + \frac{N_5}{\tau_{63}} = N_3 R_{32} + \frac{N_3}{\tau_{31}} \tag{3.32b}
\]

\[
(N_2 - N_4)\sigma_{42}p + N_5 R_{54} = \frac{N_4}{\tau_{42}} \tag{3.32c}
\]

\[
(N_1 - N_5)\sigma_{15}p + (N_3 - N_5)\sigma_{35}p = \frac{N_5}{\tau_{53}} + \frac{N_5}{\tau_{51}} + N_5 R_{54} + N_5 R_{52} \tag{3.32d}
\]

\[
N_1 + N_2 + N_3 + N_4 + N_5 = N_0 \tag{3.32e}
\]

The solution gives values of \(N_1\), \(N_2\), \(N_3\), \(N_4\) and \(N_5\). Substitute these values into the equation for imaginary part of susceptibility to give,

\[
\text{Im}\chi^{(3)}(\omega) = \frac{n_0 c}{\omega} \left[ (N_1 - N_3)\sigma_{13} + (N_2 - N_4)\sigma_{42} + (N_1 - N_5)\sigma_{15} + (N_3 - N_5)\sigma_{35} \right] \tag{3.33}
\]

and use the approximation \(R_{52} \cong 0\) and assuming there is no decay from level 5 to level 3. This gives,

\[
\text{Im}\chi_{\text{eff}}(\omega) = \frac{n_0 c}{\omega} \left\{ \frac{N_0 \sigma_{42}(\sigma_{13} + \sigma_{15})}{B} \right\} \tag{3.34}
\]

where \(B\) is defined as

\[
(R_{32}\tau_{31}(\sigma_{13} + \sigma_{15}) + \sigma_{42}(-1 - 2p\sigma_{13}\tau_{31} - p\sigma_{15}\tau_{31} + p\sigma_{35}\tau_{31} + R_{32}\tau_{31}(-1 + 2p\sigma_{13}\tau_{42} + 2p\sigma_{15}\tau_{42})))
\]

Now this should be expanded in terms of flux density \(p'(= I/\hbar\omega)\) and compared with the expression

\[
\chi_{\text{eff}} = \chi^{(1)} + \chi^{(3)}|E|^2 = \chi^{(1)} + \chi^{(3)} \frac{2I_0}{\varepsilon_0 n_0 c} \tag{3.35}
\]

Thus the spectral dependence for \(\text{Im}\chi^{(3)}\) can be written as

\[
\text{Im}\chi^{(3)} = k_1 k_2 \left( k_3[4\mu_{13}\mu_{31} + 2\mu_{15}\mu_{51}\tau_{31}] - k_4[\mu_{13}\mu_{31} + \mu_{15}\mu_{51}] \right) \tag{3.36}
\]

To get the nature of the excited state absorption spectrum, the dependence of
$\text{Im}\chi^{(3)}$ as given above is sufficient. Values of $g$'s defined in equation 3.31 are obtained from the linear absorption spectrum, by giving a Lorentzian fit to the absorption peaks. The inclusion of the term ‘$g$’ contains a detuning factor $\delta\nu$, that effectively incorporates the spectral dependence in susceptibility.

### 3.7 Conclusion

We have studied the nonlinear optical properties of 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 an RSA based optical limiter in the wavelength range from 527 to 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 $\text{Im}\chi^{(3)}$ for a wavelength change from 656 to 686 nm towards the resonant peak.
References


