Asian Journal of Physics Vol 9, No 2, (2000) 145-149

Excited state enhancement of third-order optical nonlinearity in AuTTP studied by degenerate four wave mixing at 532 nm

D NARAYANA RAO and S VENUGOPAL RAO
School of Physics, University of Hyderabad, Hyderabad – 500 046, India.
E-mail: dnrsp@uohyd.ernet.in

We present our experimental results on the enhancement in the third-order nonlinear susceptibility in tetratolyl porphyrins measured using Degenerate Four Wave Mixing at 532 nm. The enhancement, by a factor of about 3, is attributed to the strong excited state absorption at this wavelength.

1 Introduction

Porphyrins are a ubiquitous class of naturally occurring compounds having important biological representatives including hemes, chlorophyll and vitamin B_{12} among several others. They are also involved in oxygen binding, electron transfer, light harvesting, and catalysis.[1] Heme and chlorophyll are iron and magnesium derivatives of cyclic pyrrole pigments. Hemoglobin in blood is responsible for the transfer of molecular oxygen to tissues. Manganese derivatives are thought to be responsible for the decomposition of water via photosynthesis in organisms found in nature. Zinc porphyrins take part in metabolic processes. Colors of feathers in some birds are due to copper derivatives of porphyrins. In addition there are multitudes of synthetic porphyrinoid molecules that have been prepared and studied for purposes ranging from basic research to functional applications. All these molecules share the porphyrin macrocyclic substructure in common. The basic structure of the porphyrin macrocycle consists of four pyrrolic subunits linked by four methine bridges. Although the porphyrin ring is a macromolecule, it is highly flexible and a number of structural changes involving different central metal ions and peripheral substituents can be introduced without compromising its excellent chemical and thermal stability. This architectural aspect is relevant to nonlinear optics in developing materials with optimum nonlinearity and response times. The high π electron density, resulting in an extended electron de-localization makes porphyrins useful for observing a variety of nonlinear optical effects. Their sharp absorption bands in the visible and NIR can be used for resonance enhancement of $\chi^{(3)}$ as well. They have enormous potential for applications on the technological front, which include optical limiting, optical switching, optical data processing and opto-electronic device fabrication. They have also been used as organic semiconductor, bistable device, in magnetic resonance imaging and photodynamic therapy.[2,3] Because of these vital roles played by porphyrins and their derivatives a vast amount of research has been directed towards understanding the detailed mechanisms responsible for nonlinearity. Here we present our results on the measurement, and enhancement, of the third order optical nonlinearity observed in Gold Tetratolyl Porphyrin (AuTTP) and other similar porphyrins. The techniques of Degenerate Four Wave Mixing (DFWM) and Z-Scan have been employed.

2 Experimental

Fig. 1 shows the structure of the compound used in the study. The central metal could be varied from Au to Cr, Mn, or Fe. DFWM in the standard backward configuration is employed for nonlinearity and dynamics measurements. The sample used in this study shows the linear absorption features typical of metalloporphyrins, namely the high energy B (Soret) band and the low energy Q band(s). All the experiments are carried out with sample having a concentration in the range of 10^{-4} to 10^{-5} M corresponding to an absorbance of less than 0.3. During the DFWM experiments, the cubic dependence of the phase conjugate signal with respect to input intensity and the linear dependence of the PC signal with respect to concentration (shown in fig..2) have been verified for all the samples. The values of the cubic hyperpolarizability <γ> are calculated using equations (1) – (4).

$$\chi_s^{(3)} = \left(\frac{n_0}{n_{ref}}\right)^2 \left(\frac{l_{ref}}{l}\right)\left(\frac{A}{A_{ref}}\right)^{\frac{1}{2}} \left(\frac{\alpha l \exp(\alpha l/2)}{1-\exp(-\alpha l)}\right)\chi_{ref}^{(3)} \tag{1}$$

and

$$<\gamma> = \frac{\chi^{(3)}}{L^4 N}\ ;\ L = \frac{n^2+2}{3} \tag{2}$$

Where n is the refractive index, l is the length of the sample, A is the coefficient of the cubic term of a least squares fit to the plot of PC signal versus input intensity, and α is the absorption coefficient. For a solution of non-interacting particles, the effective $\chi^{(3)}$ assuming a pairwise additive model is given by

$$\chi_{solution}^{(3)} = L^4\ [N_{solvent}\gamma_{solvent} + N_{solute}\gamma_{solute}] \tag{3}$$

where N_{solute}, $N_{solvent}$ ate the number densities of molecules of the solute and the solvent respectively. For dilute solutions with:

$N_{solute} = ((A*C)/M)$, we may write

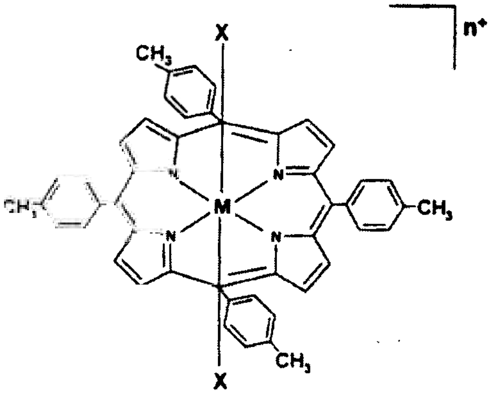
$$\chi_{solution}^{(3)} = \chi_{solvent}^{(3)} + \frac{L^4\gamma_{solute}A}{M} * C \tag{4}$$

with A being the Avagadro's number, M being the molecular weight and C the concentration of the solute in g/ml. For lower concentrations the $|\chi^{(3)}|$ of the solution follows a linear relationship with respect to the concentration of the solute. $\chi^{(3)}$ may have both real and imaginary components originating from the solute as well as solvent. The real part is responsible for the nonlinear refraction whereas the imaginary part is responsible for nonlinear absorption, either TPA or ESA. The real part can be positive or negative. The figure of merit, independent of concentration, F is given as $\chi^{(3)}/\alpha$. We have taken the value of $\chi^{(3)}$, for the reference sample CS_2, as 1.7×10^{-12} esu for ns pulses the sake of consistency although other value of 6.8×10^{-13} esu have been reported. L is the local field correction factor and N is the number density of the solute molecules in solution. The $\chi^{(3)}$ contribution from solvent is taken to be zero, as it is negligibly small in comparison to the solute.

3 Results and Discussion

The value of γ calculated, using the above equations, for AuTTP is found to be $7.25*10^{-28}$ esu. The values of other compounds are found to be less than AuTTP but of the same order of magnitude.[4] On comparing the <γ> values of our compounds with other porphyrins, the ns values are found to be three orders of magnitude larger than any of them. When the probe polarization is made normal to the pump beams, the PC signal gets reduced by only one-third of the original value (when all beams are co-polarized) indicating that the nonlinearity is predominantly electronic in origin and thermal effects are not dominant. However, there should be a significant contribution to this large value of $\langle\gamma\rangle$ from the excited singlet and triplet states, since we observe very strong ESA in all the open aperture Z-scan data. The concentration dependence of the $\chi^{(3)}$ value indicates the strong contribution of imaginary part to the total nonlinearity compared to real part. It is well established that ESA is an intensity dependent process and will dominate at higher intensity levels. This is well supported by our $\chi^{(3)}$ measurements at different input intensity levels whereby we observe an enhancement by a factor of three to four in its value. Measurements on the sample AuTTP yield a value of 10×10^{-12} esu at an input of ~ 2 mW (corresponding peak intensity at focus is ~ 100 MW/cm^2) and a value of ~ 30×10^{-12} esu at an input of ~ 6 mW (corresponding peak intensity at focus is ~ 300 MW/cm^2) for the same sample concentration. Furthermore, the intensity dependence of PC signal shows a different behavior at high intensities. A log-log plot of input energy versus PC signal shown in fig. 12 gives a slope of < 3 at lower intensities and a slope of ~ 5 at higher intensities suggesting nonlinearity contributions from higher excited states. The $\chi^{(3)}$ versus the intensity data obtained for the samples CS_2 and RhB do not show any deviation from the cubic dependence. This is well understood since there is no excited state absorption in either of the samples and hence no contribution of the excited states to the total nonlinearity. The other samples investigated, CoTTP and NiTTP with γ values of $1.4675 * 10^{-28}$ esu and $1.7725 * 10^{-28}$ esu respectively, also exhibited similar behavior at higher intensities.

Open aperture Z-scan,[5] depicted in fig. 4, shows a valley indicating strong ESA/RSA. Depending on the pulse duration, pump intensity and wavelength, nonlinear absorption can be from (a) the ground state S_0 to higher excited singlet states S_n (two-photon or multi-photon excitation), (b) the first excited singlet state S_1 to higher excited states S_n, or from (c) the T_1 to T_n states in the triplet manifold. The last two processes are known as excited state absorption (ESA), but if their cross sections are larger than that of linear absorption, then these are referred to as reverse saturable absorption (RSA). We attribute the observed nonlinear absorption to strong ESA or RSA. All the samples are found to exhibit similar behavior, indicating a negative nonlinearity as evidenced by the peak occurring at negative z values in the scan. It is the near-resonant excitation that leads to thermal excitation of the medium, resulting in this negative nonlinearity. Open aperture Z-scan obtained for RhB clearly shows saturation of absorption.



M = Au n = 1 X = Cl

Fig. 1 Structure of the compounds

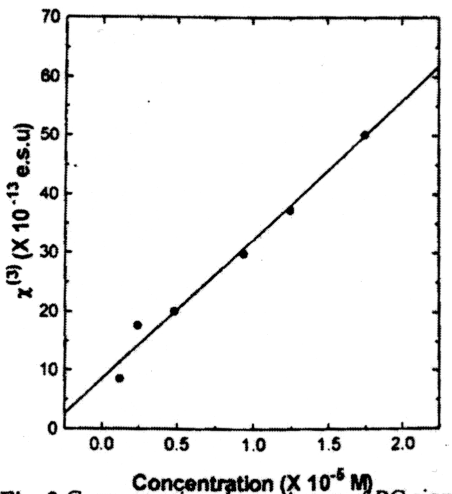


Fig. 2 Concentration dependence of PC signal

Equally large $\langle\gamma\rangle$ value have been observed using dye laser pumping also, when excited at 595 nm. At this wavelength these compounds have a stronger two-photon absorption as compared to 532 nm. Earlier reports show the excited state enhancement of the nonlinearity in linear conjugated molecules and a square planar complex. Those experiments were performed in the presence of a strong pump beam. In porphyrins, larger excited state cross-section probes the nonlinearity due to S_n and T_n apart from S_1 and T_1 states. Time resolved studies using incoherent light and ps pulses do suggest the population in different excited states and very fast relaxation time for these molecules.[4]

Rodenberger et al.[6] found a new way to achieve large nonlinearities through excited-state population. In their case a strong pump beam acting on the molecule excites the molecule to higher states and a probe is used for measurement of the nonlinearity. In our case due to strong excited state absorption the population is distributed among the excited states with the pump pulse itself. Si et al. reports the fluence dependence of nonlinear optical response of cadmium texaphyrin[7] using time-resolved DFWM at 532 nm. They argue that at lower fluences of excitation, the nonlinearity mainly arises from the first excited singlet and triplet states since the population in the higher excited states is small. In their case two response times, one fast and one slow, characterized the NLO response. The fast component was from the singlet state and the slow one from triplet state. At higher fluences the higher excited states also contribute, due to significant amount of population, to the total nonlinearity and the response will have three components, fastest one due to the higher states added to the fast and slow components observed at lower fluences. We have also performed measurements on nonlinearity and excited state dynamics for the same sample with 35 ps pulses and when compared to ns pulses we find the magnitude of the nonlinearity to be two orders less[5]. It has been already been shown that while using ns pulses the excitation could lead the population to any of the higher excited states[8]. The time response of the PC signal, at 600 nm using ns pulses, has three components and it is found to be independent of the input intensity. This again confirms the contribution of different excited states to the total nonlinearity. With ps pulses we observed only one component in the decay measurements by recording the PC signal as a function of the backward beam delay. We attribute this decay to the S_1 state population relaxation. This implies that the low nonlinearity observed, when compared to ns pulses, in the case of ps pulses is due to the population in singlet state only. The intersystem crossing takes place in ~ few hundred ps in these systems and hence the triplet population contribution to the nonlinearity is negligible. However, more studies are in progress to identify the exact

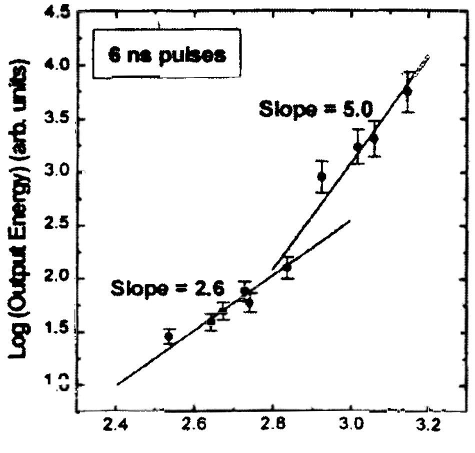


Fig. 3 PC signal versus input intensity

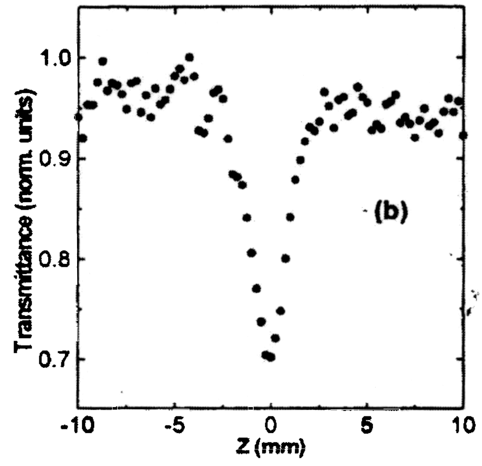


Fig. 4 Open aperture Z-scan of AuTTP

contribution of each level to the total nonlinearity. A proper combination of chemical engineering and systematic studies could lead to development of new materials with very high nonlinearity and fast response.

Acknowledgments

D N Rao is thankful to DST, Government of India, for financial support.

References

1 Gouterman M, *The Porphyrins*, Vols I-VII, D Dolphin Ed , Academic Press, New York, (1978); K Smith, Porphyrins & Metalloporphyrins, Amsterdam, The Netherlands: Elsevier/North-Holland Biomedical Press, (1976); Nalwa H S & Miyata S, eds, *Nonlinear Optics of Organic Molecules and Polymers*, CRC Press Inc, USA, 1997; Ravikanth M & Kumar G R, *Current Sci*, 68 (1995) 1010.

2 Rao D V G L N, Aranda F J, Remy D E, Roach J F, *Int J Nonlinear Opt Phys*, 3 (1994) 511.

3 Blau W, Byrne H, Dennis W M, & Kelly J M, *Opt Commun*, 56 (1985) 25; Sevian A, Ravikanth M, Kumar G R, *Chem Phys Lett*, 263 (1996) 241.

4 Rao S V, Srinivas N K M N, Giribabu L, Maiya B G, Philip R, Kumar G R & Rao D N, Submitted to *Opt Commun*; Rao S V, Srinivas N K M N, Giribabu L, Maiya B G, Philip R, Kumar G R, & Rao D N, submitted to JOSA B.

5 Sheik-Bahae M, Said A A, Wei T -H, Hagan D J, Van Stryland E W, *IEEE J Quantum Electron*, 26 (1990) 760.

6 Rodenberger D C, Heflin J R & Garito A F, *Nature* 359 (1992) 309; Rodenberger D C, Heflin J R, & Garito A F, *Phys Rev,A* 51 (1995) 3234.

7 Si J, Wang Y, Zhao J, Ye P, Wang D, Sun W & Dong S, *Appl Phys Lett* 67 (1995) 1975; J Si, Yang Q, Wang Y, Ye P, Wang S, Qin J & Liu D, *Opt Commun*, 132 (1995) 311.

8 Rao S V, Rao D N, Akkara J A, DeCristofano B S & Rao D V G L N, *Chem Phys Lett*, 297 (1998) 491.

[*Received* 1.2.2000]