Excited state dynamics in porphyrins in relevance to third-order nonlinearity and optical limiting

D. Narayana Rao *
School of Physics, University of Hyderabad, Hyderabad 500046, Andhra Pradesh, India

Abstract

Role of nonlinear optical phenomena forms the basis for many optical devices. Suitability of the material depends on its large magnitude of the relevant nonlinear effect. Tetra tolyl porphyrins (TTP) are investigated in the present work in order to study the enhancement in third order susceptibility ($\chi^{(3)}$) through the higher excited states. TTPs with different metal ions are investigated to evaluate the second order hyperpolarizability $\gamma$, using both ps and ns lasers. An incoherent laser spectroscopic technique is used to evaluate the excited state dynamics. Optical limiting properties are investigated by altering the intersystem crossing rates from singlet to triplet states.

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1. Introduction

Last two decades have witnessed an extensive research activity in the nonlinear optical, photo-physical and photochemical properties of organic materials in general and metallo-porphyrins/re- lated compounds in particular. The interest in metallo-porphyrins is many-fold. These molecules are found to have strong nonlinearity and fast response times, the desired criteria for making useful photonic devices. Previous theoretical and experimental studies have shown that there is an enhancement in the optical nonlinearity through population of the excited state [1]. In the present studies we look at the excited state contribution to nonlinear optical properties of tetra tolyl porphy-

rins as a function of the input intensity and the metal ions. The aim of the present studies has been to incorporate structural modifications to the porphyrins for application towards optical limiting. Optical limiting devices show linear absorbance at lower intensities and limit to a threshold transmittance at higher intensities due to reverse saturation of absorption (RSA). Such a nonlinear absorption can be achieved through excited state absorption (ESA) and two-photon absorption (TPA) in porphyrins. As the porphyrins possess very strong excited state absorption from both the triplet as well as the singlet states, they serve as the one of the best optical limiting materials. $S_1$ has a shorter lifetime and transfers the excited state energy to $T_1$ through inter system crossing (ISC). Longer lifetime of $T_1$ helps increase the ESA due to $T_1 \rightarrow T_n$ transitions in addition to the $S_1 \rightarrow S_n$ absorption. ISC thus plays important role. The lifetime of higher excited states also play a major role Які впливи можливо експериментовати в майбутньому?
in optical limiting. Longer lifetimes of $S_n$ and $T_n$ states lead to saturation of absorption at very high intensities. Therefore an optimum system for optical limiting would be the ones with large $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ absorption compared to $S_0 \rightarrow S_1$ absorption, very fast ISC, and fast relaxation from $S_n \rightarrow S_1$ and $T_n \rightarrow T_1$. Study of the nonlinearity and elucidation of the dynamics associated with excited states of such molecules is therefore important from a fundamental as well as technological point of view.

2. Experimental

Tetra tolyl porphyrins (TTP) with different metal ions (H, Co, Ni, Cu, Zn, Ag, Cd, Hg, Cr, Mn, Fe, Au, In, Ge, Sn, V, P) in the ring and O, OH and Cl in the axial positions are synthesized and purified according to the reported procedures in literature [2]. The structure of these molecules is given in our earlier article [3]. The samples are dissolved in highly purified spectroscopic grade chloroform with a concentration in the range of $10^{-4}$–$10^{-5}$ M corresponding to an absorbance of approximately 0.3. All samples showed linear absorption features typical of metalloporphyrins, namely the high energy B (Soret) band and the low energy Q band. We employed standard degenerate four wave mixing in phase conjugate geometry. Source for the DFWM-IL [4–6] is a 10 Hz, 6 ns Nd:YAG pumped broad band dye laser (600 nm, $\Delta \lambda = 10$ nm). Source for the ps ChH measurements is a hybrid mode-locked Nd:YAG laser (35 ps, 532 nm, 10 Hz). Experimental setup is similar to the ns system except that the beams are loosely focused in ps experiments. The peak intensities for ns and ps studies are $\sim 600$ MW/cm$^2$. Open aperture Z-scans [7] were recorded using ps and ns lasers. The input beam is spatially filtered using a 1 mm aperture to obtain a good gaussian profile before focussing the beam with a 120 mm focal length lens on to the sample kept in a 1 mm path length cuvette.

3. Results and discussion

A typical picture of the recording of DFWM-IL is shown in Fig. 1. Two beams with wave vectors $k_1$ and $k_3$ are focussed on to the sample at an angle $\theta$, and the third beam $k_2$ is made to counter propagate with respect to $k_1$. The delay between $k_1$ and $k_2$ beams and that between $k_1$ and $k_3$ are denoted as $s$ and $s$ respectively. The phase conjugate signal $k_4$ propagating in the $-k_3$ direction is detected. Two peaks are observed. The main intense peak appears when $s = 0$ and is due to the coherence of beams 1 and 3. The broader and weaker peak is due to the coherence of beams 2 and 3 and appears at time $s = \delta$. In the limiting condition that the lower excited state ($S_n$ and $T_n$ in present experiments) has life time longer than the higher excited states ($S_1$ and $T_1$), it has been shown [8] that the ratio of the peak intensities at $s = 0$ to that at $s = \delta$ corresponds to $(1/c_{gg}) * \tau_c$, where $c_{gg}$ is the relaxation rate of the lower excited state and $\tau_c$ is the correlation time.

It is clearly seen that the first peak follows the autocorrelation trace indicating that the dephasing time in the $S_n$ states is less than 170 fs. The vibrational relaxation times in the $S_1$ state ($\tau_{S1}$) is about 3–6 ps (from the width of the second peak) and the $S_1$ population relaxation is in the range of 30–70 ps [9]. However, our data does not rule out the existence of the longer lifetimes of $S_1$ state observed by other workers. What is seen in
DFWM-IL experiments is the fast component of the \( S_1 \) state. Such fast relaxation rates are expected since all these porphyrins are either nonfluorescent rendering the de-excitations generally nonradiative. \( \chi^3 \) and \( \gamma \) are estimated by measuring the FWM signal for different concentrations at 532 nm using both the ps and ns lasers. Figure of merit, \( F \), defined as \( \chi^3 \) is estimated. The largest value of \( \gamma \) is found to be \( \sim 725 \times 10^{-30} \) esu for AuTTP with ns pulses and \( \sim 1.43 \times 10^{-30} \) esu for CoTTP using ps pulses. It is also seen that for ns pulses SnTTP has the largest value of \( F \) (\( \sim 323 \times 10^{-13} \) cm esu) whereas for ps pulses \( H_2 \) TTP has the largest value (\( \sim 7.24 \times 10^{-11} \) cm esu) [3]. A plot of \( \gamma \) and \( F \) as a function of atomic number for both the ps and ns data does not reveal any steady increase in the third order nonlinearity with atomic number. We could not therefore establish a relationship between \( \gamma \) and the atomic number of the corresponding metal ion. Similarly, the plot of \( \gamma \) and the redox potential (measure of the extent of delocalization of the \( \pi \) electron cloud) does not reveal an immediate relationship. Open aperture Z scans with ns pulses show deeper valleys for those samples which are found to have higher \( \gamma \) values. Closed aperture Z scans show negative nonlinearity for all the samples. On comparing the \( \gamma \) values of our compounds with other porphyrins reported in the literature, 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, phase conjugate signal gets reduced by only one-third of the signal with all beams co-polarized, indicating that the nonlinearity is predominantly electronic in origin. ns data exhibits very strong ESA due to \( T_1 \rightarrow T_n \) absorption. A significant contribution to \( \gamma \) comes from the long-lived excited triplet states. Longitudinal relaxations of these porphyrins were measured (Fig. 2) with 35 ps, 532 nm pulses using the DFWM set-up. Temporal evolution of the signal has been checked for all the samples at longer delays >400 ps, and no thermal contribution was observed as has been reported previously in certain other porphyrins [10].

DFWM signals (ns data) as a function of input intensity shows a slope \( \sim 2.6 \) at lower intensities and \( \sim 5 \) at higher intensities for most of these samples. For example AuTTP gives a value of \( 10 \times 10^{-12} \) esu at an input of \( \sim 2 \) mw (corresponding to a peak power of 100 MW/cm\(^2\)) and a value of \( \sim 30 \times 10^{-12} \) esu at an input of 6 mw (corresponding to a peak intensity at the focus \( \sim 300 \) MW/cm\(^2\)) for the same sample concentration. As the porphyrins exhibit a strong ESA from both \( S_1 \) and \( T_1 \) states, the enhancement in \( \chi^3 \) at higher intensities is attributed to higher excited states [3]. Porphyrins, therefore exhibit \( \gamma \) predominantly due to the \( S_n \) and \( T_n \) states at higher intensities with contribution from the \( S_1 \) and \( T_1 \) states. This is similar to that of the pump-probe experiments [1].

Larger ESA cross-sections are expected depending on the contribution of the triplet and in turn the intersystem crossing rates. Shorter lifetimes for \( S_1 \) reduces the effect of excited state absorption from \( S_1 \) to \( S_n \). Since \( T_1 \) state has much larger lifetime compared to \( S_1 \), lower threshold limits for the optical limiting can be achieved with larger intersystem crossing rate from \( S_1 \) to \( T_1 \). Environment around the molecule is expected to play an important role in the modification of the intersystem crossing rates [10]. With this goal we have undertaken the study of the effect of solvent.
ZnmpTBP (TBP is chosen for the solvent effects as it has been reported well in the literature) is dissolved in six different solvents. ns and ps second data are collected for TBP dissolved in spectral grade solvents, THF, pyridine, DCM, Toluene, Acetone and Toluene +1% pyridine. The ps spectra are identical for all the solvents indicating that the contribution for RSA behavior is predominantly from the ESA coefficient, $\sigma_1$, from $S_1$ to $S_0$ levels and TPA coefficient, $\beta$, from $S_0$ to $S_n$ levels. The experiment carried out with ns laser shows a drastic difference with the different solvents. A particular broadening of the wings of the Z-scan can be seen for Toluene and the DCM. From the theoretical fit of the observed data, we infer various parameters involved for RSA behavior. $\sigma_2$ is the ESA coefficient from $T_1$ to $T_n$ levels. The results summarized in Table 1 give values of $\sigma_1$, $\sigma_2$, $\beta$ and $\tau_{\text{ISC}}$ for ns and ps pulses. $\sigma_2$, $\beta$ and $\tau_{\text{ISC}}$ for the ps data are taken as $0$, $2.67 \times 10^{-8}$ cm/w and $2000$ ps respectively. Ground state absorption cross-section $\sigma_0$ given as $\lambda/N_0$ is around $10^{-18}$ cm$^2$.

Z-scan widths with nano-second excitation shows the contribution from the triplet through a variation in the intersystem crossing rates from $S_1$ to $T_1$. The theoretical fits show a reduced value for the intersystem crossing time from nearly $2000$ ps for THF to $50$ ps for the DCM case [11]. Fig. 3 shows the curves for ZnmpTBP in THF and DCM for both ps and ns excitations.

As ISC rate play a very important role, we made a study of the heavy atom effect on the porphyrin molecule. As can be seen from the data in Fig. 4, we observe a very strong RSA behavior in [(TTP)$^{P(\pi)Cl_2}$] in comparison with [(TTP)$^{P(\pi)(OH)_2}$]. Degenerate four wave mixing measurements and Z-scan data recorded on these materials show an enhancement in the $\langle \gamma \rangle$ by one order and also much larger RSA, the valley reaching $0.2$ in the normalized transmittance.

![Fig. 3. Z-scan curves for the ZnmpTBP in THF and DCM for ns and ps excitations.](image)

<table>
<thead>
<tr>
<th>Solvent</th>
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<th>6 ns experiment</th>
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<tr>
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<tr>
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<td>Pyridine</td>
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![Fig. 4. Open aperture Z-scan transmittance for [(TTP)$^{P(\pi)(OH)_2}$], CdTTP and [(TTP)$^{P(\pi)Cl_2}$], recorded with 6 ns laser, 532 nm.](image)
Fig. 5. Optical limiting curves for CuTTP, [(TTP)P(V)Cl2]+, [(TTP)P(V)(OH)2]+, [(TTP)P(OPh)2]+ recorded with 6 ns laser, 532 nm.

4. Conclusions

From the widths and ratios of the two peaks observed with DFWM-IL, we estimate three response times ($\tau_{S_n T_n}, \tau_{S_1}, \tau_{S_1 V}$) for these molecules. The large nonlinearity exhibited by these molecules when pumped by ns pulses is attributed to strong ESA/RSA and partly due to the thermal contributions. DCM and Pyridine as solvents shows fastest intersystem crossing times from $S_1$ to $T_1$. Optical limiting studies with different central metal atoms and different axial substitutions shows lowest threshold for [(TTP)P(V)Cl2]+.

Acknowledgement

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References