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Excited state dynamics in tetra tolyl porphyrins studied using degenerate four wave mixing with incoherent light and ps pulses

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Abstract

We present our experimental results on the excited state dynamics in several tetra tolyl porphyrins (with different central metal-ions) studied using degenerate four wave mixing with nanosecond incoherent light (DFWM-IL) and picosecond time-resolved four wave mixing (DFWM-PS). Incoherent light studies indicate three lifetimes, which have been attributed to different excited states. The shortest component with a decay constant of <170 fs is due to the vibrational relaxation in the higher excited singlet states $S_n(T_2)$, 3–6 ps component is due to the vibrational relaxation of the Franck-Condon states in $S_1(\tau_{vib})$, and the long component of 20–100 ps is due to the population relaxation (T_1) from S_1 to S_0 . The population relaxation times obtained from time-resolved DFWM studies using a picosecond laser substantiates these results. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The last decade has witnessed an extensive research activity in the nonlinear optical, photo-physical and photochemical properties of organic materials in general and metalloporphyrins/related compounds in particular. These are found to have

strong nonlinearities and fast response times, the desired criteria for making useful photonic devices. Study of the nonlinearity and dynamics associated with excited states of such molecules is important from a fundamental as well as technological point of view and there are several reports on such measurements [1–6]. The measured values of cubic hyperpolarizabilities are as high as 10^{-29} esu [7] with response times as fast as a few hundreds of femtoseconds [8–10]. Methods for the study of excited state solvation and vibrational relaxation dynamics, fluorescence from high lying states

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in a variety of metalloporphyrins (and similar molecules) has included transient absorption spectroscopy, pump–probe studies and Raman spectroscopy [11–32]. Different relaxation pathways as well as the effects of solvent, temperature and metal-ions have been extensively investigated using picosecond (ps) and femtosecond (fs) laser pulses.

Recently, we synthesized tetra tolyl porphyrins (TTP) with 16 different metal-ions in the ring and studied their third-order optical nonlinearity and nonlinear absorption using the techniques of degenerate four wave mixing (DFWM) and Z-scan [6]. Our studies, using both ns and ps excitations, showed that these molecules exhibit large nonlinear absorption and a strong refractive nonlinearity. In this paper, we extend these studies to the excited state dynamics in these molecules. We use two different experimental methods for DFWM, namely nanosecond incoherent light spectroscopy (DFWM-IL) using a broad band dye laser, and picosecond time-resolved spectroscopy (DFWM-PS) using a frequency-doubled Nd:YAG laser. Incoherent studies are carried out for all the 17 samples whereas, due to source constraints, only eight samples are studied using the ps pulses. The use of incoherent light spectroscopy for the measurement of ultrafast relaxation times is well established [33–36]. For example, our previous experiments in porphyrins and C_{60} using incoherent light yielded ps resolution using ns input pulses, and lifetimes of high lying excited states in these molecules could be estimated [5,37,38]. In this paper, we report the measurement of ultrafast excited state relaxation times in the TTP compounds from DFWM-IL experiments. In addition, time-resolved DFWM-PS experiments have been performed using 35 ps pulses for the measurement of population relaxation time (T_1) in the samples, and the results are compared with those obtained from incoherent light experiments.

2. Experiment

All the samples are dissolved in highly purified spectroscopic grade chloroform and the absorption spectra are recorded using an UV–VIS

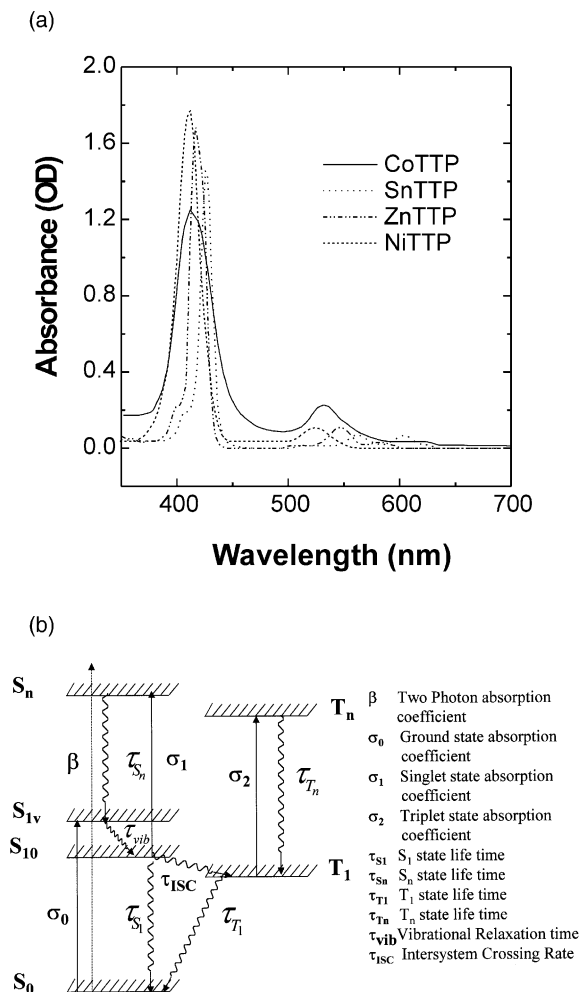


Fig. 1. (a) Absorption spectra of the representative compounds, dissolved in chloroform, used in the present study. (b) A general energy level (six-level) diagram to explain the observed signals in DFWM-IL and DFWM-PS experiments. Solid line indicates radiative decay and curved line indicates nonradiative decay (additional CT states can also exist for some porphyrins which is not shown).

recording spectrometer (model UV-160 A, Shimadzu). Fig. 1(a) shows the UV–VIS spectra for some representative samples used in this study. All of them show the typical linear absorption features of metalloporphyrins, namely the low energy Q band(s) and the high energy B (Soret) band. All experiments are carried out in samples of 10^{-4} – 10^{-5} M concentrations corresponding to an absorbance of <0.3 . Fig. 1(b) shows the energy level

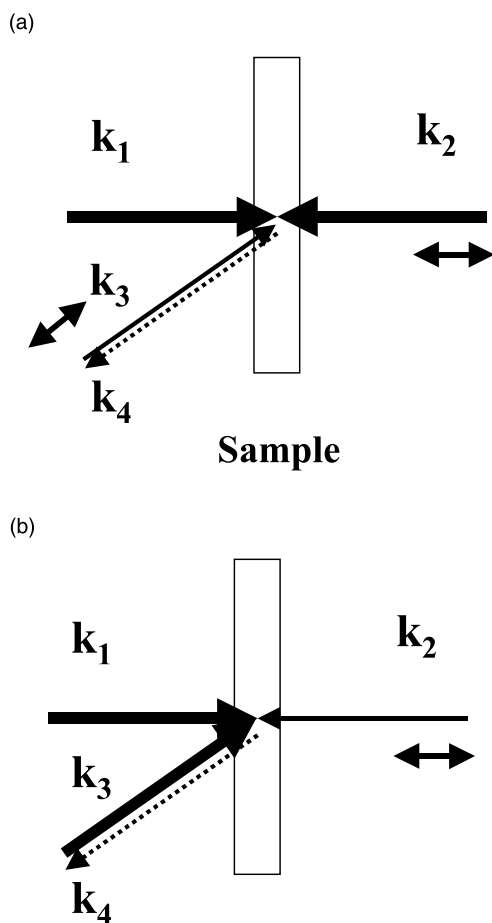


Fig. 2. Schematic of the time-resolved DFWM setup. (a) Beam 3 (thin line) is the probe for incoherent measurements using ns pulses and (b) Beam 2 (thin line) is the probe for the ps measurements. The ratio of intensities of the beams 1, 2 and 3 are 1:1:0.2 and 1:0.2:1 for (a) and (b) respectively.

diagram of a typical porphyrin and the relevant decay mechanisms.

Essential details of our experimental setup [37, 38] used for DFWM-IL are as follows. Schematic of the setup is shown in Fig. 2. An Nd:YAG laser (6 ns, 100 mJ in 532 nm, 10 Hz) is used for pumping a home built Rhodamine B dye laser. The dye laser output peaks at 594 nm and has a line width (FWHM) of ~ 7.5 nm corresponding to a correlation time (τ_c) of 160–170 fs. Three beams of equal intensity are derived from this beam. Beam 1 (k_1) and beam 2 (k_2) are designated as pumps and beam 3 (k_3) is the probe (Fig. 2(a)). The forward

pump and probe beams make an angle of 10° with each other. All three beams are focused down to a beam waist of about $100 \mu\text{m}$ and intersect in the sample kept in a 1 mm cuvette. The peak intensities reached are about $300\text{--}500 \text{ MW/cm}^2$. Beam 1 is fixed, whereas beams 2 and 3 pass through variable optical delays. The resolution of each delay line is $5 \mu\text{m}$, which corresponds to a temporal resolution of 33 fs (with a retro-reflector). The PC signal (in $-k_3$ direction) is recorded as a function of τ (delay between beams 1 and 3) for different values of δ (delay between beams 1 and 2). An optional half wave plate (HWP) is used to rotate the state of polarization of any given beam as desired. Data acquisition part consists of a fast photodiode, lock-in amplifier, an ADC card and a PC.

The source for DFWM-PS is a frequency-doubled, hybrid mode-locked Nd:YAG laser giving 532 nm, 35 ps pulses at a 10 Hz repetition rate. Beam geometry is the same as that for DFWM-IL. In this case beams 1 and 2 are focused using a 2 m lens and beam 3 is focused using a 1 m lens. PC signal is recorded by delaying the beam 2 with the other two beams at zero delay. Hence beams 1 (k_1) and 3 (k_3) are designated as pumps and beam 2 (k_2) will be the probe now (Fig. 2(b)). The sample is kept away from the focus so that the peak intensities are limited to about $200\text{--}400 \text{ MW/cm}^2$. The angle between the beams 1 and 3 is about 5° . The delay line in the probe beam is microprocessor controlled and has a maximum resolution of $1.3 \mu\text{m}$ corresponding to a temporal resolution of 8.7 fs (with a retro-reflector). The DFWM signal picked up by a fast photodiode is fed to a digital storage oscilloscope where it is averaged over several successive pulses before recording. Appropriate neutral density filters are used to attenuate the probe beam and the PC signal to avoid saturation of the photodiode (PD). The ratio of intensities of the beams 1, 2 and 3 are 1:1:0.2 and 1:0.2:1 for DFWM-IL and DFWM-PS measurements respectively.

3. Results and discussion

In an earlier work, we had reported certain aspects of the excited state dynamics of three

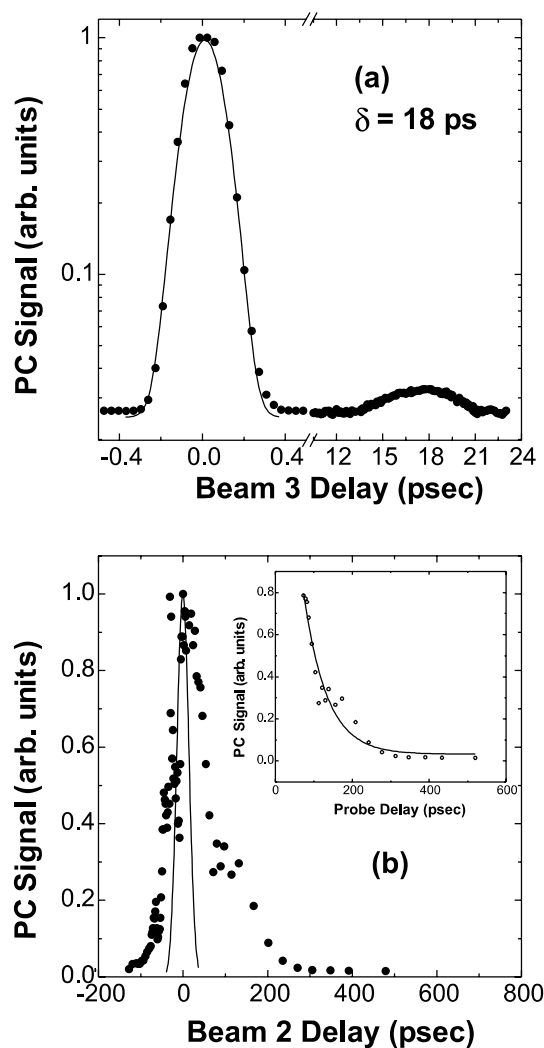


Fig. 3. (a) DFWM-IL signal for AuTTP with $\delta = 18.0$ ps. Solid line is the auto-correlation curve in the sample RhB (for all samples) (b) DFWM-PS signal for the same sample. Solid line is the auto-correlation curve in CS_2 (for all samples). Inset shows the fit to the decay part of the signal.

compounds used in this study, namely TTP, CoTTP, and NiTTP [5]. Here we extend these DFWM-IL studies to other related molecules, and besides, seek corroboration of the results thus obtained by performing DFWM-PS experiments. Figs. 3(a)–10(a) show the typical results obtained from DFWM-IL. A double-peak structure (viz. a sharp, intense peak and a broad, weak hump) has

been observed in all samples. It had been already shown by Okamoto [35] that the ratio of these peaks leads to the population relaxation time ($T_1 = \text{Ratio of the intensity of two peaks} \times \tau_c$) and we had shown earlier [5,37,38] that the widths of the peaks give information on (a) the vibrational relaxation time (T_2) of the higher excited singlet states S_n , (b) the vibrational relaxation time (τ_{vib}) of the Franck–Condon states of the first excited singlet ($S_{1v}-S_{10}$) (Fig. 1(b)).

The calculated lifetimes are summarized in Table 1. For the ns studies, since the signal involves the contribution from the triplet states (intersystem crossing is \sim few hundred ps) one has to consider the relaxation times of the T_1 state and the vibrational relaxation times in the higher excited states (T_n and T_1) as well. As the energy level structure of the singlets and the triplets are similar, the relaxation times within each manifold are also expected to be similar. The contribution for the first peak, due to the coherence of beams 1 and 3, would therefore come from the vibrational relaxation in the high-lying singlet and triplet states, which is known to be in the fs time scale. Similarly, we expect the indistinguishability of the contribution from the first excited singlet and the triplet manifolds. However the population relaxation of the singlet S_1 level and not that of the triplet T_1 level will dominate the ratio between the two peaks. This is because the triplet state has a very long lifetime and in such a situation its contribution to the ratio of the two peaks is negligible. The ratio of the two peaks is therefore attributed purely to the population relaxation of the singlet S_1 state. In S_n states the vibrational levels are closely spaced leading to a faster relaxation indicated by the sharp width of the first peak. All vibrational relaxation times in the S_n levels are found to be less than 170 fs, the vibrational relaxation times of the S_1 levels are about 3–6 ps and the population relaxation times of S_1 to S_0 are in the range of 20–70 ps. Further such fast population relaxation may be expected since all these porphyrins are either nonfluorescent or very weakly fluorescent rendering the de-excitations generally nonradiative. There are also several reports on vibrational relaxation measurements yielding, approximately, the same values in differ-

Table 1

The lifetimes of different excited states calculated using DFWM-IL and 35 ps pulses

Sample	Dephasing time of the S_n state (T_2) in fs (DFWM-IL)	Vibrational relaxation in S_1 state (τ_{vib}) in ps (DFWM-IL)	Population relaxation time (T_1) in ps (DFWM-IL)	Population relaxation time (T_1) in ps (DFWM-PS)
H ₂ TTP	<170	5.40 ± 1.10	40.0 ± 8.00	–
[P(TTP)(OH) ₂] ⁺	<170	3.50 ± 0.70	27.0 ± 5.40	–
V(O)TTP	<170	5.30 ± 1.10	22.0 ± 4.40	–
Cr(TTP)Cl	<170	5.10 ± 1.00	30.6 ± 6.10	–
Mn(TTP)Cl	<170	4.90 ± 1.00	32.6 ± 6.60	–
Fe(TTP)Cl	<170	5.10 ± 1.00	54.0 ± 10.8	150.0 ± 30.0
CoTTP	<170	5.60 ± 1.10	37.0 ± 7.40	109.0 ± 22.0
NiTTP	<170	5.00 ± 1.00	45.0 ± 9.00	40.0 ± 8.00
CuTTP	<170	4.50 ± 0.90	37.0 ± 7.40	535.0 ± 107.0
ZnTTP	<170	5.50 ± 1.10	49.0 ± 9.80	55.0 ± 11.0
Ge(TTP)(OH) ₂	<170	5.70 ± 1.10	30.0 ± 6.00	–
Ag(TTP)Cl	<170	4.20 ± 0.80	60.0 ± 12.0	46.0 ± 9.00
CdTTP	<170	5.70 ± 1.10	40.0 ± 8.00	–
In(TTP)(OH)	<170	3.80 ± 0.80	21.0 ± 4.20	–
Sn(TTP)(OH) ₂	<170	5.20 ± 1.00	51.0 ± 10.2	74.0 ± 15.0
Au(TTP)Cl	<170	4.10 ± 0.80	62.0 ± 12.4	73.0 ± 15.0
HgTTP	<170	5.40 ± 1.10	37.6 ± 0.75	–

ent classes of porphyrins [10,14,29,31] corroborating our present results.

Time-resolved studies using 35 ps pulses at 532 nm have been performed on the samples AuTTP, AgTTP, CoTTP, CuTTP, FeTTP, NiTTP, SnTTP, and ZnTTP. The signal obtained for different TTPs are shown in Figs. 3(b)–10(b). Solid dots are the experimental data for the samples and the solid line is for the reference sample CS₂. Since the two orientational relaxation times of CS₂ are 200 fs and 2 ps [34], which are much smaller than the 35 ps, half-width of the pump pulse, the CS₂ signal serves as an auto-correlation trace of the pump pulse. On the other hand, for all the TTP samples there is an obvious slower component in the decay. The decays are fitted to an exponential, from which the T_1 values are estimated. These values are summarized in Table 1. Temporal evolution of the signal has been checked for all samples at longer time delays (>400 ps) also, and no thermal contribution was observed, as has been reported previously in certain other porphyrins (e.g. basket handle porphyrins) [4]. All the values are quoted with an experimental error of 20% arising from the calibration of the neutral density filters, movement of the stepper motor, and the fitting procedures. Observed T_1 values for different samples show

faster population relaxation times if the absorption extends to lower energies below the excitation energy of 532 nm. Ni, Sn, and Zn TTPs show very long T_1 values as 532 nm falls either at the lower edge of the absorption peak or that the absorption is weaker for wavelengths longer than 532 nm.

Fig. 3(a) and (b) shows the signals obtained for AuTTP. DFWM-IL studies yield a relaxation time of 4.10 ± 0.82 ps for the S_{1v} vibrational state and 62.0 ± 12.4 ps for T_1 , whereas DFWM-PS studies give a very close value of 73.0 ± 15.0 ps for T_1 . For Zn porphyrin Kobayashi et al. [39] have observed a long excited state lifetime of ~2.6 ns. However our results depicted in Fig. 4(a) and (b) indicate lifetimes of 49 ± 10 and 55 ± 11 ps which are in excellent agreement with each other. Longer lifetime of 2.6 ns may not be observed in our recordings as the ratio of the two peaks would be ~15000:1, rendering the second peak below the noise level. Our results, though supports the presence of a fast decaying component, does not rule out the presence of the longer component of S_1 state lifetime. Fig. 5(a) and (b) shows the results for the sample SnTTP. The T_1 values obtained are 51 ± 10.2 and 74 ± 14.8 ps respectively. In the case of FeTTP (Fig. 6(a) and (b)) the values obtained are 54 ± 11 and 150 ± 30 ps respectively which do

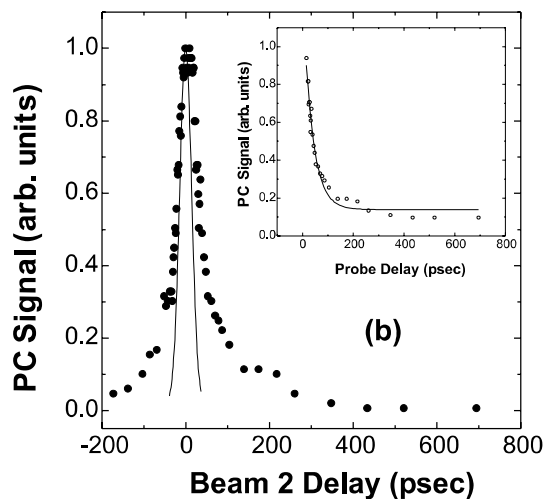
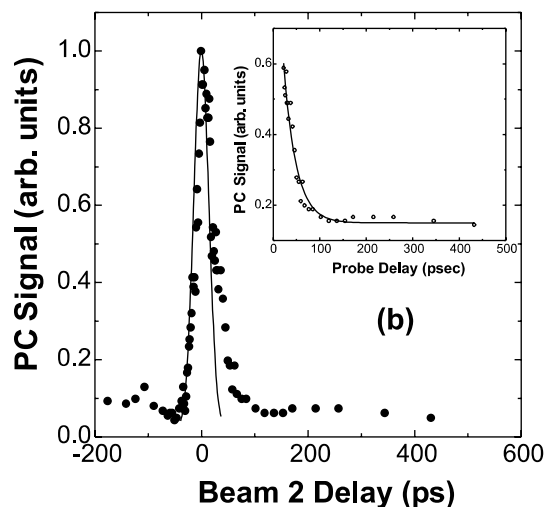
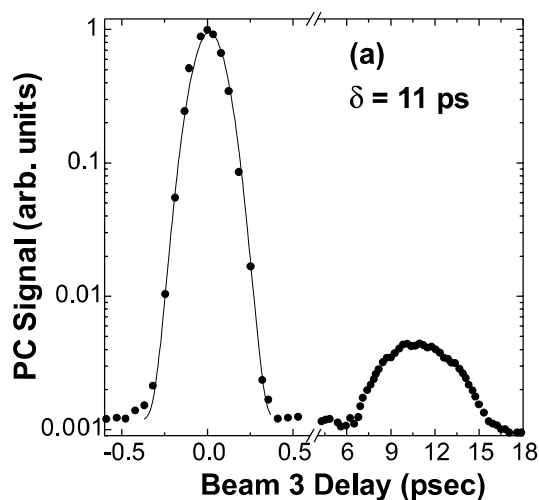
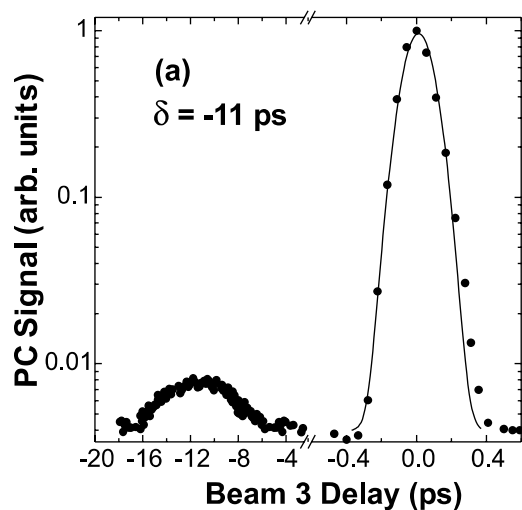


Fig. 4. (a) DFWM-IL signal for ZnTTP with $\delta = -11.0$ ps and (b) DFWM-PS signal.

Fig. 5. (a) DFWM-IL signal for SnTTP with $\delta = 11.0$ ps and (b) DFWM-PS signal.

not match with each other. One of the previous studies in iron porphyrins has been by Cornelius et al. [40] who observed a 100 ps transient in the relaxation, using a broadband ps continuum probe.

According to Kobayashi et al. [41] for Ag porphyrin, ps excitation to the 2S_1 state results in energy relaxation to 2T_1 state within 8 ps, which is followed by equilibrium between 2T_1 and 4T_1 with a time constant of ~ 12 ps. From our incoherent light measurements T_1 is found to be 60 ± 12 ps for AgTTP (Fig. 7a), and the corresponding value

obtained from time-resolved measurements is 46 ± 9 ps (Fig. 7b). Chirvonyl et al. [42] have observed transient species lifetimes of 250 ± 50 and 15 ± 8 ps respectively for Ag(II) and Ni(II) porphyrins respectively from flash photolysis experiments.

From ps transient absorption spectroscopy of donor-appended Co(II) porphyrins, Loppnow et al. [43] have estimated their ground state recovery time to be less than 50 ps. Tait et al. [44] also have reported similar studies of Co^{II} and Co^{III} octaethylporphyrins (in toluene) and they observe two

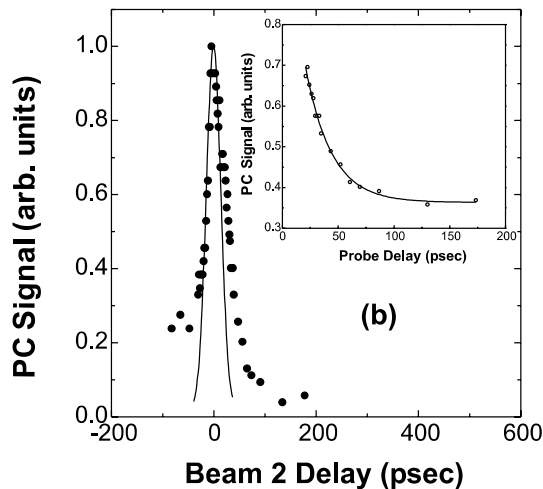
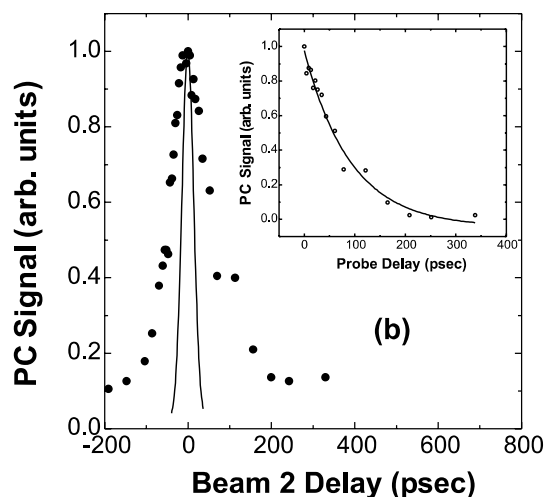
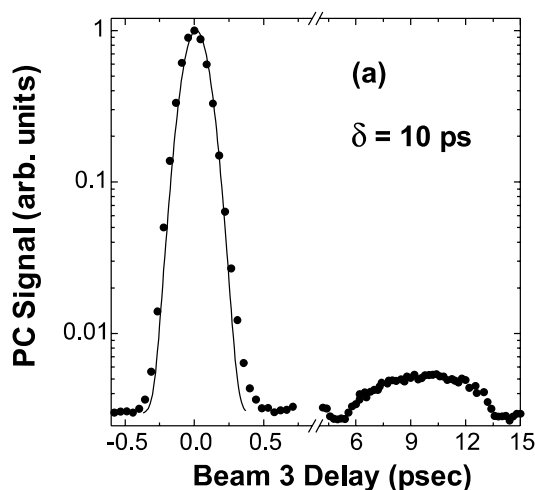
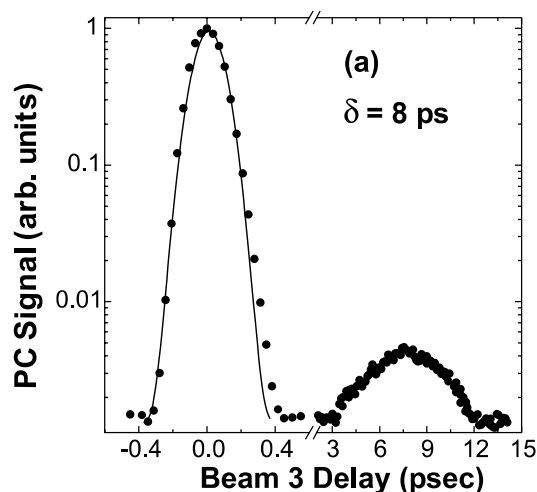


Fig. 6. (a) DFWM-IL signal for FeTTP with $\delta = 8.0$ ps and (b) DFWM-PS signal.

Fig. 7. (a) DFWM-IL signal for AgTTP with $\delta = 10.0$ ps and (b) DFWM-PS signal.

distinct time scales of transient absorption decay with different spectral signatures. In Co^{II} porphyrin the mixing of the state, which is due to the unpaired d electron with the normal singlet and triplet states produces doublets and quartets. The ground state becomes a doublet; the lowest excited states become the singdoublet [$^2\text{Q}(\pi, \pi^*)$], the tripdoublet [$^2\text{T}(\pi, \pi^*)$], and tripquartet [$^4\text{T}(\pi, \pi^*)$]. The two lifetimes of the former were estimated to be <10 and $10\text{--}20$ ps, which were attributed to the deactivation of the $^2\text{T}(\pi, \pi^*)$ and the charge transfer (CT) state. The lifetime for Co^{III} sample

was found to be ~ 5 ns. Femtosecond dynamics in $\text{Co}(\text{II})\text{TTP}$ were reported by Yu et al. in solvents of varying polarity and structure [8]. They have observed the relaxation time-scales to be 0.2, 2, and 20–200 ps in different solvents. The longest component is found to be different for each of the solvent benzene (16 ps), dichloroethane (23 ps), pyridine (40 ps) and piperidine (190 ps). This effect is attributed to the presence of a charge transfer state. Our results, shown in Fig. 8(a) and (b), give T_1 values of 37 ± 7.4 ps from DFWM-IL and 109 ± 22 ps from DFWM-PS studies. We recorded

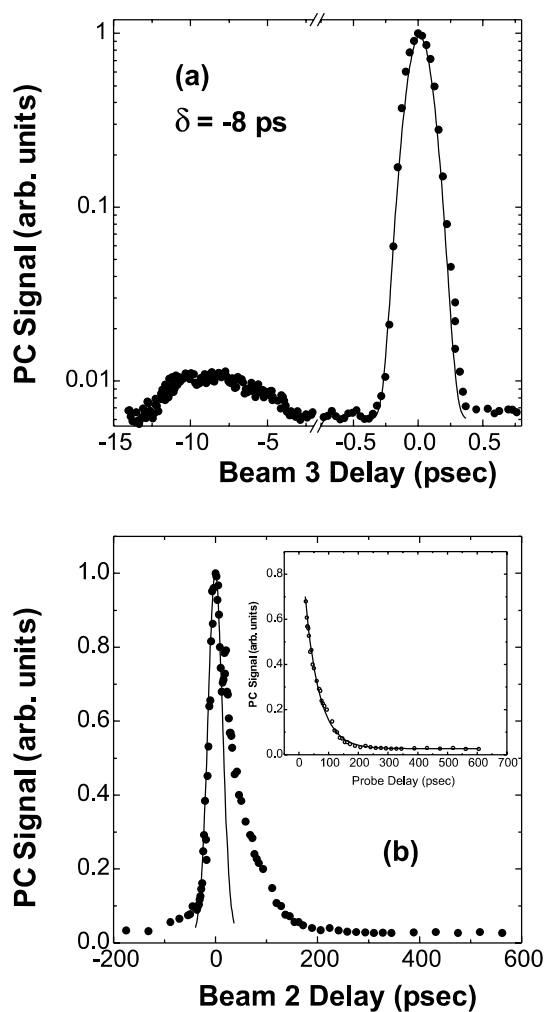


Fig. 8. (a) DFWM-IL signal for CoTTP with $\delta = -8.0$ ps and (b) DFWM-PS signal.

the DFWM-IL signal with two different solvents (chloroform, which is a nonpolar solvent, and piperidine, which is a polar solvent), but observed no change in the signal structure and the lifetimes measured, within the limits of experimental error. Thus the involvement of a CT state in the relaxation pathway could not be inferred from our measurements.

Hilinski et al. [45] have observed that the ground state recovery time of excited Cu(II) protoporphyrins increases rapidly from highly polar solvents like pyridine (~ 45 ps) to nonpolar sol-

vents like benzene (~ 400 ps). They indicate the possibility of a CT state being involved which is possible with axial coordination of more polar solvents. For Cu(II) porphyrin, Kobayashi et al. [41] have observed that after ps excitation a Franck-Condon state of 2S_1 is populated which decays into the 2T_1 state within 8 ps. This state relaxes with time constant of ~ 450 ps to the 2T_1 state and 4T_1 equilibrium state from which phosphorescence is emitted. Another report is from Yan and Holten [46] who found the lifetime of photoexcited CuTTP to be even longer, as high as 30–40 ns, and attributed it to the CT state. Jeoung et al. [47] reports the relaxation dynamics of the excited states to be completed within 100 ps for a water-soluble Cu porphyrin. The different time scales observed were 100 fs, 1.2, 4 and 25 ps and they are attributed to the split triplet states and a new quenched state. Our measurements for CuTTP yielded a τ_{vib} of 4.5 ± 0.9 ps and T_1 of 37 ± 7.4 ps from DFWM-IL, and T_1 of 535 ± 107 ps from DFWM-PS (Fig. 9(a) and (b)). Again the effect of solvent polarity could not be established from DFWM-IL experiments. The 535 ps lifetime obtained by DFWM-PS is in good agreement with that reported by Hilinski et al. However, the present DFWM-IL setup is not ideally suited for measuring large lifetimes of this order. This is because T_1 is calculated from the ratio of the peaks ($T_1 = \text{ratio} \times \tau_c$), and to obtain a lifetime of 500 ps with a τ_c of 160–170 fs the ratio has to be as high as 3000 which is beyond the dynamic range of our experiment. If one uses a dye that has a correlation time of about 50–100 ps (or use a grating in the dye laser cavity to reduce line width) there is a possibility of measuring the 500 ps component. Moreover the excitation at 532 leads the population to S_1 state primarily whereas the excitation at 600 nm leads the population directly to the S_n states through TPA. It is well understood that the effect of unpaired electrons in Cu is to split the singlet S_1 and the triplet T_1 thereby creating new pathways of relaxation (which includes the presence of a CT state or metal state). Therefore the decay mechanism could be different in these two cases and each of them could be detecting different mechanism. More detailed studies are necessary, which are underway, to resolve this discrepancy.

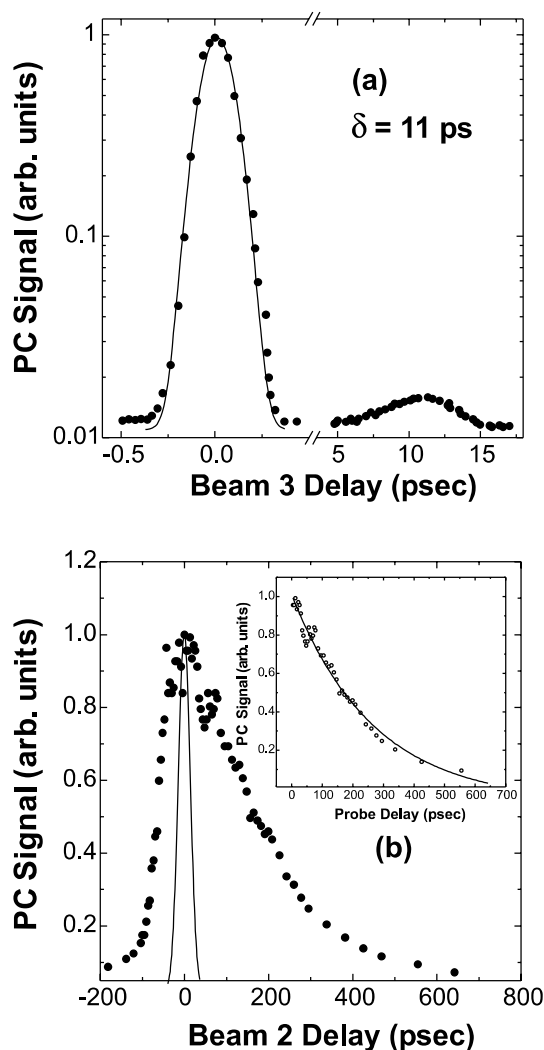


Fig. 9. (a) DFWM-IL signal for CuTTP with $\delta = 11.0$ ps and (b) DFWM-PS signal.

Kim et al. [48] have previously investigated the picosecond photophysics and photochemistry of Ni(II) porphyrin. While studying its conformational dynamics using time-resolved Raman and absorption spectroscopy, Courtney et al. [49] have observed relaxation processes on a ps time scale. In addition, the femtosecond transient absorption studies of Eom et al. [50] have yielded lifetimes of 1 and 250 ps for NiTTP in toluene. Fig. 10(a) and (b) shows our results for NiTTP giving T_1 values of 45 ± 9 and 30 ± 6 ps, which are in good agree-

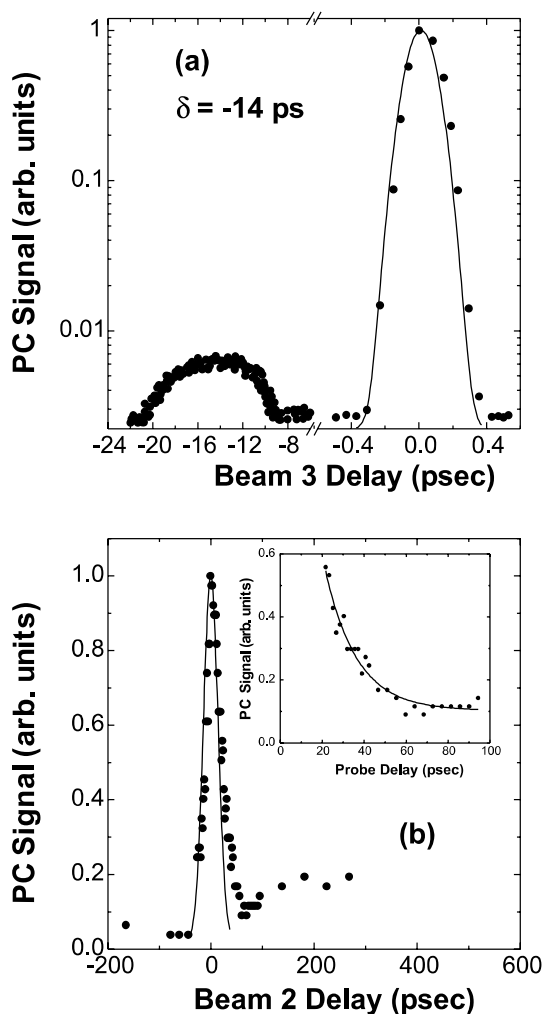


Fig. 10. (a) DFWM-IL signal for NiTTP with $\delta = -14.0$ ps and (b) DFWM-PS signal.

ment with each other and also with the reported values of Kobayashi et al. [39]. According to Drain et al. [51], the metal excited state of NiT(*t*-Bu)P exhibits a lifetime that is critically dependent on the solvent dielectric properties and temperature. He found that the lifetime varied from 2 ps in highly polar solvents to about 50 ns in nonpolar solvents, and increased to several microseconds in both kinds of solvents as the temperature was reduced to 80 K.

Brodard and Vauthey [52] reports the ground state recovery time of ~ 250 ps for NiTPP, dissolved in toluene, THF, DCM, and DCE, using

various transient grating techniques. Temperature dependence has been investigated by Gentemann et al. [17] also, who reported that H₂T (alkyl) porphyrins have ultrashort lifetimes of 10–50 ps at 296 K, which slow down to 10–15 ns at 78 K. According to them it is the ability of the nonplanar ruffled porphyrins to undergo additional structural deformations in the excited state that is responsible for the dramatically enhanced rates of internal conversion, which leads to this slowing down. Our results indicate lifetimes of 40.00 ± 8.00 ps in H₂TTP, with incoherent light.

We have brought a very generalized six-level model for all the porphyrins studied. Our initial theoretical/numerical results suggest that this model suits very well for explaining the different widths of the peaks in terms of the vibrational relaxation in excited states [53] and these will be published at a later stage.

4. Conclusions

In conclusion, we have investigated the excited state dynamics in several TTP using the DFWM-IL and DFWM-PS techniques. Our studies with incoherent light show that there are three response times for the photoexcited molecules (derived from the widths and the ratio of the two peaks in the DFWM signal). These are explained using a typical four-level model (S_0 , S_{10} , S_{1v} , and S_n). The fastest response (<170 fs), limited by the correlation time, is attributed to the vibrational relaxation in S_n state, the slower component (~3–6 ps) is attributed to the S_{1v-10} relaxation and the slowest component (~20–70 ps) is attributed to the population relaxation. The population relaxation time for each of these molecules depends on various factors like the oscillator strengths, the density of states of vibronic energy levels, energy gap between the interacting electronic states, and vibronic overlapping (Frank–Condon factor) etc. T_1 values of these compounds obtained with 532 nm excitation appear to be decreasing with the increased absorption tail for energies lower than 532 nm. The values obtained by both the measurements (DFWM-IL and DFWM-PS) are in excellent agreement, within experimental errors, for five

of the samples (Ni, Zn, Ag, Au, Sn TTPs). One major disadvantage of this present DFWM-IL setup is the measurement of population relaxation times much longer than the correlation time. This could be overcome by using incoherent light with large correlation time (~50–100 ps). Thus using incoherent light with different correlation times one can probe the shorter time scales (phase relaxation) and the longer time scales (population relaxation) as well. With their high nonlinearity, strong nonlinear absorption and ultrafast response times, these molecules prove to be attractive candidates for photonic applications.

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