Ultrafast relaxation times of metalloporphyrins by time-resolved degenerate four-wave mixing with incoherent light

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We present experimental results on the measurement of the population-relaxation times of the excited states of some metalloporphyrins such as zinc meso-tetra-phenylporphyrin (ZnmTPP), zinc meso-tetra (*p*-methoxyphenyl) tetrabenzporphyrin (ZnmpTBP), tetratollylporphyrin (TTP), cobalt tetratollylporphyrin (CoTTP) and nickel tetratollylporphyrin (NiTTP) with time-resolved degenerate four-wave mixing with the incoherent emission of a nanosecond pumped-dye laser. The experiments are carried out in the counterpropagating geometry ($\mathbf{k}_4 = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$), where $\mathbf{k}_1$ and $\mathbf{k}_2$ are counterpropagating to one another and $\mathbf{k}_3$ is at angle θ ($<90°$ with respect to $\mathbf{k}_1$). Excited-state and ground-state relaxation times are calculated based on the theoretical formalism developed by Hiromi Okamoto [J. Opt. Soc. Am. B, **10**, 2353, 1993]. The signals are recorded by delaying the probe beam ($\mathbf{k}_3$) for different fixed delays of the backward pump beam ($\mathbf{k}_2$). We observe strong signal at a second peak owing to the coherence of beams $\mathbf{k}_2$ and $\mathbf{k}_3$ for samples exhibiting excited-state absorption and a narrow peak corresponding to the coherence of beams $\mathbf{k}_1$ and $\mathbf{k}_3$ for samples that do not exhibit excited-state or reverse-saturable absorption. The nonlinear absorption is studied with the Z-scan technique. From the experimental data, we estimate the relaxation times of excited states. © 1997 Optical Society of America [S0740-3224(97)00210-5]

1. INTRODUCTION

Relaxation processes associated with excited states of materials are very important in an understanding of the dynamic behavior of light–matter interaction. Most organic materials, because of their complex structure, have many vibrational and rotational bands leading to very fast nonradiative transitions within each electronic band. These relaxations normally occur in the picosecond and the femtosecond domain. To probe these, one requires a femtosecond laser source. Different spectroscopic techniques have been developed to derive the fast relaxation times without the use of a femtosecond laser.[1] Morita and Yajima[2] in 1984 proposed a new technique in which an incoherent light source with ($\tau_c = 1/\Delta\nu$) was used. This technique has been applied to the studies of both dephasing times in the femtosecond regime and longitudinal relaxation times in the picosecond regime. A temporally incoherent light source has a short coherence time, and it thus appears as a single pulse of width τ_c in autocorrelation measurements. The time resolution in this case is determined by τ_c. Advantages of this technique are that it is easier to construct and to operate a laser with long pulses rather than a picosecond or femtosecond system and both broad tunability and time resolution are not affected by dispersion. Theoretical studies developed by Morita and Yajima[2] are based on the three-beam degenerate four-wave mixing (DFWM) technique. Two beams with wave vectors $\mathbf{k}_1$ and $\mathbf{k}_3$ are focused on the sample at an angle θ, and the third beam $\mathbf{k}_2$ is made to counterpropagate with respect to $\mathbf{k}_1$. The delay between the $\mathbf{k}_1$ and the $\mathbf{k}_2$ beams and that between the $\mathbf{k}_1$ and the $\mathbf{k}_3$ beams are denoted as δ and τ, respectively. The phase-conjugate signal $\mathbf{k}_4$ propagating in the $-\mathbf{k}_3$ direction is detected. Kobayashi *et al.*[3] derived a generalized formula for the signal $\mathbf{k}_4$ when one of the beams is delayed with respect to the other beams. Hiromi Okamoto[4] extended these studies by looking at systems having different excited- and ground-state relaxation times and showed that a second peak appears along with the main coherent peak. He also showed that the ratio of the two peaks is related to the lifetime of the ground state. We applied the technique of four-wave mixing with incoherent light to the study of porphyrins as there is considerable interest in these materials[5] with regard to their optical nonlinearity and excited-state dynamics. They participate in a variety of ultrafast photophysical and biophysical processes. They serve as functional groups in a wide variety of biological systems, such as chlorophyll, hemeproteins, and vitamin B_{12}. These compounds are readily accessible, and they can be tailored

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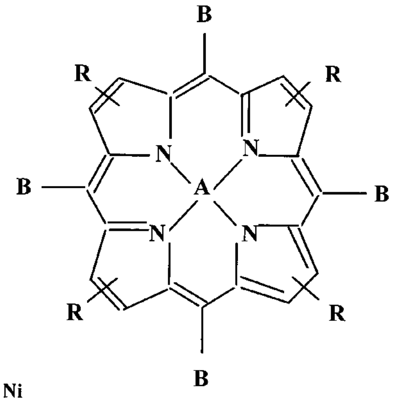
simply by changing the central metal and the nature of the organic substituents in the molecule. By tuning the electronic transitions in the visible region, one can effectively use them in the fabrication of optoelectronic devices.[5] Porphyrins are attractive because of their large nonlinearity[6] (~10^{-8} esu), their sharp absorption bands in the visible and the near IR, which can be used for resonance enhancement of $\chi^{(3)}$, and their easy derivation along with excellent thermal and chemical stabilities. Furthermore, these compounds have the potential for various applications, such as optical limiting,[7] mirrorless optical bistability,[8] organic semiconductors,[9] magnetic-resonance imaging,[10] catalysis of organic reactions, and photodynamic therapy,[11] to name a few. Organic materials with π-electron delocalization are studied for possible device applications in optical communication and optical data processing.[12,13] In this study, we record DFWM signals by delaying $\mathbf{k}_3$ for different fixed delays of $\mathbf{k}_2$ with respect to $\mathbf{k}_1$. We observe different linewidths as compared with Okamoto's results, and these are explained in terms of the relaxation times of different excited states.

2. EXPERIMENTAL DETAILS

The dye laser used in the study consists of an oscillator and a single-stage amplifier. The laser medium, rhodamine B in methanol, is pumped by the second harmonic of a Nd:YAG (Continuum, USA, 6 ns, 10 Hz) with an output of ~300 mJ at 1064 nm and ~100 mJ at 532 nm. The oscillator is pumped by 8% of the power, and the remaining 92% of the power is used for signal amplification. The oscillator consists of a plane mirror and a glass plate (~8% R) combination that produces broadband light. The FWHM of the output is ~7 nm. The corresponding coherence time[14] τ_c is ~170 fs.

The beam is collimated before being split into three beams. Two beam splitters (30/70 and 50/50) are used to obtain three beams of almost equal intensity. Beam 1 is fixed, whereas beams 2 and 3 pass through variable delays. Beam 1 is the forward pump, beam 2 is the backward pump, and beam 3 is the probe. Beam 3 makes an angle of ~10° with the forward pump. Using lenses of ~20-cm focal length, we focused all the beams onto the sample contained in a 1-mm- or 100-μm-thick quartz cell. The beam waist at the focus was ~100 μm. Neutral-density filters were used to attenuate the probe beam. We isolated the phase-conjugate beam (in the $-\mathbf{k}_3$ direction) with a beam splitter and focused it onto a fast photodiode. The samples used in the study are porphyrins such as zinc meso-tetra-phenylporphyrin (ZnmTPP), zinc meso-tetra (p-methoxyphenyl) tetrabenzporphyrin (ZnmpTBP), tetratollylporphyrin (TTP), cobalt tetratollylporphyrin (CoTTP), nickel tetratollylporphyrin (NiTTP), commercially available Camel Ink (manufactured by Camlin Ltd., India), rhodamine B, and Rose Bengal. Figure 1 shows the structure of the porphyrins. The output of the photodiode is given to a data-acquisition system, which consists of a lock-in amplifier, an analog-to-digital converter card, and an IBM PC. The concentration of the samples used is typically ~0.1 optical density. The typical intensities at the focus are of the order of a few megawatts per square centimeter.



A = Zn, Co, Ni
B = p-methoxy phenyl, Tollyl
R = Benzyl, phenyl

Fig. 1. Structure of the different compounds used in the study.

3. THEORY

We calculated the relaxation times based on the theoretical studies done by Okamoto,[4] assuming that the incoherent light-correlation time at the sample is a delta function. A rigorous theory that includes the finite-correlation time was recently presented by Ulness and Albrecht.[15] The equations that are relevant for our studies follow. For transient gratings the signal in the direction $\mathbf{k}_4 = \mathbf{k}_1 + \mathbf{k}_2 - \mathbf{k}_3$ has contributions from two different gratings[16]:

- $\mathbf{k}_2$ at time t_3 gets diffracted in the direction of $\mathbf{k}_4$ by the grating formed through the interaction of the fields propagating with $\mathbf{k}_1$ and $\mathbf{k}_3$ wave vectors.
- $\mathbf{k}_1$ at time t_3 gets diffracted by the grating formed through the interaction of the fields propagating with $\mathbf{k}_2$ and $\mathbf{k}_3$ wave vectors.

When two or more levels of the system are populated, we must consider the effect of excited-state relaxation, which is not the same as ground-state relaxation. The signal intensity is proportional to the statistical average of the polarization $\mathbf{P}_3$,

$$J(\tau, \delta) = \int_{-\infty}^{\infty} \mathrm{d}t_0 \langle |\mathbf{P}_3(t_0; \tau, \delta)|^2 \rangle, \tag{1}$$

where $\langle\ \rangle$ denotes statistical average.

The polarization induced by the three wave vectors amounts to a total electric field given by

$$\begin{aligned} \mathbf{E}(t) = {} & \boldsymbol{\epsilon}(t)\exp[-i\omega_0(t) + i\mathbf{k}_1 \cdot \mathbf{r}] + \boldsymbol{\epsilon}(t-\delta) \\ & \times \exp[-i\omega_0(t-\delta) - i\mathbf{k}_2 \cdot \mathbf{r}] + \boldsymbol{\epsilon}(t-\tau) \\ & \times \exp[-i\omega_0(t-\tau) + i\mathbf{k}_3 \cdot \mathbf{r}] + \text{c.c.} \end{aligned} \tag{2}$$

The total signal intensity at time t is calculated in the homogenous broadening limit when the integration for the polarization of the fields at the times t, τ, and $t \pm \delta$ is performed. The relative intensities for the signals at time $t = 0$ and $t = \delta$ are given by

$$I_0 \alpha [4/(\gamma_{gg} + \gamma_{ee}) + 1/\gamma_{gg} + 1/\gamma_{ee}](1/\tau_c),$$

$$I_\delta \alpha (1/\gamma_{gg} + 1/\gamma_{ee})^2 (1/\tau_c)^2 + (1/\gamma_{gg} + 1/\gamma_{ee})(4/\tau_c), \quad (3)$$

where γ_{ee} and γ_{gg} are the excited- and the ground-state relaxation rates, respectively. These signals overide the background owing to the broad temporal duration of the pump pulse (6 ns in our case):

$$I_b \alpha [4/(\gamma_{gg} + \tau_{ee}) + 1/\gamma_{gg} + 1/\gamma_{ee}](1/\tau_c) + 8. \quad (4)$$

In the limiting condition in which the excited-state relaxation is much faster than ground-state relaxation (that is, $\gamma_{ee}\tau_c \gg \gamma_{gg}\tau_c$) the intensities of the main peak, the second peak, and that of the background asymptotically reach a certain value:

$$I_0 \alpha 1/(\gamma_{gg}\tau_c),$$

$$I_\delta \alpha 1/(\gamma_{gg}\tau_c)^2,$$

$$I_b \alpha 1/(\gamma_{gg}\tau_c), \quad (5)$$

and the ratios would then be 1, $(1/\gamma_{gg}\tau_c)$, and 1, respectively, from which we can evaluate the ground-state population-relaxation time.

4. RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra for some of the samples: CoTTP (in chloroform), ink (in distilled water) and Rhodamine B (in methanol). All the spectra are taken with a Jasco ultraviolet/visible spectrometer (Model 7800). Figure 3 shows time-resolved profiles, for different values of δ, for ZnmTPP. Figure 4 shows the profiles for different compounds TTP, CoTTP, and NiTTP for the same value of δ. The main intense peak appears at $\tau = 0$ and is due to the coherence of beams 1 and 3, and it has a width (FWHM) of ~160–180 fs. This width coincides with the width of the autocorrelation curve. This has been confirmed by the fact that when the sample is replaced with Rhodamine B in methanol, we get the autocorrelation function (Fig. 5, inset) at time $\tau = 0$ (as the response time in Rhodamine B is known to be a few femtoseconds), and we do not observe the second peak. Different values of δ were used for recording the signal; the data in Fig. 5 is for $\delta = +1.5$ ps. The broader and weaker peak in Fig. 3 is due to the coherence of beams 2 and 3. It has a width of ~3 ps for the porphyrin and appears at $\tau = |\delta|$. Although a previously mentioned study[4] reported that the second peak had the same width as the first peak, we observed, for the first time in porphyrin dyes, the broader second peak.

Open-aperture Z scans[17] were run for all the materials to assess their nonlinear absorption results, which are shown in Fig. 6. The Z-scan technique is a simple, sensitive, single-beam method that uses the principle of spatial beam distortion to measure both the sign and the magnitude of refractive nonlinearities and nonlinear absorption of optical materials. Reverse-saturable absorption in tetraphenylporphyrins, implying that there is excited-state absorption, is well established.[7,18] Open-aperture Z-scan studies of ZnmpTBP, ZnmTPP, CoTTP, NiTTP, TPP, and ink show reverse-saturation absorption, whereas Rhodamine B and Rose Bengal show saturable absorption. Materials that exhibited reverse-saturable absorption showed two peaks. For Rhodamine B solution, we do not observe a second peak. Experiments were also conducted for other dyes such as Rose Bengal, which shows saturable absorption, and also for which we did not observe a second peak. To confirm our observations, we replaced the porphyrin dye with a commercial blue ink, which exhibits reverse-saturable absorption. The recorded signal once again showed two peaks. The width of the broader peak in this system, however, was 1–1.5 ps. This supports our argument that the second peak appears whenever there is excited-state absorption. We observed similar recordings for other porphyrins such as CoTTP, NiTTP, and TTP. The width of the second peak varied from sample to sample. These variations in the width of

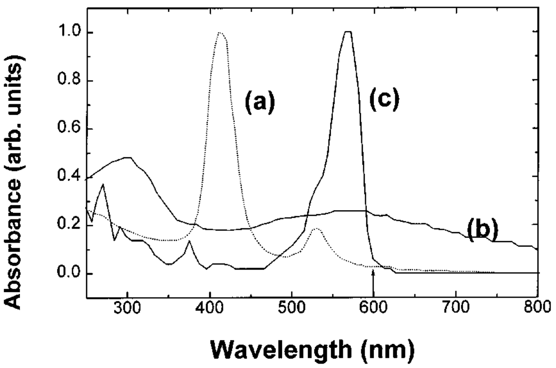


Fig. 2. Absorption spectra of (a) CoTTP (in chloroform), (b) ink (in distilled water), and (c) Rhodamine B (in methanol).

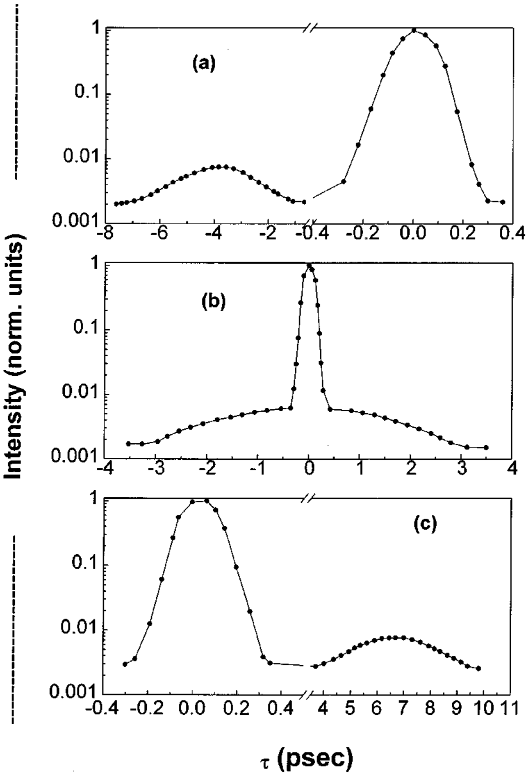


Fig. 3. Phase-conjugate intensity as a function of delay τ for ZnmTPP: (a) $\delta = -4$ ps (b) $\delta = 0$ ps and (c) $\delta = +6.5$ ps.

second peak is due to the variations in the excited-state dynamics of the different samples.

Figure 7 shows the energy-level diagram for the porphyrins, indicating the different transitions. Femtosecond pump–probe studies on dye molecules revealed the presence of subpicosecond transients, which have been attributed to redistribution of excitation energy among the vibrational modes in excited states S_n of the molecule.[19] Also it has been found from Raman linewidths of most metalloporphyrins that the minimum vibrational population lifetime is ~0.5 ps.[20] Our samples also show the same behavior. The input pulses excite molecules from the ground state S_0 into the higher vibrational states of the excited singlet state $S_{1\nu}$. The relaxation of the molecules out of this state occurs rapidly into an equilibrium level in the singlet state S_1. This level relaxes either by nonradiative decay into first triplet state T_1 (intersystem crossing rate K_{isc}) or by both radiative and nonradiative decay within the singlet system. Depending on the intersystem crossing rates, the excited-state absorption may be from singlet S_1 or triplet states T_1 into S_n or T_n, respectively. In our case, since the correlation time is ~170 fs, there is little probability of intersystem crossing at such short time scales. Pumping of the molecules, with sufficient intensity, can lead the population to the excited state S_n. These upper states S_n will relax back

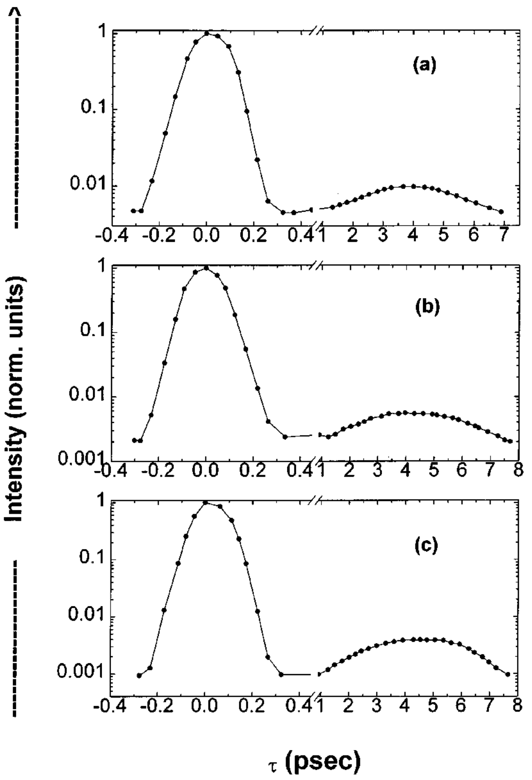


Fig. 4. Phase-conjugate intensity as a function of delay τ for (a) TTP, (b) CoTTP, and (c) NiTTP. $\delta = +4$ ps for all samples.

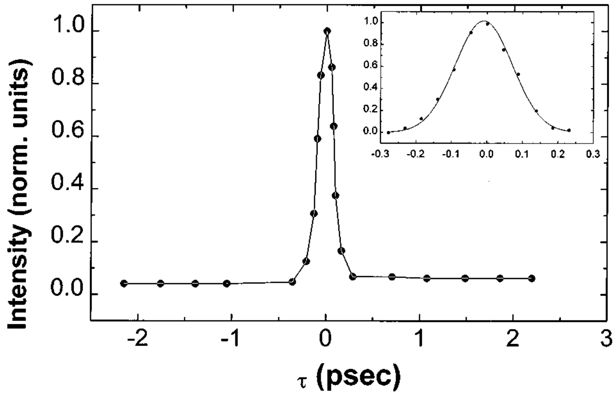


Fig. 5. Phase-conjugate intensity as a function of delay τ for Rhodamine B for $\delta = +1.5$ ps. Inset: autocorrelation trace.

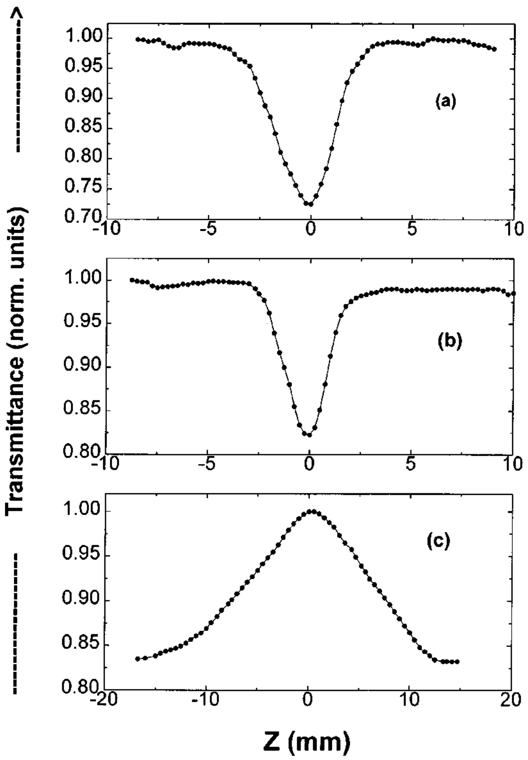


Fig. 6. Open aperture z-scans for different samples (a) CoTTP, (b) Ink, and (c) Rhodamine B.

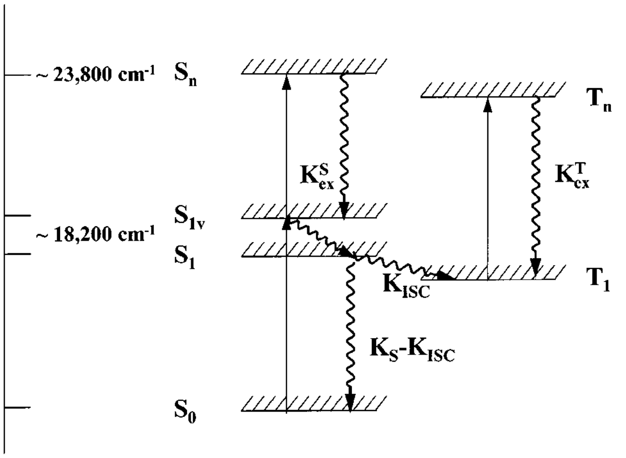


Fig. 7. Energy-level diagram for the porphyrins. K, transition rate.

to the S_1 state on a femtosecond time scale and, in the process, generate a vibrationally excited state. The different line shapes for the observed signal can be explained if we take the S_n levels as the excited upper state, the S_1 as the excited lower level (ground state as given in the theory), and the γ_{ee} and γ_{gg} as the relaxation rates of S_n and S_1, respectively. Because of the fast response time in femtoseconds, we attribute the signal at peak 1 as due to the excited states S_n of porphyrins. The relaxation within the vibrational levels, in metalloporphyrins, is reported to be of the order of a few picoseconds. We attribute the width of the second peak to vibrational relaxation ($S_{1\nu}$ to S_1) within the molecule, which is of the order of 3 to 4 ps (FWHM). The variations in the intensities of the two peaks can be explained as being due to the efficiencies of the two gratings. The main intense peak is due to the coherence of beams 1 and 3, while beam 2 gets diffracted in the $\mathbf{k}_4$ direction and can be thought of as a transmission grating. Whereas the broader peak is due to the coherence of beams 2 and 3, beam 1 gets diffracted in the $\mathbf{k}_4$ direction and can be thought of as a reflection grating. The difference in the signal intensities can be seen as the difference in the diffraction efficiencies of the two gratings.

Changing the polarization state of the probe beam such that it is perpendicular to pump polarization dropped the signal intensity by 7 to 8 times. There was no change in the widths or ratio of the peaks. Although a previously mentioned study[4] reports that the second peak had the same width as the first peak, we observed a broader second peak. There is no decay observed in the coherence peak owing to beams 1 and 3, from which we infer that T_2 of the excited states of S_n for the samples is much less than the 170-fs correlation time of the pulses. As porphyrins are known to exhibit very strong reverse-saturable absorption, we conclude that the first peak is due to the fast relaxations occurring in the S_n excited states. The second peak moves symmetrically across the main peak with a delay of beam 2 appearing exactly at $\tau = \delta$. The width of the second peak remains constant for large values of δ. A constant background appears in all of the profiles. The thermal effects that occur in the slower (nanosecond) time scales produce this background signal, over which the signals owing to coherent processes override. The values of T_1 calculated with relation (5) are of 48, 32, 40, 37, and 45 ps for ZnmTPP, ZnmpTBP, TTP, CoTTP and NiTTP, respectively. The ratio of I_δ to I_b is 1:2, which is in good agreement with theory. The signal profile remained the same with different solvents such as tetrahydrofuran, dichloromethane, benzene, and chloroform. The open-aperture Z-scan studies also show reverse-saturation absorption.

5. CONCLUSION

In conclusion, we have estimated the population-relaxation times for a few metalloporphyrins using DFWM with incoherent light. We observe two peaks, one sharp and intense owing to the coherence of the forward pump beam and the probe beam, and the other weaker and broader owing to the coherence of the backward pump beam and the probe beam. By just calculating the intensity ratio of these peaks, we could estimate the population-relaxation time. We could also estimate the phase-relaxation times of the excited states of these samples. From the width of the first peak, we conclude that the vibrational relaxations in the excited states S_n are in the femtosecond scale. From the width of the second peak we estimate the vibrational relaxation time within the singlet state S_1. Using an incoherent nanosecond laser source, we could estimate both relaxation times.

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