

Electronic and Vibrational Relaxation of Porphycene in Solution

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Received: June 5, 2008; Revised Manuscript Received: August 19, 2008

The relaxation of electronically excited porphycene in acetonitrile solution has been studied by transient absorption spectroscopy supported by global analysis techniques. Three processes following the femtosecond pulse excitation to the S_2 state have been identified: the intramolecular vibrational redistribution on the time scale of tens of femtoseconds, the internal conversion $S_2 \rightsquigarrow S_1$ (750 fs) and thermal equilibration of the molecule by energy exchange with the solvent (16 ps). The recorded transient absorption kinetics exhibit oscillations which have been assigned to the evolution of wavepackets in both S_1 and S_0 states.

1. Introduction

Porphycenes,¹ structural isomers of porphyrins (Figure 1), have in recent years been attracting much attention, especially due to their potential applications as efficient photosensitizers in photodynamical therapy of cancer.² Thus a significant effort has been put into fully characterizing their photochemical properties. In particular the relaxation pathways of electronically excited porphyrins and porphycenes^{3–10} have been thoroughly investigated. Due to the lack of dipole moments in these molecules, the relaxation may be conveniently observed without being obscured by solvation effects. For free base tetraphenylporphyrin, a very fast (< 100 fs) internal conversion (IC) $Q_y \rightsquigarrow Q_x$ and intramolecular vibrational energy redistribution (IVR) occurring on a time scale of 100–200 fs have been observed even for the excitation energy exceeding the energy of the fluorescent state (S_1) by several thousands cm^{-1} . The ultrafast relaxation was followed by two slower processes occurring on time scales of 1.4 and 10 ps. They have been attributed to interactions with solvent molecules: collisions-assisted redistribution of vibrational energy and thermal equilibration by energy exchange with the solvent,⁴ respectively. An analogous scheme for zinc tetraphenylporphyrin is more complicated due to the presence of additional relaxation pathways.^{5–7}

The experiments probing the relaxation routes in porphycenes conducted so far have been focused on the case when the electronic excitation to the S_3 and S_4 states (the Soret bands) provides an excess energy as large as 11 000 cm^{-1} .^{8–10} An unexpectedly slow relaxation of the molecules embedded in a cryogenic gas matrix has been found by picosecond transient absorption and time-resolved fluorescence measurements with the temporal resolution of the order of 30 ps. It has been established that a relaxed S_1 state is reached after more than 100 ps.^{8,9} On the other hand, the relaxation time was shorter than the resolution of the apparatus when the molecules in the gas matrix were excited to the S_2 state (energy excess of 900 cm^{-1}) or the experiment was performed in a solution (regardless of the excitation energy). These observations have been interpreted in terms of a slow energy transfer from vibrational levels of the chromophore to the adjacent layer of matrix atoms,

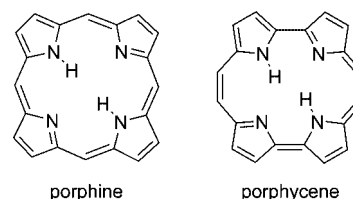


Figure 1. Chemical structures of porphine (the parent porphyrin) and porphycene.

due to a mismatch of the vibrational frequencies of porphycene and of the lattice phonons.

In this work we augment the existing knowledge of the relaxation mechanisms of porphycene with the results of time-resolved measurements of absorption spectra following the excitation of the molecules in solution to the S_2 state. With a temporal resolution below 50 fs, we have been able to determine the rate of $S_2 \rightsquigarrow S_1$ IC and to estimate the time scale of IVR. We have also measured the thermalization time of the molecules in the S_1 state obtaining a result similar to that reported for free base tetraphenylporphyrin.⁴

In addition, we have observed that the kinetic traces of the transient signals contain oscillations with periods in the range of tens of femtoseconds. By comparing the frequencies of these oscillations with those of the molecular vibrations we conclude that the observed oscillations are manifestations of the evolving vibrational wavepackets excited with the broadband laser pulses.

2. Experimental Details

Porphycene has been synthesized as described elsewhere.¹¹ The solvent used for preparation of liquid samples, acetonitrile (ACN), was of spectral grade and was used as supplied. The solutions were prepared at concentrations of the order of 10^{-4} M, so that the absorbance at 630 nm in a 1 mm-thick cell was in the range of 0.3–0.5. The samples were not deaerated.

Transient absorption measurements were carried out at room temperature using two experimental setups. In each setup the liquid sample was contained in a 1 or 2 mm-thick fused silica cell. Because of high photostability of porphycene and low power deposition in the sample (low Stokes shift and high quantum yield of the fluorescence) we could use conventional cells instead of flow-through cells usually required in the

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experiments of this kind. The molecules were excited by the pulses from a 1 kHz repetition rate noncollinear optical parametric amplifier (NOPA, model Topas-White from Light Conversion) pumped by a Ti:sapphire regenerative amplifier and tunable within the range of 530–780 nm with approximately 20 fs pulse-duration. The energy of the pulses was in the range of 5–15 μJ and the beam diameter in the sample was approximately 0.5 mm. The light was linearly polarized.

The two experimental arrangements differed by the method of probing the transient absorption. In the first one, a part of the beam from a femtosecond Ti:sapphire regenerative amplifier was focused in a rotating CaF_2 plate in order to generate white-light supercontinuum¹² pulses. The supercontinuum beam was first filtered spatially and spectrally (down to 325–800 nm range) and then split into two beams, one of which (probe) was overlapped with the excited region of the sample. The second beam (reference) also passed through the sample, several mm away from the first one and served as a monitor of the stationary absorption. The spectra of the beams were recorded by a single imaging spectrograph equipped with a 2-dimensional CCD camera. In this configuration the scatter from the pump beam obscured the transient absorption spectra in the spectral range close to that of the excitation pulses. In order to overcome this problem the kinetics of the absorption at wavelengths close to the excitation were recorded in the second setup with a quasi-monochromatic probe beam obtained by dividing the pump beam with a beam-splitter. In this “single color” case the intensity of the probe beam was measured with a photodiode and no reference beam was used. The optically induced changes of the signal were separated from the stationary absorption by a periodical blocking of the pump beam with an electro-mechanical shutter.

The probe beams in both setups were linearly polarized along the axis rotated by 45° with respect to the polarization of the pump beam. After leaving the sample the probe beams passed through a calcite polarizer which separated the two polarization components, parallel and perpendicular to that of the excitation. The intensity of the resulting beams was measured independently, either as a signal coming from different vertical areas of the CCD camera (in the supercontinuum setup) or with two photodiodes (in the “single color” setup). In such an arrangement one can measure either the anisotropy of the transient absorption or the kinetics of the signal disentangled from the rotational diffusion effects (equivalent to the measurements at the magic angle between the probe and pump beams). In this work we concentrate on the latter data.

The temporal resolution of the setups was equal to 150 fs for the supercontinuum probing and below 50 fs for quasimonochromatic probing. The range of pump–probe delays was up to 1 ns and 100 ps in the two setups, respectively.

3. Results and Discussion

The stationary absorption spectrum of an acetonitrile solution of porphycene in the spectral range covering the Q bands is shown in Figure 2a. It consists of three main bands, centered at approximately 560, 590, and 630 nm. The two shorter-wavelength bands correspond to absorption to the S_2 electronic state, while the band centered at 630 nm results from $S_1 \leftarrow S_0$ absorption.¹³ This band partially overlaps the fluorescence spectrum which exhibits very low Stokes shift.

The most informative transient spectra were recorded for the excitation wavelengths equal to 630 and 555 nm (Figure 2b,c) corresponding to $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ transitions, respectively. In the case of 630 nm excitation, the transient absorption

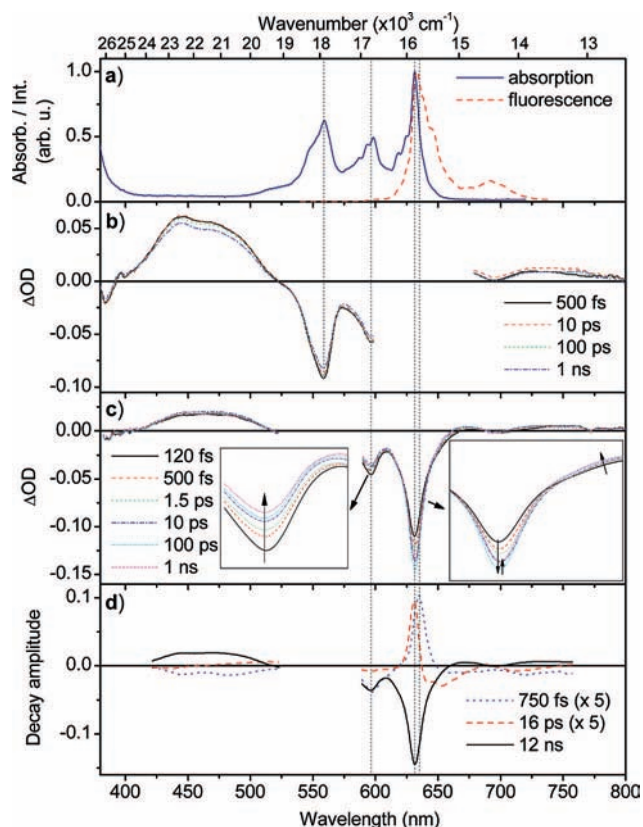


Figure 2. (a) Stationary absorption and fluorescence spectra of porphycene in ACN. (b) Transient absorption spectra of porphycene in ACN for the excitation wavelength 630 nm. (c) Transient absorption spectra of porphycene in ACN for excitation wavelength 555 nm. (d) Decay associated difference spectra computed from the transient spectra measured for the excitation at 555 nm.

spectrum consists of two excited-state absorption (ESA) bands (400–525 and 700–800 nm) and the bleaching band visible in the spectral region corresponding to the $S_2 \leftarrow S_0$ absorption. The $S_1 \leftarrow S_0$ absorption and $S_1 \rightarrow S_0$ emission are obscured by the scattered excitation light. The transient signal decays monoexponentially in the whole spectral region covered in this experiment. The monoexponential decay was confirmed by the global fit¹⁴ of the kinetics at all wavelengths in this spectral range. The decay time determined by this procedure is equal to (10 ± 1) ns and corresponds to the lifetime of the S_1 state.^{15,16} The influence of the oxygen present in the nondeaerated sample, which in principle increases the rate of the $S_1 \leftrightarrow T_1$ intersystem crossing, seems to be insignificant here because the S_1 state’s lifetime measured in a deaerated solution in acetonitrile is only slightly longer (11.9 ns according to ref 16). Thus it can be safely assumed that the much faster relaxation processes are undisturbed by the presence of the oxygen in the sample. It is worth noting that this decay time has been determined from the data which covers only 1 ns delay range. However, one should keep in mind that the calculated decay time is a result of the simultaneous fitting of several hundreds kinetics. No evidence of IVR or thermal equilibration is visible in the spectral range available in this experiment.

More complicated dynamics was found in the transient spectra recorded with excitation at 555 nm (Figure 2c). The main spectral features are very similar to those observed in the previous case, however the spectra evolve on three distinct time scales, subpicosecond, picosecond, and nanosecond. The kinetics of the signal at characteristic wavelengths are shown in Figure 3.

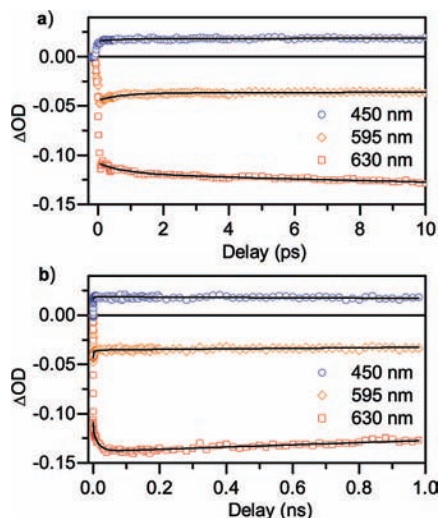


Figure 3. Selected kinetics of transient absorption of porphycene in ACN recorded for the excitation wavelength 555 nm in a short (a) and long (b) delay time window.

The subpicosecond evolution is most prominent in the decay of the gain signal at 595 nm and the simultaneous rise at 630 nm (Figure 3a). A slower process is visible in the kinetics at 630 nm, as a rise of the signal within the first 50 ps after the excitation (Figure 3b). At long delays the absorption at all wavelengths decays on a nanosecond time scale in the fashion very similar to that observed with excitation of the molecules to the S_1 state.

The results discussed so far suggest that the fastest process is related to the $S_2 \rightsquigarrow S_1$ relaxation and the slowest one corresponds to the decay of the S_1 excited-state resulting in repopulation of the ground-state and population of the triplet state. This preliminary interpretation was confirmed by means of the global analysis. The experimental data was subjected to the procedure in which the kinetic traces $\Delta A(t, \lambda)$ at each wavelength λ in the analyzed spectral range were fitted with a multiexponential function of the form

$$\Delta A(t, \lambda) = \sum_{i=1}^n A_i(\lambda) \exp\left(-\frac{t}{\tau_i}\right) \quad (1)$$

A common set of the decay times τ_1, \dots, τ_n was used for all kinetics. The set of amplitudes $A_i(\lambda)$ constitutes the so-called decay associated difference spectra¹⁷ (DADS) which greatly simplify the association of the kinetic behavior with the observed spectral features.

Three different decay times were necessary to fit the data recorded for the excitation wavelength of 555 nm. Their values are equal to (750 ± 170) fs, (16 ± 3) ps, and (12 ± 1) ns. The respective DADS are shown in Figure 2d. The one corresponding to the 750 fs decay consists of the following bands:

- (1) A broad negative band in the range of 400–525 nm and the shape identical to the shape of the ESA band from the S_1 state,
- (2) A narrow negative band around 590 nm partially overlapping the $S_2 \leftarrow S_0$ absorption spectrum,
- (3) A narrow positive band which resembles the $S_1 \leftarrow S_0$ absorption band slightly shifted to the red.

Comparison of these bands with the transient spectra (Figure 2b,c) leads to the conclusion that (1) and (3) evidence the rise of the population of the S_1 state which, in turn, results in the rise of the ESA (1) and the bleaching accompanied by the rise of the stimulated emission (3). The stimulated emission (SE) from

the S_2 state, whose spectral characteristics (2) reflects the $S_2 \leftarrow S_0$ absorption spectrum, decays simultaneously with the increase of the signals originating from the S_1 state. These facts strongly support the identification of the decay time equal to 750 fs as the lifetime of the S_2 state and the deactivation process as the $S_2 \rightsquigarrow S_1$ internal conversion.

The slower process occurring on the time scale of 16 ps leads to the decay of the red wing of the gain band in the spectral range 610–670 nm and the rise of its maximum (inset in Figure 2c). Due to the low Stokes shift of the fluorescence spectrum, both the bleaching and the SE from the S_1 state contribute to this band. Taking this into account it is reasonable to assume that the observed spectral evolution results from the narrowing of the SE band with its simultaneous shift to the blue. A very similar behavior, the narrowing and the blue shift, was observed in the time-resolved fluorescence spectra of porphycene in both cryogenic gas matrices and tetrahydrofuran solution and interpreted as a manifestation of the thermal relaxation of the molecules.⁹ Also, the thermal relaxation of free base tetraphenylporphyrin dissolved in benzene was observed as the similar spectral evolution on the comparable time scale (10–20 ps).⁴ We believe that in the case of porphycene dissolved in ACN described here this particular feature of the transient spectrum may be identified with the thermal equilibration of the molecule by the energy exchange with the solvent.

The DADS corresponding to the 12 ns decay reflects the transient spectra observed after the excitation of the molecules to the S_1 state. Thus, as in the previous case, this decay time may be identified as the S_1 state lifetime.

It should be pointed out that no evidence for IVR has been found in the evolution of the transient spectra recorded with the supercontinuum setup. The reason for the lack of IVR signature can be 2-fold: (1) the IVR process is faster than the temporal resolution of our apparatus or (2) it affects only the parts of the spectrum obscured by the scattered pump light. In order to decide which is the case, the data taken with the supercontinuum probe beam were supplemented by the results of the experiment with quasi-monochromatic probing (“single color” setup). Three kinetic profiles of the transient signal, measured at the wavelengths corresponding to each of the absorption maxima are shown in Figure 4.

The negative signal measured at 545 nm (Figure 4a) rises within 40 fs and then rapidly decays to approximately 2/3 of the maximum amplitude (we verified that the contribution of the artifact signal due to solvent is at zero delay significantly lower than the true transient absorption of porphycene). This ultrafast evolution appears only after excitation to the S_2 state with a high energy excess, therefore we associate the fast-decaying gain with the stimulated emission from primarily excited vibrational states of S_2 . The intramolecular vibrational redistribution which leads to the depopulation of the Franck–Condon states is visible as the decay of the gain within 50 fs. This value, however, should not be considered as a time of a complete vibrational relaxation of the S_2 state. Instead, it should be understood as a time after which the SE spectrum from the molecules still undergoing vibrational redistribution moves out of the spectrum of the probe pulse. Nevertheless, this indicates that the characteristic time scale of IVR is of the order of tens of femtoseconds.

The ultrafast decay is not present in the kinetics measured at 595 nm (Figure 4b), when the molecules are also excited to the S_2 state but with little energy excess. The signal exhibits some oscillations at early delays (they will be discussed later) but its mean value decays much more slowly than in the previous case.

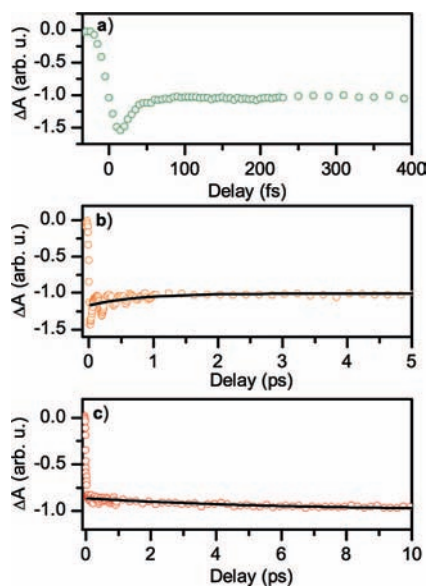


Figure 4. Kinetics of transient absorption probed with quasi-monochromatic pulses with the central wavelength equal to 545 (a), 595 (b), and 625 nm (c).

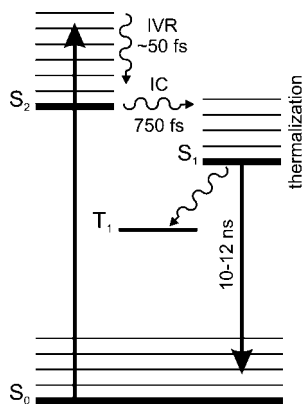


Figure 5. Relaxation scheme of porphycene in solution derived from the results of transient absorption experiments with broadband and quasi-monochromatic probing. The formation of the T_1 state is not evidenced by femtosecond time-resolved experiments but it has been observed previously.¹⁶

The monoexponential curve with a decay time equal to the determined lifetime of the S_2 state (solid curve in Figure 4b) shows that the evolution of the gain reflects the population of S_2 . This result is a further confirmation of the association of the 750 fs process found in the transient absorption spectra after excitation at 555 nm with the $S_2 \rightsquigarrow S_1$ IC.

The gain signal observed at 625 nm after excitation to the S_1 state (Figure 4c) also oscillates at early delays and slowly rises on the time scale of picoseconds. This rise is similar to the process described by the 16 ps decay time visible in the kinetics of transient absorption at similar wavelengths after excitation to the S_2 state. In this case, however, the characteristic time is shorter and it equals to (6.2 ± 0.5) ps. This difference may be attributed to the different amount of the excess energy to be dissipated if we assume that the evolution of the kinetics measured at around 630 nm is due to thermal equilibration of the molecules, regardless of the excitation wavelength.

The observations that have been already discussed lead to the relaxation scheme of a porphycene excited to the S_2 state depicted in Figure 5. Summarizing, after the excitation to the S_2 state a molecule relaxes from the Franck–Condon vibrational

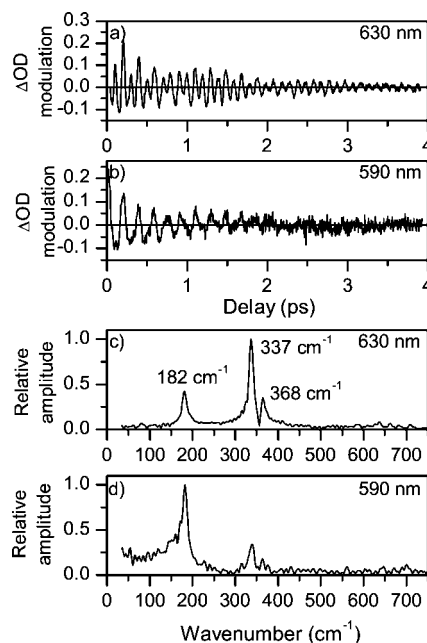


Figure 6. Periodic modulation of the transient absorption curves after excitation and probing at 630 (a) and 590 nm (b) and their Fourier transforms (c and d).

states on a time scale of tens of femtoseconds. The internal conversion to the S_1 state takes approximately 750 fs and the characteristic time of thermal equilibration of the molecule with the solvent is equal to 16 ps (this time is shortened to 6 ps, when the energy excess is lower). The ground-state is repopulated with the characteristic time of approximately 10–12 ns. It should be noted that we have found no evidence for the population of the triplet state, although it is known to be formed with a significant quantum yield.¹⁶ The reason is the too short time delay range in our experiments; the triplet state would dominate the spectrum only after the decay of the S_1 state, i.e., for delays $\gg 10$ ns.

In order to examine the oscillations visible in the transient traces observed at 595 and 625 nm, separate measurements have been performed. The sample was placed in a thinner (1 mm) cell; therefore, the temporal resolution was improved so that the fast oscillations could be well resolved. The modulation curves (obtained by fitting the experimental traces with a monoexponential function, then dividing the experimental trace by the fitted function and finally subtracting 1) are shown in Figure 6.

Although the modulation curves measured at 590 and 630 nm (Figure 6a,b) seem to be different, they both represent superpositions of three distinct oscillations of the same frequencies, which can be found by the Fourier transform (Figure 6c,d). Their corresponding wavenumbers are equal to (181.7 ± 0.3) , (337.3 ± 0.1) , and (367.7 ± 0.3) cm^{-1} . These values are very close to vibrational frequencies of porphycene measured in solidified gas matrices:¹³ 178, 341, and 362 cm^{-1} (S_1 state in N_2 matrix; the lowest vibrational mode, 141 cm^{-1} , is not present in the oscillations). This similarity is consistent with the most natural identification of the oscillations as the evolution of the vibrational wavepacket excited by a spectrally broad laser pulse. In fact the wavepacket may be directly excited in the S_1 state or, through the Raman interaction, in S_0 . This cannot be distinguished on the ground of the vibrational frequencies because they are very similar in the ground state (184, 344, and 362 cm^{-1} in N_2 matrix)¹³ and in the excited state.

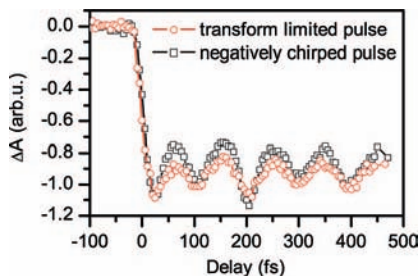


Figure 7. Transient signals measured at 630 nm with transform limited and negatively chirped pulses.

This ambiguity can be resolved if one uses tailored laser pulses. As pointed out by Bardeen et al.¹⁸ a negative chirp in the pulse increases the amplitude of the oscillations (as to the transform limited pulse) if the wavepacket is excited also in the ground state. As it can be seen in Figure 7, this is the case for porphycene excited to S_1 . Therefore we conclude that the observed oscillations result from the evolution of wavepackets in both S_0 and S_1 states. Nevertheless, the oscillations on the kinetic trace measured at 630 nm decay monoexponentially with a time constant equal to (1.6 ± 0.1) ps, which indicates that the dephasing times must be similar in both states.

The oscillations on the curve for 590 nm also decay monoexponentially (with a decay time equal to (850 ± 50) fs). Interpretation of this value is more difficult, however, because the decay of oscillations after excitation into S_2 is affected not only by vibrational dephasing but also by the $S_2 \rightsquigarrow S_1$ internal conversion. Indeed, this time is close to the lifetime of the S_2 state, which may imply that the decay of S_2 contributes significantly to the decay of the oscillations.

4. Conclusions

The relaxation of electronically excited porphycene dissolved in acetonitrile has been investigated by means of transient absorption spectroscopy. The results were interpreted using global analysis techniques. The relaxation scheme inferred from the experimental data is as follows: a molecule excited to the S_2 state with a large energy excess undergoes an ultrafast intramolecular vibrational redistribution on a time scale of tens of femtoseconds. In the next step the S_1 state is populated through internal conversion with a characteristic time of (750 ± 170) fs. The molecule in the S_1 state dissipates the excess vibrational energy into the solvent and thermalizes with a time constant equal to (16 ± 3) ps. The thermalization time decreases to approximately 6 ps when the molecule is excited directly to

S_1 with less excess energy. Finally, the S_1 state decays with a decay time of 10–12 ns, in agreement with previous observations.

The oscillations present at early delays in the kinetic traces measured with quasimonochromatic probing have been attributed to the evolution of the wavepacket excited by the broadband ultrashort laser pulse. This has been confirmed by the identification of the 3 distinct frequencies revealed by the Fourier transform with the vibrational frequencies of porphycene measured in cryogenic gas matrices. The presence of wavepackets in both S_0 and S_1 states has been shown on the grounds of the dependence of the amplitude of oscillations on the chirp of the pump pulse.

Acknowledgment. We thank Natalia Urbanska for the synthesis and purification of porphycene used in the experiments.

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JP8049697