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Picosecond Time-Resolved Resonance Raman Scattering from Zinc(II) Octaethylporphyrin

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Light-induced charge separation in the photosynthetic reaction center is initiated by photoexcitation of a chlorophyll complex into its first excited singlet (S_1) state.[1] To understand this critical biological process better, more insight into the electronic structure and conformation of singlet excited porphyrin-like molecules is essential. Time-resolved resonance Raman scattering is an ideal technique for providing this insight and has been used recently to characterize the vibrational properties of electronically excited porphyrins.[2–4] However, due to a limited time resolution, this approach could only focus on relatively long-lived excited states like the T_1 and d,d states of metalloporphyrins[2–4] and the S_1 and T_1 states of free-base derivatives.[2d,4] Moreover, dynamic processes, such as vibrational relaxation of electronically excited macrocycles, could not be studied at all. These latter issues are likely to be of fundamental importance in understanding the details of the photosynthetic process.[5] To increase the time resolution of the Raman technique we have developed picosecond pump–probe methods[6] that allow us to monitor the time evolution of a metalloporphyrin in its excited-state manifold. Here, we present our initial results on Raman scattering from excited electronic states of Zn(II) octaethylporphyrin (ZnOEP).[7] In the S_1 state the number and symmetry of the bands indicate weak or absent Jahn–Teller distortion. ZnOEP in the T_1 state, in agreement with previous work on the ZnTPP T_1 state,[2] shows relatively strong enhancement of depolarized modes. The latter observation indicates Jahn–Teller distortion and shows that metalloporphyrin excited states of different spin multiplicity exhibit qualitatively different Jahn–Teller effects.

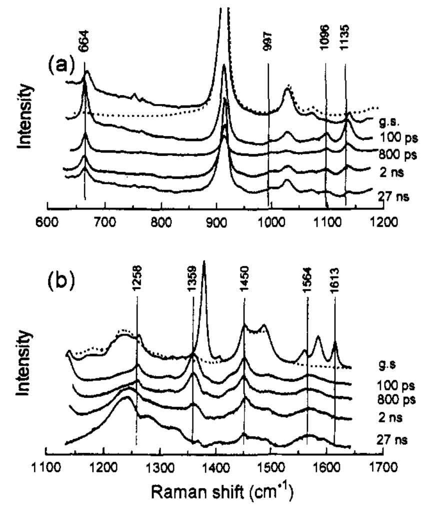

Figure 1. Time-resolved resonance Raman spectra of ZnOEP in THF in the low-wavenumber range (a) and in the high-wavenumber range (b). The pump and probe pulses were at 572 and 450 nm, respectively. The time evolution of the Raman scattering is represented by spectra obtained at time delays between the pump pulse and probe pulse of 100 ps, 800 ps, 2 ns, and 27 ns, as indicated. The concentration of ZnOEP was 5 × 10^{-4} M. The spectra of the ground state (gs) and of the solvent (dotted line) were obtained in the absence of the pump pulse. The spectra at high frequency at the various time delays were obtained by subtracting the ground-state spectra from the original data so that no negative peaks appeared. The peak positions of the vibrational modes are collected in Table 1. At low frequencies the ground-state subtraction was not performed. Judging from the intensities at 669 and 753 cm^{-1}, we conclude that the intensity of ground-state features in the excited-state spectra is negligible.

To induce the S_1 state we excited ZnOEP dissolved in tetrahydrofuran (THF) or pyridine at the maximum of its Q(0,0) absorption band.[8] The Raman spectrum of the sample was probed in the blue with a second laser pulse. To refresh the sample between excitation pulses, we used a flowing liquid jet assembly similar to that of Atkinson et al.[9]

Figure 1 shows Raman spectra of ZnOEP obtained with the excitation pulse preceding the probe pulse by 100 ps, 800 ps, 2 ns, and 27 ns, respectively. The spectra of the solvent THF and of the ground state are also shown in Figure 1. Polarization dependent measurements were carried out to determine the symmetry species of the Raman modes (Table 1). At short time delays (100 ps, 800 ps), ZnOEP is in its S_1 state and the spectrum is dominated by totally symmetric modes, although some weak nontotally symmetric modes are also visible. After 27 ns only the triplet state remains. At this time delay, the spectrum resembles that obtained by Kumble et al.[2e] in a nanosecond pump–probe experiment, although some line-shape and intensity differences

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(7) Excited-state absorption spectra and lifetimes on a picosecond time scale have been measured by Rodriguez et al.: Rodriguez, J.; Kirmaier, C.; Holten, D. W. *J. Am. Chem. Soc.* **1989,** *111,* 6500–6501. The S_1 state of ZnOEP has an absorption maximum at 450 nm; the ground-state absorption at this wavelength is low. With high yield, the S_1 state converts into the T_1 state, which has an absorption maximum at 435 nm.

(8) A pyrromethene 567 dye laser (Coherent 702) generated pulses (7 ps fwhm) at 572 nm. The laser is synchronously pumped by the second harmonic of a mode-locked Nd:YAG (Coherent Antares). The third harmonic is used to pump a Stilbene 420 dye laser with an output wavelength of 450 nm. A cavity dumper on each dye laser is used to create a time delay of 790 ns between subsequent pulses and to increase the peak power of the individual pulses. The pulse energies of the pump and probe lasers were 80 and 30 nJ, respectively. A microscope objective was used to focus these beams to 15-μm spots on the sample. Time delays between the pump and probe pulses were created electronically with the cavity dumpers or spatially by changing the path length of the pump pulse. The Raman spectrum was dispersed by a single monochromator (Jobin Yvon HR 640, 2400 grooves/mm grating) and detected with a CCD detector (Princeton Instruments. Model LN/CCD 1152UV). The spectral resolution was 7 cm^{-1}.

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Table 1. Raman Shifts, Polarizations, and Assignments of the Observed Raman Modes of ZnOEP in Its Ground and S_1 and T_1 Excited States in Tetrahydrofuran and Pyridine

tetrahydrofuran			pyridine					
S_0	S_1	T_1	S_0	S_1	T_1	ρ^a	assignment^b	character^b
669	664	665	669	663	663	p	ν_7	$\nu(C_aN)$, $\delta(C_aC_mC_a)$, $\delta(C_aC_m)$
	710^c					p		
730^c	731^c		733^c	729^c		p		
753		753	752^c			dp		
765^c	764^c					p		
		781				p		
1025^d	997	996	*e*	*e*	*e*	p	$\nu(C_1C_2)$	$\nu(C_1C_2)$
	1096	1097		1097	1096	dp		
1138	1135	1138	1135	1136	1135	p	ν_5	$\nu(C_aC_b)$, $\nu(C_bC_1)$
1211			*e*			dp	ν_{13}	$\delta(C_mH)$, $\nu(C_aC_b)$
		1239			1240	dp		
1261	1258		1262	1258		p	CH_2 twist	$\delta(C_bC_1H)$, $\delta(C_2C_1H)$
		1276			1276	dp		
1320	1313		1319	1315		p	CH_2 wag	$\delta(C_bC_1H)$, $\delta(C_2C_1H)$
1375	1359		1373	1353		p	ν_4	$\nu(C_aN)$, $\nu(C_aC_b)$
	1429^f			1429		dp		
1486	1450	1450	*e*	1447		p	ν_3	$\nu(C_aC_m)$, $\nu(C_bC_b)$
1558	1582^f	1582^f	*e*	*e*	*e*	dp	ν_{11}	$\nu(C_bC_b)$
1584	1564	1564	*e*	*e*	*e*	p	ν_2	$\nu(C_bC_b)$
1613			1611			dp	ν_{10}	$\nu(C_aC_m)$

^{a} p, polarized; dp, depolarized. ^{b} From ref 12b. ^{c} Weak. ^{d} Evident at higher porphyrin concentrations. ^{e} Obscured by solvent modes. ^{f} Identified by polarization measurements.

are apparent. These differences do not arise from the use of picosecond pulses in the present study.[10] At a pump–probe time delay of 2 ns (Figure 1), modes characteristic of both S_1 and T_1 are seen. Overall, the temporal evolution of the singlet into the triplet, as monitored by the Raman spectra in Figure 1, shows excellent agreement with earlier optical work in which the lifetime of the singlet state was determined to be 2.5 ns.[7]

In Table 1, ZnOEP modes in the S_1 and T_1 states are labeled with reference to those reported for NiOEP.[11] Assignments for excited-state vibrations were made by analogy to ground-state vibrations. For totally symmetric modes this was facilitated by the 1:1 correlation that appears to exist between modes in the ground and excited states, respectively. For the S_1 spectra, the depolarized modes are almost all of low intensity, and some could only be identified by polarization measurements. We discuss the S_1 spectrum below and then consider the T_1 data briefly.

The electronic configurations of metallooctaethylporphyrins in the ground and first excited singlet states are $a_{1u}a_{1u}$ and $a_{1u}e_g$, respectively.[12] Molecular orbital calculations predict that the individual modes should show sensitivity to the electron occupancy of the a_{1u} and e_g orbitals.[13] Modes involving primarily stretches of C_aC_m, C_aC_b, or C_aN bonds are predicted to shift to lower frequencies in the S_1 state, whereas modes comprising mostly C_bC_b stretches are predicted to shift to higher frequencies. Earlier work on both metalloporphyrin π-cation and π-anion radicals has demonstrated the generality of these orbital occupancy arguments in the assignment of vibrational modes and electronic state ordering.[14] In general, our assignments of the vibrational modes in S_1 agree with predictions based on the orbital occupancy assignments above. An exception to this is the behavior of ν_2, which apparently shifts to lower, rather than higher, frequency in the S_1 state. Perng and Bocian[14c] observed similar behavior for some modes in the ZnOEP π-anion radical, that is, frequency shifts that were counter to those predicted for e_g orbital occupancy, and suggested that structural changes of the macrocycle in the anion radical state were responsible. From the behavior of ν_2, it appears that similar phenomena may occur to some extent in the S_1 state.

As opposed to our previous work on the T_1 state of ZnTPP[2a,b] and that described below for T_1 of ZnOEP, Jahn–Teller distortion occurs to only a minor extent, if at all, in the S_1 state. This conclusion follows from our observations in Figure 1 and Table 1 that only weak enhancement of depolarized modes occurs, and that the number of totally symmetric modes does not increase relative to the ground state. This conclusion agrees with theoretical predictions that Jahn–Teller effects in the S_1 state will be minimized by configuration interaction.[15]

In the T_1 state, the Raman shifts of many modes coincide with those in the S_1 state. The depolarized modes, though, are significantly stronger than in the S_1 state (Figure 1 and Table 1). The broad feature at 1239 cm^{-1} with a shoulder at 1276 cm^{-1} may comprise several underlying modes. This spectral feature was independent of whether THF or pyridine was used as the solvent. Ethyl modes are expected to occur in this frequency range, and, although they are not strongly enhanced in the ground state,[11] they may gain intensity in the excited state and account for the spectral congestion. The shift of ν_2 in the triplet state, as in S_1, does not follow the predictions based on the molecular orbital calculations. As in H_2OEP and ZnTPP,[2] ν_4 is not strongly enhanced in the T_1 state of ZnOEP. The enhancement of depolarized modes in the T_1 state strongly suggests that Jahn–Teller distortion is present in this state, in agreement with the now general observation of structural rearrangement in triplet states of metalloporphyrin chromophores.[2,16] To conclude, the observations presented here on the S_1 and T_1 states of ZnOEP test and confirm theoretical predictions that Jahn–Teller distortion is significantly more pronounced in the triplet than in the singlet state.

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(10) We determined the Raman spectrum in the T_1 state with nanosecond Q-switched Nd:YAG laser pulses as pump and probe as well. A back-scattering arrangement was chosen with the sample in a spinning EPR tube. The wavelengths of the pump and probe lasers, respectively, were 532 and 435.7 nm. The spectra were identical to those in Figure 1.

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