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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · NOVEMBER 1991

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unreasonable to expect that the polar tensor errors for CH_2F_2 and CD_2F_2 are also somewhat larger than those used here, in which case both alternative sign sets considered in this study will satisfy the isotopic invariance criterion. The principal component analyses then strongly indicate that the $(-0--)$ $(-+)$ $(+-)^H$ and $(-+--)$ $(-+)^D$ alternative pair is to be preferred, in light of the molecular orbital results. It is encouraging that the polar tensor invariant quantities for methylene fluoride for this preferred sign set are in excellent agreement with those predicted from the

equations of the electronegativity model.

Acknowledgment. We gratefully acknowledge partial financial support from CNPq, FAPESP, and FINEP. E.S. is supported by a CNPq graduate student fellowship. GAUSSIAN 86 calculations were carried out on a VAX 11/750 computer of the Departamento de Quimica Fundamental of the Universidade Federal de Pernambuco.

Registry No. CH_2F_2 , 75-10-5; CD_2F_2 , 594-24-1.

Resonance Raman Characterization of the Radical Anion and Triplet States of Zinc Tetraphenylporphine

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Resonance Raman (RR) spectra are reported for the anion radical and for the photoexcited triplet state of ZnTPP. The anion radical was prepared by controlled-potential electrolysis in dry dimethylformamide, and care was taken to avoid phlorin contamination. RR spectra were obtained by excitation at 457.9 nm, at the anion absorption band maximum. Bands were assigned with the aid of pyrrole- d_8 and phenyl- d_{20} isotopomers. The pattern of isotope shifts and polarizations was found to be quite similar to that of the neutral parent, ZnTPP, and meaningful mode correlations are possible: ν_2 , ν_{10} , ν_{27} , and ν_{29} shift down 15–20 cm^{-1} upon reduction, while ν_1 , ν_4 , and the phenyl mode ϕ_4 are essentially unaffected. This frequency shift pattern is discussed in terms of the expectations for placing an electron in the e_g^* orbital, including the anticipated Jahn-Teller (J-T) effect. Although band overlaps make depolarization ratios difficult to quantitate, the ν_{10} band is found to be essentially depolarized, indicating that the J-T effect is dynamic, rather than static in character, at least with respect to stretching of the $\text{C}_\alpha\text{C}_m$ bonds. The ν_2 and ν_{10} downshifts are attributable to porphyrin core expansion upon reduction, but the ν_{27} and ν_{29} reductions are probably manifestations of the J-T effect. Triplet-state RR spectra were produced with 416-nm photolysis and 459-nm probe pulses (7 ns) from electronically timed Q-switched Nd:YAG lasers equipped with H_2/D_2 Raman shifters. The RR peaks were assigned via their polarizations and the d_8 and d_{20} isotopomer shifts. The spectrum contains three strong bands of predominantly phenyl character. Their frequencies are unshifted relative to the ground state, implying negligible electronic involvement of the phenyl groups in the T_1 state, but their enhancements indicate substantial involvement in the resonant T_n state. This state is suggested to be produced by charge transfer from the porphyrin e_g^* to the phenyl π^* orbitals. There are also four weak bands, which are assigned to the porphyrin skeletal modes ν_2 , ν_{10} , ν_{11} , and ν_{27} . The first three of these are at frequencies which are 40–50 cm^{-1} lower than in the ground state. For ν_2 the shift is comparable to the sum of the shifts seen upon forming the ZnTPP cation radical and anion radical, but for ν_{10} the shift is much larger than this sum, indicating that the J-T effect is more pronounced in the triplet state than in the radical anion. Consistent with this conclusion, the ν_{10} band of $^3\text{ZnTPP}$ is partially polarized, suggesting a static J-T distortion along the $\text{C}_\alpha\text{C}_m$ bonds. However, the ν_{11} band is depolarized, implying that the $\text{C}_\beta\text{C}_\beta$ bonds remain equivalent. The ν_{27} band shifts up 15 cm^{-1} and broadens significantly, suggesting a dynamic B_{2g} J-T effect along the C_m -phenyl bonds.

Introduction

The photophysical properties of metalloporphyrins are important to a range of current research areas, ranging from solar energy conversion to photodynamic therapy. Our view of porphyrin excited states has evolved from the concurrent development of theoretical calculations¹ and of static and time-resolved electronic (emissive and absorptive)^{1–5} and magnetic^{6,7} spectroscopy. The structures of these excited states can be elucidated by vibrational spectroscopies, especially resonance Raman⁸ (RR) and resonance coherent anti-Stokes Raman⁹ (RCAR) spectroscopy. These techniques have been used to characterize the triplet excited states of Ni^{II}P (P = octaethylporphyrin, uroporphyrin, or protoporphyrin IX dimethyl ester), in which the antibonding metal orbital in $d_{x^2-y^2}$ is populated.^{8–10}

In this paper, we explore the character of the excited states produced by the population of porphyrin orbitals, using a closed-shell metal ion, Zn(II), in tetraphenylporphine (TPP).^{1,2} A structural diagram of the molecule is shown in Figure 1, while the energy levels of the valence orbitals and states are shown

schematically in Figure 2. The highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) are the

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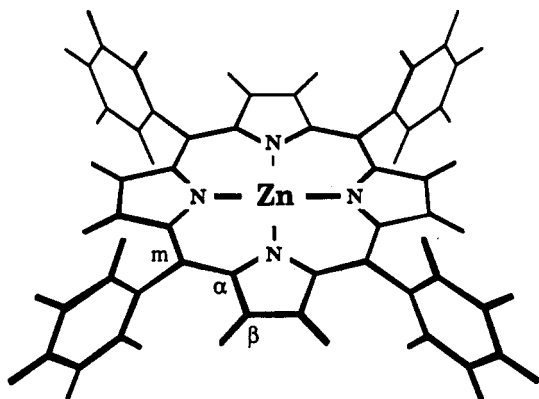


Figure 1. Structural diagram for ZnTPP, with atom labeling.

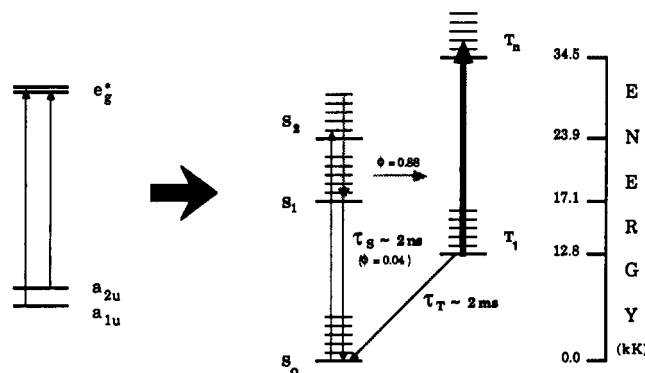


Figure 2. Orbital (left) and state (right) energy levels for ZnTPP.

porphyrin a_{2u} and e_g^* π orbitals. The next lowest occupied orbital, a_{1u} , is close to a_{2u} in energy, and two electronic transitions, Q and B, are found in the visible region of the spectrum. Excitation into either singlet state (S_1 , S_2) is followed by efficient intersystem crossing to the lowest triplet state (T_1). A strong triplet-triplet absorption, T_1 - T_n , is found in the visible region. We are able to probe the character of both triplet states by analyzing the RR spectrum produced by populating and probing the T_1 state with a two-pulse experimental arrangement. Preliminary results of a similar experiment on the same molecule have been published by Walters et al.,¹¹ during the preparation of this paper. In the present study, we have assigned the $^3\text{ZnTPP}$ RR bands definitively using polarization measurements and isotopic substitution. The band assignments and polarizations permit deductions about bonding changes and the Jahn-Teller (J-T) effect in the T_1 state and the character of the electronic excitation of the T_n state.

Because the T_1 state involves promotion of an electron from the a_{2u} to the e_g^* orbital, we have also examined the effects on the RR spectrum of placing an electron in the e_g^* orbital separately to form the ZnTPP^- radical. RR spectra of ZnTPP^- have been reported previously,¹² but the assignments have been problematic. The effects of removing an electron from the a_{2u} orbital can be gauged from the recent analysis of TPP radical-cation spectra.¹³

Experimental Section

Tetrahydrofuran (Baker Analyzed reagent) was freshly distilled from sodium/benzophenone under nitrogen, and CD_3CN (Aldrich) was used as received. Dimethylformamide (Burdick and Jackson) was dried by codistilling with benzene and then further dried over 4-Å molecular sieves and sodium. Chlorin-free H_2 -[TPP] was purified¹⁴ from commercial H_2 [TPP] (Aldrich).

H_2 [TPP]- d_{20} was synthesized by the method of Wagner et al.¹⁵ involving condensation of benzaldehyde- d_5 , which was prepared by Ce(IV) oxidation¹⁶ of toluene- d_8 (Aldrich, Gold Label), and pyrrole (Aldrich, purified on alumina before use) in CH_2Cl_2 (Baker Analyzed, reagent grade) and a few percent ethanol. Isotopic purity was assessed by NMR to be 99%. H_2 [TPP]- d_8 was prepared¹⁵ by condensing pyrrole- d_5 (isotopic purity >95%), prepared by isotopic exchange of pyrrole in 0.1 M DCl ¹⁷ (three extractions), and benzaldehyde (Fisher Scientific, purified on alumina) in CDCl_3 (Cambridge Isotope Laboratories) and a few percent CH_3OD (Aldrich, Gold Label). Deuterated solvents were necessary to avoid significant isotope exchange in the condensation reaction.¹⁸ Isotopic purity was determined by ^1H NMR to be >90%. Zinc insertion was carried out by standard methods,¹⁴ and the ZnTPP complexes were purified on silica. Samples were prepared by dissolving the appropriate isotopomer in a 1:1 $\text{CD}_3\text{CN}/\text{THF}$ solution, placed in a standard 1-mm quartz cuvette, and sealed under an inert atmosphere.

CW RR spectra were obtained with 457.9-nm Ar^+ ion laser incident on ca. 1 mM ZnTPP/THF in spinning NMR tubes, employing a 135° backscattering geometry.¹⁹ The scattered light was focused on the slits of a SPEX Triplemate spectrograph and analyzed with a computer-controlled diode array detector (Princeton Instruments). Polarization ratios were measured with a polarizer between the sample and the entrance slit of the monochromator.

Resonance Raman spectra of anion radicals were obtained by in situ electrochemical reduction at a Pt gauge (-1.20 V vs Ag wire in 0.20 M tetrabutylammonium perchlorate in DMF) of ca. 1 mM porphyrin solutions. A three compartment glass cell (the Ag wire pseudoreference and Pt wire auxiliary were separated by medium frits) was purged by O_2 -scrubbed argon throughout the experiment. Raman light was collected in 135° backscattering.

Transient absorption experiments involved timing control among a Q-switched Nd:YAG laser (Quanta Ray DCR, 10 Hz and ca. 7-ns fwhm) equipped with an H_2 Raman shifter, a xenon flashlamp (EG&G, 4- μs fwhm), and a gated dual-diode array detector (Princeton Instruments) with home-built electronic circuitry. The electronic absorption of the ZnTPP triplet state in the 1:1 $\text{CD}_3\text{CN}/\text{THF}$ solution was measured in a 200-ns time window beginning 100 ns after a 7-ns incident pulse at 416 nm (first Stokes H_2 shift of the 355-nm YAG third harmonic), a wavelength close to the ground-state Soret band maximum. The transmitted light was dispersed with a 0.22-m monochromator (ISA).

Two color time-resolved resonance Raman spectra were obtained by spatially overlapping a second laser pulse at 458.9 nm (first anti-Stokes $^2\text{H}_2$ shift of the 532-nm YAG second harmonic), in the T_1 absorption of ZnTPP . The delay between the two lasers was adjusted with the same electronic timing circuitry. The scattered light was collected with a SPEX Triplemate spectrograph and detected with an intensified diode array (Princeton Instruments). Difference spectra were obtained by subtracting the ground-state spectrum (458.9-nm probe only) from spectra obtained with the same laser but now delayed by a fixed time after a spatially overlapped 416-nm pump pulse.

Results

A. Ground-State Vibrations. Figure 3 shows RR spectra of ground-state ZnTPP and of its phenyl- d_{20} and meso- d_8 isotopomers obtained with 457.9-nm Ar^+ laser excitation, near resonance with the Soret ($S_0 \rightarrow S_2$) electronic transition (Figure 2). The bands

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TABLE I: Ground-State Vibrational Frequencies (cm^{-1}) of ZnTPP and NiTPP

vibrational mode ^a	polarizn	NiTPP ^b	Δ_8^c	Δ_{20}^c	ZnTPP ^d	Δ_8	Δ_{20}	ZnTPP ^e	Δ_8	Δ_{20}	$\Delta^{0/-e}$
ϕ (phenyl)	p	1599	0	-40	1598	+1	-33	1595	+1	-34	-4
ν_{10} , $\nu(\text{C}_\alpha\text{-C}_m)$	dp	1594	-2	-2	1547	+4	+6	1528	-10	-3	-19
ν_2 , $\nu(\text{C}_\alpha\text{-C}_m)$	p	1572	-15	+4	1548	-19	-1	1532	-21	-3	-16
ν_{11} , $\nu(\text{C}_\beta\text{-C}_\beta)$	dp	1504	-47	0	1493	-44	-1				
ν_{28} , $\nu(\text{C}_\alpha\text{-C}_m)$	dp	1485	-8	-8				(1487 d_8)			
ν_3 , $\nu(\text{C}_\beta\text{-C}_\beta)$	p	1470	-50	+8				1439	-40	+3	
ν_{29} , $\nu(\text{C}_\alpha\text{-C}_\beta)$	dp	1377	-34	-25	1360	-39	-14	1345	-26	-11	-15
ν_4 , $\nu(\text{C}_\alpha\text{-N})$	p	1374	-7	-11	1352	-6	-1	1351	-11	0	-1
ν_{20} , $\delta(\text{C}_\beta\text{-H})$	ap	1341	-466	+1				1334		0	
ν_{12} , $\nu(\text{C}_\alpha\text{-N})$	dp	1302	-3	+1				1295		+1	
ν_{27} , $\nu(\text{C}_m\text{-Ph})$	dp	1269	-7	-40	1272	0	-41	1257	0	-42	-15
ν_1 , $\nu(\text{C}_m\text{-Ph})$	p	1235	-1	-50	1237	-1	-50	1231	-2	-51	-4

^aSee ref 20 for assignments and mode description. ^bFrom ref 20. ^cFrequency shifts for d_8 and d_{20} . ^dPresent work. ^eFrequency shift between ZnTPP and ZnTPP⁻.

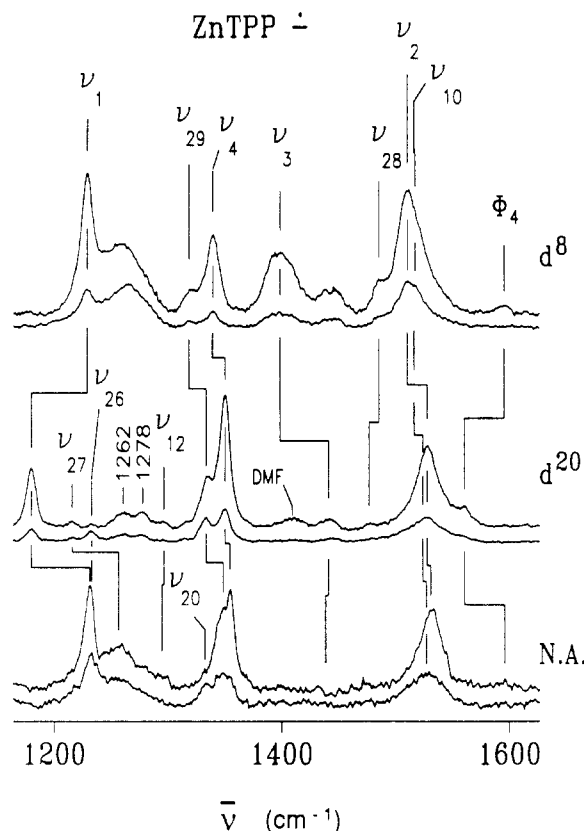


Figure 3. Resonance Raman spectra (457.9-nm Ar⁺ laser excitation) of ground-state, natural-abundance ZnTPP (NA), ZnTPP- d_8 (d_8), and ZnTPP- d_{20} (d_{20}) in THF (ca. 1 mM) parallel and perpendicular (bottom) polarized light collections. A standard spinning NMR tube (5 mm) with 135° backscattering geometry¹⁹ was used. Typical incident laser powers were <50 mW. Conditions: laser power, <50 mW; 50 μm slit width; 16-min collection time.

are readily assigned with reference to the NiTPP normal modes which have recently been analyzed.²⁰ Large d_{20} shifts identify the phenyl mode, ϕ_4 , and the phenyl ring stretch, ν_1 , while large d_8 shifts identify the $\text{C}_\beta\text{C}_\beta$ modes ν_{11} and ν_2 .²⁰ The remaining porphyrin skeletal modes— ν_{10} , ν_{29} , ν_4 , and ν_{27} —show smaller d_8 shifts. The prominent vibrational bands are of A_{1g} character (ν_2 , ν_4 , and ν_1 ; $\rho \approx 0.15$) as expected for near-Soret excitation, although B_{1g} (ν_{10} and ν_{11}) and B_{2g} modes (ν_{29} and ν_{27} ; $\rho \approx 0.75$) are also observed. The activation of non totally symmetric modes in resonance with the Soret band is commonly observed in metal-porphyrin RR spectra and is attributed to Jahn–Teller distortion in the degenerate (resonant) excited state, S_2 .²¹ The enhancement

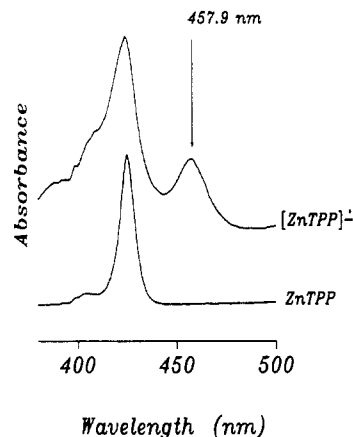


Figure 4. Absorption spectrum for ZnTPP in 0.2 M TBAP/DMF partially reduced to the radical anion via thin-layer electrochemical cell at an applied voltage of -1.2 V (vs Ag wire).

factors and isotope shifts are similar to those seen for NiTPP,²⁰ but the frequencies are somewhat lower (Table I), due to the larger core size of ZnTPP.²²

B. Radical Anion. Figure 4 shows the absorption spectrum obtained by partial electrolysis of ZnTPP solution in DMF containing 0.2 M supporting electrolyte (TBAP, tetrabutylammonium perchlorate). ZnTPP is converted cleanly to ZnTPP⁻, that is without formation of phlorin, which absorbs strongly at 810 nm. The RR spectrum of the anion can be obtained selectively with laser excitation at 457.9 nm, where the neutral parent absorbs very little. Phlorin contamination was carefully avoided by limiting the electrolysis time and potential and by rigorously drying and deoxygenating the solvent. Zinc tetraphenylphlorin also has an absorption band (457 nm) overlapping that of ZnTPP⁻, so its presence is an obvious concern in the resonance Raman experiment. We found, however, that the RR spectrum was altered dramatically under conditions favoring phlorin formation, new bands appearing at 1541, 1438, 1346, and 1297 cm^{-1} . The absence of these bands was therefore used as a test of sample integrity.

Figure 5 shows RR spectra of ZnTPP⁻ and of its d_8 and d_{20} isotopomers. The natural-abundance spectrum is in agreement with that reported by Atamian et al.¹² and with those of previous studies, although the perpendicularly polarized spectrum has not been shown previously. Atamian et al. stated that “essentially all the ZnTPP⁻ modes are polarized”, but it can be seen in Figure 5 that several weak bands are depolarized or even anomalously polarized; in the latter category, we point out the band assigned to ν_{20} in the natural-abundance spectrum and the one assigned to ν_{26} in the d_{20} spectrum. A point of interest in connection with the Jahn–Teller effect (see below) is the polarization state of the band we assign to ν_{10} , the B_{1g} $\text{C}_\alpha\text{C}_m$ stretching mode, at 1528 cm^{-1} . This band underlies the strong polarized ν_2 mode at 1532 cm^{-1} ,

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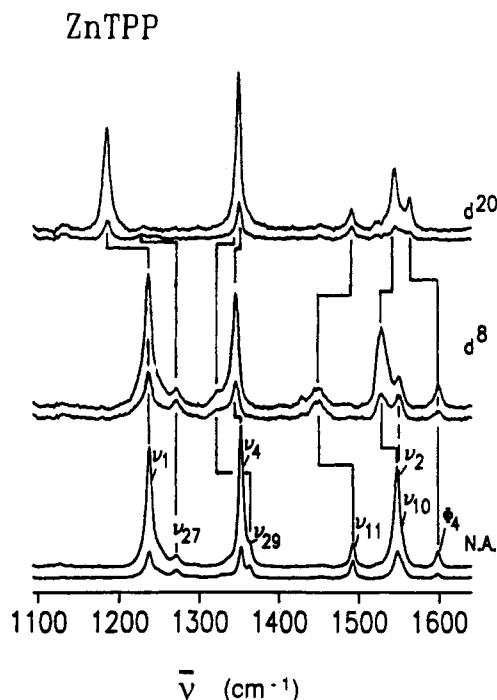


Figure 5. Resonance Raman spectra (457.9-nm Ar⁺ laser excitation) of ZnTPP^{•−} (ca. 1 mM), natural-abundance ZnTPP^{•−} (NA), ZnTPP^{•−}-d₈ (d⁸), and ZnTPP^{•−}-d₂₀ (d²⁰) generated by bulk electrolysis at −1.2 V (vs Ag wire) in 0.2 M TBAP/DMF with parallel (top) and perpendicular (bottom) polarized light collections. A standard three-compartment electrochemical cell with stirring and 135° backscattering geometry was used. Typical incident laser powers were <50 mW. Conditions: see Figure 3.

but the perpendicularly polarized spectrum shows the peak maximum to be offset. This effect is shown more clearly in the expanded view given in Figure 6. The same band is also shown for MgTPP^{•−}, where the offset is greater. Comparison of the perpendicularly polarized MgTPP^{•−} band with the low-frequency shoulder of the parallel polarized peak shows ν_{10} to be essentially depolarized.

Atamian et al.¹² reported RR spectra for the pyrrole-d₈ and meso-¹³C isotopomers of ZnTPP^{•−}, but their d₈ spectrum differs significantly from ours. It contains prominent bands which we have come to associate with phlorin and other reduced species (the frequencies of the contaminating bands for the d₈ isotopomer differ from those cited above for the natural-abundance species), and we suggest that their d₈ sample contained such species. Because of this difference, and because a different third isotopomer was used, it is impossible to compare isotope shifts between the two studies. Atamian et al. did not correlate the spectra of ZnTPP^{•−} and ZnTPP, but instead assigned the anion spectra on the basis of a normal-mode calculation with a D_{2h} force field adjusted empirically, using CuTPP as a starting point. With this force field, they found only a tenuous connection between the eigenvectors calculated for ZnTPP^{•−} and for CuTPP and attributed this effect to a B_{1g} J–T distortion, as indicated by a QCFF/Pi calculation.

In Table I, we assign the ZnTPP^{•−} bands to idealized D_{4h} porphyrin modes on the basis of their polarizations and isotope shifts. The resemblance of the isotope shift pattern to those observed for the parent ZnTPP, and also for NiTPP, is unmistakable, even if there are quantitative differences. For example, the d₂₀ sensitivity of ν_4 is 11 cm^{−1} for NiTPP but zero for ZnTPP^{•−}. It is only 1 cm^{−1} for the neutral parent, ZnTPP, however, showing that the normal-mode composition is somewhat metal dependent, perhaps because of the core size difference. ν_4 , which is a “quarter ring stretch,”²⁰ involves an out-of-phase combination of C_αN and C_αC_β stretches, and it is not surprising that the mode composition might be sensitive to changes in the force constants. Similar considerations apply to other modes showing quantitative differences in the isotope shifts among the three species. In all cases, however, the qualitative pattern (large or small d₈ and d₂₀ shifts)

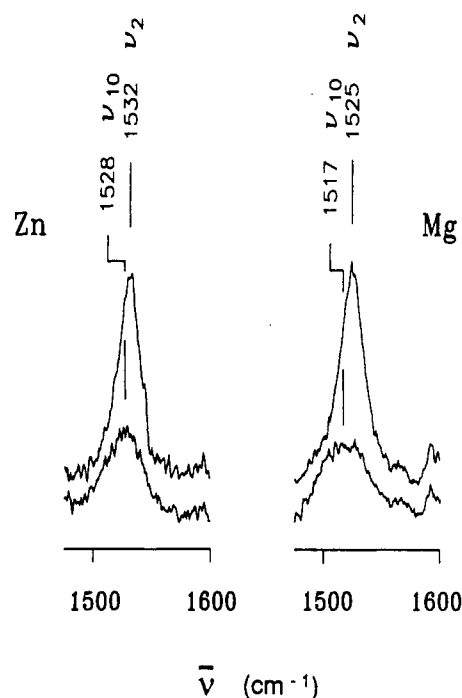


Figure 6. Expanded view of polarizations in the ν_2/ν_{10} region for ZnTPP^{•−} and MgTPP^{•−}.

is maintained, and there is no reason to doubt that the modes are correlated, even if their compositions change slightly.

Within this correlation, a pattern of selective frequency shifts is associated with ZnTPP reduction: ν_2 , ν_{10} , ν_{29} , and ν_{27} shift down by 15–20 cm^{−1}, while ν_1 , ν_4 , and the phenyl mode ϕ_4 are essentially unaffected. Two weak bands are unaccounted for in the d₂₀ isotopomer spectrum, at 1262 and 1278 cm^{−1}. They might be present in the natural-abundance and d₈ spectra, in which this region is crowded. They may arise from modes that are upshifted in the anion or else from overtone or combination modes that become activated.

The enhancement pattern is much the same for ZnTPP and ZnTPP^{•−}, suggesting that the 455-nm absorption band of the latter is similar in character to the Soret band of the former. For both species, there are three strong RR bands arising from the A_{1g} modes ν_1 , ν_2 , and ν_4 , while the fourth A_{1g} mode in the region, ν_3 , is very weak (undetectable for ZnTPP), although it becomes prominent in the d₈ isotopomer of ZnTPP^{•−} (a solvent band occurs at the same frequency, but the strength of the 1399-cm^{−1} band in relation to the solvent band in the isotopomer spectra makes assignment to ν_3 highly probable). The weakness of ν_3 in metallotetraphenylporphyrins has been attributed²⁰ to mixing of C_αC_m and C_βC_β stretching coordinates in ν_2 and ν_3 , the intensity accumulating in the in-phase mode (ν_2) and canceling for the out-of-phase mode (ν_3).

For both neutral and anionic species, modest enhancement is seen for the depolarized bands associated with ν_{10} , ν_{29} , ν_{27} , and (for ZnTPP) ν_{11} (not seen in ZnTPP^{•−}). This enhancement has been linked to Jahn–Teller activity in the Soret excited state of metalloporphyrins.²³ Similar activity may be experienced by the 455-nm excited state of ZnTPP^{•−}. The anion, but not the neutral parent, also shows enhancement of anomalously polarized, A_{2g} modes ν_{20} and ν_{26} . ν_{26} appears as a shoulder on the strong ν_1 band, where the intensity is stronger in perpendicular than parallel scattering, but is a well-separated peak in the d₂₀ spectrum, at 1233 cm^{−1}. The ν_{20} band shows up clearly in the perpendicularly polarized spectrum of the natural-abundance sample, at 1334 cm^{−1}. A_{2g} modes are not J–T active and require interstate vibronic coupling for RR enhancement. Their appearance in the ZnTPP^{•−} spectra suggests that the 455-nm transition is coupled vibronically

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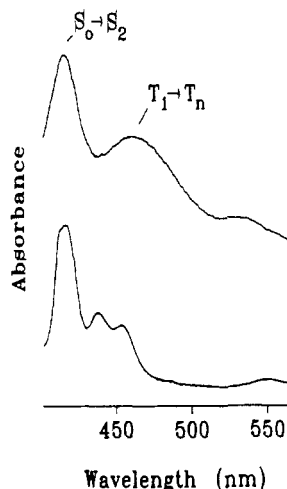


Figure 7. Top: 416-nm laser pulse induced absorption spectrum of ZnTPP (ca. 0.05 mM in 1:1 CD_3CN/THF), showing ground-state (S_0) and triplet-state (T_1) absorption bands, measured with a gated OMA in a 200-ns window beginning 100 ns after photoexcitation. Bottom: Electronic absorption spectrum (HP 8045A spectrophotometer) of ZnTPP in methylene chloride after being exposed to a 416-nm YAG pulse train (10 Hz, first Stokes H_2 shifted, 355-nm output) for ca. 1 h. The absorption bands below S_0 are due to photodegradation.

with other anion electronic transitions.

C. ZnTPP Excited State. The photodynamics of ZnTPP have been studied in detail.^{1,2,24,25} Excitation into the B (418 nm) or Q (540–590 nm) band region populates the lowest energy excited singlet state, S_1 , which fluoresces with a low quantum yield ($\phi = 0.04$, $\tau^{1/2} = 2$ ns at 298 K) and crosses efficiently ($\phi = 0.88$) to the lowest triplet excited state, T_1 ($\tau^{1/2} = 2$ ms at 298 K)²⁶ (Figure 2). The S_1 and T_1 state absorption maxima are 460²⁷ and 480 nm,²⁸ respectively.

Figure 7 (top) shows the transient absorption spectrum of ZnTPP in 1:1 CD_3CN/THF , measured in a 200-ns window initiated 100 ns after a 7-ns (fwhm) 416-nm pulse. Significant population of the triplet state is demonstrated by the large T_1 absorption, comparable in strength to the remnant S_0 absorption. This mixed solvent was chosen to be unreactive with 3ZnTPP while minimizing interference from solvent bands in the transient RR spectrum (see below). CD_3CN serves to dilute the THF bands in the 1000–1700- cm^{-1} region. (Pure CD_3CN does not dissolve ZnTPP sufficiently.) While methylene chloride is a better Raman solvent, it reacts with 3ZnTPP , as demonstrated by the appearance of photoproduct absorption bands (Figure 7, bottom) when a methylene chloride solution of ZnTPP is irradiated with 416-nm laser pulses (the solution turns from violet to green). Chlorinated solvents have been shown to react with photoexcited porphyrins.²⁹ This photoreactivity is the likely source of the discrepancy between the present results and an early 3ZnTPP RR spectrum³⁰ reported from this laboratory. The earlier spectrum, which showed only small shifts from the ground-state bands, was produced by subtracting the ground-state CW spectrum, obtained with a spinning sample, from the CW spectrum of a stationary sample, in which a photostationary state was allowed to build up. Unfortunately, the solvent was methylene chloride, and it seems likely that photoproducts in the stationary sample contributed to the difference spectrum. In the present experiments, care was taken to

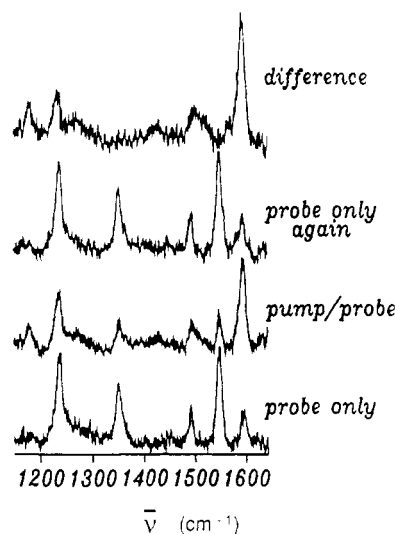


Figure 8. Resonance Raman spectrum (probe only) of ground-state ZnTPP (458.9-nm excitation (first anti-Stokes 2H_2 shifted, 532 nm YAG output) taken in 1:1 CD_3CN/THF (ca. 1 mM) and of the same solution 100 ns after a spatially coincident 416-nm pulse (first Stokes H_2 shifted, 355-nm output from a second YAG laser). Subsequent elimination of the 416-nm pump pulses results in a return to the original ground-state spectrum (probe only again). The difference spectrum (difference, attributed to 3ZnTPP ; see text) is obtained by subtracting the probe only spectrum from the pump/probe spectrum. The intensity ratio for subtraction was adjusted to avoid negative peaks.

ascertain the absence of undesired photoproducts in the CD_3CN/THF mixture, even with prolonged exposure to 416-nm laser pulses.

The RR spectrum of ZnTPP, taken with 7-ns (fwhm) 458.9-nm pulsed laser excitation (Figure 8, probe only), contains bands with identical frequencies and relative intensities similar to those seen in the 457.9-nm excitation CW spectrum (Figure 3) and clearly arises from ground-state ZnTPP. Introduction of a 416-nm pump pulse 100 ns before the probe pulse results in significant changes in the RR spectrum (Figure 8, pump/probe). Subsequent removal of the pump beam results in reappearance of the ground-state spectrum (Figure 8, probe only again), showing that the system is totally reversible both chemically (i.e., no photodegradation, confirmed by UV/vis and TLC) and photophysically. The difference spectrum (Figure 8, difference) is produced by subtracting the probe only spectrum from the pump/probe spectrum, using an intensity factor just sufficient to avoid negative difference peaks associated with ground-state bands. The difference spectrum is attributed to the excited triplet state (T_1) since the excited singlet state (S_1 ; $\tau^{1/2} = 2$ ns) is depleted during the 100-ns pump/probe delay, and the probe excitation is in resonance with the $T_1 \rightarrow T_n$ transition (Figure 7). Difference spectra obtained with longer delays, 200, 300, 400, 500, and 600 ns (not shown), reflect the decay of the excited triplet state (the decay is hastened by triplet-triplet annihilation³¹ at the 0.5 mM concentrations used) and repopulation of the ground state, with no evidence of other transient species.

In order to assign the RR features of 3ZnTPP , pump/probe difference spectra were obtained for ZnTPP- d_{20} and ZnTPP- d_8 isotopomers (Figure 9). The vibrational frequency shifts are given in Table II. Large d_{20} shifts establish that the 1596-, 1233-, 1179- cm^{-1} bands have significant phenyl character. As shown in Figure 10, they are polarized and are assigned to ϕ_4 , ν_1 , and ϕ_6 , respectively.²⁰ These bands occur at the same frequency as their ground-state analogues (Table I), implying that the phenyl electronic structure is unperturbed in the T_1 state. They are by far the strongest bands in the 3ZnTPP RR spectrum, however, and must have large Franck-Condon factors to the resonant upper state (T_n).

The band at 1287 cm^{-1} also shows a large d_{20} isotope shift and is assigned to ν_{27} , the only d_{20} -sensitive TPP Raman mode in this spectral region¹⁷ other than the nearby ν_1 . Both ν_1 and ν_{27} pri-

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TABLE II: Triplet-State Vibrational Frequencies (cm^{-1}) of ZnTPP

vibrational mode	polarizn	$^3\text{ZnTPP}^*$	Δ_8^a	Δ_{20}^a	$\Delta_{S_0-T_1}^b$	$\Delta_{S_0-P^+}^c$	$\Delta_{S_0-P^-}^b$
ϕ_4 (phenyl)	p	1596	-1	-36	-2	-4	+2
ν_{10} , $\nu(\text{C}_\alpha\text{-C}_m)$	dp	1493	+2	0	-54	+4	-19
ν_2 , $\nu(\text{C}_\alpha\text{-C}_m)$	p	1508	-28	0	-40	-32	-16
ν_{11} , $\nu(\text{C}_\beta\text{-C}_\beta)$	dp	1445	-22	0	-48	-5	
ν_4 , $\nu(\text{C}_\alpha\text{-N})$	p					-10	+3
ν_{27} , $\nu(\text{C}_m\text{-Ph})$	dp	1287	-10	-44	+15		-15
ν_1 , $\nu(\text{C}_m\text{-Ph})$	p	1233	0	-50	-4	-3	-3
ϕ_6 (phenyl)	p	1179	0	<i>d</i>			

^a Isotope shift for d_8 and d_{20} substitution. ^b Shift from the ZnTPP ground-state frequency for the T_1 state and for the ZnTPP radical anion (P^-). The radical-cation frequencies were obtained from RR spectra (unpublished) of electrogenerated species. ^c Shift between CuTPP and its radical cation (P^+).¹³ ^d A large downshift, $\sim 300 \text{ cm}^{-1}$, is expected for this mode.

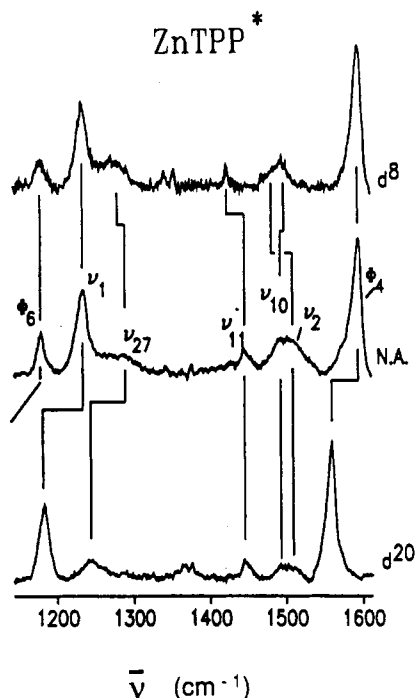


Figure 9. Difference RR spectra of $^3\text{ZnTPP}$ (NA), $^3\text{ZnTPP-d}_8$ (d^8), and $^3\text{ZnTPP-d}_{20}$ (d^{20}) isotopomers (458.9-nm probe and 416-nm pump) taken in 1:1 $\text{CD}_3\text{CN/THF}$ (ca. 1 mM) solutions. Vibrational assignments were based on the isotope shift patterns (Table I). The pump/probe delay was 10 ns.

marily involve stretching of the porphyrin-phenyl bond and are the two Raman-active modes, A_{1g} and B_{2g} , formed from this coordinate. The 1287-cm^{-1} band is unusually broad, but the polarization spectra (Figure 10) show the entire envelope to be largely depolarized, as expected for ν_{27} . Moreover, the d_{20} spectrum (Figure 9) shows an equally broad band at the shifted position, so the breadth does not appear to be attributable to extra modes. Three other bands are seen in the $^3\text{ZnTPP}$ spectrum (Figure 9), at 1508 , 1493 , and 1445 cm^{-1} , which exhibit negligible d_{20} sensitivity but show substantial d_8 shifts. Comparison with the ground-state ZnTPP isotope shifts allows us to assign these bands to ν_2 , ν_{10} , and ν_{11} , respectively. The polarization spectra (Figure 11) show ν_{11} to be depolarized, consistent with its B_{1g} symmetry; its d_8 shift is only about half that seen in the ground state, however, indicating an appreciable change in composition. The ν_2 and ν_{10} bands are overlapped, but the polarization spectra identify ν_{10} as the low-frequency component from the prominent perpendicularly polarized contribution.

On the other hand, ν_{10} and ν_{27} seem to be less completely depolarized than is ν_{11} . This can be seen in the difference polarization spectrum shown in Figure 10, in which the perpendicular spectrum is subtracted from the parallel spectrum, with an intensity ratio (close to the expected 3:4) sufficient to cancel the ν_{11} intensities. A strong shoulder at the ν_{10} position is seen in this difference spectrum, showing a significant remnant polarized component; some remnant intensity is also seen for ν_{27} . Thus, the ν_{10} and ν_{27} depolarization ratios appear to be less than 3:4. A

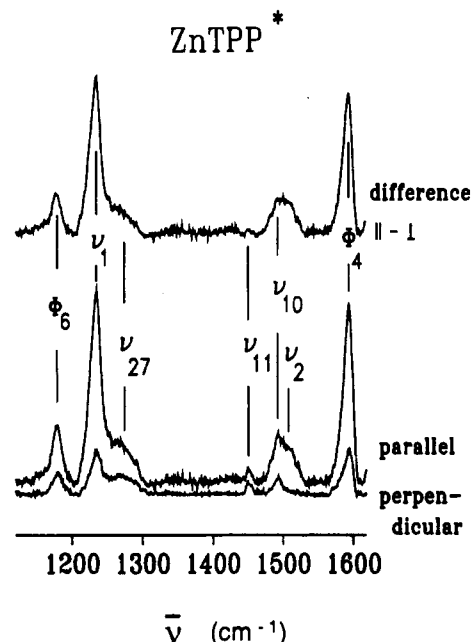


Figure 10. Parallel (\parallel) and perpendicular (\perp) polarized difference RR spectra of $^3\text{ZnTPP}$ (ca. 1 mM in 1:1 $\text{CD}_3\text{CN/THF}$) solutions with 458.9-nm excitation 10 ns following a spatially coincident 416-nm pump pulse. The parallel-perpendicular difference is plotted above.

lowering of the symmetry is implied by this observation, and its consequences are discussed in the next section.

The isotope shifts of ν_2 and ν_{10} match those seen in the ground-state spectra, even though their frequencies are lowered by 40 and 54 cm^{-1} ; the ν_{11} frequency is lowered by 48 cm^{-1} . ν_2 is the only A_{1g} skeletal mode seen in the $^3\text{ZnTPP}$ spectrum and is therefore the only one with an appreciable Franck-Condon factor to the T_n state. It is striking that ν_4 , the strongest band in the S_2 -resonant RR spectrum of ground-state ZnTPP, is undetectable in the $^3\text{ZnTPP}$ spectrum. The excited-state RR frequencies and assignments are listed in Table II.

The $^3\text{ZnTPP}$ RR spectrum reported by Walters et al.¹¹ contains the same strong phenyl modes, ϕ_4 , ν_1 , and ϕ_6 , as does our spectrum and also a broad band which was suggested to contain unresolved ν_2 and ν_{10} components. There are some differences between their spectra and ours, however. They assigned a 1427-cm^{-1} band to ν_{11} , but the frequency of our ν_{11} band is 1445 cm^{-1} . Additional bands were reported by Walters et al. at 1389 and 1357 cm^{-1} (the latter is coincident with the strong ground-state ν_4), but these are not seen in our spectra. Finally, Walters et al. found two components, at 1265 and 1290 cm^{-1} , where we see a single broad band, ν_{27} , with a 1287-cm^{-1} central frequency, which is not resolvable by isotopic or polarization measurements. It is possible that the low temperature, -80°C , employed by Walters et al., is responsible for some of these differences, but their significance is difficult to assess.

Discussion

Skeletal Modes: The Jahn-Teller Effect. The three observed skeletal modes of $^3\text{ZnTPP}$ — ν_{10} , ν_2 , and ν_{11} —all experience large

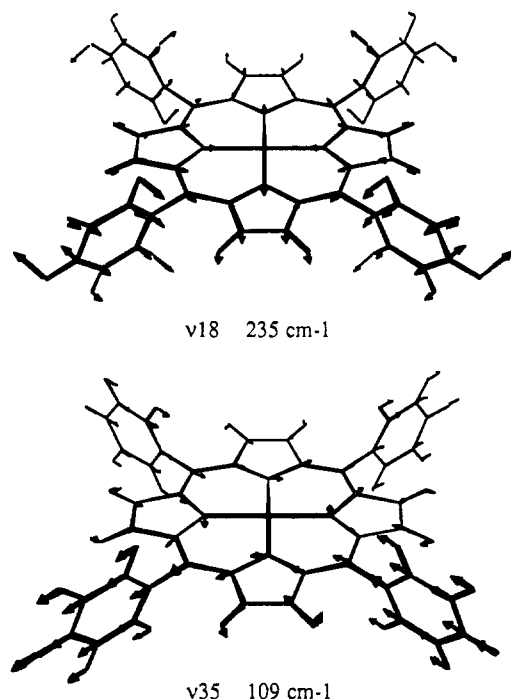


Figure 11. Eigenvectors²⁰ for the two possible Jahn-Teller distortion coordinates, ν_{18} (B_{1g} , 235 cm^{-1}) and ν_{35} (B_{2g} , 109 cm^{-1}).

downshifts from their ground-state frequencies. ν_{10} and ν_{11} involve stretching of the methine $C_{\alpha}C_m$ and pyrrole $C_{\beta}C_{\beta}$ bonds, respectively, while ν_2 involves a mixture (along with ν_3) of both coordinates.²⁰ Since the lowest excited state has an electronic configuration based on a hole in the HOMO and an electron in the LUMO of the porphyrin ring (d orbitals are not involved in the closed-shell ZnTPP), the downshifts are consistent with the expected weakening of the ring π bonds. Indeed, it is instructive to compare these downshifts to those observed upon addition of an electron to ZnTPP, to form the radical anion, or extraction of an electron to form the radical cation. The frequency shifts of ZnTPP⁻ relative to ZnTPP are listed in Table I. An RR spectrum of ZnTPP⁺ has been reported by Yamaguchi et al.,³² but the assignments are not obvious and we use instead the frequency shifts between CuTPP and CuTPP⁺, for which reliable assignments are available from isotope shifts and polarizations.¹³

The comparison in Table II shows that the ν_2 frequency shift upon electronic excitation of ZnTPP, 40 cm^{-1} , is not far from the sum of the frequency shifts upon addition and extraction of an electron, 16 and 32 cm^{-1} . This is the only A_{1g} skeletal mode seen for ³ZnTPP, and since it is a combination of $C_{\alpha}C_m$ and $C_{\beta}C_{\beta}$ stretching, we conclude that the expansion of the π bonds is about as expected from the simple addition of one-electron effects. For ν_{10} , however, the one-electron effects are not additive in the electronically excited state. The radical-cation shift is very small, while the radical-anion shift is only one-third as large as the ³ZnTPP shift.

The B_{1g} and B_{2g} modes provide distortion coordinates appropriate for the Jahn-Teller effect.^{11,12} The ZnTPP LUMO, e_g^* , is degenerate, and both ³ZnTPP and ZnTPP⁻ are therefore subject to J-T distortion. The ZnTPP HOMO is a_{2u} , but it is only slightly higher in energy than the a_{1u} orbital, as evidenced by essentially zero intensity in $Q_{0,0}$ electronic transition. The configurations produced by promotion of an electron to the e_g^* orbital from the a_{2u} and a_{1u} orbitals mix with one another to produce the two lowest excited singlet states, Q and B (S_1 and S_2 in Figure 2); this configuration interaction has the effect of suppressing J-T activity, which is expected to vanish, within the four-orbital model, when a_{2u} and a_{1u} are degenerate.^{21,33} In the triplet state, however, this

configuration interaction is prohibited by symmetry and the Jahn-Teller effect should find full expression.³³ EPR spectroscopy on the T_1 state of zinc porphine⁶ has established that there is a J-T distortion of B_{1g} symmetry.³⁴ We therefore interpret the large ³ZnTPP downshifts of ν_{10} as resulting from the same distortion.

The J-T effect produces a linear force along a distortion coordinate, resulting in a flattened or double-minimum potential. If the barrier between the minima is substantially larger than a vibrational quantum, then the distortion is static and the symmetry of the molecule is lowered. In that event, the Raman scattering tensor conforms to the lowered symmetry and the depolarization ratio is affected. The J-T-active modes, which are depolarized in the parent symmetry, become polarized in the lower symmetry. As noted above, the ν_{10} band does indeed appear to be substantially polarized (Figure 10), but on the other hand the ν_{11} band remains depolarized. This difference must reflect the specifics of the J-T distortion coordinate. If it leads to an inequivalence of the two $C_{\alpha}C_m$ bonds at each methine bridge, then the α_{xx} and α_{yy} tensor elements would become unequal for the B_{1g} mode involving $C_{\alpha}C_m$ stretching, i.e., ν_{10} , resulting in $\rho < 3/4$. This distortion could, however, leave the $C_{\beta}C_{\beta}$ bonds essentially equal so that the α_{xx}/α_{yy} inequality might be negligible for the $C_{\beta}C_{\beta}$ stretch, ν_{11} , leaving $\rho = 3/4$. The suggested static distortion along the $C_{\alpha}C_m$ bonds is unlikely to be along the ν_{10} coordinate per se, since its frequency is high, but rather along the lowest frequency B_{1g} coordinate, ν_{18} , whose eigenvector²⁰ is shown in Figure 11. This mode involves displacement of the metal-N(pyrrole) bonds primarily but also produces inequivalent $C_{\alpha}C_m$ bonds.

The ν_{27} band of ³ZnTPP is broad and is shifted up slightly from its ZnTPP frequency. As noted above, the assignment of this band seems unequivocal, because of its large d_{20} shift, and the downshift of the entire band envelope makes it unlikely that the breadth could be explained by overlapping bands. ν_{27} is the B_{2g} porphyrin-phenyl stretch. Although the main Jahn-Teller distortion coordinate is B_{1g} , a subsidiary B_{2g} distortion cannot be excluded.³⁴ Zero-field EPR measurements on T_1 of ZnTPP find E_0 to be temperature dependent, which argues for multiple conformational states in T_1 . A subsidiary J-T distortion along ν_{35} (Figure 11), the lowest frequency porphyrin skeletal mode,²⁰ which is of B_{2g} symmetry, could account for the EPR result. Since ν_{27} appears to be partially polarized, a static B_{2g} J-T distortion is suggested. The breadth of the band indicates, however, that there is a distribution of static distortions involving the phenyl rings.

Anion. Porphyrin radical anions are generally assumed to undergo a B_{1g} J-T distortion¹² since the e_g^* orbitals individually have B_{1g} nodal patterns.²⁷ Configuration interaction could, however, mix the e_g^* orbitals and introduce a B_{2g} pattern. The EPR spectrum of ZnTPP⁻ is broad, and while the width is consistent with the hyperfine parameters calculated on the basis of a B_{1g} distortion,³⁵ structural interpretation is not definitive.

The RR spectra indicate that the distortion is much less pronounced than in ³ZnTPP. The band frequencies are closer to those of the neutral parent, and there is no clear evidence of symmetry lowering from depolarization ratios. In particular, the ν_{10} band is essentially depolarized, in contrast to ³ZnTPP, indicating that the B_{1g} distortion must have a sufficiently low barrier to be dynamic. A barrier of $<200 \text{ cm}^{-1}$ has indeed been estimated by Maslov³⁶ and by Felton and Linschitz.³⁵ As noted above, the RR enhancement is similar for ZnTPP and the anion, suggesting that there is no large distortion for the latter in its ground state.

The ν_{10} and ν_2 modes shift down 19 and 16 cm^{-1} upon reduction of ZnTPP. Since these involve $C_{\alpha}C_m$ and $C_{\beta}C_{\beta}$ stretches primarily, the downshifts may reflect net antibonding character of the e_g^* orbitals for these bonds. Alternatively, both modes are markers of the porphyrin core size,²² and core size expansion is expected on the basis of the large e_g^* orbital coefficients of opposite phase

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on opposite pyrrole N atoms.²⁷ The downshift in ν_2 can be explained by a core size expansion of 0.05 Å on the basis of the correlations given in ref 22. This expansion is predicted to shift ν_{10} down by 27 cm⁻¹, 9 cm⁻¹ more than observed. The elevated frequency might reflect a B_{1g} contraction of C_αC_m bonds from the bond length expected on the basis of the core size.

On the other hand, there is some evidence for a B_{2g} J-T effect because the two B_{2g} modes which are observed in the parent ZnTPP as well as the anion, ν_{27} and ν_{29} , shift down upon reduction, although the relevant bond orders are not expected to decrease. ν_{27} is a C_m-phenyl stretch as is the A_{1g} mode ν_1 , but ν_1 does not shift upon reduction. ν_{29} is a C_αC_β stretch primarily, and if anything, the C_αC_β bond order should increase upon reduction, since the major interaction is bonding in the e_g* orbitals.²¹ The adjacent A_{1g} mode ν_4 does not shift, although it is a combination of C_αC_β and C_αN stretching, perhaps because the antibonding C_αN interaction cancels the bonding C_αC_β interaction. Thus, there appears to be a selective softening of B_{2g} modes. We note that this effect apparently does not preclude a predominantly B_{1g} J-T distortion. Hoffman and Ratner³⁷ have analyzed the complexities of the J-T effect in D_{4h} symmetry and concluded that under some conditions the modes less strongly coupled can show the greater softening.

Phenyl Mode Dominance in ³ZnTPP: Charge-Transfer Character for the T_n State? The most striking aspect of the ³ZnTPP RR spectrum is the dominance of the ϕ_4 , ϕ_6 , and ν_1 bands. The first two of these arise from internal modes of the phenyl ring, while ν_1 , the A_{1g} porphyrin-phenyl stretch, also has a strong contribution from the internal phenyl bonds.²⁰ These bonds must therefore be significantly altered in the resonant excited state, T_n, leading to large Franck-Condon products for the phenyl modes, as pointed out by Walters et al.¹¹ It seems likely that the relatively low intensity of the porphyrin ν_2 band may also be borrowed from the nearby strong ϕ_4 . Certainly, the Franck-Condon products are much smaller for the porphyrin skeletal modes than for the phenyl modes; no other A_{1g} skeletal mode is observed besides ν_2 .

We suggest that the reason for the phenyl mode dominance is that the T₁-T_n transition involves charge transfer from the porphyrin e_g* to a phenyl π* orbital. The T_n energy can be estimated to be 34.5 kK by adding the frequency of the T₁-S₀ phosphorescence band maximum, 12.8 kK (780 nm), to that of the T₁-T_n absorption band maximum, 21.7 kK (460 nm). This energy is not far from that of the first excited state, 38.4 kK, of benzene,³⁸ whose π* energy should be lowered somewhat in TPP because of the inductive effect of the porphyrin. Thus, the porphyrin e_g*-phenyl π* assignment does not seem unreasonable. The proposed charge-transfer transition would produce a phenyl anion, resulting in a large change in the phenyl geometry and thereby accounting for the phenyl mode enhancements. The porphyrin mode enhancements would be much lower because the e_g* orbital is spread over a much larger number of bonds so its depopulation has a smaller geometric effect.

The phenyl mode frequencies, however, are essentially the same for ³ZnTPP and ZnTPP. There is very little electronic communication between the phenyl and porphyrin rings in the TPP ground

state,³⁹ presumably because they are kept nearly orthogonal by the steric repulsion between phenyl and pyrrole H atoms. The unshifted RR frequencies imply that this electronic insulation is maintained in the T₁ state as well. Although the ground-state RR intensities were at one time interpreted⁴⁰ as implying electronic delocalization on the phenyl rings in the resonant S₂ state, the most recent analysis²⁰ suggests that vibrational mixing with porphyrin modes may be sufficient to account for the phenyl mode intensities. Only in the T_n state does electronic involvement of the phenyl rings come clearly into play. The proposed charge-transfer transition would be coupled to rotation of the phenyl groups into the porphyrin plane, since the resulting favorable orbital overlap would increase the transition moment. This coupling might help to explain the large bandwidth of the T₁-T_n absorption band (Figure 7). A large RR enhancement would be expected for the phenyl torsion mode were it possible to record the spectrum at low enough frequency. (Assignment of this mode to a 23-cm⁻¹ band in the cold jet fluorescence spectrum of ZnTPP has been suggested,⁴¹ although a somewhat higher frequency seems more likely.²⁰)

Conclusions

1. The RR spectrum of ZnTPP⁻ is similar to that of ZnTPP, both in enhancement patterns and in d_8 and d_{20} isotope shifts. There are modest frequency downshifts for ν_{10} and ν_2 which may be understood qualitatively on the basis of the e_g* orbital pattern. Downshifts of the B_{2g} modes, ν_{27} and ν_{29} , however, are suggested to arise from the J-T effect. Depolarized and anomalously polarized bands appear in the spectrum, indicating that D_{4h} symmetry is maintained. Consequently, the J-T distortion is inferred to be dynamic in character.

2. The RR spectrum of ³ZnTPP, in contrast, shows a large downshift in ν_{10} , much larger than expected from orbital occupancy considerations, and its band shows an appreciable polarized component. These effects are interpreted in terms of a static distortion along a B_{1g} coordinate, probably ν_{18} , which involves the C_αC_m bonds. At the same time, an upshift and broadening of the B_{2g} mode, ν_{27} , which is also partially polarized, suggests a simultaneous B_{2g} J-T distortion, probably along ν_{35} , which involves the porphyrin-phenyl bonds.

3. The ³ZnTPP RR spectrum is dominated by phenyl modes, suggesting that the T₁-T_n electronic transition at 480 nm involves a porphyrin e_g* to phenyl π* orbital excitation. The resulting charge transfer to the phenyl ring produces large displacements along the phenyl ring coordinates.

Acknowledgment. We thank Dr. Jack Fajer for helpful discussions. This work was supported by DOE Grant DE-AC02-81ER10861. R.A.R. was the recipient of NIH Individual National Research Service Award GM12197-02. R.P. was supported by a grant from the Italian Consiglio Nazionale delle Ricerche.

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