Time-Resolved Resonance Raman Spectroscopic Study on Metallo-tetraphenylporphyrins: Effects of Metal Sizes

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The variation of Jahn-Teller (J-T) distortion imposed on various metallo- tetraphenylporphyrins (MTPPs: M = Zn^{II}, Pd^{II}, Pt^{II} and Rh^{III}) has been investigated by time-resolved resonance Raman spectroscopy. B_{1g} and B_{2g} modes of the triplet (π,π^*) states for the heavy-metal porphyrins exhibit the enhancement of their intensities compared with those of $^3Zn^{II}TPP$. while the enhancement of phenyl internal mode is reduced. These results suggest that the J-T distortion becomes manifest as the metal size increases, and consequently the porphyrin-to-phenyl ring charge transfer in the excited triplet state is inhibited.

Introduction

The photophysical properties of metalloporphyrins and related molecules have been a concern of current investigation.[1] Recently. much attention has been drawn to their excited state structures and dynamics. because the excited states are known to act as primary intermediates in electron transfer,[2] photodynamic therapy[3] and solar energy conversion processes.[4] Since the frequencies of the time-resolved resonance Raman (TR^3) bands are much sensitive to the changes in bonding, structure, and charge transfer processes in the excited states. the TR^3 spectroscopy has been extensively applied to the investigation on the excited state structural changes of metalloporphyrins[5-17] and free-base porphyrins.[18-23]

Especially. there have been numerous investigations to characterize the Jahn-Teller (J-T) distortion in the excited triplet state (T_1) of *meso*-substituted tetraphenylporphyrin (TPP) derivatives. From the previous TR^3 studies[5-7] it has been found that the J-T effects of $Zn^{II}TPP$ are attributed to the distortion along the B_{1g} and B_{2g} coordinates. Because of the J-T distortion. the molecular symmetry is reduced, and the electronic structure of porphyrin ring undergoes a change. Such structural changes would give rise to an increase in the dihedral angle between phenyl groups and porphyrin ring. and likely result in a variation of the porphyrin-phenyl electronic conjugation in the highly excited triplet states (T_n). Furthermore. the J-T distortion in the triplet state is expected to be affected by the central metal size and the axial ligation. Thus. we report the TR^3 spectra of some heavy-metal porphyrins such as $Pd^{II}TPP$, $Pt^{II}TPP$ and $Rh^{III}T$-PPCl in noncoordinating and coordinating solvents in order to address the consequences of metal size and solvents on the excited state J-T distortion. The comparison of these results with those of $Zn^{II}TPP$ has been made to correlate the relationship between the J-T distortion and the porphyrin ring-to-phenyl charge transfer of these porphyrins.

Experimental Section

$Zn^{II}TPP$. $Pd^{II}TPP$. $Pt^{II}TPP$. and $Rh^{III}TPPCl$ were purchased from Porphyrin Products. Inc. (Logan. Utah) and used without further purification. The ground-state absorption and Raman spectra of these compounds agree with the published spectra.[24,25] All the solvents used were spectroscopic grade and further purified by fractional distillation.

The TR^3 spectra were obtained with a pump pulse of 532 nm (5 ns fwhm at 10 Hz. and 0.03 mJ/pulse) by using a nanosecond Q-switched Nd : YAG laser.[9,21] The pump pulses at 565 nm were generated from the dye laser system pumped by the 532 nm outputs of the Nd : YAG laser. The probe pulses at 435 and 458 nm (3.5 ns fwhm at 10 Hz. and 0.01 mJ/pulse) were prepared as the first anti-Stokes shifted Raman line of H_2. excited by the 532 and 565 nm. respectively. 416 nm pulse is the first Stokes line of a H_2 Raman shifter pumped from the third harmonic (355 nm) of the Nd : YAG laser. The intensities of pump and probe pulses were adjusted by employing neutral density filters. The percentage of excited porphyrin molecules was estimated to be around 50-60% as compared with the solvent Raman peaks. The time delay between pump and probe pulses was controlled with an optical delay line. The Raman scattering signal was collected by a HR 640 spectrograph (Jobin Yvon) connected with a delay generator (Stanford Research DG535). a pulse generator (Princeton Instruments FG135). and a gated intensified photodiode array detector (Princeton Instruments IRY700). The sample solutions (*ca.* 1 mM) were flowed through a glass capillary (0.8-mm i.d.) at a rate sufficient to ensure that each pulse encountered a fresh volume of sample. We carefully checked the sample decomposition by monitoring the ground state Raman spectra of the samples. Ground state absorption spectra were measured on a Varian UV-visible spectrophotometer (Cary 5E). and the ground state Raman spectra were recorded by employing a continuous wave (cw) Ar ion laser. a Raman U1000 double

monochromator (Jobin-Yvon), and a photon counting electronics (Hamamatsu). All the Raman modes were assigned following the mode assignment of $Zn^{II}TPP$ and $Ni^{II}TPP$, because Raman spectra for high-frequency porphyrin skeletal modes of these metalloporphyrins are well known and quite similar with other heavy-metalloporphyrins.

We obtained the ground state Raman spectra using the probe pulses in resonance with T_1-T_n absorption bands of metalloporphyrins investigated here. And we just employed the pump pulses in resonance with Q-bands to generate excited triplet state species with an appropriate time delay between these two pulses. As for the pure triplet state Raman spectra, we subtracted the ground state Raman spectral intensities from the transient Raman spectra with $_2$ and $_4$ modes as reference. The T-T absorption bands of metalloporphyrins investigated in the present work exhibit much broader spectral features (fwhm is *ca.* 65 nm) than the corresponding ground state Soret bands.[26,27] Therefore, the variations in excitation wavelength do not show any significant intensity changes when all the transient peaks are normalized with $_2$ and $_4$ modes. Actually, the TR^3 spectra of MTPPs obtained with 435 nm probe pulses are identical to those measured by the different probe pulses such as 416 and 456 nm. Therefore, in this paper, we report the TR^3 spectra measured by the probe pulses in resonance with T_1-T_n absorption maximum of MTPPs. The different delay times were also employed for each porphyrin due to the difference in the singlet state lifetimes. The delay time we employed was believed to be sufficient enough to monitor only the triplet state species. We also changed the delay times between pump and probe pulses to see whether there exist any changes in Raman enhancement pattern depending upon delay times. It was found that there are no substantial changes in Raman intensities.

Results

$Zn^{II}TPP$. Figure 1 shows the TR^3 spectra of $Zn^{II}TPP$ in THF obtained by 565 nm pump and 458 nm probe pulses, which are in resonance with Q(0,1) and T_1-T_n absorption bands, respectively.[26] The bottom spectrum was obtained with an excitation of 458 nm probe only. The overall spectral
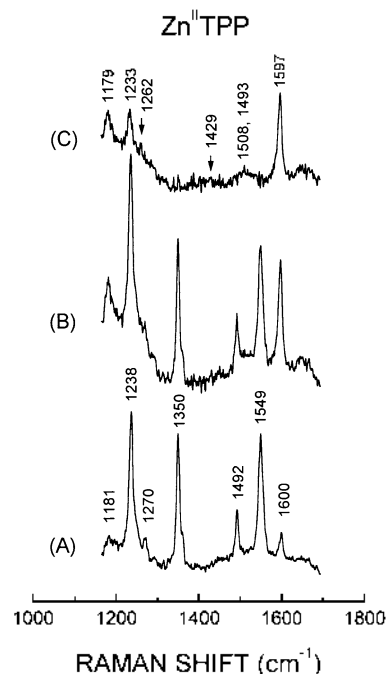

ZnⅡTPP

Figure 1. Nanosecond TR^3 spectra of $Zn^{II}TPP$ in THF measured with 565 nm pump and 458 nm probe pulses: (A) probe only, (B) pump and probe (time delay: 17 ns), and (C) difference (B-A) with a proper subtraction factor.

features of this spectrum are identical to those obtained by 457.9 nm cw Ar ion laser line: ϕ_4 (phenyl) mode at 1600 cm^{-1}, v_2 and v_{10} modes around 1549 cm^{-1}, v_{11} mode at 1492 cm^{-1}, v_4 mode at 1350 cm^{-1}, v_{27} mode at 1270 cm^{-1}, v_1 mode at 1238 cm^{-1} and ϕ_6 (phenyl) mode at 1181 cm^{-1}, respectively (Table 1). Since the S_1 and T_1 state lifetimes of $Zn^{II}TPP$ were reported to be about 2.7 ns and 1.2 ms, respectively.[27] the TR^3 spectrum of $Zn^{II}TPP$ in the T_1 state was recorded by the 458 nm probe pulse at 17 ns delay after pumping at 565 nm. The characteristic feature in the TR^3 spectra of $^3Zn^{II}TPP$ was manifest in the phenyl mode (ϕ_4) enhancemental at 1597 cm^{-1} as shown in the difference spectrum (Figure 1C). These results are consistent with the TR^3 spectra of $^3Zn^{II}TPP$ reported by Walters *et al.*[6] and Reed *et al.*[7] From the previous reports, the v_2 and v_{10} bands around 1549 cm^{-1} shifted to 1508 and 1493 cm^{-1}; the frequency shifts of these two bands

Table 1. Vibrational frequencies and assignment of the S_0 and T_1 states of $Zn^{II}TPP$, $Pd^{II}TPP$, $Pt^{II}TPP$ and $Rh^{III}TPPCl$

assignment	symmetry	$Zn^{II}TPP$		$Pd^{II}TPP$		$Pt^{II}TPP$		$Rh^{III}TPPCl$	
		S_0	T_1	S_0	T_1	S_0	T_1	S_0	T_1
Φ_4. (phenyl)	a_{1g}	1600	1597	1600	1600 (1598)	1600	1597 (1597)	1600	1598 (1598)
v_2. $(C_\beta C_\beta)$. $(C_\alpha C_m)$	a_{1g}	} 1549	1508	} 1562	} 1515	} 1562	1506	} 1557	} (1539)
v_{10}. $(C_\alpha C_m)$	b_{1g}		1493				1496		
v_{11}. $(C_\beta C_\beta)$	b_{1g}	1492	1429	1498	1450	1494	1452 (1451)	1496	(1441)
v_4. $(C_\alpha C_\beta)$. $(C_\alpha N)$	a_{1g}	1350	–	1367	–	1371	1368 (1371)	1364	(1367)
v_{12}. (Pyr half-ring)$_{svs}$	b_{1g}	–	–	–	1304 (1304)	–	1308 (1308)	–	(1301)
v_{27}. $(C_m C_{ph})$	b_{1g}	1270	1262	(1274)	(1267)	–	(1267)	1273	(1285)
v_1. $(C_m C_{ph})$. $(C_\alpha N)$	a_{1g}	1238	1233	1238	1233 (1232)	1235	1235	1237	1231 (1236)
Φ_6. (phenyl)	a_{1g}	1181	1179	1185	1183	1187	1186	1181	1181

Values shown in parentheses were obtained in piperidine solvent.

in the triplet state Raman spectrum were different, and consequently observed to be broad in this region.[6,7] The relative intensity of the v_1 band was diminished in the TR[3] spectrum, indicating no spectral shift for this band between the ground and triplet states. The v_{11} band at 1492 cm[1] and v_2- band at 1270 cm[1] shifted to 1429 and 1262 cm[1]. Intensities of both ϕ_6 and v_1 bands at 1179 and 1233 cm[1] were moderately enhanced in the triplet state.

Pd[II]TPP. The ground state absorption spectrum of Pd[II]TPP in THF denotes Q(0,0) and Q(0,1) bands at 550 and 521 nm, respectively, as well as B band at 414 nm. The T_1-T_n absorption maximum of Pd[II]TPP was reported to be around 450 nm.[26] and the S_1 and T_1 state lifetimes to be about 20 ps and 380 ms, respectively.[27] Thus, the TR[3] spectrum of photoexcited Pd[II]TPP was measured by employing 435 nm probe pulses at 3 ns time delay after an excitation of 532 nm pumping. In the probe only spectrum of Pd[II]TPP in THF (Figure 2(1)A), ϕ_1 mode at 1600 cm[1], v_2 and v_{10} modes around 1562 cm[1], v_{11} mode at 1498 cm[1], v_1 mode at 1367 cm[1], v_1 mode at 1238 cm[1] and ϕ_6 mode at 1185 cm[1] were observed, respectively (Table 1). In the difference Raman spectrum (Figure 2(1)C), the ϕ_1 band at 1600 cm[1] was observed to be enhanced in comparison with that observed in the probe only spectrum. The v_2 and v_{10} bands around 1562 cm[1] in the ground state exhibit different frequency downshift each other and become broad around 1515 cm[1] in the T_1 state. The v_1 band at 1238 cm[1] and the ϕ_6 mode at 1185 cm[1]

show 3-5 cm[1] downshift with an increase in its intensity. Also, the v_{12} mode at 1304 cm[1] and v_{11} mode at 1450 cm[1] were observed in contrast to ground state spectrum. The Raman spectral changes of the ϕ_1, ϕ_6 and v_1 modes accompanied by the T_1 state formation are not so significant as compared with those of [3]Zn[II]TPP. On the contrary, when the triplet state Raman spectrum was recorded for Pd[II]TPP in piperidine as shown in Figure 2(2), the v_{10}, v_{11} and v_2- modes at 1515, 1450 and 1304 cm[1] were not so strongly enhanced as those in THF. On the other hand, the TR[3] spectra of [3]Pd[II]TPP in piperidine show a pronounced increase in intensities particularly for the ϕ_1 band at 1598 cm[1] and the v_1 mode at 1232 cm[1] as compared with other B_{1g} modes such as the v_{11} and v_{12} modes (Figure 2(2)C).

Pt[II]TPP. The ground state absorption spectrum of Pt[II]TPP in THF exhibits Q(0,0) and Q(0,1) bands at 537 and 508 nm as well as B band at 400 nm. As in the case of Pd[II]TPP, the S_1 state lifetime of Pt[II]TPP is very short (~20 ps) due to the heavy atom effect, and the T_1 state lifetime was reported to be about 54 ms.[27,28] Thus, the transient Raman spectrum attributable to the T_1 state was obtained by the probe pulse at 416 nm at 3 ns time delay after 532 nm excitation (Figure 3). The ground state Raman spectra (Figure 3(1)A) obtained by the low power probe only excitation exhibit the ϕ_1 mode at 1600 cm[1], the v_2 and v_{10} modes at 1562 cm[1], the v_{11} mode at 1494 cm[1], the v_4 mode at 1371 cm[1], the v_1 mode at 1235 cm[1] and the ϕ_6 mode at 1187 cm[1], respectively (Table 1). In the excited triplet state Raman spectrum of Pt[II]TPP as shown

Pd[II]TPP

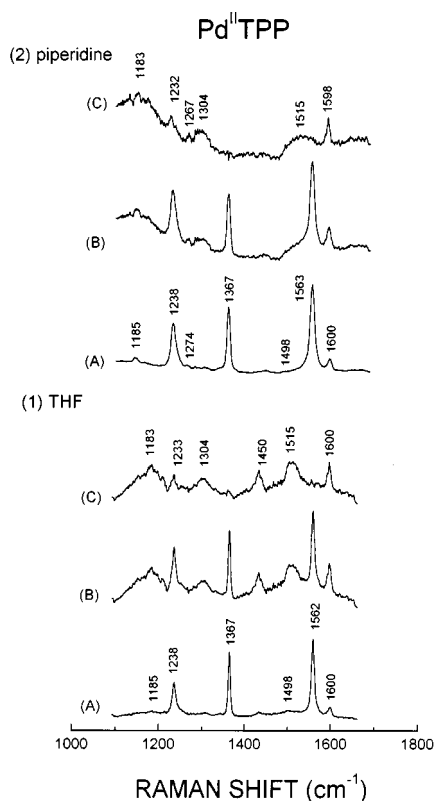(2) piperidine

(1) THF

RAMAN SHIFT (cm^{-1})

Figure 2. Nanosecond TR[3] spectra of Pd[II]TPP in (1) THF and (2) piperidine measured with 532 nm pump and 435 nm probe pulses. (A) probe only, (B) pump and probe (time delay: 1 ns), and (C) difference (B-A) with a proper subtraction factor.
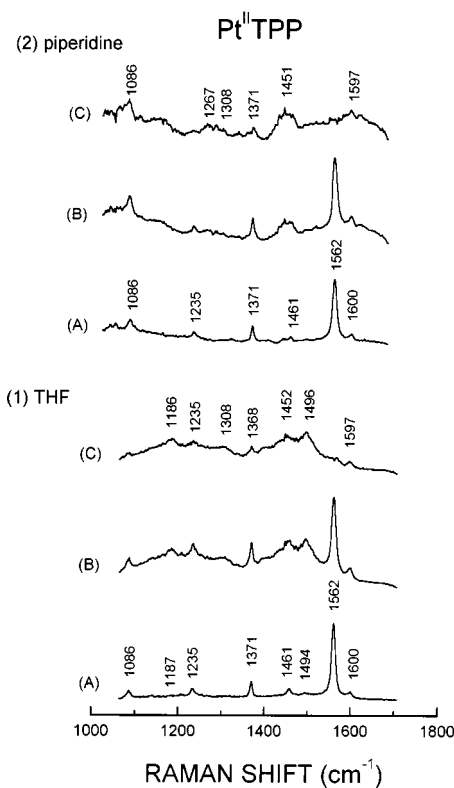

Pt[II]TPP

(2) piperidine

(1) THF

RAMAN SHIFT (cm^{-1})

Figure 3. Nanosecond transient resonance Raman spectra of Pt[II]TPP in (1) THF and (2) piperidine measured with single pulse at 416 nm: (A) the low power, (B) the high power, and (C) the difference spectrum (B-A) with a proper subtraction factor.

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in the difference spectrum of Figure 3(1)C, the ϕ_4 band at 1597 cm^{-1} is only slightly enhanced and the ϕ_6 band at 1186 cm^{-1} becomes broader relative to the corresponding ground state Raman band. In addition, the v_{10}, v_{11} and v_{12} bands at 1496, 1452 and 1308 cm^{-1} were observed to be relatively strong in comparison with the slight enhancement of the ϕ_4 mode in ^{3}Pt^{II}TPP (Figure 3C). In piperidine, the overall spectral features of ^{3}Pt^{II}TPP(pip) are similar to those for ^{3}Pt^{II}TPP in THF.

Rh^{III}TPPCl. Figure 4 shows the TR^3 spectra of Rh^{III}TPPCl in THF and piperidine acquired by probe (435 nm) pulses at 7 ns time delay after pumping at 532 nm. The T$_1$ state lifetime was reported to be around 115 ms.[28] Figure 4(1)A shows the Raman spectrum obtained with an excitation of 435 nm probe pulse only. The overall spectral features of the probe only spectrum are identical to those obtained by 457.9 nm cw Ar laser line: ϕ_4 mode at 1600 cm^{-1}, v_2 and v_{10} modes around 1557 cm^{-1}, v_{11} mode at 1496 cm^{-1}, v_4 mode at 1364 cm^{-1}, v_2- mode at 1273 cm^{-1}, v_1 mode at 1237 cm^{-1} and ϕ_6 mode at 1181 cm^{-1}, respectively.

The TR^3 spectra of Rh^{III}TPPCl in THF show a pronounced increase of intensities particularly in the ϕ_4 band at 1598 cm^{-1} and the v_1 mode at 1231 cm^{-1} (see Figure 4(1)C). In piperidine, the TR^3 spectra of Rh^{III}TPPCl show that the ϕ_4 mode at 1598 cm^{-1} is also enhanced. The B$_{1g}$ modes such as the v_{11} mode at 1441 cm^{-1} and the v_{12} mode at 1301 cm^{-1} become more enhanced relative to those of Rh^{III}TPPCl in THF (see Figure 4(2)C).

Rh^{III}TPPCl

(2) piperidine

(C) 1236 1301 1367 1441 1539 1598

(B)

(A) 1237 1273 1364 1496 1557 1600

(1) THF

(C) 1181 1231 1557 1598

(B)

(A) 1181 1237 1364 1496 1557 1600
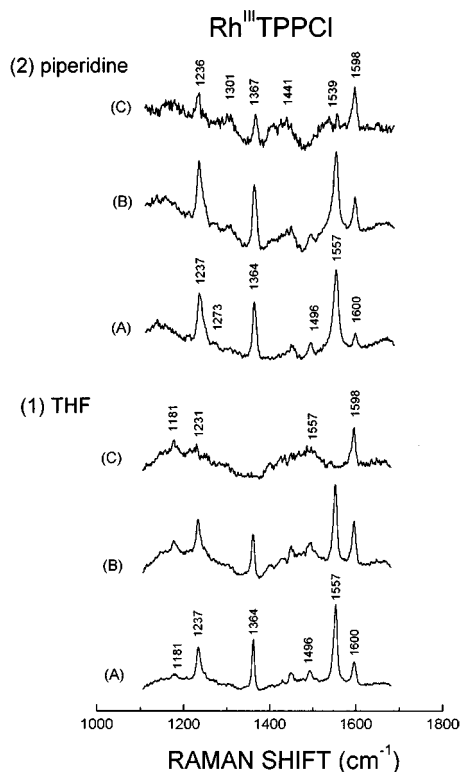
RAMAN SHIFT (cm^{-1})

Figure 4. Nanosecond TR^3 spectra of Rh^{III}TPPCl in (1) THF and (2) piperidine measured with 532 nm pump and 435 nm probe pulses; (A) probe only, (B) pump and probe (time delay: 7 ns), and (C) difference (B-A) with a proper subtraction factor.

Discussion

The most prominent aspect in the TR^3 spectrum of ^{3}Zn^{II}TPP appears to be the enhancement of the Raman bands in the 1100-1700 cm^{-1} region as compared with those of the ground state spectrum. This phenomenon was interpreted in terms of the symmetry lowering caused by J-T distortion, and the enhancement of some Raman bands can be correlated with the nontotally symmetric Raman modes (B$_{1g}$ or B$_{2g}$).[6,7] It has been recognized that the excited singlet state of metalloporphyrins has (a$_{1u}$e$_g$) and (a$_{2u}$e$_g$) orbital configurations which are almost degenerate, and a strong configurational interaction takes place. Thus, in the excited singlet state the configurational interaction minimizes the J-T effect normally. Conversely, in the T$_1$ state this configurational interaction is prohibited by symmetry,[29] and the J-T effect should be manifest.[30] The J-T distortion in D$_{4h}$ symmetry is known to occur along the B$_{1g}$ and/or B$_{2g}$ normal coordinates, causing the B$_{1g}$ and B$_{2g}$ vibrational modes to be totally symmetric in the reduced symmetry. The B$_{1g}$ and B$_{2g}$ modes include the v_{10}, v_{12}, v^-, and v_{29} modes providing distortion coordinates appropriate for the J-T effect.

In the cases of closed-shell heavy-metal metalloporphyrins (Pd^{II}TPP and Pt^{II}TPP), the enhancements of B$_{1g}$ modes were observed in the excited triplet states, but the ϕ_4 mode enhancement is not so significant as compared with the B$_{1g}$ modes. The ϕ_4 modes of ^{3}Pd^{II}TPP and ^{3}Pt^{II}TPP around 1600 cm^{-1} are rather weaker than that of ^{3}Zn^{II}TPP. It was reported that the ϕ_4 mode enhancement in the TR^3 spectra of ^{3}H$_2$TPP and ^{3}Zn^{II}TPP are mainly attributable to the charge transfer coupled to a rotation of the phenyl groups into the porphyrin ring.[21] In other words, the ϕ_4 mode enhancement in the excited triplet state was suggested to be contributed by the T$_1$-T$_n$ electronic transition in B band region involving a porphyrin e$_g$* to phenyl π* orbital excitation. The charge transfer from the porphyrin to the phenyl ring produces a large displacement along the phenyl ring coordinate. Therefore, a relatively weak ϕ_4 mode enhancement of Pd^{II}TPP and Pt^{II}-TPP in the excited triplet state indicates a decrease in the electronic conjugation between the porphyrin ring and phenyl groups. Thus, it can be suggested that the structural distortion by the J-T effects may increase the dihedral angle between the phenyl groups and porphyrin ring, and consequently inhibit the charge transfer process. These phenomena could account for the observation that the relative intensities of the ϕ_4 modes of heavy-metal TPPs are reduced whereas the B$_{1g}$ and B$_{2g}$ modes related to the J-T distortion are enhanced in the T$_1$ state.

The v_2 and v_4 bands in the ground state of closed-shell metallo-TPPs were observed at higher frequencies in the order of Rh < Pd < Pt metal compared with those of Zn^{II}-TPP. This indicates that the core sizes are decreased in the same order. It is noteworthy that the core size of porphyrin ring does not increase linearly as the metal size increases due to the out-of-plane geometry of the central metal in the porphyrin ring.[31] Nevertheless, it is important to note that the downshifts of the v_2 and v_{10} modes in the TR^3 spectra com-

pared to those of ground state are attributable to the porphyrin core-size expansion as the metal size increases. Since the v_2 and v_{10} modes are contributed by methine $C_\beta C_\beta$ and pyrrole $C_\alpha C_m$ bond stretchings, the downshifts of these modes in the T_1 state are consistent with the weakening of the ring π bonds. This suggests that a significant distortion of porphyrin ring take place to result in an expansion of the core size of $Pd^{II}TPP$ and $Pt^{II}TPP$ in the T_1 state. In other words, the distortion of heavy-metal porphyrin macrocycle becomes manifest as compared with the D_{4h} symmetry of $Zn^{II}TPP$, because of the more effective J-T distortion in the T_1 state. The v_4 mode of heavy-metal porphyrins in the T_1 state remains unchanged in its intensity and frequency, although it is a combination of $C_\alpha C_\beta$ and $C_\alpha N$ stretching. The behavior probably reflects the fact that the antibonding $C_\alpha N$ interaction cancels the bonding $C_\alpha C_\beta$ interaction.[7]

In the case of the TR[3] spectrum of $Rh^{III}TPPCl$ in THF, the ϕ_4 mode is markedly enhanced relative to the other modes. This is because chlorin axial ligand pulls the rhodium metal out of the porphyrin ring plane slightly making the porphyrin ring relatively undistorted, and consequently enhances the electronic resonance between the phenyl groups and porphyrin ring. In piperidine, other Raman bands, especially B_{1g} and B_{2g} modes, of $^3Rh^{III}TPPCl$ were observed to be enhanced, because piperidine solvent is ligated to the central rhodium metal as the sixth ligand so that the metal is located near the center of porphyrin ring to induce the J-T distortion. For $Pd^{II}TPP$ in piperidine, it is likely that $^3Pd^{II}TPP$ partially makes the five-coordinated complex through ligating with piperidine in the T_1 state. However, the transient Raman band at 1450 cm^{-1} was observed in THF in contrast to the lack of this mode indicating the contribution of the nontotally symmetric v_{11} mode (B_{1g}). This finding implies that the THF solvent is not ligated to the central metal ion in the triplet state and Pd metal is located near the center of porphyrin ring to induce the J-T distortion. Thus the structure of $^3Pd^{II}TPP(pip)$ should be similar to that of $Rh^{III}TPPCl$ in THF, while the structure of $Pd^{II}TPP$ in THF is similar to that of $^3Rh^{III}TPPCl(pip)$ in piperidine. Actually, in the TR[3] spectrum of $^3Pd^{II}TPP$ in piperidine, only the ϕ_4 mode was observed to be largely enhanced (Figure 2(2)C). Therefore, the relatively strong enhancement of the ϕ_4 mode of $^3Pd^{II}TPP(pip)$ in piperidine could be explained by the same reason for the enhancement of the ϕ_4 mode in $^3Rh^{III}TPPCl$ in THF. It is noteworthy that the enhancement of the ϕ_4 modes in the triplet states decreases in the order of Zn^{II}, Pd^{II}, and $Pt^{II}TPP$. This indicates that more ruffling structure of porphyrin ring is probably expected as the metal size increases, and thus the structural changes may reduce the dihedral angle between the phenyl groups and porphyrin ring. Therefore, the five-coordinated complexes, $Pd^{II}TPP(pip)$ in piperidine or $Rh^{III}TPPCl$ in THF, may have the doming structure due to the out-of-plane geometry of the central metal. In addition, the TR[3] spectra between $^3Pt^{II}TPP(pip)$ and $^3Pt^{II}TPP$ show the identical features. That is probably due to the similarity in structure between four- and five-coordinated species. From the previous report[25] that even the large metal

size of platinum does not increase the core size of porphyrin ring in piperidine and CH_2Cl_2 solvents, one expects severe distortion and ruffling for $Pt^{II}TPP(pip)$ and $Pt^{II}TPP$. Since this severe already-distortion exists in the ground state, the difference in distortion between the ground and excited states is not expected as the axial ligand is coordinated.

A similar structural change was recently investigated in free-base *meso*-tetraalkylporphyrins, $H_2T(alkyl)P$.[32] Particularly, the introduction of bulky tertiary-butyl or adamantyl substituents at the meso positions induced ruffling distortions. Those porphyrins deviate substantially from planarity, as is likely evidenced by the extremely short S_1 state lifetime, and the distortion consists primarily of severe ruffling of the macrocycle. It was suggested that the ultrafast radiationless deactivation of the ruffled porphyrins derives largely from the ability of these already-distorted molecules to easily undergo additional structural changes in the excited state compared to the ground state, resulting in an enhanced Franck-Condon factor for internal conversion. In concomitant with these observations, the extremely short S_1 lifetimes of heavy-metalloporphyrins are likely attributable to the structural distortion in addition to the heavy-metal effect.

Conclusions

The TR[3] spectra of closed-shell heavy-metal TPPs (Pd^{II}, Pt^{II}, Rh^{III}) show marked enhancements and large downshifts of the v_2 and v_{10} modes. These effects are interpreted in terms of the J-T distortion along the B_{1g} coordinate, which involves methine $C_\beta C_\beta$ and pyrrole $C_\alpha N$ bond stretchings. At the same time, the enhancement of the ϕ_4 mode in the T_1 state decreases as the metal size increases. This also suggests that a simultaneous charge transfer from porphyrin to phenyl rings is inhibited by the large displacements along the phenyl ring coordinates by the J-T distortion.

References

1. Rodriguez, J.; Kirmaier, C.; Holten, D. *J. Am. Chem. Soc.* **1989**, *111*, 6500.
2. Wasilewski, M. R. In *Photoinduced Electron Transfer, Part A*; Fox, M. A., Chanon, W., Eds.; Elsevier: Amsterdam, 1988; p 303.
3. (a) Roberts, J. E.; Dillon, J. *SPIE J.* **1987**, *847*, 134. (b) Chang, C. K.; Takamura, S.; Musselman, B. D.; Kessel, D. In *Porphyrins: Excited States and Dynamics*; *ACS Symp. Ser.* 321; Gouterman, M., Rentzepis, P. M., Straub, K. D., Eds.; Am. Chem. Soc.; Washington, 1986; p 347.
4. (a) Aizawa, M.; Hirano, M.; Suzuki, S. *Electrochim. Acta* **1979**, *24*, 89. (b) Harriman, A.; Porter, G.; Wilowska, A. *J. Chem. Soc., Faraday Trans. II* **1984**, *80*, 191.
5. Kumble, R.; Hu, S.; Loppnow, G. R.; Vitols, S. E.; Spiro, T. G. *J. Phys. Chem.* **1993**, *97*, 10521.
6. Walters, V. A.; de Paula, J. C.; Babcock, G. T.; Leroi, G.

E. *J. Am. Chem. Soc.* **1989**, *111*, 8300.

7. Reed, R. A.; Purrello, R.; Prendergast, K.; Spiro, T. G. *J. Phys. Chem.* **1991**, *95*, 9720.

8. Sato, S.; Kamogawa, K.; Aoyagi, K.; Kitagawa, T. *J. Phys. Chem.* **1992**, *96*, 10676.

9. (a) Jeoung, S. C.; Kim, D.; Cho, D. W.; Yoon, M. *J. Phys. Chem.* **1995**, *99*, 5826. (b) Jeoung, S. C.; Kim, D.; Cho, D. W.; Yoon, M. *J. Phys. Chem.* **1996**, *100*, 3072.

10. Vitols, S. E.; Terashita, S.; Blackwood, Jr. M. E.; Kumble, R.; Ozaki, Y.; Spiro, T. G. *J. Phys. Chem.* **1995**, *99*, 7246.

11. de Paula, J. C.; Walters, V. A.; Jackson, B. A.; Cardozo, K. *J. Phys. Chem.* **1995**, *99*, 4373.

12. Strahan, G. D.; Lu, D.; Tsuboi, M.; Nakamoto, K. *J. Phys. Chem.* **1992**, *96*, 6450.

13. Kruglik, S. G.; Apanasevich, P. A.; Chirvony, V. S.; Kvach, V. V.; Orlovich, V. A. *J. Phys. Chem.* **1995**, *99*, 2978.

14. (a) Kruglik, S. G.; Galievsky, V. A.; Chirvony, V. S.; Apanasevich, P. A.; Ermolenkov, V. V.; Orlovich, V. A.; Chinsky, L.; Turpin, P.-Y. *J. Phys. Chem.* **1995**, *99*, 5732. (b) Mojzes, P.; Chinsky, L.; Turpin, P.-Y. *J. Phys. Chem.* **1993**, *97*, 4841. (c) Chinsky, L.; Turpin, P.-Y.; Al-Obaidi, A. H. R.; Bell, S. E. J.; Hester, R. E. *J. Phys. Chem.* **1991**, *95*, 5754.

15. Kumble, R.; Loppnow, G. R.; Hu, S.; Mukherjee, A.; Thompson, M. A.; Spiro, T. G. *J. Phys. Chem.* **1995**, *99*, 5809.

16. Asano-Someda, M.; Sato, S.; Aoyagi, K.; Kitagawa, T. *J. Phys. Chem.* **1995**, *99*, 13800.

17. Sato, S.; Kitagawa, T. *Appl. Phys. B* **1994**, *59*, 415.

18. Sato, S.; Asano-Someda. M.; Kitagawa, T. *Chem. Phys. Lett.* **1992**, *189*, 443.

19. Bell, S. E. J.; Al-Obaidi, A. H. R.; Hegarty, M.; Hester, R. E.; McGarvey, J. J. *J. Phys. Chem.* **1993**, *97*, 11599.

20. Bell, S. E. J.; Al-Obaidi, A. H. R.; Hegarty, M.; McGarvey, J. J.; Hester, R. E. *J. Phys. Chem.* **1995**, *99*, 3959.

21. Jeoung, S. C.; Kim, D.; Ahn, K.-H.; Cho, D. W.; Yoon, M. *Chem. Phys. Lett.* **1995**, *241*, 533.

22. de Paula, J. C.; Walters, V. A.; Nutaitis, C.; Lind, J.; Hall, K. *J. Phys. Chem.* **1992**, *96*, 10591.

23. Sato, S.; Aoyagi, K.; Haya, T.; Kitagawa, T. *J. Phys. Chem.* **1995**, *99*, 7766.

24. Gouterman, M. In *The Porphyrins, Vol. III*; Dolphin, D., Ed.; Academic Press: New York, 1978; Chapters 1 and 8.

25. Seo, J.-C.; Chung, Y.-B.; Kim, D. *Appl. Spectrosc.* **1987**, *41*, 1199.

26. Harriman, A. *J. Chem. Soc. Faraday Trans. II* **1981**, *77*, 1281.

27. Darwent, J. R.; Douglas, P.; Harriman, A.; Porter, G.; Richoux, M. *Coord. Chem. Rev.* **1982**, *44*, 83.

28. Kalyanasundaram, K. *Chem. Phys. Lett.* **1984**, *104*, 357.

29. Ake, R. L.; Gouterman, M. *Theor. Chim. Acta* **1974**, *15*, 20.

30. Gouterman, M. *Ann. N. Y. Acad. Sci.* **1973**, *206*, 70.

31. Becker, R. S.; Allison, J. B. *J. Phys. Chem.* **1963**, *67*, 2662 and references cited therein.

32. (a) Gentemann, S.; Medforth, C. J.; Forsyth, T. P.; Nurco, D. J.; Smith, K. M.; Fajer, J.; Holten, D. *J. Am. Chem. Soc.* **1994**, *116*, 7363. (b) Gentemann, S.; Medforth, C. J.; Ema, T.; Nelson, N. Y.; Smith, K. M.; Fajer, J.; Holten, D. *Chem. Phys. Lett.* **1995**, *245*, 441.