because of the effect of conjugation. It is notable that the bandwidths for the skeletal modes are somewhat larger in the triplet than in the ground state spectra (~15 vs. 12 cm^{-1} FWHM). The skeletal mode frequencies are expected to be less sensitive to phenyl conjugation because the electronic influence is spread over a larger ring, but their increased width may nevertheless be a reflection of the proposed inhomogeneous distribution.

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Registry No. MgTPP, 14640-21-2; ZnTPP, 14074-80-7; PdTPP, 14187-13-4.

Laser-Induced Excited-State Ligation Changes for Nickel Tetraphenylporphine Monitored by Raman Spectroscopy

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Metalloporphyrins offer the interesting possibility of undergoing changes in axial ligation associated with the pumping of excited ligand field states via intersystem crossing from initially populated porphyrin π–π* states.[1,2] One example is the extremely rapid[3] and efficient photodissociation of the CO adduct of heme proteins, which has been widely exploited in studying the heme-linked protein dynamics of these O_2-carrying and -activating macromolecules.[4] Nickel porphyrins offer an attractive system for investigation since they are 4-coordinate and low spin in noncoordinating and weakly coordinating solvents but 6-coordinate and high spin in strongly coordinating solvents.[5] Holten and coworkers have shown with transient optical spectroscopy that the accessible excited state (low spin) of the 6-coordinate species rapidly loses its axial ligands, while the excited state of 4-coordinate nickel porphyrin (high spin) becomes ligated, thanks to the hole created in the d_{z^2} orbital. It should therefore be possible to shift the equilibrium between 4- and 6-coordinate species with photons. In this report we demonstrate such pumping with CW laser excitation of stationary samples of NiTPP (nickel tetraphenylporphine) in pyridine and piperidine, using resonance Raman (RR) spectroscopy to monitor the ligation changes. The RR spectra also allow assessment of the structural change attendant upon ligation, and they permit identification of a 5-coordinate species in piperidine solution, with a ground state that is probably high spin.[6] The same spinning vs. stationary sample technique was used which has allowed us to obtain triplet-state RR spectra of TPP complexes of Mg, Zn, and Pd.[7]

Figure 1 shows 406.7-nm-excited Raman spectra, in the region of the ν_4 skeletal mode,[8] for a stationary sample of NiTPP in pyridine. Two ν_4 bands are seen, at 1369 and 1346 cm^{-1}. The former is at the frequency seen for NiTPP in noncoordinating solvents and is attributed to the low-spin 4-coordinate complex. The latter band is attributed to the 6-coordinate high-spin complex, by comparison with the spectrum of NiTPP in piperidine (see Figure 3) in which the 6-coordinate species is dominant.[1,5] The porphyrin core is expanded in the 6-coordinate species due to electron promotion to the in-plane antibonding $d_{x^2-y^2}$ orbital; the porphyrin center-to-pyrrole nitrogen distance (C_t–N) is ~1.95 Å in 4-coordinate nickel porphyrins,[9] but 2.038 Å in the bis-imidazole adduct of nickel tetramethylpyridylporphine.[14] We attribute the ν_4 down shift upon pyridine or piperidine coordination at least in part to the core-size expansion; the porphyrin skeletal mode frequencies are known to be sensitive to the core size, as well as to electronic effects.[15]

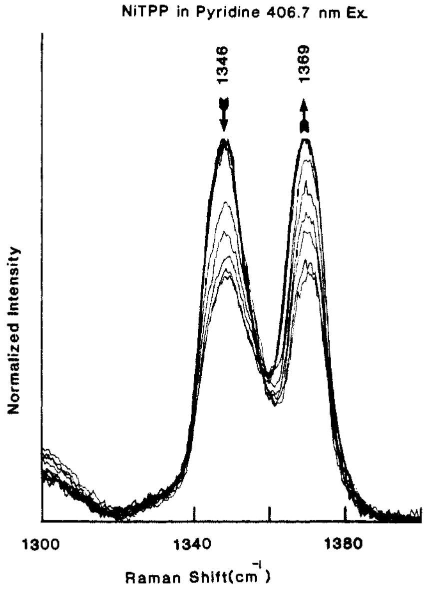

Figure 1. ν_4 Raman peaks for a stationary sample of NiTPP (purchased from Porphyrin Products and purified by chromatography on alumina A540, 0.2 mM) in pyridine, with 406.7-nm excitation. Arrows indicate the decreasing (1346 cm^{-1}) and increasing (1369 cm^{-1}) relative intensities at increasing laser power levels (1.5, 5, 10, 15, 20, 25, 50, 75, 90, 125, and 140 mW). In the absence of an internal standard (pyridine peaks are obscured by those of NiTPP) the spectra were scaled to whichever peak was stronger. (The intrinsic scattering factors are not the same for the two peaks.) Spectra were obtained via backscattering (135°) from a NMR sample tube, using a Spex 1401 double monochromator: 7-cm^{-1} slit width; 1-s time constant; 0.5 cm^{-1}/s scan rate.

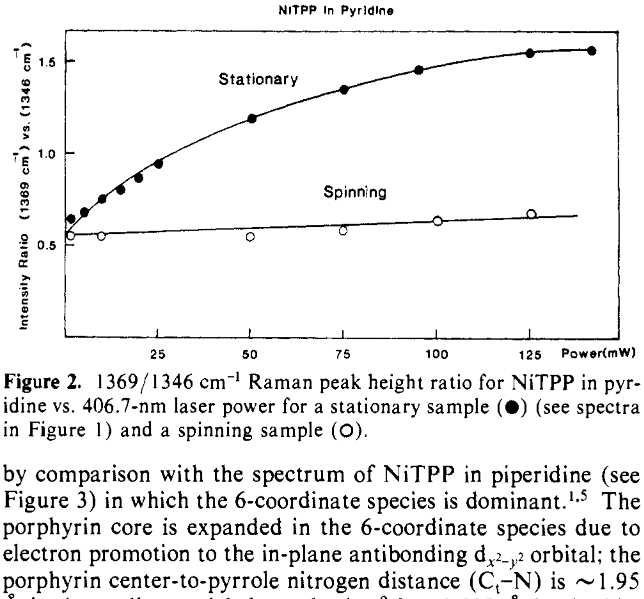

Figure 2. 1369/1346 cm^{-1} Raman peak height ratio for NiTPP in pyridine vs. 406.7-nm laser power for a stationary sample (●) (see spectra in Figure 1) and a spinning sample (○).

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(9) 1.929 Å in tetragonal (D_{2d}, ruffled)[10] and 1.958 Å in triclinic (D_{4h}, planar)[11] nickel octaethylporphyrin; 1.960 Å in nickel deuterioporphyrin;[12] 1.957 Å in nickel etioporphyrin.[13]

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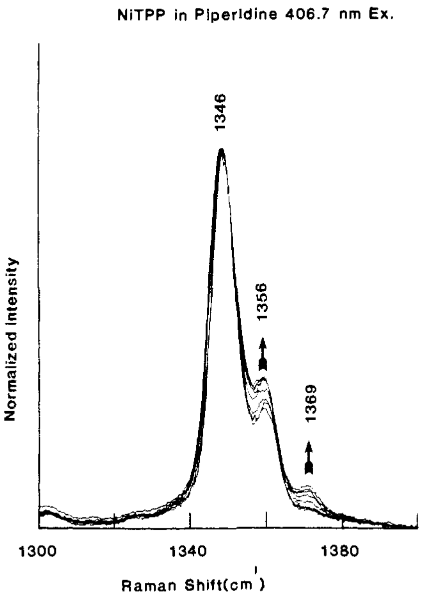

Figure 3. ν_4 Raman peaks for a stationary sample of NiTPP, 0.5 mM in piperidine, with 406.7-nm excitation. Arrows indicate the increasing relative intensities of the 1356- and 1369-cm^{-1} peaks with increasing laser power (5, 15, 25, 50, 75, 100, 125, and 150 mW): 5-cm^{-1} slit width; 1-s time constant; 0.5 cm^{-1}/s scan rate. The spectra were scaled to the 1346-cm^{-1} peak.

The spectra in Figure 1 show a progressive augmentation of the 1369-cm^{-1} band and diminution of the 1346-cm^{-1} band with increasing incident laser power levels. The intensity ratio is plotted against laser power in Figure 2, where it is seen to increase monotonically from a starting value of 0.54 to a limiting value of ~1.6. When the sample was spun through the laser, the spectral changes shown in Figure 1 were largely abolished, and the ratio of the bands was nearly independent of laser power, as shown in Figure 2. We attribute these effects to a laser-induced photostationary state in which the ligation equilibrium is shifted toward 4-coordination; evidently the movement of the sample through the laser beam in the spinning cell (3000 rpm) is sufficient to abolish this effect.

The solid line in Figure 2 represents the equation

$$\frac{I_4}{I_6} = \frac{j_4(k_6 + I_0\sigma_6\phi_6)}{j_6(k_4 + I_0\sigma_4\phi_4)}$$

Where I_i, j_i, and σ_i are the observed Raman intensity, the molar scattering factor, and the molar absorptivity of NiTPP ($i = 4$) and (py)$_2$NiTPP ($i = 6$), ϕ_4 and ϕ_6 are the quantum yields for converting $4 \rightarrow 6$ or $6 \rightarrow 4$ via light absorption, k_4 and k_6 are the thermal interconversion rates, and I_0 is the incident laser flux. This equation derives from a simple photokinetic scheme in which photoexcited NiTPP and (py)$_2$NiTPP are interconverted via capture or loss of ligands or else return to their own ground state. From the limiting values of I_4/I_6 one can calculate $k_6\sigma_4\phi_4/k_4\sigma_6\phi_6 = 1.6/0.54 = 3.0$. From the optical absorption spectra (and the assumption that the (py)$_2$NiTPP spectrum is given by that of NiTPP in piperidine, for which (pip)$_2$NiTPP predominates) one can estimate $\sigma_4/\sigma_6 \simeq 90$ (at 406.7 nm) and k_4/k_6 (the (4)/(6) equilibrium ratio) $\simeq 1.5$, whence $\phi_4/\phi_6 \simeq 0.05$. A low ratio of quantum yields is reasonable since ligation of the photoexcited NiTPP is a bimolecular process, while ligand loss from photoexcited (py)$_2$NiTPP is unimolecular.

Figure 3 shows laser-induced changes in RR spectra of NiTPP in piperidine; again these changes are abolished by spinning the sample. The major species is the 6-coordinate complex, with $\nu_4 = 1346$ cm^{-1}. Another band is seen at 1356 cm^{-1}, which increases with increasing laser power. In addition a band grows in at 1369 cm^{-1}, the frequency of the 4-coordinate species. Thus photopumping of the deligation process is seen in piperidine as well as pyridine. The new species responsible for the 1356-cm^{-1} band is suggested to be a 5-coordinate complex, with a single piperidine ligand. The 13-cm^{-1} ν_4 decrease between the 4- and 5-coordinate species suggests an appreciable core-size expansion consistent with high-spin character for the latter, as predicted by Ake and Gouterman;[6] adding an axial ligand to NiTPP without a change in spin state would not be expected to change the core size very much. The 10-cm^{-1} increase in ν_4 of the 5-coordinate species relative to that of the 6-coordinate (pip)$_2$NiTPP (which is also high spin) may reflect partial relaxation of the core size, due to the out-of-plane displacement of the Ni atom expected for a 5-coordinate high-spin adduct, by analogy with the relaxation seen for (2-MeImH)FeTPP (2.045 Å C$_t$-N; Fe 0.5 Å out of plane)[16] relative to high-spin (THF)$_2$FeTPP (2.057 Å C$_t$-N, Fe in plane.[17] If changes in the (pip)NiTPP concentration resulted simply from adjustments of the thermal equilibrium the growth of the 1356-cm^{-1} peak would be expected to track that of the 1369-cm^{-1} peak, but the former appears to saturate with increasing laser power while the latter does not. This behavior suggests that (pip)NiTPP forms directly by photopumping (pip)$_2$NiTPP and loss of a single ligand. If the (pip)NiTPP ground state is high spin, then electronic deexcitation must be competitive with loss of a second ligand from the low-spin primary photoproduct.

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Rapid Precipitation of Low Vapor Pressure Solids from Supercritical Fluid Solutions: The Formation of Thin Films and Powders

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Supercritical fluids have been shown to have excellent solvating properties above their critical densities, and supercritical fluid solutions of solutes having negligible vapor pressures can be readily prepared.[1-5] We are currently investigating the rapid expansion of supercritical fluid solutions (RESS) to better understand the process and to evaluate the range of solute products that can be produced by the rapid loss of solvating power which occurs during expansion. Products include films, fine powders having narrow size distributions, and amorphous mixtures produced under the nonequilibrium conditions inherent in the expansion process.

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