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Resonance Raman Spectra of the Nitrogen-Bridged Iron Porphyrin Dimer, (μ -Nitrido)bis[(5,10,15,20-tetraphenylporphinato)iron]

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Abstract: Resonance Raman (RR) spectra are reported for the nitrogen-bridged iron porphyrin dimer (TPPFe)₂N (TPP = tetraphenylporphyrin) with excitation at a large number of wavelengths throughout the Soret and visible regions of the absorption spectrum. RR bands due to in-plane porphyrin and phenyl ring vibrations are assigned by analogy to those observed for the oxygen-bridged dimer (TPPFe)₂O. As in the case for (TPPFe)₂O, no evidence is found for dimer vibrational splittings in the porphyrin modes of (TPPFe)₂N, despite the substantially smaller separation of the porphyrin rings of the nitrogen-bridged complex. RR bands sensitive to the spin and oxidation states of the metal ions are observed for (TPPFe)₂N at 1567 and 1538 cm⁻¹, indicating that the iron ions in the complex are best characterized as low-spin Fe(III), in agreement with X-ray photoelectron studies. The symmetric Fe-N-Fe stretching mode is assigned to a RR band at 424 cm⁻¹ via a 6-cm⁻¹ shift observed upon ⁵⁴Fe substitution. This mode is strongly resonance enhanced with Soret excitation, as are other out-of-plane polarized modes at 267, 226, and 194 cm⁻¹. With excitation to the blue side of the Soret band, near an intense 390-nm (25 640 cm⁻¹) absorption band of (TPPFe)₂N, the out-of-plane polarized modes completely dominate the RR spectrum. It is suggested that an out-of-plane A_{2u} ← A_{1g} charge transfer in which a nonbonding metal electron is promoted to an orbital that is delocalized throughout the Fe-N-Fe linkage contributes to the absorption to the blue of the Soret band. The very low frequency RR bands are attributed to the fundamental and nonfundamental vibrational transitions associated with the out-of-plane deformation of the Fe(N_{pyrrole})₄ cores, which along with the Fe-N-Fe stretch become resonance enhanced via the charge-transfer transition. The visible-region excitation profiles for (TPPFe)₂N indicate that the 533-nm (18 800 cm⁻¹) absorption is the vibronic satellite of the Q-state absorption and that the Q-state origin, which is not observed in the electronic spectrum, is at 578 nm (17 300 cm⁻¹). The profiles observed for (TPPFe)₂N are different from those of other metallotetraphenylporphyrin complexes in that only anomalously polarized modes (1342 and 1226 cm⁻¹) exhibit Q(0,2) maxima, whereas only polarized and depolarized modes of the latter complexes exhibit Q(0,2) maxima. A depolarized band at 1506 cm⁻¹ in the RR spectrum of (TPPFe)₂N shows evidence for Jahn-Teller activity in that it has appreciable intensity with blue excitation. The polarized phenyl ring vibrations of (TPPFe)₂N exhibit considerably more resonance enhancement than do those of (TPPFe)₂O. The 996-cm⁻¹ phenyl mode exhibits a profile that maximizes near the Q(0,1) position for the symmetric C_{methine}-C_{phenyl} stretching mode at 1235 cm⁻¹, indicating that this latter vibration is the "helping mode" for resonance enhancement of the phenyl vibration. The differences in the vibronic activity of the in-plane porphyrin and phenyl ring modes of (TPPFe)₂N relative to (TPPFe)₂O are consistent with the increased ruffling (S₄ distortion) of the pyrrole rings in (TPPFe)₂N compared to the oxygen-bridged complex.

I. Introduction

The characterization of the structural and electronic properties of aggregates of metalloporphyrin molecules is essential to the elucidation of energy transduction mechanisms in biological systems. Of the many types of oligomeric metalloporphyrins known, axially bridged dimeric species are particularly useful as model systems for the characterization of interchromophore-induced perturbations because they are generally quite stable and exhibit minimal flexibility of their molecular stereochemistries. These features allow the examination of the physical properties of the dimers for well-defined structures. The most common axially bridged metalloporphyrin dimers are the μ -oxo species,¹ which are known for Fe,² Al,³ Sc,³ Nb,⁴ Mo,⁵ Re,⁵ W,⁵ Os,⁶ Ru,⁷ and Mn⁸ porphyrins. Metalloporphyrin dimers that are axially bridged either via direct metal-metal bonds or via single atoms

other than oxygen are also known^{7,9,10} but are far less common and not well characterized.

A particularly sensitive probe of the structural and electronic properties of metalloporphyrin complexes is resonance Raman (RR) spectroscopy. Metalloporphyrins produce extremely intense and detailed RR spectra that have been successfully interpreted in terms of theoretical models for vibronically induced scattering.¹¹⁻¹⁴ Despite the utility of RR spectroscopy for characterizing metalloporphyrin complexes, few applications have been made to dimeric species. In fact, the only metalloporphyrin dimer that has been thoroughly investigated with RR spectroscopy is the μ -oxo dimer of iron tetraphenylporphyrin, (TPPFe)₂O.^{15,16} The RR spectrum of this complex was originally examined by Adar and Srivastava¹⁵ who derived selection rules for the vibrational modes of the complex in the presence of intermediate to strong coupling of the monomer electronic excited states and who, on the basis of these selection rules, attributed the doubling observed from several RR bands to intradimer (exciton) coupling of the porphyrin units. A reexamination of the RR spectrum of (TPPFe)₂O

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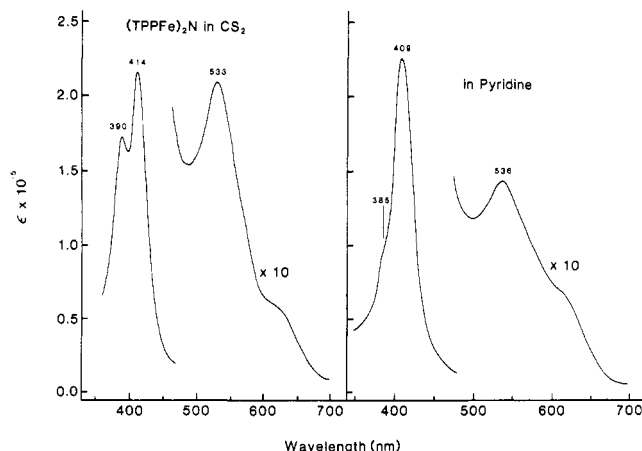


Figure 1. Absorption profile of (TPPFe)₂N in CS₂ and pyridine. The vertical axes are in units of cm⁻¹ M⁻¹.

by Spiro and co-workers¹⁶ led to the conclusion that the reported dimer-split bands are actually unrelated vibrational modes that are accidentally nearly degenerate. The data of the latter study was interpreted in terms of monomer selection rules, and it was concluded that the porphyrin units in (TPPFe)₂O are too greatly separated to induce measurable perturbations on the electronic properties of one another.

In order to further investigate the question of intradimer coupling in axially bridged metalloporphyrin complexes, we have examined in detail the RR spectrum of the single-atom nitrogen-bridged dimer (μ -nitrido)bis[(5,10,15,20-tetraphenylporphyrinato)iron]¹⁰ ((TPPFe)₂N). (We have previously reported a preliminary RR study of this complex.¹⁷) The mean porphyrin planes in (TPPFe)₂N are separated by 4.2 Å compared to 4.6 Å in (TPPFe)₂O,^{18,19} thus increasing the prospects for observing the effects of intradimer coupling in the RR spectrum. In addition to the potential usefulness of (TPPFe)₂N as a model system for probing intradimer coupling, the complex is interesting in that it is the only known μ -nitrido species bridging first-row transition-metal atoms.^{10,20} Consequently, considerable experimental^{10,17,18,21–25} and theoretical²⁶ efforts have been directed toward characterizing the physical properties of the complex. Although many analogies can be made between the properties of (TPPFe)₂N and the analogous oxygen-bridged species, certain distinct differences between the two dimers are clearly evident. In particular, the electronic absorption spectra of the two complexes are quite different. The spectrum of (TPPFe)₂N (Figure 1) exhibits a strong band at 390 nm in CS₂ solutions in addition to the Soret (B(0,0)) band at 414 nm, whereas (TPPFe)₂O exhibits no strong absorption to the blue of the Soret band. The 390-nm absorption intensity is quite solvent dependent, being significantly reduced in pyridine solutions while the Soret intensity is not particularly affected. The visible region of the absorption spectrum of (TPPFe)₂N is characterized by bands at ~610 and ~533 nm. The separation of these bands (~2400 cm⁻¹) is clearly too large to be attributed to the splitting between the α (Q(0,0)) and β (Q(0,1)) absorptions of the complex; thus, the assignment of the 610- and 533-nm bands is not obvious. In contrast, bands attributable to the α and β

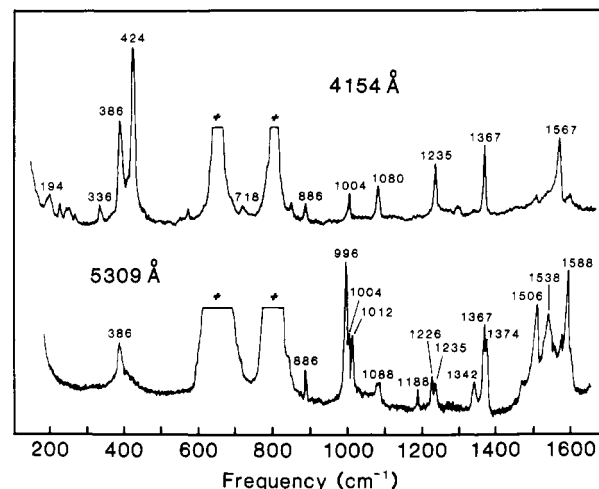


Figure 2. Resonance Raman spectra of (TPPFe)₂N in CS₂. Solvent peaks are denoted by *. See Experimental Section for spectral conditions.

absorptions of (TPPFe)₂O are clearly observed.¹⁵ The characterization of the absorption spectrum of (TPPFe)₂N as well as the nature of the other physical properties of the complex should be facilitated by thorough RR studies.

In this paper, we first present the assignment of the RR bands observed for (TPPFe)₂N and then, in the context of these assignments, consider the evidence for intradimer coupling of the porphyrin units in the complex. Next, we analyze the visible-region excitation profiles for several RR bands and compare these profiles with those observed for other metallotetraphenylporphyrin complexes. Finally, we discuss some specific electronic properties of (TPPFe)₂N including the spin and oxidation states of the iron centers and the characterization of the electronic absorption spectrum.

II. Experimental Section

The (TPPFe)₂N complex was prepared and purified by the method of Summerville and Cohen.¹⁰ Substitution of ⁵⁴Fe (from ⁵⁴Fe₂O₃, 97.08% in ⁵⁴Fe, Oak Ridge National Laboratories) was accomplished in a manner similar to that outlined in ref 16. The identities of the compounds were confirmed by using UV-visible and infrared spectroscopies. All solvents were spectral grade and were used without further purification.

The RR spectra were recorded with the optics in a 90° scattering configuration on a computer-controlled Spex Industries Ramalog 6 spectrometer equipped with a thermoelectrically cooled Hamamatsu R955 photomultiplier tube and a photon-counting detection system. Excitation wavelengths were provided by a tunable dye laser (Coherent Radiation Model 590) utilizing the tuning ranges of Rhodamine 6G and Coumarin 6 dyes (Exciton Chemical Company) and by the discrete lasing outputs of Ar ion (Spectra-Physics Model 164-05), Kr ion (Coherent Radiation Model CR-2000K), and He-Cd (Liconix) lasers.

For excitation in the Soret region, RR spectra were collected at 1-cm⁻¹ intervals at a rate of 5 s/point. Sample concentrations were typically 0.074 mM (0.10 mg/mL), and the incident power was less than 5 mW. The spectral slit width for this region was 3 cm⁻¹. Spectra used to measure isotope shifts were recorded on a strip chart recorder with a spectral slit width of 0.5 cm⁻¹. For excitation in the visible region, spectra were collected at 2-cm⁻¹ intervals at rates of 30–70 s/point, depending on experimental conditions. Sample concentrations were 0.74 mM (1.0 mg/mL), and incident powers ranged from 20 to 80 mW. Samples were flowed to prevent decomposition. The spectral slit width for this region was 5 cm⁻¹. Sample integrity was monitored with UV-visible absorption spectroscopy.

Excitation profiles were measured with respect to the 656- and 796-cm⁻¹ bands of the CS₂ solvent. The profiles are corrected for the ν^4 dependence of scattered light, sample reabsorption, and instrument and photomultiplier responses.

III. Results and Discussion

A. Assignment of the Vibrational Modes. The RR spectra of (TPPFe)₂N in CS₂ observed with excitation near the maxima of the Soret (λ_{ex} 4154 Å) and visible (λ_{ex} 5309 Å) absorption bands are shown in Figure 2. The frequencies and depolarization ratios,

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Table I. Resonance Raman Bands of (TPPFe)₂N and (TPPFe)₂O

band	(TPPFe) ₂ N		(TPPFe) ₂ O ^a	
	frequency, cm ⁻¹	profile type ^b	frequency, cm ⁻¹	assignment
A_{1g}				
A	1599 (p) ^c	IIb	1599 (p) ^c	phenyl
1	1567 (0.125)	I	1553 (0.09)	$\nu(\text{C}_\beta\text{-C}_\beta) + \delta(\text{C}_\beta\text{-H})^d$
2	~1450 vw		1450 (0.09)	$\nu(\text{C}_\alpha\text{-C}_\beta) + \delta(\text{C}_\beta\text{-H})$
3	1367 (0.125)	I	1359 (0.06)	$\nu(\text{C}_\alpha\text{-N}) + \delta(\text{C}_\beta\text{-H})$
4	1235 (0.125)	I	1237 (0.08)	$\nu(\text{C}_m\text{-Ph})$
	1188 (p)	IIa, b		
5	1080 (0.125)	I	1083 (p)	$\delta(\text{C}_\beta\text{-H})$
B	~1030 vw		1030 (p)	phenyl
6	1004 (0.125)	I	1004 (0.06)	$\nu(\text{C}_\alpha\text{-C}_m)$
C	996 (p)	IIb	995 (p)	phenyl
D	886 (p) ^e	I	886 (p)	
	718 (p)		719 (p) ^f	
7	640 (p)		640 (p)	porphyrin deformation
	570 (p)		571 (p) ^f	
	424 (0.17)	IIa		$\nu(\text{Fe-N-Fe})^f$
8	386 (0.07-0.17) ^g	I	390 (p)	porphyrin deformation
			363 (0.07)	$\nu(\text{Fe-O-Fe})$
	336 (p)	I	330 (p) ^f	
	267 (~0.25)	IIa		
	252 (p)			
	226 (~0.25)	IIa		
	194 (0.17)	IIa		
A_{2g}				
9	1538 (7.5)		1511 (13.7)	$\nu(\text{C}_\alpha\text{-C}_m)$
10	1342 (ap)		1333 (10.9)	$\nu(\text{C}_\alpha\text{-C}_\beta) + \delta(\text{C}_\beta\text{-H})$
11	1226 (1.3)		1234 (4.3)	$\nu(\text{C}_\alpha\text{-N}) + \delta(\text{C}_\beta\text{-H})$
12			n.o. ^h	$\delta(\text{C}_\beta\text{-H})$
13			827 (ap) vw	
14			n.o.	
15			n.o.	
B_{1g} and B_{2g}				
16	1588 (0.75)		1561 (dp)	$\nu(\text{C}_\alpha\text{-C}_m)$
17	1506 (0.7)		1495 (0.8)	$\nu(\text{C}_\beta\text{-C}_\beta)$
	1374 (0.75)		1368 (dp) ⁱ	
	1295 (0.75) ^j	IIa		
18	~1270 vw		1271 (dp)	$\nu(\text{C}_\alpha\text{-N})$
19	1088 (0.7)		1087 (0.52)	$\delta(\text{C}_\beta\text{-H})$
20	1012 (0.7)		1014 (0.68)	$\delta(\text{C}_\beta\text{-H})$
21	846 (0.7)		848 (0.87)	
22	~257 ^k		257 (0.75)	
23	~195 ^k		195 (dp)	

^a Taken from ref 16 unless otherwise specified. ^b Intensity profile types exhibited by bands of (TPPFe)₂N in the blue region. A type I profile reaches maximum intensity in resonance with the Soret band at 414 nm in CS₂ (see Figure 1); a type II profile reaches maximum intensity in resonance to the blue of the Soret band. The a and b labels on the type II profiles refer to whether the RR band intensity in pyridine solutions diminishes, paralleling the behavior of the 390-nm absorption band (IIa), or remains reasonably the same magnitude with respect to those bands exhibiting type I profiles (IIb). ^c p, polarized; dp, depolarized; ap, anomalously polarized. Depolarization ratios are given in parentheses for bands for which values could be measured with reasonable accuracy. ^d The subscripts are used in the assignment labels to identify the α - and β -pyrrole and the methine-bridging carbon atoms in the porphyrin macrocycle. Ph refers to the phenyl groups (see Figure 1 of ref 16). ^e This band is assigned as a phenyl mode in ref 16. More recent studies indicate this assignment may be incorrect (T. G. Spiro, private communication). ^f This work. ^g This band of (TPPFe)₂N exhibits a marked dispersion in its depolarization ratio in the B-state region (see text). ^h Expected, not observed. ⁱ Taken from ref 28. ^j Observed only with excitation to the blue of the Soret band (see section III.A.3 of the text). ^k Appears as a shoulder on the more intense, nearly coincident polarized mode. The depolarized assignment is made by analogy to the RR spectrum of (TPPFe)₂O.

ρ , of the observed RR bands are listed in Table I by polarization according to the D_{4h} symmetry classifications: A_{1g}, $\rho < 0.75$ (polarized); A_{2g}, $\rho > 0.75$ (anomalously polarized); and B_{1g} and B_{2g}, $\rho = 0.75$ (depolarized). The spectrum observed with λ_{ex} 4154 Å exhibits mostly polarized bands, indicative of the Franck-Condon scattering mechanism typically in effect upon excitation of the intense Soret band of metalloporphyrins.²⁷ Conversely, the RR spectrum observed with λ_{ex} 5309 Å exhibits many depolarized and anomalously polarized bands, indicative of the vibronic scattering mechanisms operative upon excitation of the less-intense visible bands.^{13,14,27} There are a significant number of polarized bands observed with visible-region excitation, in part due to the substantial Soret intensity underlying the visible absorption at 533 nm (Figure 1). However, certain polarized RR bands do exhibit significant Q-state scattering and will be discussed

further in conjunction with the visible-region excitation profiles.

1. In-Plane Porphyrin Modes. Virtually all of the RR bands of (TPPFe)₂N observed with Soret and visible-region excitation are in-plane porphyrin modes and have analogues in the RR spectrum of (TPPFe)₂O. Accordingly, we have assigned the majority of the RR bands of the nitrogen-bridged complex by comparison with those of the oxygen-bridged species. The RR frequencies of bands observed for the latter molecule are also given in Table I along with the assignments made by Spiro and co-workers.¹⁶

Three weak polarized bands are observed at 718, 570, and 336 cm⁻¹ in the RR spectrum of (TPPFe)₂N that have no reported analogues in the spectrum of (TPPFe)₂O. However, a reexamination of the RR spectrum (not shown) of (TPPFe)₂O reveals the presence of these bands. The frequencies and low intensities of these bands of the two complexes suggests that they could be difference bands of the intense C-C and C-N stretching vibrations.

We also observe a fairly intense depolarized RR band at 1374 cm^{-1} in the RR spectrum of $(\text{TPPFe})_2\text{N}$ for which an analogous band was not reported for $(\text{TPPFe})_2\text{O}$ by Spiro and co-workers.¹⁶ However, Chottard et al.²⁸ have reported a depolarized band at 1368 cm^{-1} in the spectrum of $(\text{TPPFe})_2\text{O}$. We also observe this band, which is nearly obscured by the strong 1359- cm^{-1} band in the oxygen-bridged complex. The frequency and intensity of the 1374- cm^{-1} band indicates that it can be attributed to one of the nontotally symmetric stretching vibrations of the porphyrin skeleton.

The depolarization ratios of the high-frequency in-plane totally symmetric vibrations of $(\text{TPPFe})_2\text{N}$ observed with both λ_{ex} 4154 Å and λ_{ex} 5309 Å are $\rho = 0.125$ and show no dispersion. This value of ρ is expected for a strictly planar scattering mechanism in molecules possessing a 4-fold axis of symmetry and corresponds to $\alpha_{xx} = \alpha_{yy}$ and $\alpha_{zz} = 0$ for the diagonal elements of the scattering tensor.²⁹ In contrast, the analogous totally symmetric vibrations of $(\text{TPPFe})_2\text{O}$ have values of $\rho < 0.125$ and show a small dispersion.¹⁶ The lowering of ρ implies a nonnegligible contribution of α_{zz} to the scattering tensor,²⁹ which in turn implies the contribution of a z-polarized (out-of-plane) electronic transition. It has been suggested that an out-of-plane charge-transfer transition localized in the Fe–O–Fe linkage is responsible for the lowering of the ρ values for the polarized bands of $(\text{TPPFe})_2\text{O}$.¹⁶ Apparently, the analogous transition in $(\text{TPPFe})_2\text{N}$ does not contribute to the scattering tensor with excitation between the two $\pi^* \leftarrow \pi$ transitions. This point will be discussed in more detail below.

2. Out-of-Plane Modes. There are several RR bands observed in the spectrum of $(\text{TPPFe})_2\text{N}$ with Soret-region excitation that have no analogues in the RR spectrum of $(\text{TPPFe})_2\text{O}$. A very intense polarized band is observed at 424 cm^{-1} , and weaker polarized bands are observed at 267, 252, 226, and 194 cm^{-1} . The depolarization ratios for the 424- and 194- cm^{-1} bands are 0.17 and for the 267- and 226- cm^{-1} bands are 0.2–0.3. The value of ρ for the 252- cm^{-1} band cannot be determined accurately. The values of $\rho > 0.125$ are indicative of a substantial contribution of a z-polarized electronic transition to the scattering tensor. The values $\rho = 0.17$ observed for the 424- and 194- cm^{-1} bands imply as much as a 75% z-polarized contribution to the scattering tensor, while the values $\rho = 0.2$ –0.3 observed for the 267- and 226- cm^{-1} bands could indicate an even larger contribution.

a. Symmetric Fe–N–Fe Stretch. In our preliminary RR study of $(\text{TPPFe})_2\text{N}$,¹⁷ we tentatively assigned the intense 424- cm^{-1} band to the symmetric Fe–N–Fe stretching mode. This assignment was made by analogy to the frequency of the symmetric and asymmetric Fe–O–Fe stretching modes of $(\text{TPPFe})_2\text{O}$. The symmetric stretching mode of the oxygen-bridged complex is observed at 363 cm^{-1} in the RR spectrum,¹⁶ while the companion asymmetric Fe–O–Fe stretching mode is observed at 872 cm^{-1} in the infrared spectrum.³⁰ The asymmetric Fe–N–Fe stretching mode of $(\text{TPPFe})_2\text{N}$ has been tentatively assigned to an infrared band at 910 cm^{-1} .¹⁰ The increase in frequency of the asymmetric Fe–X–Fe stretching vibration upon substitution of the nitrogen for the oxygen bridge is expected as a result of the superior π -bonding capabilities of the μ -nitrido ligand; thus, it is also expected that the symmetric Fe–N–Fe stretching vibration should occur at a higher frequency in the RR spectrum than the analogous Fe–O–Fe mode of the oxygen-bridged species.

We have confirmed the assignment of the 424- cm^{-1} band of $(\text{TPPFe})_2\text{N}$ as the symmetric Fe–N–Fe stretching vibration by substitution of ^{54}Fe into the complex. RR spectra of $(\text{TPP}^{56}\text{Fe})_2\text{N}$ and $(\text{TPP}^{54}\text{Fe})_2\text{N}$ in the region 360–460 cm^{-1} are compared in Figure 3. The substitution of ^{54}Fe results in a shift of the 424- cm^{-1} band 6 cm^{-1} to higher frequency. No shifts are detectable in the frequencies of any of the other RR bands. The shift of 6 cm^{-1}

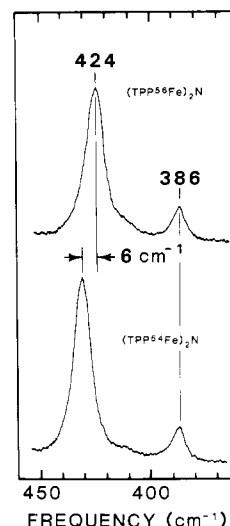


Figure 3. Low-frequency resonance Raman spectra of $(\text{TPPFe})_2\text{N}$ in CS_2 showing the observed isotope shift of the 424- cm^{-1} band. The spectra were recorded by using 4067-Å excitation (see Figure 4 (top)), sample concentrations of 0.074 mM (0.10 mg/mL), and resolution of 0.5 cm^{-1} .

represents 75% of the theoretical shift of 8 cm^{-1} expected on the basis of the change in reduced mass of the symmetric stretching mode of the linear Fe–N–Fe bridge. Recall that the depolarization ratio observed for the 424- cm^{-1} band is also indicative of a 75% out-of-plane character for the vibrational mode. Undoubtedly, the remaining 25% character of the 424- cm^{-1} mode is represented by contributions from the various other totally symmetric in- and out-of-plane vibrations of the FeN_4 porphyrin cores.

The frequencies of the symmetric and asymmetric Fe–N–Fe stretches in $(\text{TPPFe})_2\text{N}$ can be used to calculate the valence force constants for the vibration. The observed frequencies correspond to an Fe–N stretching constant of 4.5 $\text{mdyn}/\text{\AA}$ with a stretch-stretch interaction constant of 1.4 $\text{mdyn}/\text{\AA}$. The Fe–N stretching force constant, although larger (as expected) than the 3.8 $\text{mdyn}/\text{\AA}$ Fe–O stretching constant observed for $(\text{TPPFe})_2\text{O}$,¹⁶ is considerably smaller than that observed for μ -nitrido complexes of second- and third-row transition metals.³¹ The latter result is consistent with the lower bond order of the metal–N–metal bridge in $(\text{TPPFe})_2\text{N}$ ^{24–26} compared to that of μ -nitrido second- and third-row transition-metal complexes.³¹

b. FeN_4 Core Modes. The very low frequencies ($< 300 \text{ cm}^{-1}$; see Table I) of the z-polarized vibrations suggest that these modes are associated with out-of-plane deformations of the FeN_4 cores in $(\text{TPPFe})_2\text{N}$.³² Indeed, low-frequency RR bands assigned to out-of-plane deformations have been observed in the spectra of a number of metalloporphyrins.³³ There are four out-of-plane vibrational modes of A_{2u} symmetry³⁴ (D_{4h} point group) associated with the basic metalloporphyrin (excluding all peripheral substituents) of which one is the “umbrella” motion of the FeN_4 core. In the dimeric complex, the in-phase linear combination of this motion on the two porphyrin units is a totally symmetric z-polarized deformation. Such a motion would be expected to couple to the symmetric Fe–N–Fe stretching vibration. It is not obvious which of the four low-frequency z-polarized vibrations corresponds to the in-phase “umbrella” motion since all four bands are within 75 cm^{-1} of one another. However, the 194- cm^{-1} band is clearly the strongest of the four bands and possesses a depolarization ratio ($\rho = 0.17$) similar to that observed for the Fe–N–Fe stretch. If the 194- cm^{-1} mode is the fundamental of the out-of-plane deformation, then the 226- cm^{-1} band could be a difference band of the 194- cm^{-1} band and the intense 424- cm^{-1} band. This assign-

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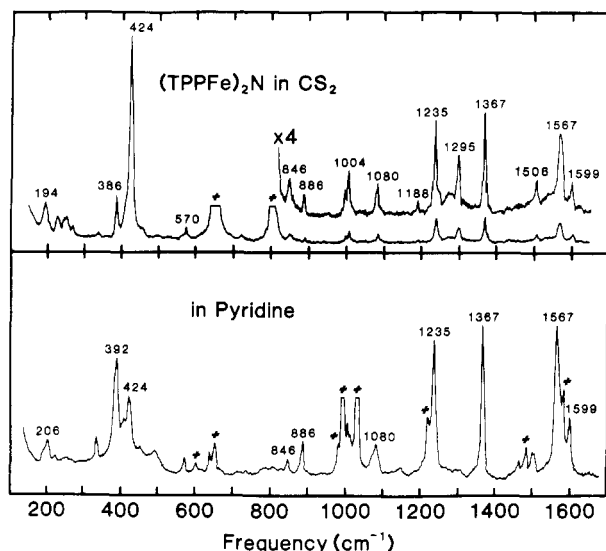


Figure 4. Resonance Raman spectra of (TPPFe)₂N in 0.074 mM (0.10 mg/mL) solutions of CS₂ and pyridine observed with 4067-Å excitation. Solvent peaks are denoted by #. See Experimental Section for spectral conditions.

ment leaves several vibrations unaccounted for, but it is also possible that an in-phase linear combination of one of the other A_{2u} vibrations of the porphyrin unit is also contributing to the low-frequency region.

The characterization of the core "umbrella" motion as a strictly out-of-plane vibration is actually somewhat misleading. The iron ions in (TPPFe)₂N are displaced substantially from the planes of the porphyrin rings. This distortion (C_{4v}) mixes the out-of-plane deformation with the "in-plane" symmetric stretching vibration of the FeN₄ core (both modes are totally symmetric in C_{4v} symmetry). The in-plane stretching vibration of the FeN₄ cores in (TPPFe)₂N occurs at 386 cm⁻¹ and is observed with excitation in both the Soret and visible regions (Figure 2). Unlike the high-frequency porphyrin vibrations that exhibit $\rho = 0.125$ with no dispersion, the ρ value for the 386-cm⁻¹ band exhibits a dramatic dispersion: ρ (4579 Å) = 0.10; ρ (4416 Å) = 0.07; ρ (4131 Å) = 0.12; and ρ (4067 Å) = 0.17. The value $\rho = 0.10$ observed with λ_{ex} 4579 Å is indicative of a primarily in-plane scattering mechanism with a small amount of z-polarized character, as is expected for scattering primarily from the Soret excited state. The out-of-plane contribution increases with increasing excitation energy and with λ_{ex} 4067 Å, $\rho = 0.17$, indicative of a substantial z contribution to the scattering tensor. The observed behavior of the depolarization ratio for the 386-cm⁻¹ band illustrates the significant mixing of the in- and out-of-plane FeN₄ core vibrations.

With λ_{ex} 4154 Å, slightly to the red of the Soret maximum of (TPPFe)₂N in CS₂ (Figure 1), the resonance enhancements of the out-of-plane FeN₄ core deformations and symmetric Fe-N-Fe stretching vibration are $\sim 4 \times 10^4$ and 4×10^5 , respectively (relative to the 796-cm⁻¹ band of CS₂), comparable to or greater than those of the in-plane porphyrin modes (Figure 2). The very large intensity enhancements of the out-of-plane vibrations suggest that a z-polarized electronic transition (A_{2u} ← A_{1g} in D_{4h} symmetry) associated with the Fe-N-Fe linkage contributes to the absorption in the Soret region. In attempts to investigate this point further, we examined the RR spectrum of (TPPFe)₂N at several different excitation wavelengths in the blue region. The RR spectrum of the complex in CS₂ with excitation between the Soret and 390-nm absorption bands (λ_{ex} 4067 Å) is shown in Figure 4 (top). The intensities of the out-of-plane vibrations increase by $\sim 50\%$ over those observed with λ_{ex} 4154 Å, while the intensities of the in-plane porphyrin modes are approximately the same as those observed with the longer excitation wavelength. This differential enhancement of the in-plane and out-of-plane vibrations at the two excitation wavelengths is consistent with a z-polarized electronic transition contributing to the absorption to the blue of the Soret band. However, it should be noted that it is also possible

that the differential enhancements to some degree reflect B-state scattering with the two types of modes exhibiting differentially blue-shifted excitation maxima. Blue-shifted Soret excitation maxima have been observed for certain high-frequency polarized modes of cytochrome c.³⁵

The relative contribution to the scattering tensors of the in-plane and out-of-plane vibrations by absorption to the blue of the Soret, particularly near the intense 390-nm band, is better illustrated by comparing the RR spectrum of (TPPFe)₂N in CS₂ and pyridine (Figure 4). In pyridine, the 390-nm band is shifted to 385 nm and the Soret band is observed at 409 nm (Figure 1). The intensity of the 390-nm band is reduced approximately 5-fold in pyridine compared to that in CS₂, while the Soret bands are of comparable intensity in the two solvents. The resonance enhancements of the in-plane porphyrin vibrations with λ_{ex} 4067 Å in pyridine are $\sim 10^5$ (scaled to the 796-cm⁻¹ band of CS₂), comparable to those observed with this excitation wavelength in CS₂. In contrast, the intensities of the out-of-plane vibrations are drastically reduced in pyridine solution, with the 424-cm⁻¹ band decreasing in intensity by a factor of ~ 25 . This large decrease in intensity cannot be attributed to the difference in the position of the Soret maximum in pyridine vs. that in CS₂ relative to the excitation wavelength, since varying λ_{ex} from 4154 to 4067 Å in the latter solvent results in only a 50% change in the RR intensity. In fact, the observed 25-fold decrease in the intensity of the 424-cm⁻¹ band, in conjunction with the 5-fold decrease in the absorption coefficient of the 390-nm band, suggests an ϵ^2 dependence for the RR intensity that could occur if this mode is predominantly enhanced by Franck-Condon scattering from a single excited state. The very large RR intensity along with the enhancement pattern for the non-porphyrin symmetric Fe-N-Fe stretching vibration strongly suggests that a z-polarized electronic transition does contribute to the absorption to the blue of the Soret in the region of the B(0,1) absorption.

3. Other Modes. Certain other RR bands also gain intensity at λ_{ex} 4067 Å compared to λ_{ex} 4154 Å, most notably the two phenyl modes at 1599 and 996 cm⁻¹ and unidentified bands at 1295 and 1188 cm⁻¹ that have no analogues in the RR spectrum of (TPPFe)₂O. The 1599-, 1188-, and 996-cm⁻¹ bands are all polarized and are also observed with excitation in the visible region, whereas the 1295-cm⁻¹ band is depolarized and not observed in the visible region (Figure 2 (bottom)). The 1188-cm⁻¹ band cannot be assigned as a totally symmetric porphyrin mode since all of those vibrations are accounted for (Table I). The pattern of enhancement of the 1188-cm⁻¹ band most closely parallels that of the phenyl modes. The phenyl vibrations (1599 and 996 cm⁻¹) are observed to be most intense with excitation to the blue side of the Soret and visible absorption bands (compare, for example, the intensities of the 1599- and 996-cm⁻¹ bands with λ_{ex} 4154 Å (Figure 2) and λ_{ex} 4067 Å (Figure 4)). Given the pattern of intensity enhancement of the 1188-cm⁻¹ band and considering the fact that monosubstituted benzenes exhibit strong polarized Raman bands near 1200 cm⁻¹, attributable to a phenyl ring deformation,^{36,37} it seems reasonable that the 1188-cm⁻¹ band is this same mode in (TPPFe)₂N. It is possible that the 1295-cm⁻¹ band is also a phenyl mode; however, the observation of a depolarized phenyl vibration in the RR spectrum of a TPP complex is unprecedented. This band cannot be assigned as an out-of-plane vibration since the frequencies of these latter vibrations are all expected to be less than 1000 cm⁻¹.³² It is more likely that the 1295-cm⁻¹ band is one of the "missing" B_{1g} or B_{2g} in-plane porphyrin modes.

The solvent dependence of the intensity enhancement for the 1188- and 1295-cm⁻¹ bands are different from those of the 1599- and 996-cm⁻¹ phenyl modes and the other in-plane porphyrin vibrations. Both the 1188- and 1295-cm⁻¹ bands are strongly enhanced to the blue of the Soret maximum in CS₂, as are the

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1599- and 996-cm⁻¹ bands; however, the intensities of the former bands are significantly reduced in pyridine compared to CS₂ (Figure 4), while those of the latter are not. Thus the behavior of the 1188- and 1295-cm⁻¹ bands seems to more closely parallel that of the out-of-plane modes than that of the other phenyl and in-plane porphyrin vibrations.

The behavior of the various RR bands at different wavelengths and in different solvents establishes that there are several different mechanisms of resonance enhancement of the Raman intensities. To distinguish the different behaviors of the RR bands, we have used the following scheme in Table I. Bands that are principally enhanced with Soret excitation are labeled by I. Bands principally enhanced with excitation between the Soret and 390-nm absorption bands and that lose Raman intensity in pyridine solution are labeled by IIa. Bands principally enhanced with excitation between the Soret and 390-nm absorption band whose intensities are unaffected in pyridine solution are labeled by IIb.

B. Intradimer Coupling. In that all of the in-plane vibrational modes of (TPPFe)₂N observed with Soret- and visible-region excitation can be correlated with those of (TPPFe)₂O, which in turn can be correlated with those of monomeric TPPFe complexes,¹⁶ it must be concluded that exciton coupling between the π, π^* excited states of the porphyrin units comprising the dimer is weak or nonexistent. The appearance in the RR spectrum of bands attributable to the in-phase out-of-plane deformations of the FeN₄ cores cannot be considered to be the result of intradimer coupling, since motions of the atoms in the Fe-N-Fe linkage are coupled directly through kinetic and potential energy terms in the vibrational Hamiltonian of the ground electronic state. Any type of electronic coupling between the in-plane π, π^* excited states that is mediated by the perpendicular electronic excited states must also be small, since the depolarization ratios observed with excitation throughout the Soret and visible regions for all of the high-frequency porphyrin modes are characteristic of a strictly in-plane scattering mechanism (see section III.A.1).

Spiro and co-workers¹⁶ noted that a measure of intradimer coupling more sensitive than attempting to observe dimer splittings in the RR spectrum would be to search for Raman-active modes in the infrared spectrum and vice versa, since the out-of-phase combinations of monomer vibrations active under one set of selection rules will become active under the other. Under this premise, these workers tentatively assigned a weak band observed at 1358 cm⁻¹ in the infrared spectrum of (TPPFe)₂O to the out-of-phase combination of the monomer A_{1g} mode observed at 1359 cm⁻¹ in the RR spectrum. The 1200–1600-cm⁻¹ region of the infrared spectrum of (TPPFe)₂N is shown in Figure 5 along with the spectra of TPPFeCl and (TPPFe)₂O. Three relatively weak bands are observed at 1235, 1368, and 1564 cm⁻¹ in the infrared spectrum of (TPPFe)₂N, which do not appear in the spectrum of the monomer TPPFeCl and which correspond very closely in frequency to strong polarized bands observed in the RR spectrum. These infrared bands could be assigned to the respective out-of-phase combinations of the monomer modes. However, in view of the fact that the out-of-phase frequencies are essentially coincident with those of the in-phase modes, the excited-state interaction between the porphyrin units in (TPPFe)₂N cannot realistically be described as any stronger than in (TPPFe)₂O. A more likely source of any type of increased interaction between the porphyrin macrocycles of (TPPFe)₂N relative to (TPPFe)₂O (presuming the interactions were increased) would be increased vibrational kinetic and potential energy coupling facilitated by the higher bond order of the μ -nitrido bridge.

The apparent lack of any appreciable exciton coupling in (TPPFe)₂N and (TPPFe)₂O is in itself interesting. The porphyrin macrocycles of the two complexes are separated by >4 Å;^{18,19} thus, a large spacial separation may be the origin of the lack of coupling. However, oxygen-bridged dimers of scandium porphyrins do show evidence of exciton splittings, reported to be on the order of ~1000 cm⁻¹ in the B state and ≤50 cm⁻¹ in the Q state.³⁸ In that the

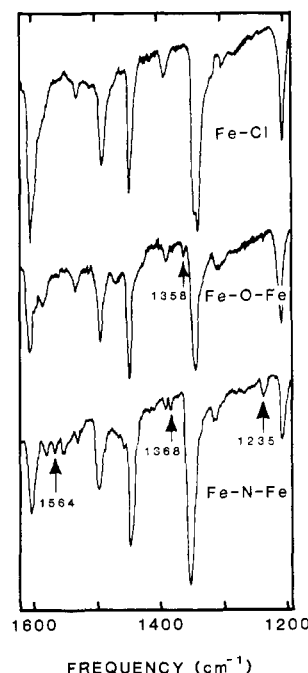


Figure 5. Infrared absorption spectra of TPPFeCl, (TPPFe)₂O, and (TPPFe)₂N. Weak bands having frequencies coincident with those of strong polarized RR bands are labeled. The spectra were recorded from KBr pellet samples on a Perkin-Elmer Model 283 IR spectrometer. Resolution is approximately 5 cm⁻¹.

mean porphyrin separations and absorption coefficients of the bridged iron- and scandium-porphyrin dimers are similar to one another, the exciton couplings in (TPPFe)₂N and (TPPFe)₂O are expected to be similar to those observed for the scandium species. A possible explanation for the apparent lack of appreciable exciton coupling in the iron complexes is that the lifetimes of the excited states are too short to facilitate the interaction. This is equivalent to saying that the excitation does not have time to move from one porphyrin unit to the other before relaxation occurs, resulting in an excited state which is de facto "localized" on one (or the other) of the porphyrins. These excited states are best represented as a degenerate pair of monomer excited states. This situation can be contrasted with one in which the excitation has time to become "delocalized" over both porphyrin units, a case in which the excited states are best represented as an exciton split pair arising from linear combinations of the two monomer excited states. In this connection, many iron porphyrins are thought to have excited-state lifetimes on the order of 10⁻¹³–10⁻¹⁵ s,^{35,39–42} and although the excited-state lifetimes of (TPPFe)₂N and (TPPFe)₂O are not known, they would be expected to be within this range. Exciton splittings of hundreds to thousands of wavenumbers would be required in order for the excitation to appear delocalized in systems with excited-state lifetimes of this order of magnitude. Thus, exciton splittings may not be observable in the iron porphyrin dimers.

C. Visible-Region Excitation Profiles. The visible-region excitation profiles of several RR bands of each polarization observed for (TPPFe)₂N are shown in Figure 6 along with the absorption spectrum. The profiles are plotted on a linear scale with the different bands displaced for clarity of presentation. The resonance enhancements of the Raman bands in the visible region are ~10³ (relative to the 796-cm⁻¹ band of CS₂), and the errors in the intensity measurements are on the order of ±10%. These uncertainties in the experimental intensities result in an error in the

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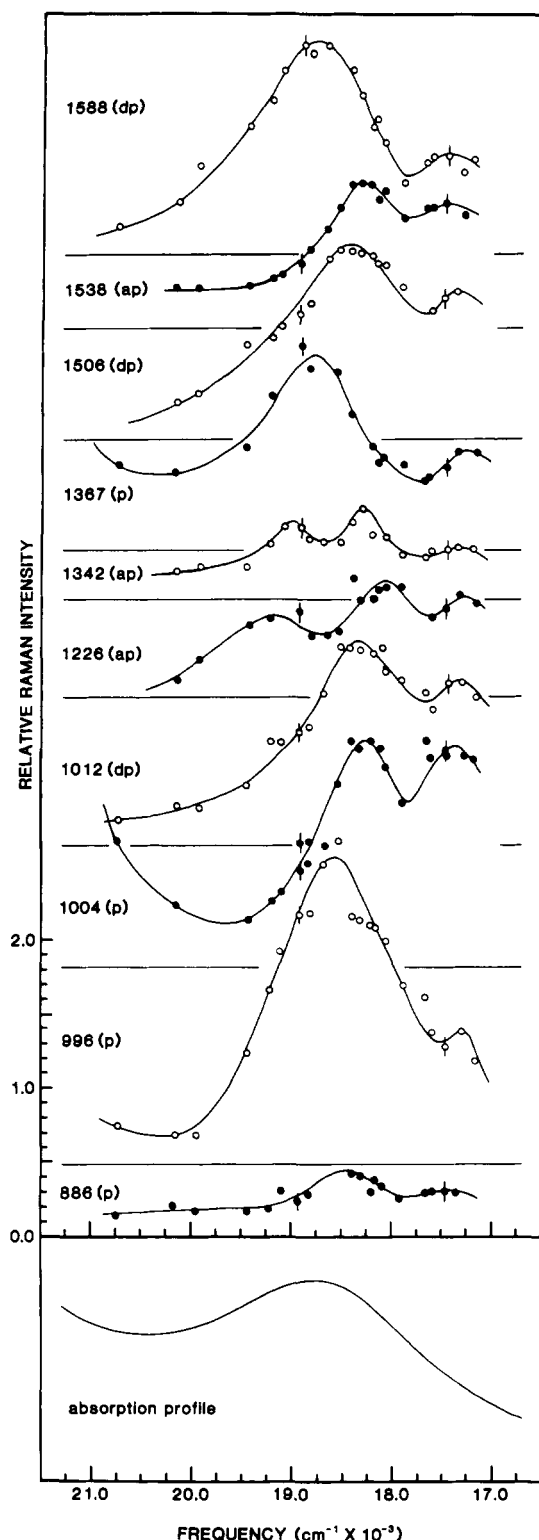


Figure 6. Excitation profiles for representative bands of $(\text{TPPFe})_2\text{N}$ in CS_2 . The intensities are plotted on a linear scale of magnitude 10^3 relative to the 796-cm^{-1} band of CS_2 , and the frequencies are given in cm^{-1} . The profiles are displaced vertically and are plotted by using alternate filled (●) and open (○) circles for clarity of presentation. The visible region of the absorption profile is also shown. abbreviations used: p, polarized; dp, depolarized; ap, anomalously polarized.

peak position in the profiles of $\pm 150\text{ cm}^{-1}$. The profiles indicate that the maximum in the absorption spectrum at $18\,800\text{ cm}^{-1}$ (533 nm) corresponds to the $\text{Q}(0,1)$ band and that the electronic origin, $\text{Q}(0,0)$, is located near $17\,300\text{ cm}^{-1}$ (578 nm), although the latter band is not observed in the absorption spectrum. The qualitative features of the excitation profiles of $(\text{TPPFe})_2\text{N}$ are similar to

those observed for TPPCrCl and $(\text{TPPFe})_2\text{O}$,^{13,16} although the quantitative features are different. The profiles for the latter complexes have been interpreted in terms of strong vibronic coupling between the Q and B states with a small amount of Jahn-Teller activity in the Q state. We also find evidence for these coupling mechanisms in $(\text{TPPFe})_2\text{N}$, although they involve different modes than in TPPCrCl and $(\text{TPPFe})_2\text{O}$.

The profiles for the anomalously polarized (A_{2g}) modes at 1538 , 1342 , and 1226 cm^{-1} all exhibit $\text{Q}(0,0)\text{--Q}(0,1)$ splittings that are significantly less than their respective ground-state vibrational frequencies. This is typical for A_{2g} modes, which are known to exhibit constructive interference in their excitation profiles, tending to bring the maxima together by filling in the intensity between the peaks.⁴³ The profiles of the A_{2g} modes of $(\text{TPPFe})_2\text{N}$ also show signs of strong vibronic coupling as is evidenced by the $\text{Q}(0,2)$ maxima observed for the 1342- and 1226-cm^{-1} modes and by the near equality of intensities of the $\text{Q}(0,1)$ and $\text{Q}(0,0)$ maxima observed for the 1538-cm^{-1} band.^{13,44} There are no $\text{Q}(0,2)$ maxima observed in the profiles of the A_{2g} modes of TPPCrCl or $(\text{TPPFe})_2\text{O}$,^{13,16} thus intermanifold (Q-B) coupling via the A_{2g} modes must be stronger in $(\text{TPPFe})_2\text{N}$ than in the other TPP complexes. [It should be noted that the $\text{Q}(0,2)$ maxima in the A_{2g} -mode profiles of $(\text{TPPFe})_2\text{N}$ cannot be attributed to intramanifold (Jahn-Teller) coupling since the A_{2g} modes are Jahn-Teller inactive.]

The depolarized mode at 1588 cm^{-1} exhibits a profile with a $\text{Q}(0,0)\text{--Q}(0,1)$ splitting very close to the ground-state frequency, as does the depolarized mode at 1012 cm^{-1} . The $\text{Q}(0,0)/\text{Q}(0,1)$ intensity ratio exhibited by the 1588-cm^{-1} profile is about 0.5, close to that expected for moderate vibronic coupling with nonadiabatic effects included.¹³ The profile of the 1506-cm^{-1} band peaks at the same position as that of the 1012-cm^{-1} band. In addition, these two bands exhibit profiles with $\text{Q}(0,0)/\text{Q}(0,1)$ intensity ratios (both 0.75) larger than expected, suggesting that the two vibrational modes are strongly coupled in the Q state.¹⁴ The 1506-cm^{-1} band is also the only depolarized mode that displays appreciable intensity with excitation in the Soret region of the spectrum (Figures 2 and 4). This behavior is indicative of Jahn-Teller activity in the vibrational motion with a moderate displacement of the Q-state potential minimum along this particular normal coordinate.⁴⁵

Several polarized vibrational modes of $(\text{TPPFe})_2\text{N}$ are observed to obtain intensity via scattering from the Q state. The profile of the 1367-cm^{-1} band exhibits $\text{Q}(0,0)\text{--Q}(0,1)$ maxima separated by $\sim 1370\text{ cm}^{-1}$ and a $\text{Q}(0,0)/\text{Q}(0,1)$ intensity ratio of 0.5, indicative of only moderate vibronic coupling with nonadiabatic effects included.¹³ The profile of the 1004-cm^{-1} polarized band also exhibits maxima separated by its approximate frequency, but the $\text{Q}(0,0)/\text{Q}(0,1)$ intensity ratio is nearly unity. This intensity ratio could reflect either strong vibronic coupling with destructive interference compensating for the expected shifts of the $\text{Q}(0,0)$ and $\text{Q}(0,1)$ maxima from the value of the vibrational frequency^{13,14} or simply moderate vibronic coupling with the absence of nonadiabatic effects. The profiles of the 1367- and 1004-cm^{-1} bands of $(\text{TPPFe})_2\text{N}$ are also characterized by the absence of $\text{Q}(0,2)$ maxima, which are typically observed in the profiles of A_{1g} modes of other TPP complexes.^{13,14,16} Apparently, the Q-state-origin shifts for these modes in the nitrogen-bridged dimer are smaller than in the other complexes. This conclusion is further emphasized by the Q-state behavior of the intensity of the 386-cm^{-1} symmetric FeN_4 core stretching mode in $(\text{TPPFe})_2\text{N}$. This mode is only weakly resonance enhanced and displays a profile (not shown) with no particular features. In contrast, the intensities of the analogous core modes of TPPCrCl , TPPCu , and $(\text{TPPFe})_2\text{O}$ are strongly enhanced with Q-state excitation and exhibit supernumerary maxima in their excitation profiles at the position of a high-frequency porphyrin vibration.^{13,14,16} This "helping mode" behavior is characteristic of the large Q-state-origin shifts for the A_{1g} modes

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of TPPCrCl , TPPCu , and $(\text{TPPFe})_2\text{O}$, which are not present for those of $(\text{TPPFe})_2\text{N}$.

It is not clear to what extent distortions in the porphyrin molecular stereochemistry such as doming of the core (C_4v distortion) or ruffling of the pyrrole rings (S_4 distortion) are responsible for strong vibronic activity of the various porphyrin modes since detailed excitation profiles have not been obtained for a sufficient number of metal TPP (or any other metalloporphyrin) complexes to develop a reliable correlation between structural perturbations and observed Raman activity. It is interesting to note that the only RR bands of $(\text{TPPFe})_2\text{N}$ that do exhibit $Q(0,2)$ maxima in their excitation profiles (Figure 5) are attributable to A_{2g} vibrations involving the N_{pyrrole} , C_{α} , and C_{β} atoms (1342 and 1226 cm^{-1}). One possible explanation for the strong vibronic activity of the A_{2g} modes in $(\text{TPPFe})_2\text{N}$ is that the porphyrin pyrrole rings of this complex exhibit a significantly larger amount of ruffling than do those of $(\text{TPPFe})_2\text{O}$. The A_{2g} modes are totally symmetric with respect to the S_4 distortion and could provide an extremely effective coupling between the Q and B states.

Polarized RR bands at 996 and 886 cm^{-1} are resonance enhanced with visible-region excitation (Figure 2). Both of these bands have been previously attributed to internal vibrations of the phenyl rings;¹⁶ however, more recent studies suggest that the 886-cm^{-1} band may not be a phenyl mode (T. G. Spiro, private communication). Indeed, the excitation profiles for the 996 - and 886-cm^{-1} bands of $(\text{TPPFe})_2\text{N}$ are quite different. The 996-cm^{-1} band exhibits a profile with a $Q(0,0)$ – $Q(0,1)$ splitting of $\sim 1250\text{ cm}^{-1}$, substantially more than the ground-state frequency, and shows an extremely strong $Q(0,1)$ maximum. Recall that this mode is also most strongly enhanced to the blue side of the Soret maximum (compare Figure 2 (top) and Figure 4 (top)) in the region of the $B(0,1)$ state. On the other hand, the 886-cm^{-1} band does not exhibit any pronounced intensity maxima with excitation in either the Soret or visible regions. It is possible that the 996-cm^{-1} phenyl mode is enhanced via a "helping mode" mechanism by the 1235-cm^{-1} C_m –Ph vibration (Table I). This in-plane porphyrin mode is also observed in the RR spectrum with visible-region excitation, although its intensity is somewhat less than the $\nu(C_{\alpha}$ –N) (1367 cm^{-1}) and the $\nu(C_{\alpha}$ – C_m) (1004 cm^{-1}) A_{1g} porphyrin vibrations (Figure 2). Spiro and co-workers¹⁶ have suggested that the Raman activity of the phenyl modes occurs in the excited state where the phenyl rings and the porphyrin macrocycle may be more nearly coplanar. These workers further suggested that ruffling of the porphyrin rings may facilitate the rotation of the phenyl rings toward the porphyrin plane in the Q state. The increased Raman activity observed for the phenyl modes of the highly ruffled $(\text{TPPFe})_2\text{N}$ complex relative to those of the less ruffled $(\text{TPPFe})_2\text{O}$ molecule is clearly consistent with this suggestion.

D. Spin and Oxidation States of the Iron Centers. The structural and spectroscopic features exhibited by $(\text{TPPFe})_2\text{N}$ have resulted in some ambiguity in the assignment of the formal spin and oxidation states of the metal ions in the complex.^{10,17,18,21,22} The iron centers in $(\text{TPPFe})_2\text{N}$ are situated well out of the porphyrin planes ($\sim 0.32\text{ \AA}$), a feature normally characteristic of high-spin iron porphyrin systems.¹⁸ Nevertheless, X-ray photoelectron studies indicate that the iron ions in $(\text{TPPFe})_2\text{N}$ are best characterized as low-spin Fe(III).²² On the other hand, we reported in a preliminary RR study that certain spin- and oxidation-state-sensitive marker bands in the spectrum of $(\text{TPPFe})_2\text{N}$ are observed at frequencies similar to those of $(\text{TPPFe})_2\text{O}$.¹⁷ The iron ions in the oxygen-bridged complex are known to be high-spin Fe(III), so we concluded that this is also the case for the nitrogen-bridged molecule.

The results of the detailed RR study reported here indicate that our previous assignment of the spin state of the metal centers in $(\text{TPPFe})_2\text{N}$ is incorrect and that the RR data are indeed consistent with those observed for low-spin $\text{TPPFe}^{\text{III}}$ complexes. In particular, spin-state-sensitive RR bands^{28,46} are observed at 1567

cm^{-1} (p), 1538 cm^{-1} (ap), 1367 cm^{-1} (p), and 1374 cm^{-1} (dp) in the spectrum of $(\text{TPPFe})_2\text{N}$, which are shifted to 1553 , 1511 , 1359 , and 1368 cm^{-1} in the spectrum of the high-spin $(\text{TPPFe})_2\text{O}$ complex (Table I). In our previous study, which only involved Soret-region excitation, we also observed RR bands near 1553 and 1559 cm^{-1} in the spectrum of $(\text{TPPFe})_2\text{N}$. However, we have subsequently determined that these bands occur in the spectrum of the nitrogen-bridged complex as a result of laser-induced photodecomposition. This difficulty was resolved in the present study by using a flowing sample technique and extremely low laser powers ($\sim 5\text{ mW}$) (see Section II). Another observation that reflects the difference in the spin states of the iron ions in $(\text{TPPFe})_2\text{N}$ and $(\text{TPPFe})_2\text{O}$ is that the two highest frequency depolarized-RR bands are observed at 1588 and 1506 cm^{-1} in the former complex and 1561 and 1495 cm^{-1} in the latter. These bands correspond to the TPPFe counterparts of bands III and V observed for iron mesoporphyrin(IX) complexes⁴⁷ but are not generally considered to be reliable marker bands for TPPFe complexes. Nevertheless, the differences in the frequencies of the two sets of bands observed for $(\text{TPPFe})_2\text{N}$ vs. $(\text{TPPFe})_2\text{O}$ reflect those typically observed for low- vs. high-spin TPPFe species.^{28,46}

E. Electronic Absorption Spectrum. The intensity enhancement patterns observed for the RR bands of $(\text{TPPFe})_2\text{N}$ (Figure 5 and section III.A) shows that the E_u excited states, $Q(0,0)$ and $B(0,0)$, occur $\sim 17\,300\text{ cm}^{-1}$ (578 nm) and $\sim 24\,150\text{ cm}^{-1}$ (414 nm) above the A_{1g} ground state. The RR data also confirm that the absorption band near $18\,800\text{ cm}^{-1}$ (533 nm) corresponds to the vibronic satellite, $Q(0,1)$, and suggest that an A_{2u} excited state lies slightly above the $B(0,0)$ state near the maximum of the vibronic satellite, $B(0,1)$ at $\sim 25\,600\text{ cm}^{-1}$ (390 nm). The only absorption that has yet to be assigned is the weak $16\,390\text{-cm}^{-1}$ (610 nm) band. No resonance enhancement is observed for the RR bands with excitation in this region, probably because of the low extinction of the absorption. $(\text{TPPFe})_2\text{O}$ also exhibits a weak band immediately to the red of its $Q(0,0)$ band. The 610-nm band of $(\text{TPPFe})_2\text{N}$ (and the analogue of $(\text{TPPFe})_2\text{O}$) is most likely associated with an in-plane charge-transfer transition of the FeN_4 unit.

The very large intensity enhancement observed for the symmetric Fe–N–Fe stretching mode suggests that the z-polarized electronic transition to the A_{2u} state must result in a significant transfer of charge from the bridging ligand to the metal ions or vice versa. Recently, Tatsumi and Hoffman have reported molecular orbital (MO) calculations for the bridging system of $(\text{TPPFe})_2\text{N}$.²⁶ The predicted ordering scheme for the MO's is shown in Figure 7. Recent EPR studies^{24,25} of $(\text{TPPFe})_2\text{N}$ have shown that the single unpaired electron in the complex resides in the a_{1g}^* orbital,⁴⁸ which is calculated to be 89% Fe (d_{z^2}) (44.5% on each Fe) and 1.6% nitrido $2s$. This orbital is calculated to lie within 2500 cm^{-1} of the e_u^* and a_{2u}^* orbitals, which are predicted to be 67.8% Fe ($d_{xz,yz}$) (33.9% on each Fe) and 25.7% nitrido $2p_{x,y}$, and 80.2% Fe (d_{z^2}) (40.1% on each Fe) and 11.3% nitrido $2p_z$, respectively. This group of four metal-centered, antibonding orbitals is calculated to be in excess of $30\,000\text{ cm}^{-1}$ above the ligand-based bonding counterparts and $\sim 14\,000$ and $\sim 18\,000\text{ cm}^{-1}$ above the nonbonding metal e_g and b_{2g} , b_{1u} orbitals, respectively (see ref 26).

Four transitions are possible between the MO's of the bridging system of $(\text{TPPFe})_2\text{N}$ that result in an excited state of A_{2u} symmetry: $a_{2u}^* \leftarrow a_{1g}^*$; $a_{2u}^* \leftarrow a_{1g}$; $a_{1g}^* \leftarrow a_{2u}$; and $e_u^* \leftarrow e_g$. The first of these transitions involves two antibonding orbitals and would not result in a sufficient charge redistribution to produce an origin shift necessary to account for the strong resonance enhancement of the Fe–N–Fe stretching mode. Also, the predicted transition energy is only $\sim 2500\text{ cm}^{-1}$.²⁶ The next two transitions involve bonding and antibonding orbitals and result in excited states where large amounts of electron density is redistributed from

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(48) The calculations of ref 26 (and consequently the discussions of ref 24–26) use D_{4h} symmetry labels. The pertinent $D_{4h} \rightarrow D_{4g}$ symmetry correlations are as follows: $a_{1g} \rightarrow a_1$; $a_{2u} \rightarrow b_2$; $b_{1g} + b_{2u} \rightarrow e_2$; $b_{2g} + b_{1u} \rightarrow e_2$; $e_g \rightarrow e_3$; $e_u \rightarrow e_1$.

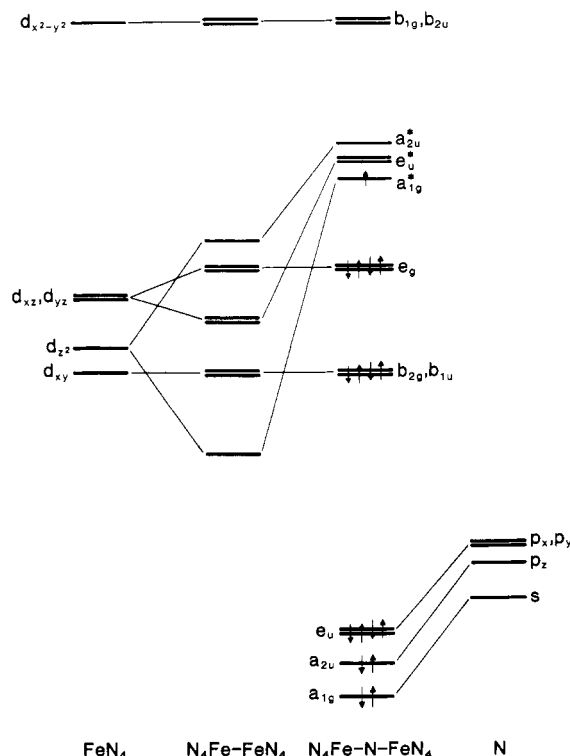


Figure 7. Molecular orbital scheme for the Fe-N-Fe bridge system of (TPPFe)₂N. *D*_{4h} symmetry labels are used. The ordering of the orbital energies is based on the MO calculations of ref 26 but is not presented to scale.

the bridging nitrogen atom to the metal ions. Excitation near either of these two transitions could result in the large observed intensity enhancement of the 424-cm⁻¹ band; however, the predicted energies are too high, well in excess of 30 000 cm⁻¹. The final transition involves the nonbonding and antibonding orbitals and corresponds to the promotion of a metal-centered electron to an orbital that is completely delocalized throughout the Fe-N-Fe-bridging system. Such a transition could also give rise to the observed out-of-plane Raman intensity enhancements, although the predicted energy is only 14 000 cm⁻¹, significantly less than is observed.

The assignment of the blue-region charge-transfer absorption band of (TPPFe)₂N to the $e_u^* \leftarrow e_g$ transition, rather than the $a_{2u}^* \leftarrow a_{1g}$ or $a_{1g}^* \leftarrow a_{2u}$ transition, is most consistent with the features observed in the RR and electronic absorption spectra of the series of single-atom bridged complexes (TPPFe)₂X, which includes, in addition to (TPPFe)₂N and (TPPFe)₂O, the carbon-bridged species (TPPFe)₂C.⁹ This conclusion is based on the following reasoning. The π -bonding capabilities of the bridging ligand increase in the order C \gg N > O. The increased π -bonding results in a destabilization of the e_u^* orbitals relative to the nonbonding e_g orbitals but does not significantly affect the energies of the a_{1g}^* and a_{2u}^* orbitals (see ref 26). Thus, the energy of an $A_{2u} \leftarrow A_{1g}$ electronic transition involving the e_u^* orbitals should increase for the series of the three bridged dimers in the order

C \gg N > O, whereas a transition involving the a_{1g}^* or a_{2u}^* orbitals should occur near the same energy in the three complexes. The calculations of Tatsumi and Hoffmann predict that the $e_u^* \leftarrow e_g$ energy separations in the carbon-, nitrogen-, and oxygen-bridged systems are $\sim 26\,000$, $\sim 14\,000$, and $\sim 10\,000$ cm⁻¹, respectively. If the predicted relative separations of the two orbitals in the different complexes are assumed to be approximately correct, the actual energy separation for the carbon- and oxygen-bridged complexes would be $\sim 37\,600$ and $\sim 21\,600$ cm⁻¹, respectively, on the basis of an estimated splitting of 25 600 cm⁻¹ for (TPPFe)₂N. A strong absorption is not observed in the spectrum of (TPPFe)₂O near 21 600 cm⁻¹; however, this band could be much weaker than the analogous absorption of (TPPFe)₂N and thus obscured by the Soret band. Evidence that a z-polarized electronic transition does contribute to the visible-region spectrum of (TPPFe)₂O is provided by the strong resonance enhancement of the Fe-O-Fe stretching mode in the RR spectrum with excitation between the Soret and visible bands (λ_{ex} 4579 Å).¹⁶ This can be contrasted to (TPPFe)₂N for which the Fe-N-Fe stretching mode is principally resonance enhanced with excitation to the blue side of the Soret band. Similarly, the large energy separation expected between the e_u^* and e_g orbitals of (TPPFe)₂C should result in the absence of any observable z-polarized absorption in its electronic spectrum. Indeed, there are no bands observed in the absorption spectrum of (TPPFe)₂C that could be attributed to such a transition.⁹ Also, no band attributable to the Fe-C-Fe symmetric stretching mode has been reported in the RR spectrum.²⁸ This band is expected near 450 cm⁻¹, on the basis of the frequency observed for the asymmetric Fe-C-Fe stretching vibration in the infrared spectrum (940 cm⁻¹)⁹ and on the frequencies of the analogous symmetric and asymmetric vibrations in (TPPFe)₂N (424 and 910 cm⁻¹) and (TPPFe)₂O (363 and 872 cm⁻¹).

One final piece of evidence for the involvement of the e_u^* and e_g orbitals in the $A_{2u} \leftarrow A_{1g}$ transition of (TPPFe)₂N and (TPPFe)₂O is provided by RR studies of non-porphyrin oxygen-bridged complexes of ruthenium and osmium.^{49,50} These complexes exhibit strong resonance enhancement of their M-O-M stretching vibrations with excitation into the strong absorption bands that occur at energies less than 20 000 cm⁻¹. These bands have been attributed to $A_{2u} \leftarrow A_{1g}$ transitions involving the e_u^* and e_g orbitals of these systems. Similar studies have not been reported for nitrogen-bridged non-porphyrin ruthenium and osmium complexes; nevertheless, the observations made for the oxygen-bridged species are consistent with those made for (TPPFe)₂N and (TPPFe)₂O.

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