A Thesis

entitled

Photodissociation of \((\text{DMSO})_2\text{Fe(II)TPP}, (\text{TMSO})_2\text{Fe(II)TPP, and (PSO})_2\text{Fe(II)TPP to form a transient Five-Coordinate Complex as Studied Using Transient Resonance Raman Spectroscopy}

by

Kenneth P. Boone

Submitted in partial fulfillment
of the requirements for the
Master of Science Degree in Chemistry

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Adviser: Dr. Eric W. Findsen

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College of Graduate Studies

University of Toledo

December 2008
An Abstract of

Photodissociation of \((\text{DMSO})_2\text{Fe(II)TPP}, (\text{TMSO})_2\text{Fe(II)TPP, and (PSO)}_2\text{Fe(II)TPP to form a transient Five-Coordinate Complex as Studied Using Transient Resonance Raman Spectroscopy}

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This work presents the results of UV-Visible absorption and Resonance Raman spectroscopic studies of three different heme complexes. \((\text{DMSO})_2\text{Fe(II)TPP (1)}\) and \((\text{TMSO})_2\text{Fe(II)TPP (2)}\) were studied in neat DMSO (dimethylsulfoxide) and neat TMSO (tetramethylene sulfoxide), respectively. A third heme complex, \((\text{PSO})_2\text{Fe(II)TPP (3)}\), required a binary solvent of benzene and PSO (phenyl sulfoxide) in order to be created and studied. Both \((1)\) and \((2)\) were studied in the same binary solvent as well. The investigation determined that all three complexes behave similarly in relation to their UV-VIS and resonance Raman spectra. Resonance Raman experiments at low incident laser power have shown that \((1), (2),\) and \((3)\) exhibit the properties of a 6-coordinate, low-spin complex in the binary solvent. \((1)\) and \((2)\) exhibit the same properties in neat
solvent. The UV-visible absorption data also provides evidence for the presence of a 6-coordinate low-spin complex for all three species in the ground state. The UV-VIS data for (2) and (3) shows a 4 and 5 nm red-shift, respectively, in their Soret bands as compared to (1) in the binary solvent. (2) displays a 3 nm red-shift in its Soret band as compared to (1) in neat solvent. These shifts are attributed to the different sulfoxide ligands bound to the iron center.

For all three complexes, at high laser power, photolysis of an axial ligand occurs and a transient 5-coordinate, high-spin photoproduct is created. This transient photoproduct has a core-size of 2.05 Angstroms and 2.04 Angstroms for (1) and (2) in neat solvent. In binary solvent, the transient photoproducts for (1), (2), and (3) all possessed a calculated core-size of 2.05 Angstroms.

The resonance Raman data provides evidence that the sulfoxides studied are moderate σ−donors and π−acceptors when compared to nitrogenous ligands such as imidazole and pyridine. However, there is no evidence in the resonance Raman data to distinguish among the three sulfoxides the strongest π-acceptor.
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I would like to first of all thank my research director, Dr. Eric W. Findsen, for his training in the lab, advice, and for taking me out to dine at Taco Bell and Ferdo’s. I would also like to thank the members of my committee Dr. Mark Mason and Dr. Xiche Hu for their assistance. I would also like to thank former graduate students Eric Yearley and Aaron Duckworth for listening when I had to vent. Aaron’s family was very helpful in allowing me to stay at their house two to three times per week. They welcomed me into their house and I will never forget them or the kindness they displayed. I cannot forget the secretaries Charlene Hansen and Pam Samples, they were life-savers when help was needed to navigate the maze of paperwork associated with working in the Chemistry Department of a large university.

Last, and certainly not least, I would like to thank my wife Sarah for her love and support. I could not have survived graduate school without her help.

Sincerely,

Kenneth Patrick Boone
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Chapter 1

Introduction

Tetraphenylporphyrins belong to the broad class of porphyrins referred to as synthetic. Some synthetic porphyrins provide ideal four-fold symmetry and while alterations to the periphery of physiological-type porphyrins produce subtle changes in the vibrational spectrum, these synthetic porphyrins present a substantially altered vibrational pattern that is still recognizable. Although natural porphyrins should serve as the best models for proteins, there are advantages in studying the synthetic porphyrins in many circumstances. One advantage of using meso-aryl substituted porphyrins is that they tend to aggregate much less\(^1\) than do natural porphyrins.\(^2\) Second, in many cases, the low symmetry of natural porphyrins limits the spectral resolution of the vibrational modes. As will be seen from the vibrational spectra, the increase in symmetry increases the resolution of the symmetrical vibrational bands of the porphyrin. A third advantage is that these porphyrins are easy to prepare and to crystallize, which has made them very useful in structural studies.\(^3,4\)

The focus of this study is on three model tetraphenylporphyrin complexes with the iron in the +2 oxidation state. This allows direct comparison to be made to model heme systems (such as iron (II) protoporphyrin IX) and to hemeproteins such as oxyhemoglobin, myoglobin, and intermediate complexes of catalase and cytochromes.
Model porphyrin systems of interest are those with one or more axial ligands which either mimic or contrast to those in the active sites of heme proteins.

Sulfoxide ligands, such as DMSO (dimethyl sulfoxide) and TMSO (tetramethylene sulfoxide) have been utilized as solvents for electrochemical applications and in ligand binding studies to iron porphyrins. However, when compared to oxygen, carbon monoxide, and nitrogen-based ligands, sulfoxide ligands have been relatively ignored. Only a few investigations have been carried out where at least one of the ligands on the ferrous model porphyrin has been a sulfoxide ligand.

In this study, several sulfoxides were used as axial ligands to study metalloporphyrin macrocycle dynamics. Investigation of model metalloporphyrin complexes with two sulfoxide ligands is important for several reasons. Most of the model metalloporphyrin complexes that have been characterized have at least one nitrogenous-base axial ligand. Investigation into other types of ligands clarifies properties of the complex which are due to nitrogenous-base ligands such as imidazole. The DMSO ligand (which has been shown to bind through the oxygen atom may be a good model for catalase and oxygen intermediates of cytochrome P450. The excited state dynamics of these model metalloporphyrin systems are useful in understanding the excited-state behavior of heme active sites and in potential applications of iron porphyrin complexes in photochemical systems.

Ligand photodissociation dynamics and the excited state decay mechanisms of other model iron (II) porphyrin complexes and heme proteins have been studied. The primary tool for the investigations, however, has been transient absorption spectroscopy. The time-resolved studies have been carried out on model iron (II) porphyrins with
ligands such as nitrogenous bases,\textsuperscript{12} carbon monoxide/mixed ligand complexes,\textsuperscript{13,14,15} isocyanides,\textsuperscript{16} and nitrosyl ligands.\textsuperscript{17} Efforts have been made to detect and characterize the electronic excited state intermediates of hemes and hemeproteins by transient absorption spectroscopy, but the number of excited-state intermediates and their timescales are in dispute.\textsuperscript{40}

Resonance Raman spectroscopy has been used to study model heme systems but those investigations have focused on the equilibrium structure of the porphyrin. Transient and time-resolved studies have primarily investigated the dynamics of hemeprotein excited-states with ligands such as O\textsubscript{2}, NO, CO, and the effects of the protein on the heme active site.\textsuperscript{11,18,19}

Resonance Raman spectroscopy is complementary to transient absorption spectroscopy in that it can provide electronic and structural information. Resonance Raman spectroscopy also has several advantages over transient absorption spectroscopy. First is the fact that resonance Raman gives definite structural information that detail the coordination and spin-state of the heme-complex (refer to Chapter 3 and 5). Electronic information can also be obtained such as the electron-withdrawing or donating ability of the axial ligand. Second is the fact that resonance Raman allows some selectivity of the excited state being observed. Transient absorption studies can be complicated by many overlapping bands from intermediate states. When this occurs, spectral deconvolution (curve-fitting) is needed to make assignments. In resonance Raman spectroscopy, the transient complex that is observed is the complex that has an absorption band in resonance with the excitation wavelength. It would be extremely useful and fruitful to the spectroscopist if these two techniques were run in conjunction with each other.
Excited-state pathways of iron porphyrin complexes are difficult to elucidate due to the mixing of the porphyrin and ligand orbitals with the metal orbitals. Theoretical calculations have been used to predict excited-state pathways\textsuperscript{20,21,22} and transition energies for iron porphyrin complexes. The photodissociative states of model porphyrins of carbonmonoxy- and oxy-hemeproteins have been assigned by spectroscopic investigations\textsuperscript{23,24} in conjunction with theoretical calculations\textsuperscript{21,22}. The photodissociative states of hemes with nitrogenous-base axial ligands has also been assigned based on transient absorption studies\textsuperscript{12} and theoretical calculations\textsuperscript{20,25,26}. The dissociative state in all of these cases has been assigned to the $d_{\pi}-d_{\sigma^*}$ state, although the energy of the state was found to be ligand dependent\textsuperscript{20,25,26}. The photodissociative states and excited state pathways for heme complexes with non-nitrogenous axial ligands still remain to be investigated. Spectroscopic characterization of model porphyrin complexes with several types of axial ligands will contribute to the understanding of the relationship between the excited-state pathway and the axial ligand.

This thesis compares the equilibrium and excited-state behavior of three (ferrous) tetraphenylporphyrin complexes having axial DMSO, TMSO, or PSO (phenyl sulfoxide) ligands. Two different solvent environments were used in this study to enable comparison of the PSO-ligated porphyrin species to the DMSO- and TMSO-ligated porphyrins. The DMSO- and TMSO-ligated species were also examined in neat solvent so as to allow direct comparison to previous studies on more physiologically related model metalloporphyrin systems. The spectroscopic methods used include equilibrium UV-visible absorption, equilibrium resonance Raman, and transient resonance Raman spectroscopy. Equilibrium UV-visible and equilibrium resonance Raman spectroscopies
were used to obtain ground-state structural and electronic information. Transient resonance Raman spectroscopy allowed the collection of structural and some electronic information on the transient photoproduct.
Chapter 2

Experimental Methods

2.1 Reduction of Iron Porphyrins

Three iron(II)tetraphenylporphyrin (TPP) species were investigated in this study, they were: \((\text{DMSO})_2\text{Fe(II)TPP (1)}, \quad (\text{TMSO})_2\text{Fe(II)TPP (2)}, \quad \text{and (PSO)}_2\text{Fe(II)TPP (3). Refer to Table 2.1 for the chemicals (and their shorthand notations) which were used in this study.}

For sample preparation, Fe(III)(TPP)Cl was obtained from Aldrich and used as received. The DMSO was obtained from Fisher and was vacuum distilled before use. The TMSO and SD were obtained from Acros Organics and the TMSO was also vacuum distilled before use. The PSO was obtained from Aldrich and used as received.

To prepare (1), Fe(III)(TPP)Cl was dissolved in neat DMSO in a one dram vial whose cap was fitted with a Teflon septum. The solution was degassed by bubbling N\(_2\) gas through the solution for at least 20 minutes. A small amount of solid SD was added to the solution. The solution was then shaken briefly to move the SD throughout the solution and the bubbling of N\(_2\) gas through the solution was sufficient to agitate the mixture. Nitrogen gas was bubbled through the solution for an additional 20 minutes with the SD in the solution to reduce the iron. The solution changed to a deep red color.
and the complete reduction of the iron porphyrin was verified by the absorption spectrum. The samples were stable for several weeks and were monitored using absorption spectroscopy. The same procedure was used to prepare (2) but with TMSO as the neat solvent.

The preparation of (3) had to be done in a different manner as PSO is a solid. The PSO was dissolved in benzene in a one-dram vial whose cap was fitted with a Teflon septum. A small magnetic stir bar was added to the solution and the solution was vortexed for one minute to ensure homogeneity. Fe(III)(TPP)Cl was then added to this solution and vortexed for several seconds. The solution was then degassed with benzene-saturated N₂ for twenty minutes. While degassing the porphyrin solution, an unsaturated aqueous SD solution was prepared and degassed by bubbling N₂ or He through the solution for at least twenty minutes. When both solutions were degassed, one milliliter of the aqueous SD solution was added to the porphyrin solution. The two immiscible solutions were mixed, using a stir bar, for 90-120 minutes while under constant benzene saturated N₂ pressure. One milliliter of degassed benzene had to be added to the container after 90 minutes due to evaporation of some of the solvent. Then the stir bar was stopped and the two solutions were allowed to separate; the aqueous SD solution on the bottom and the porphyrin/benzene solution on top. One milliliter of degassed benzene was then slowly added to the container without stirring. At first the newly added degassed benzene was clear and colorless while it mixed with the red porphyrin/benzene layer. However after twenty minutes the porphyrin/benzene layer appeared to be separated into two portions. The top portion was orange and the bottom portion was red. Overall, the container appeared to have three sections, a clear and colorless aqueous layer, a red
benzene layer, and an orange benzene layer. The orange benzene layer did not seem to disappear with time and only disappeared when the container was agitated. The orange benzene layer did reappear if more degassed benzene was added to the organic layer; this reappearance was much slower. When the red layer was extracted the resulting absorption spectrum was consistent with ferrous porphyrins and the Soret band was not split, indicating only one species was present. When the orange layer was extracted the resulting absorption spectrum was consistent with ferric porphyrins and the Soret band indicated only one species was present.

The procedure for the preparation of (3) was used in an attempt to prepare (1) and (2). Unfortunately, when the degassed benzene was added to create a third layer on top of the porphyrin solution, the layer disappeared quickly. With DMSO, the layer was gone in a matter of minutes. This indicated that the separation of the ferric and ferrous species was lost.

To be able to compare the spectra of (3) to the spectra of (1) and (2), the latter two were prepared in their neat solvents but were then diluted in degassed benzene. The dilutions were done until the concentration of the metalloporphyrin solutions matched that of the bis-PSO complex. The concentration of the porphyrin was between 0.02 and 0.05 mM.

<table>
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<th>Abbreviation</th>
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<tr>
<td>DMSO</td>
<td>Dimethyl Sulfoxide</td>
</tr>
<tr>
<td>TMSO</td>
<td>Tetramethylene Sulfoxide</td>
</tr>
<tr>
<td>PSO</td>
<td>Phenyl Sulfoxide</td>
</tr>
<tr>
<td>SD</td>
<td>Sodium Dithionite</td>
</tr>
<tr>
<td>Fe(III)(TPP)Cl</td>
<td>Tetraphenylporphine Iron (III) Chloride</td>
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Table 2.1 Abbreviations for ligands and porphyrins used for this study
2.2 Resonance Raman Protocol

Resonance Raman spectra were recorded with a Quantel 571-C 10 Nd:YAG laser that produces ~10 ns pulses with a repetition rate of 8-10 Hz. The fundamental frequency of the Nd:YAG laser is 1064 nm and can be frequency doubled to obtain 532 nm radiation with a second harmonic generator (SHG). The SHG is a crystal of potassium dideuterium phosphate (KDP). Third harmonic generation is also possible with another KDP crystal and produces radiation at 355 nm. Additional frequencies are obtained using a hydrogen or deuterium filled Raman shift cell. A number of Raman shifted wavelengths are possible using 355 nm and 532 nm excitation. Stokes shifting a 355 nm pulse with hydrogen or deuterium produces 416 nm and 397 nm radiation while anti-Stokes shifting of the 532 nm laser emission results in 459 nm and 436 nm radiation respectively.

A back-scattering sample configuration was used for all of the experiments reported in this work. The scattered radiation from the sample was collected using a Wollensack-Dumont 75mm f/1.9 Oscillo-Anastigmat lens and focused into a Sopra 1.5 m single pass spectrograph after passing through a polarization scrambler. The focused light was dispersed by a 2400 groove/mm holographic grating onto a Princeton Instruments IRY-700 gated, intensified diode array detector. Fig. 2.1 illustrates the experimental setup.

There are several advantages to using a multichannel plate intensified diode array as the detector for pulsed Raman experiments. The diode array enables a range of wavelengths to be detected simultaneously. In pulsed laser spectroscopy, one inevitably has to deal with fluctuations in pulse-to-pulse laser power. This problem becomes a
serious issue if you are using a scanning monochromator with a PMT because the peak-to-peak power fluctuations may result in altered peak intensities. These fluctuations are of no concern with an intensified diode array detector because the entire region is recorded simultaneously. To reduce contributions to the noise from stray light and dark noise in the spectrum the diode array is turned on only we there is a signal to be detected; generally referred to as “gating the detector”.

The gating is achieved by using a signal generated by the oscillator Q-switch to trigger the pulse generator (Princeton Instruments Inc. FG-100 Pulse Generator) which functions to gate, or turn on, the multichannel plate intensifier (MCP) of the photodiode array.

Raman Spectra between 700 cm\(^{-1}\) and 1650 cm\(^{-1}\) were calibrated using neat indene. Pure indene was obtained through vacuum distillation. The indene sample was stored under nitrogen to reduce the rate of decomposition or was sealed in a 5 mm NMR tube under vacuum. Low frequency Raman spectra in the range of 200 cm\(^{-1}\) to 500 cm\(^{-1}\) were calibrated using spectral grade carbon tetrachloride.

Laser power at the sample was controlled by the use of neutral density filters and the focus of the laser beam on the sample. The laser power at the sample was measured with a Scientech Mode 365 power and energy meter. The integrity of samples used in the experiments was monitored with UV-VIS absorption spectroscopy, taken both before and after irradiation at high laser power.

Absorption spectra were obtained using either a Hewlett-Packard HP 8452 spectrometer or a Cary 5 UV/Vis/NIR spectrometer.
Figure 2.1 Instrumental setup used throughout experiments. Components labeled above are: A) beam dump, B) power meter, C) prism, D) neutral density filters [if used], E) prism, F) sample area, G) sample collection optic, H) polarization scrambler, I) 1.5 m single pass spectrograph, J) optical multichannel analyzer, K) pulse generator, L) computer. Dichroic mirrors used were specific to desired wavelength with maximum reflectivity of wavelength at 45°.
Figure 2.2 Picture of the generation of the (PSO)_2Fe(II)TPP species in binary solvent. The three regions in the dram vial are the clear and colorless aqueous region at the bottom, the organic red ferrous porphyrin region in the middle, and the organic orange ferric porphyrin region at the top.
3.1 Absorption Theory of Porphyrins

The absorption spectrum of a metalloporphyrin contains a very strong transition in the near UV-VIS and two weak transitions in the visible region. The transitions in the visible region are called the \( \alpha \) and \( \beta \) bands (or collectively the Q-bands) and have an extinction coefficient \( (\varepsilon) \) of approximately \( 1 \times 10^4 \text{ M}^{-1}\text{cm}^{-1} \). The transition in the near UV is called the Soret (or B-band) and has a \( \varepsilon \) that is approximately ten times that value.

The first attempt to explain the absorption spectrum of a porphyrin was made by Simpson with his \( \pi \)-electron theory. According to Simpson, the porphyrin is an 18 member 18 \( \pi \)-electron ring (refer to Figure 3.1) in which electrons are placed in orbitals of increasing angular momentum, two in \( \ell = 0 \) and 4 each in \( \ell = 1, 2, 3, \) and 4. When an electron of angular momentum of four (in the HOMO, Highest Occupied Molecular Orbital) is excited to an angular momentum of five (the LUMO, Lowest Unoccupied Molecular Orbital), the two momenta either add or subtract. The whole molecule may then change its angular momentum by one unit (\( 5-4 \) or \( -5+4 \)) or nine units (\( 5+4 \) or \( -5-4 \)) (changes in the angular momentum of anything other than \( \pm 1 \) are forbidden). Since the LUMO in porphyrins is doubly degenerate, both values of angular momenta will generate...
doubly degenerate states. The two sets of doubly degenerate states are labeled B and Q, where B refers to one unit of angular momentum and Q refers to nine units of angular momentum. Hund’s Rule says that the state that has the highest angular momentum will be lowest in energy. In this case the Q state is lower in energy and the B state is higher in energy. This can be observed in the absorption spectrum, with Q-bands being in the visible region and the B-band being in the near-UV region. This is not to be confused with the β band which is actually the Q(0-1) vibrational side band of the Q(0,0) transition or α-band. Since the Q and B bands seen in the absorption spectrum represent a transition to a state that is doubly degenerate, each band is doubly degenerate. If the symmetry of the porphyrin ring were broken and if the degeneracy of the LUMO were broken, one would see this loss of degeneracy in the absorption spectrum as four peaks instead of two.

**Figure 3.1** Structure of a metalloporphyrin ring. The alpha-carbon position is labeled α, the beta-carbon position is labeled β, and the meso-position is labeled δ. Only one porphyrin ring system was examined in this study with hydrogens at the β-positions 1-8 and phenyl rings at all four δ positions. The metal in the center of the porphyrin ring in this study was iron.
The most important problem with Simpson’s theory is that it did not predict the intensity of the Q and B bands correctly. The model gives the same intensity for the $\alpha$, $\beta$, and B bands of the porphyrin. Further, Simpson’s model did not take into account the configuration interaction (CI) between the excited state configurations that are described below. Gouterman’s four-orbital model successfully took into account CI.$^{31}$

The early molecular orbital (MO) calculations describing the orbitals and energies involved in the absorption spectrum were done by Longuett-Higgins et al.$^{29}$ and are depicted in Figure 3.2. The Highest Occupied Molecular Orbitals (HOMOs) are labeled $a_{1u}$ and $a_{2u}$. The LUMO is doubly degenerate and is labeled the $e_g$ orbital. Since the orbital is polarized in the $x$ and $y$ directions, the individual orbitals are labeled $e_{gx}$ and $e_{gy}$. When the electron is promoted to the LUMO from the HOMO, it changes its angular momentum by $\pm 1$ or $\pm 9$ units. The transitions are denoted as $(a_{1u}e_{gx})$ and $(a_{2u}e_{gy})$. These transitions just denoted actually mix together so you have four possible transitions: $(a_{1u}e_{gx})$, $(a_{1u}e_{gy})$, $(a_{2u}e_{gx})$, and $(a_{2u}e_{gy})$. A consequence of CI is that the transition dipole strength of the two allowed transitions add (each allowed transition involves a change in angular momentum of one unit), creating an intense transition we see as the B-band in the near UV. However, the dipole strength of the two forbidden transitions (involving a change in angular momentum of nine units) will nearly cancel and is seen as the $\alpha$-band in the visible region of the spectrum. As stated above, the $\beta$-band is a vibrational side band of the $\alpha$-band.
Figure 3.2 Porphyrin frontier orbitals, redrawn from M. Gouterman, *Journal of Molecular Spectroscopy*, 1961, v 6, p 138. The top filled Molecular Orbitals are the $a_{2u}$ and the $a_{1u}$, and the lowest unfilled molecular orbital is the doubly degenerate $e_g$. The relative sizes of the orbitals (orbital coefficients) are indicated by the circles (H.C. Longuet-Higgins, C.W. Rector, and J.R. Platt, *Journal of Chemical Physics*, 1950, v 18, p 1174). Filled and empty circles indicate sign (+ and -, respectively).

The CI calculations of Gouterman also defined four parameters of the four-orbital model, which are defined in Fig 3.3. The $A_{1g}$ parameter is half the energy splitting between the $a_{1u}$ and the $a_{2u}$ orbitals. The $A'_{1g}$ parameter is the average energy splitting...
for the electronic transition (from the ground state to $E_B - E_Q$). The $A''_{1g}$ term is the configuration interaction contribution. $R$ is the total transition dipole of the transition.

![Diagram showing Gouterman’s Four-Orbital Model](image)

**Figure 3.3** Definitions of the parameters of the four-orbital model. The parameters are $A_{1g}$, $A'_{1g}$, $A''_{1g}$, and $R_1/R_2$. The Molecular Orbitals depicted in (a) are typical of metallo-tetraphenyl porphyrins (except for those with very electronegative metals such as Pd and Pt). In almost all other metallo-porphyrin complexes the $a_{1u}$ orbital is predicted to be higher in energy than the $a_{2u}$ orbital. $E_B$ and $E_Q$ are the energies of the B-band and Q-band respectively. The $\theta$ term is the “unmixing” parameter.

Figure 3.2 depicts the frontier orbitals of the four-orbital model as applied to the metalloporphyrin. The $a_{1u}$ orbital has electron density at the $\alpha$ and $\beta$ carbons of the porphyrin ring. The $a_{2u}$ orbital has electron density at the pyrrole nitrogens and at the meso-carbons. The $e_g$ orbitals are degenerate as one becomes the other by rotation of 90° about the principal axis.

Figure 3.2 also depicts ways in which the electronic structure of the metalloporphyrin may be altered. There are three ways that the electronic structure of a metalloporphyrin may be altered. The first is the substitution of different metals into the center of the porphyrin ring. The $a_{1u}$ orbital energy should not be affected by metal...
substitution as it has nodes at the pyrrole nitrogens and cannot interact with the metal orbitals. Metal substitution is expected to alter the energies of the \(a_{2u}\) orbital. As the electronegativity of the metal increases, the degree of delocalization of the electrons in the metalloporphyrin \(a_{2u}\) orbital into the metal \(p_z\) orbitals increases. The stabilization of the \(a_{2u}\) orbital is attributed to increased interaction with empty metal \(p_z\) orbitals.

The second way to alter the electronic structure of the metalloporphyrin is to change the substituents at the \(\beta\) or \(\delta\) positions of the ring (Refer to Figure 3.1). By altering the substituents at the \(\beta\) positions, the \(a_{1u}\) orbital energy is changed. For example, propionic acid, vinyl, and methyl substituents of protoporphyrin IX have an overall effect of raising the \(a_{1u}\) energy relative to the \(a_{2u}\) energy. Phenyl rings at the \(\delta\) positions (as in TPP) raise the energy of the \(a_{2u}\) orbital relative to the \(a_{1u}\) orbital. The raising or lowering of the \(a_{1u}\) or \(a_{2u}\) orbital energies is attributed to mixing of the filled \(\pi\) orbitals of the \(\alpha\)-carbons of the substituents with the filled porphyrin molecular orbitals. This mixing delocalizes charge onto the carbons and results in lowering of the electron-electron repulsion. The more electron-withdrawing a substituent, the more the substituent carbons become conjugated with the ring, and the more the charge is delocalized.

The third way to alter the electronic structure of a metalloporphyrin is by coordination of ligand(s) to the axial position(s) on the metal. The ligand will augment or inhibit a metal’s ability to withdraw electrons from the porphyrin \(\pi\)-system. For example, a ligand that is a strong Lewis acid will withdraw electron density from the metal center, and the degree of delocalization of the porphyrin \(\pi\)-electrons to the metal now increases, further stabilizing the \(a_{2u}\) orbital.
The intensity of the Q(0,0) transition, or $\alpha$ band, depends on the energy spacing of the $a_{1u}$ and $a_{2u}$ orbitals.\textsuperscript{32} For example, if the energy gap between the $a_{1u}$ and $a_{2u}$ orbitals increases, the ($a_{1u}$, $e_g$) and ($a_{2u}$, $e_g$) transition dipoles cancel to a lesser extent, and the $\alpha$ band increases in intensity. The Q(0,1) band, or $\beta$ band, derives its intensity from coupling to the Soret and $\alpha$ bands. The intensity of the $\beta$ band with respect to the Soret band has been shown to be relatively constant among porphyrins.\textsuperscript{33,34} Therefore the intensity ratio of the $\alpha$ and $\beta$ bands can be used as an empirical measure of the gap between the $a_{1u}$ and $a_{2u}$ orbitals.\textsuperscript{33} The greater the $\alpha/\beta$ intensity ratio, the greater the energy gap between the $a_{1u}$ and $a_{2u}$ orbitals of the porphyrin.

3.2 Characteristic d-orbital configurations of Iron Porphyrins

Figure 3.4 shows examples of energy level spacings of d-orbitals of ferrous (iron (II), $d^6$) porphyrin complexes with different coordination numbers.\textsuperscript{20} The energy level diagrams explain why 4-coordinate ferrous complexes are predicted to be intermediate spin, why most 5-coordinate complexes are high spin, and most 6-coordinate complexes are observed to be low spin.\textsuperscript{35}

In the Fe(II) 4-coordinate porphyrin species, the iron has no axial ligands and the iron is expected to remain in the porphyrin plane.\textsuperscript{36} The crystal structure of Fe(II)TPP shows that the iron is indeed in the plane of the porphyrin.\textsuperscript{61,62} As a result of the iron staying in-plane, the iron $d_{x^2-y^2}$ orbital overlaps with orbitals from the pyrrole nitrogens and electron-electron repulsion raises the energy of this d-orbital dramatically when compared to the other d-orbitals. Since there are no axial ligands in this case, the $d_z^2$
orbital is much lower in energy when compared to the five and six-coordinate species. The result is an intermediate spin for the four-coordinate species.

Figure 3.4 Relative metal orbital occupancy and spin state of ferrous porphine, derived and reproduced from extended Huckel calculations of M. Zerner, M. Gouterman, and H. Kobayashi in *Theoretica Chimica Acta*, 1966, v. 6, p. 373. The diagrams at the bottom are reproduced from S-C. Jeoung, D. Kim, and D-W. Cho in *Journal of Raman Spectroscopy*, 2000, v. 31, p 327.

In the Fe(II), five-coordinate species, the iron has one axial ligand in the fifth position and is removed from the plane of the porphyrin towards this ligand. In this position, the $d_{x^2-y^2}$ orbital is no longer in the porphyrin plane and therefore no longer overlaps with the pyrrole nitrogen orbitals. The result is a moderate decrease in energy.
The ligand coordinated in the fifth position of the iron moderately raises the energy of the $d_{z^2}$ orbital. The lowering of the energy of the $d_{x^2-y^2}$ orbital and raising of the energy of $d_{z^2}$ orbital allows for a high spin complex to form.

In the Fe(II) six-coordinate species, the iron is in the porphyrin plane and ligands occupy the fifth and sixth positions on the iron. Electron-electron repulsion raises the energy of the $d_{x^2-y^2}$ orbital and the sixth ligand raises the energy of the $d_{z^2}$ orbital. This allows for the formation of a low spin complex.

The descriptions of the coordination states are generalities and exceptions do exist. For the five-coordinate species, Fe(II) porphyrins can be low spin when the ligand in the fifth position is a very strong field ligand such as NO and CS.$^{37,38}$ The only known model system that is a six-coordinate, high spin Fe(II) porphyrin is the bis-THF$^{27}$ species as THF is very weak field ligand.

Table 3.1 summarizes the relationship between the iron spin state, coordination number, and geometry. The six-coordinate species are expected to be planar, while the five-coordinate species are expected to be nonplanar if they are high-spin. As shown in Table 3.2, the core size (center to nitrogen distance) for high-spin complexes are larger than for low-spin complexes. This is due to the occupation of the $d_{x^2-y^2}$ orbitals in these complexes.$^{27}$ This large change in core size allows for the identification of spin states for a given coordination number by the frequencies of the Resonance Raman core-size modes such as $v_2$ and $v_4$.

The previous section describes the $\pi-\pi^*$ electronic absorption spectra of porphyrins. Since iron does have vacant d-orbitals, weaker transitions can occur. These are classified as either charge-transfer (CT) or d-d transitions. Because these transitions
are weak, they are often masked by the stronger $\pi-\pi^*$ absorptions. CT transitions can occur from the metal to, or from, the porphyrin ring or the axial ligand. They have been identified in hemes by polarized single-crystal absorption spectroscopy. The metal d-d transitions are parity forbidden in $D_{4h}$ symmetry, but can gain intensity with symmetry distortion. These transitions are important as they have been suggested as possible photodissociative pathways for axial ligands. In these transitions, electron density is transferred to the $d_{z^2}$ or $d_{x^2-y^2}$ orbitals, and are antibonding with respect to the axial ligand.

<table>
<thead>
<tr>
<th>Ligand Field Strength</th>
<th>6-Coordinate</th>
<th>5-Coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong</td>
<td>ls, nearly planar</td>
<td>ls, nearly planar</td>
</tr>
<tr>
<td>Medium</td>
<td>ls, nearly planar</td>
<td>hs, nonplanar</td>
</tr>
<tr>
<td>Weak</td>
<td>predicted is</td>
<td>hs, nonplanar</td>
</tr>
<tr>
<td>Very Weak</td>
<td>hs, nearly planar</td>
<td>hs, nonplanar</td>
</tr>
</tbody>
</table>

Table 3.2 Expected spin states and structures for iron (II) porphyrins (from Ref. 6 and references therein). Abbreviations: hs = high spin; is = intermediate spin; ls = low spin

### 3.3 Normal Raman Scattering

When light strikes a material it is either absorbed or scattered. Scattering that results in no loss of energy (inelastic) is termed Rayleigh scattering and the frequency of the scattered light is the same as the incoming light. Scattering that results in a change of
energy of the scattered light compared to that of the incident light is termed Raman scattering. Scattered radiation that is less energetic than the incoming light is labeled Stokes shifted radiation and the more energetic scattered radiation is labeled anti-Stokes shifted radiation.

Normal Raman Scattering can be considered as radiation from an induced dipole. This induced dipole, $\mu$, can be defined as:

$$\mu = \alpha E$$

(3.3.1)

where $\alpha$ is the polarizability of the molecule and $E$ is the electric field of the incident radiation. The polarizability of a molecule is essentially a measure of how easily the molecule’s electron cloud is distorted. This distortion of the molecule’s electron cloud by the incoming radiation is the source of the induced dipole.

The term $\alpha$ is not a scalar quantity and is better represented as a tensor. This is because the induced dipole does not necessarily have the same directionality as the incoming radiation. In other words, if the electric field is aligned along the z-axis, the induced dipole may have components in the x, y, and z axes. Equation 3.3.1 may be rewritten to demonstrate this:

$$
\begin{bmatrix}
\mu_x \\
\mu_y \\
\mu_z 
\end{bmatrix} =
\begin{bmatrix}
\alpha_{xx} & \alpha_{xy} & \alpha_{xz} \\
\alpha_{yx} & \alpha_{yy} & \alpha_{yz} \\
\alpha_{zx} & \alpha_{zy} & \alpha_{zz}
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y \\
E_z
\end{bmatrix}
$$

(3.3.2)

There are nine components of the polarizability tensor and they reflect the way the magnitude of the induced dipole is related to the directionality and polarization of the incident light. The term $\alpha$ determines the induced dipole moment’s spatial orientation.
The subscripts on $\alpha$ represent the polarization of the incident and scattered light, respectively.\textsuperscript{41}

The polarizability, $\alpha_{\text{per}}$, is dependent on the nuclear positions; in other words the polarizability may vary with vibrations of the molecule. This variation is best represented by expanding each component of the tensor in a Taylor series with respect to the normal coordinates of the vibration. Using the electrical harmonic approximation,\textsuperscript{41} the expanded forms of $\alpha_{\text{per}}$ can be simplified to:

$$\alpha = \alpha_o + \alpha'_k Q_k$$

(3.3.3)

where $\alpha$ is the polarizability tensor, $\alpha_o$ is the molecule's polarizability tensor in its equilibrium position, $\alpha'_k$ is the molecule's polarizability at the $k^{\text{th}}$ normal mode (derived polarizability), and $Q_k$ is the $k^{\text{th}}$ normal mode of the molecule. Taking into account the time dependence of $Q$, eq. 3.3.3 becomes:

$$\alpha = \alpha_o + \alpha'_k Q_{k_0} \cos(2\pi v_k t)$$

(3.3.4)\textsuperscript{41}

where $Q_{k_0}$ is the amplitude of the normal coordinate mode and $v_k$ is the frequency of the $k^{\text{th}}$ normal mode.

The electric field in eq. 3.3.1 is also not constant; the intensity varies with time and can be represented as:

$$E = E_o \cos(2\pi v_o t)$$

(3.3.5)

where $v_o$ is the frequency of the incoming radiation, $t$ is time, $E$ is the electric field at time $t$, and $E_o$ is the incident electric field. Eq. 3.3.5 may be inserted into eq. 3.3.1 to demonstrate the time dependence of the induced dipole:
\[ \mu = \alpha (E_o \cos(2\pi \nu_o t)) \]  

(3.3.6)

and eq. 3.3.4 may be inserted into eq. 3.3.6:

\[ \mu = \alpha_o E \cos(2\pi \nu_o t) + \frac{1}{2} \alpha'_k Q_{ko} E_o \cos\{2\pi t(\nu_o + \nu_k)\} \]
\[ + \frac{1}{2} \alpha'_k Q_{ko} E_o \cos\{2\pi t(\nu_o - \nu_k)\} \]

(3.3.7)

Equation 3.3.7 describes the scattered radiation that has interacted with the electron cloud of a molecule. The first term of equation 3.3.7 describes Rayleigh scattering; the scattered radiation is of frequency \( \nu_o \), which is the frequency of the incident light. The second term refers to anti-Stokes scattering; in which the frequency of the scattered radiation is higher than the incident radiation by the frequency of the \( k^{th} \) normal mode. The third term refers to Stokes scattering; here the frequency of the scattered radiation is lower than the incident radiation by the frequency of the \( k^{th} \) normal mode.

The intensity of this scattered radiation \( I_s \) is proportional to the scattering frequency \( (\nu_s) \) and the square of the transition polarizability tensor between the ground state \( (g) \) and the final state \( (f) \). This is represented in eq 8:

\[ I_s = \left( \frac{8\pi\nu_s^4}{9c^4} \right) I_o \sum \left| (\alpha_{\rho\sigma})_{gf} \right|^2 \]

(3.3.8)

where \( I_o \) is the intensity of the incident radiation and \( c \) is the speed of light.

It is important to note that the values of the tensor components will depend on your coordinate system. Regardless of your choice of coordinates, an electric field
applied in one direction will produce an induced dipole that has a unique direction and
magnitude, but the components of the scattering tensor will depend on the choice of
coordinates.\textsuperscript{41} No matter what coordinate system is chosen, there are two invariants that
can be obtained from the scattering tensor which are called the mean polarizability ($a$)
and the anisotropy ($\gamma$). The mean polarizability is:

$$a = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (3.3.9)$$

and the anisotropy is defined as :

$$\lambda^2 = \frac{1}{2}\{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{xz}^2)\} \quad (3.3.10)$$

This becomes important now because in all explanations above it was assumed
the scattering was from a single molecule in a fixed position whose nuclei were allowed
to vibrate along their equilibrium positions. Raman scattering is usually performed on
bulk samples containing many molecules that rotate freely and therefore are in randomly
distributed orientations when interacting with incident radiation. For Raman Scattering
by a bulk sample, the depolarization ratio can be defined in terms of the invariants
described in equations 3.3.9 and 3.3.10. The depolarization ratio gives information on
the symmetry of the normal mode that is responsible for a given vibronic transition. If
the scattered light is observed at 90\(^{\circ}\), the depolarization ratio ($\rho$) is given by:

$$\rho = \frac{I_{\perp}}{I} = \frac{3\gamma^2}{45a^2 + 4\gamma^2} \quad (3.3.11)$$

\textsuperscript{43}
For Raman scattering, with a symmetric scattering tensor, the depolarization ratio varies between completely polarized ($\rho = 0$) to completely depolarized ($\rho = \frac{3}{4}$).

### 3.4 Resonance Raman Scattering

Resonance Raman Scattering is different than normal scattering in that the incident radiation frequency $\nu_o$ is brought close to the frequency of an electronic transition $\nu_e$ of a molecule. The polarizability tensor in Resonance Raman Scattering will be described in Quantum Mechanical terms as it gives a more detailed description of the factors that govern the intensities seen in the vibrational spectrum. According to the Kramers-Heisenberg-Dirac dispersion equation, the polarizability tensor is described by second-order perturbation theory in terms of the transition moments of the molecule:\textsuperscript{44,45}

\[
(\alpha_{\rho\sigma})_{fg} = \frac{1}{A} \sum_{e} \left( \frac{\langle f | \mu_\rho | e \rangle \langle e | \mu_\sigma | g \rangle}{\nu_{eg} - \nu_o + i\Gamma_e} + \frac{\langle f | \mu_\sigma | e \rangle \langle e | \mu_\rho | g \rangle}{\nu_{ef} - \nu_o + i\Gamma_e} \right) \quad (3.4.1)
\]

where $(\alpha_{\rho\sigma})_{fg}$ is the polarizability tensor of the molecule involved in the Raman transition between states $g$ and $f$ with incident and scattered polarizations indicated by $\rho$ and $\sigma$. $\mu_\rho$ and $\mu_\sigma$ refer to the dipole moments before and after scattering, $|g\rangle$, $|f\rangle$, and $|e\rangle$ are the initial, final, and excited electronic states ($|e\rangle$ has a half-bandwidth of $\Gamma_e$), and $\nu_{eg}$ and $\nu_{ef}$ are the frequencies of transition.

When the incident light is of a frequency that is near to the frequency of an electronic transition, the first term in eq. 3.4.1 becomes dominant as the numerator becomes very large. This term is responsible for the resonance enhancement of
vibrational intensities seen in the vibrational spectrum and is referred to as the resonant term. The second term is referred to as the nonresonant term and is ignored.

According to the Born-Oppenheimer Approximation the electron’s movement is ~1000 times faster than the nucleus and it allows for the separation of vibrational and electronic terms in wavefunctions that describe electronic transitions. Doing so for parts of eq. 3.4.1 gives:

\[ \langle f | \mu | e \rangle = \langle j | M_e | \nu \rangle \quad \langle e | \mu | g \rangle = \langle \nu | M_e | i \rangle \]

where \( i \) and \( j \) are the initial and final vibrational wavefunctions of the electronic ground state, \( \nu \) is the vibrational state of the excited electronic state \( e \). \( M \) is the pure electronic transition moment between states \( g \) and \( e \).

The electronic transition moment is not purely independent of the nuclear motions as there is a non-negligible amount of nuclear motion during an electronic transition. This means the pure electronic transition moment may be expanded in a Taylor’s Series about the equilibrium geometry:

\[ M_e = M_e^O + \left( \frac{\partial M}{\partial Q} \right)^O Q \ldots \]  

(3.4.2)

where \( Q \) is a given normal mode of the molecule. With the nonresonant term in eq.1 and the polarization of the molecule being ignored, the first two terms of eq. 3.4.2 give the following for the polarizability:

\[ \alpha = A + B \]

(3.4.3)

\[ A = \left( M_e^O \right)^2 \frac{1}{A} \sum_{\nu} \frac{\langle j | \nu \rangle \langle \nu | i \rangle}{\nu_i - \nu_o + i \Gamma_v} \]

(3.4.4)
The transition frequency $\nu_{i\nu}$ is the frequency between the ground vibrational level, $i$, and the vibrational level $\nu$ of the excited state $e$.

The first term in eq. 3.4.3 is called A-term scattering and is defined in eq 3.4.4. It is the dominant factor in the Resonance Raman intensity. In this term, the Raman intensity is mostly dependent on the Frank-Condon integrals in the numerator. The magnitude of the integrals increases with the amount of displacement of the electronic excited state potential well along the normal coordinate. This means that a vibrational band will be enhanced depending on its displacement in the excited state. Typically only vibrational modes that are totally symmetric will be enhanced by the A-term. In the absence of an origin shift, the numerator in eq. 3.4.4 goes to zero.

The second term is called B-term scattering and it allows non-totally symmetric vibrations to gain intensity. Non-totally symmetric modes do not see a displacement of the equilibrium distance during the course of a vibration. The dependency on the normal mode of the vibrational integrals in eq. 3.4.5 allow for this. The normal coordinate $Q$ connects the vibrational levels that differ by one quantum, so that both $\langle 1 | Q | 0 \rangle \langle 0 | 0 \rangle$ and $\langle 1 | Q | 0 \rangle \langle 1 | 1 \rangle$ can contribute to the B-term for Raman fundamentals.

In Resonance Raman Scattering, the polarizability tensor $\alpha$ is not the same as with Normal Raman Scattering. The equation for the depolarization ratio for a randomly oriented molecule is:

$$B = M e \left( \frac{\partial M}{\partial Q} \right)^O \sum \frac{\langle j | Q | \nu \rangle \langle \nu | i \rangle + \langle j | \nu \rangle \langle \nu | Q | i \rangle}{\nu_{vi} - \nu_o + i \Gamma \nu} \right)$$

(3.4.5)
\[ \rho_l = \frac{I_\perp}{I} = \frac{3\gamma^2}{(45a^2 + 4\gamma^2)} \]  

Equation 3.4.6 is identical to eq 3.3.11 in the previous section and the parameters were defined in eq 3.3.9 and 3.3.10 of the previous section. When the incident frequency approaches the frequency of an electronic transition, theory predicts the scattering tensor may become asymmetric.\(^4\) Placzek considered this in his treatment of the Raman effect\(^4\) and he came up with the following expression for the depolarization ratio:

\[ \rho_l = \frac{(3g^s + 5g^a)}{(10g^o + 4g^s)} \]  

where:

\[ g^o = 3a^2 \]  

\[ g^s = \frac{1}{3}\left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{yy} - \alpha_{zz})^2 \right] \]  

\[ + \frac{1}{2}\left[ (\alpha_{xy} + \alpha_{yx})^2 + (\alpha_{xz} + \alpha_{zx})^2 + (\alpha_{yz} + \alpha_{zy})^2 \right] \]  

\[ g^a = \frac{1}{2}\left[ (\alpha_{xy} - \alpha_{yx})^2 + (\alpha_{xz} - \alpha_{zx})^2 + (\alpha_{yz} - \alpha_{zy})^2 \right] \]  

These three variables are called, respectively, the isotropic \((g^o)\), the quadrupole \((g^s)\), and the magnetic dipole components of the scattering tensor. Eq.3.4.7 can more easily be compared to eq 3.4.6 if the quadrupole and the magnetic dipole variables are redefined as two anisotropy invariants of the scattering tensor, a symmetric part:
The subscripts on $\gamma$ in eq 11 and eq 12 refer to the fact that they are symmetric and asymmetric components (respectively) of the scattering tensor. With the invariants now defined, eq 6 can be restated:

$$\rho_l = \frac{3\gamma_s^2 + 5\gamma_{as}^2}{45a^2 + 4\gamma_s^2}$$

(3.4.13)

The depolarization ratio observed in Resonance Raman Scattering is defined by eq 3.4.13 and allows for an asymmetric scattering tensor. If the scattering tensor were symmetric, then it’s obvious that $\gamma_s^2$ would equal $\gamma^2$ and the asymmetric component $\gamma_{as}^2$ would be equal to zero. Then eq 3.4.13 would reduce to eq 3.4.6.

The depolarization ratio in eq 6 applies far from resonance and implies that a ratio can be no larger than $\frac{3}{4}$. This is the value of $\rho_l$ for all non-totally symmetric modes because $a$ equals zero; these bands are depolarized. For totally symmetric modes, $a$ has non-zero values and $\rho_l$ varies between $\frac{3}{4}$ and zero and is referred to as polarized. From looking at eq 3.4.13, one can see how $\rho_l$ can be larger than $\frac{3}{4}$. This results from non-totally symmetric bands; and these bands are called anomalously polarized. The phenomenon of inverse polarization, $\rho_l$ equals infinity, requires $a$ and $\gamma_s$ to be zero$^{30}$ and for $\gamma_{as}$ to be non-zero. This will only happen for a non-totally symmetric band for which the scattering tensor is antisymmetric (i.e. $\alpha_{ij} = -\alpha_{ij}$). Inversely polarized bands can be
seen when the incident frequency is near the frequency of a forbidden band such as the $\alpha$ or $\beta$ band.
Chapter 4

UV-Visible Absorption Spectroscopy of Ferrous Tetraphenylporphyrin Complexes

Three iron (II) tetraphenylporphyrin (TPP) complexes were studied, (DMSO)$_2$Fe(II)TPP, (TMSO)$_2$Fe(II)TPP, and (PSO)$_2$Fe(II)TPP. The UV-visible absorption spectra were run under anaerobic conditions where the samples were reduced as described in Chapter 2. The concentrations of the porphyrin samples varied between 0.02 and 0.1 mM.

Two solvent environments were used in the study because of the conditions needed to generate the (PSO)$_2$Fe(II)TPP complex. Phenyl sulfoxide is a solid at room temperature so a co-solvent was needed to dissolve both the phenyl sulfoxide and the iron (III) tetraphenylporphyrin chloride. Benzene was chosen since it will dissolve the tetraphenylporphyrin and the phenyl sulfoxide, and is non-coordinating to the porphyrin and sulfoxide. The bis-DMSO and bis-TMSO complexes were also examined in this solvent environment. The molar ratio of benzene to sulfoxide was kept around 0.9 : 0.1. This benzene/sulfoxide environment will be referred to as a “binary solvent”. The bis-DMSO and bis-TMSO complexes were also examined in neat solvent. This allows straight-forward comparison to previous studies of (DMSO)$_2$Fe(II)PPIX$^{40}$ and
(TMSO)$_2$Fe(II)PPIX$^{48}$ (PPIX = protoporphyrin IX). The complexes in neat solvent will be examined first followed by the complexes in the binary solvent.

4.1 Ferrous TPP complexes in neat solvent

The absorption spectrum of (DMSO)$_2$Fe(II)TPP in neat DMSO has peak maxima at 429, 532, and 560 nm, which correspond to the Soret, beta, and alpha bands, respectively. The $\alpha/\beta$ intensity ratio was determined to be 0.20. This could not be determined directly from the spectra. A spectral curve-fitting program in Grams AI, Thermo-Galactic, was used in the determination of the ratio. (TMSO)$_2$Fe(II)TPP in neat TMSO has Soret, beta, and alpha peak maxima at 432, 532, and 566 nm, respectively. The $\alpha/\beta$ intensity ratio was determined to be 0.781. The absorption spectra are displayed in Figure 4.1.

The visible absorption spectra of these ferrous TPP complexes are also distinguishable from their PPIX counterparts. The Soret in the ferrous TPP complexes are 2-5 nm red-shifted from the position of their PPIX counterparts. In the visible region the $\alpha$ band for the ferrous TPP complexes is weaker than in the ferrous PPIX complexes. This leads to $\alpha/\beta$ intensity ratios, for the ferrous TPP complexes, of less than half that of the ferrous PPIX complexes. This is demonstrated by examining Table 4.1.

4.2 Ferrous TPP complexes in binary solvent

(PSO)$_2$Fe(II)TPP in the binary solvent was found to have Soret band of 433 nm but the Q bands could not be determined directly from the sample spectrum. The Q-
bands appear as a broad peak around 551 nm. The Soret, beta, and alpha bands for the bis-DMSO complex are 428, 531, and 578 nm, respectively, with an $\alpha/\beta$ intensity ratio of 0.512. The bis-TMSO complex has the Soret, beta, and alpha bands at 432, 531, and 564 nm, respectively, with an $\alpha/\beta$ intensity ratio of 0.685. The absorption spectra of all three bis-sulfoxide complexes are shown in Figure 4.3. The band positions and intensity ratios of these three complexes and similar complexes are listed in Table 4.1.

<table>
<thead>
<tr>
<th>Complex</th>
<th>solvent</th>
<th>Soret (nm)</th>
<th>$\beta$ (nm)</th>
<th>$\alpha$ (nm)</th>
<th>$\alpha/\beta$ ratio</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(DMSO)$_2$Fe(II)TPP</td>
<td>binary</td>
<td>428</td>
<td>531</td>
<td>578</td>
<td>0.51</td>
<td>this work</td>
</tr>
<tr>
<td>(TMSO)$_2$Fe(II)TPP</td>
<td>binary</td>
<td>432</td>
<td>531</td>
<td>564</td>
<td>0.69</td>
<td>this work</td>
</tr>
<tr>
<td>(PSO)$_2$Fe(II)TPP</td>
<td>binary</td>
<td>433</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>this work</td>
</tr>
<tr>
<td>(DMSO)$_2$Fe(II)TPP</td>
<td>neat</td>
<td>429</td>
<td>532</td>
<td>560</td>
<td>0.2</td>
<td>this work</td>
</tr>
<tr>
<td>(TMSO)$_2$Fe(II)TPP</td>
<td>neat</td>
<td>432</td>
<td>532</td>
<td>566</td>
<td>0.78</td>
<td>this work</td>
</tr>
<tr>
<td>(DMSO)$_2$Fe(II)PPIX</td>
<td>neat</td>
<td>423</td>
<td>524</td>
<td>555</td>
<td>1.33</td>
<td>10</td>
</tr>
<tr>
<td>(TMSO)$_2$Fe(II)PPIX</td>
<td>neat</td>
<td>426</td>
<td>527</td>
<td>558</td>
<td>1.38</td>
<td>48</td>
</tr>
<tr>
<td>(ImH)$_2$Fe(II)PPIX</td>
<td>neat</td>
<td>423</td>
<td>525</td>
<td>557</td>
<td>NA</td>
<td>49</td>
</tr>
<tr>
<td>(CO)(DMSO)Fe(II)PPIX</td>
<td>neat</td>
<td>416</td>
<td>536</td>
<td>567</td>
<td>1.12</td>
<td>14</td>
</tr>
<tr>
<td>(CO)(TMSO)Fe(II)PPIX</td>
<td>neat</td>
<td>415</td>
<td>536</td>
<td>568</td>
<td>1.10</td>
<td>48</td>
</tr>
</tbody>
</table>

**Table 4.1** UV-vis absorption band wavelengths for some six- and five-coordinate iron (II) porphyrin complexes. (Im = Imidazole, PPIX = protoporphyrin IX). * absorption spectra recorded in binary solvent. # absorption peaks in neat solvent.
Figure 4.1 Uv-vis spectra of A) \((\text{DMSO})_2\text{Fe(II)TPP}\) in neat DMSO and B) \((\text{TMSO})_2\text{Fe(II)TPP}\) in neat TMSO. Insets show an expansion of the visible region. Sample concentrations of the insets are \(~0.1\) mM, while sample concentrations of the spectra that are not expanded were 0.01-0.06 mM.
Figure 4.2 UV-vis spectra of A) (DMSO)$_2$Fe(II)TPP in binary solvent, B) (TMSO)$_2$Fe(II)TPP in binary solvent, and C) (PSO)$_2$Fe(II)TPP. Insets show an expansion of the visible regions. Concentrations of all samples in this Figure were 0.02-0.05 mM.
Chapter 5

Nanosecond Resonance Raman Spectroscopy of Tetraphenylporphyrin Complexes

This study will focus on the high frequency modes of the porphyrins. These modes provide information on the structural characteristics of both the ground state and the transient photoproducts of the porphyrin macrocycle. The resonance Raman spectra of all three species in all environments studied here were taken with 10 ns laser pulses. Resonance Raman spectra were recorded at high and low power densities. The spectra taken at low power density describe the ferrous, six-coordinate ground state species. The spectra taken at high power densities describe transient photoproducts formed from photodissociation within the 10 ns laser pulse. The high frequency modes of the complexes in neat solvent will be examined first, followed by the porphyrin complexes in a binary solvent environment.

5.1 High Frequency Modes in neat solvent

Figure 5.1 shows the resonance Raman spectra of (DMSO)$_2$Fe(II)TPP and the transient photoproduct in neat DMSO, which were obtained using 416 nm radiation. The resonance Raman spectrum taken at low power has mode frequencies of 1363, 1494, and
1562 cm\(^{-1}\). These are assigned to the porphyrin normal-mode vibrations of \(\nu_4\), \(\nu_{11}\), and \(\nu_2\), respectively. These assignments are based upon mode frequencies reported in the literature\(^6\) where the author was able to generate the \((\text{DMSO})_2\text{Fe(II)TPP}\) species by reducing \(\text{Fe(III)TPPCl}\) in neat DMSO. Assignments were also made with the help of mode frequencies reported in the literature for three low-spin, 6-coordinate model porphyrins, namely \((1\text{-methylimidazole})_2\text{Fe(II)TPP}\)\(^{5,3}\), \((\text{piperidine})_2\text{Fe(II)TPP}\)\(^{5,3}\), and \((\text{pyridine})_2\text{Fe(II)TPP}\).\(^{5,3}\) Polarization ratio studies were also carried out to verify the polarization of the bands.

Figure 5.2 shows the resonance Raman spectra of \((\text{TMSO})_2\text{Fe(II)TPP}\) and the transient photoproduct in neat TMSO obtained with 416 nm radiation. The low power spectrum has mode frequencies of 1361, 1498, and 1561 cm\(^{-1}\). These modes are assigned to the porphyrin normal modes of \(\nu_4\), \(\nu_{11}\), and \(\nu_2\), respectively. The assignments are based on the same reasoning as for the bis-DMSO complex. The \((\text{TMSO})_2\text{Fe(II)TPP}\) ground state is assigned as a low-spin, six-coordinate complex.

At high laser power, as seen in Figures 5.1 and 5.2, different vibrational modes are observed for both the bis-DMSO and bis-TMSO \(\text{Fe(II)TPP}\) complexes. Mode frequencies for the bis-DMSO complex are 1344, 1486, and 1539 cm\(^{-1}\). These are assigned to the porphyrin normal-modes \(\nu_4\), \(\nu_{11}\), and \(\nu_2\) respectively. Mode frequencies for the bis-TMSO complex are 1345, 1440, 1489, and 1542 cm\(^{-1}\). These are assigned to the porphyrin normal-modes of \(\nu_4\), \(\nu_3\), \(\nu_{11}\), and \(\nu_2\) respectively. These new mode frequencies are very similar to those reported for the five-coordinate, high-spin model system of \((2\text{-methylimidazole})\text{Fe(II)TPP}\)\(^{5,3}\). Therefore, the shifts in frequencies of the modes indicate the formation of a transient high-spin, five-coordinate complex. In all
cases, the samples were examined via UV-vis absorption after the high power experiments to check for photodegradation of the porphyrin and no sample showed any signs of degradation. Upon lowering the laser power density back to its original level, the vibrational modes of the low-spin, six-coordinate complex were observed. This affirmed that the creation of the transient species is a reversible process.

The mode frequencies for the intermediate-spin, four-coordinate Fe(II)TPP are shown in Table 5.2. These mode frequencies do not correspond to those of the transient photoproduct. This supports the assignment of the transient species to a five-coordinate complex. Photolysis studies of other six-coordinate ferrous porphyrin complexes show photodissociation of only one axial ligand to form a five-coordinate complex.16, 55, 56

Attempts were made to obtain resonance Raman spectra of bis-DMSO and bis-TMSO Fe(II)TPP complexes and their transient photoproducts using Q-band excitation at 532 nm. In physiological porphyrins, excitation with radiation resonant with the visible absorption bands enhances the intensity of non-totally symmetric vibrational bands. These non-symmetrical bands are not seen or are very weak in TPP complexes.51 Upon excitation with 532 nm radiation, no vibrational modes are seen for any of the TPP complexes examined in this study.

5.2 High Frequency Modes in binary solvent

Figure 5.3 shows the resonance Raman spectra of (PSO)2Fe(II)TPP and the corresponding transient photoproduct in the binary solvent, obtained using 416 nm radiation. The resonance Raman spectrum for (PSO)2Fe(II)TPP, taken at low power, has mode frequencies of 1361, 1447, 1495, and 1553 cm\(^{-1}\). These are assigned to the
porphyrin normal-mode vibrations of ν₄, ν₃, ν₁₁, and ν₂ respectively. The transient photoproduct produced at high laser power has mode frequencies at 1346, 1487, and 1540 cm⁻¹. These are assigned to the porphyrin normal-mode vibrations of ν₄, ν₁₁, and ν₂, respectively. The (PSO)₂Fe(II)TPP ground state is assigned as a low-spin, six-coordinate complex.

Figure 5.4 shows the resonance Raman spectra of (TMSO)₂Fe(II)TPP and the corresponding transient photoproduct in the binary solvent, obtained using 416 nm radiation. The resonance Raman spectrum for (TMSO)₂Fe(II)TPP, taken at low power, has mode frequencies of 1362, 1502, and 1557 cm⁻¹. These are assigned to the porphyrin normal-mode vibrations of ν₄, ν₁₁, and ν₂, respectively. The transient photoproduct produced at high laser power produces mode frequencies at 1344, 1434, 1489, and 1539 cm⁻¹. These are assigned to the porphyrin normal-mode vibrations of ν₄, ν₃, ν₁₁, and ν₂, respectively. The (TMSO)₂Fe(II)TPP ground state is assigned as a low-spin, six-coordinate complex.

Figure 5.5 shows the resonance Raman spectra of (DMSO)₂Fe(II)TPP and the corresponding transient photoproduct in the binary solvent, obtained using 416 nm radiation. The resonance Raman spectrum for (DMSO)₂Fe(II)TPP, taken at low power, has mode frequencies of 1362, 1496, and 1561 cm⁻¹. These are assigned to the porphyrin normal-mode vibrations of ν₄, ν₁₁, and ν₂, respectively. The transient photoproduct produced at high laser power produces mode frequencies at 1344, 1435, 1487, and 1540 cm⁻¹. These are assigned to the porphyrin normal-mode vibrations ν₄, ν₃, ν₁₁, and ν₂, respectively. The (DMSO)₂Fe(II)TPP ground state is assigned as a low-spin, six-coordinate complex.
5.3 Important High Frequency Modes

The $\nu_4$ vibrational mode is a totally symmetric mode; it is the pyrrole ring “breathing mode” whose major component consists of the \(C_\alpha-N\) stretch. The $\nu_4$ mode is sensitive to changes in the $\pi$-electron delocalization between the iron $d_{\pi}$ orbitals and the ligand and to changes in the iron oxidation state.

When the iron in the porphyrin has a ligand (or ligands; L) coordinated, there is overlap between the iron $d_{\pi}$ ($= d_{xz}$ and $d_{yz}$) and $d_{z^2}$ orbitals and the ligand $\pi$ and $\sigma$ orbitals. This leads to two distinct types of interactions, $d_{z^2}$ (Fe)-$\sigma$(L) and $d_{\pi}$(Fe)-$\pi$(L), which are referred to as $\sigma$-type and $\pi$-type interactions, respectively. Since the $d_{z^2}$ orbital is of $a_{1g}$ symmetry it does not affect the $\pi$-state of the porphyrin. However, the $d_{\pi}$ orbitals are of $e_g$ symmetry and do interact with the LUMO of the porphyrin. Since there are 4 and 2 electrons in the low-spin, ferrous and high-spin, ferrous iron $d_{\pi}$ orbital respectively, the low spin, ferrous species has two more electrons to delocalize to the LUMO of the porphyrin ring. According to ab initio calculations, the $\pi^*$ orbital of the porphyrin ring (the LUMO) is anti-bonding with respect to the $C_\alpha-N$ bond.\textsuperscript{57} Therefore, the more electrons occupying this orbital, the weaker the $C_\alpha-N$ stretch will be, consequently the force constant for that vibration will decrease. This is why ferrous, low-spin porphyrins have a lower frequency for $\nu_4$ than ferrous, high-spin species. If the axial ligand has $\pi$-acidity, the empty or partially occupied $\pi^*$ (L) orbital withdraws electron density from the $d_{\pi}$ orbitals, which in turn, withdraws electron density from the $\pi^*$ orbitals on the porphyrin ring. This causes $\nu_4$ to shift to a higher frequency. If the axial ligand was $\pi$-
basic in nature, the frequency of $v_4$ would shift to a lower frequency because of the weaker bond strength due to increased electron density in the $\pi^*$ orbitals.

Several Raman bands, most notably $v_2$ and $v_3$, have been shown to be sensitive to the core size of the porphyrin ring. The sensitivity of the modes has been found to be related to the $C_\alpha$-$N$-$C_\alpha$ bond angle and not to the center-to-pyrrole nitrogen distance ($C_\text{r}$-$N$). The $C_\text{r}$-$N$ distances were calculated for all three species (see Table 5.2) examined in this study and the values calculated are in agreement with other low-spin, six-coordinate ferrous porphyrins.

<table>
<thead>
<tr>
<th>Complex</th>
<th>solvent</th>
<th>Spin State</th>
<th>$v_4$ (cm$^{-1}$)</th>
<th>$v_3$ (cm$^{-1}$)</th>
<th>$v_{11}$ (cm$^{-1}$)</th>
<th>$v_2$ (cm$^{-1}$)</th>
<th>reference</th>
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</thead>
<tbody>
<tr>
<td>(DMSO)$_2$Fe(II)PPIX#</td>
<td>neat</td>
<td>ls</td>
<td>1368</td>
<td>1496</td>
<td>--</td>
<td>1584</td>
<td>48</td>
</tr>
<tr>
<td>(DMSO)Fe(II)PPIX##</td>
<td>neat</td>
<td>hs</td>
<td>1358</td>
<td>1469</td>
<td>--</td>
<td>1560</td>
<td>48</td>
</tr>
<tr>
<td>(TMSO)$_2$Fe(II)PPIX#</td>
<td>neat</td>
<td>ls</td>
<td>1368</td>
<td>--</td>
<td>--</td>
<td>1591</td>
<td>48</td>
</tr>
<tr>
<td>(TMSO)Fe(II)PPIX##</td>
<td>neat</td>
<td>hs</td>
<td>1360</td>
<td>1477</td>
<td>--</td>
<td>1563</td>
<td>48</td>
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<tr>
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<td>ls</td>
<td>1363</td>
<td>--</td>
<td>1494</td>
<td>1562</td>
<td>this work</td>
</tr>
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<td>hs</td>
<td>1344</td>
<td>--</td>
<td>1486</td>
<td>1539</td>
<td>this work</td>
</tr>
<tr>
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<td>ls</td>
<td>1361</td>
<td>--</td>
<td>1498</td>
<td>1561</td>
<td>this work</td>
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<td>hs</td>
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<td>1440</td>
<td>1489</td>
<td>1542</td>
<td>this work</td>
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<td>binary</td>
<td>ls</td>
<td>1362</td>
<td>--</td>
<td>1496</td>
<td>1561</td>
<td>this work</td>
</tr>
<tr>
<td>(DMSO)Fe(II)TPP*#</td>
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<td>hs</td>
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<td>1435</td>
<td>1487</td>
<td>1540</td>
<td>this work</td>
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<tr>
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<td>ls</td>
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<td>--</td>
<td>1502</td>
<td>1557</td>
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<td>1344</td>
<td>1434</td>
<td>1489</td>
<td>1539</td>
<td>this work</td>
</tr>
<tr>
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<td>ls</td>
<td>1361</td>
<td>1447</td>
<td>1495</td>
<td>1553</td>
<td>this work</td>
</tr>
<tr>
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<td>binary</td>
<td>hs</td>
<td>1346</td>
<td>--</td>
<td>1487</td>
<td>1540</td>
<td>this work</td>
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</table>

*indicates transient species, ls and hs are low-spin and high-spin, respectively.

Table 5.1 Comparison of experimentally determined resonance Raman frequencies for ferrous iron porphyrin complexes containing either DMSO, TMSO, or PSO ligands.
Table 5.2 Resonance Raman frequencies for various four-, five-, and six-coordinate complexes as previously reported.

<table>
<thead>
<tr>
<th>Complex</th>
<th>(v_4 (\text{cm}^{-1}))</th>
<th>(v_3 (\text{cm}^{-1}))</th>
<th>(v_{11} (\text{cm}^{-1}))</th>
<th>(v_2 (\text{cm}^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ImH)(_2)Fe(II)PPIX</td>
<td>1359</td>
<td>1493</td>
<td>1584</td>
<td>1539</td>
<td>39</td>
</tr>
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<td>(OH)(_2)Fe(II)PPIX</td>
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<td>1469</td>
<td>1559</td>
<td>1541</td>
<td>39</td>
</tr>
<tr>
<td>(ImH)(_2)Fe(II)TPP</td>
<td>1354</td>
<td>1448</td>
<td>1557</td>
<td>1545</td>
<td>39</td>
</tr>
<tr>
<td>(pip)(_2)Fe(II)TPP</td>
<td>1356</td>
<td>--</td>
<td>1561</td>
<td>--</td>
<td>51</td>
</tr>
<tr>
<td>(py)(_2)Fe(II)TPP</td>
<td>1360</td>
<td>--</td>
<td>1558</td>
<td>--</td>
<td>51, 53</td>
</tr>
<tr>
<td>(pic)(_2)Fe(II)TPP</td>
<td>1360</td>
<td>--</td>
<td>1558</td>
<td>--</td>
<td>51, 53</td>
</tr>
<tr>
<td>(2-MeImH)(_2)Fe(II)PPIX</td>
<td>1357</td>
<td>1471</td>
<td>1562</td>
<td>1547</td>
<td>39</td>
</tr>
<tr>
<td>(2-MeImH)(_2)Fe(II)TPP</td>
<td>1341</td>
<td>1431</td>
<td>1538</td>
<td>--</td>
<td>51, 53</td>
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<tr>
<td>Fe(II)TPP</td>
<td>1370</td>
<td>--</td>
<td>1565</td>
<td>--</td>
<td>51, 53</td>
</tr>
</tbody>
</table>

Table 5.3 Ferrous TPP center-to-Nitrogen (C\(_r\)-N) distances calculated from core-size sensitive Raman modes using linear correlation parameters of Spiro et al.\(^54\) The core size calculated from the individual bands is shown as is the average calculated C\(_r\)-N distance.

* indicates transient species, # indicates binary solvent, and n indicates neat solvent.
Figure 5.1 Resonance Raman spectra of (DMSO)$_2$Fe(II)TPP taken with 416 nm radiation in neat DMSO. Solid line is the ground-state species, the dashed line is the excited-state species.
Figure 5.2 Resonance Raman spectrum of (TMSO)$_2$Fe(II)TPP in neat TMSO with 416 nm radiation. Solid line is the ground-state species, the dashed line is the excited-state species.
Figure 5.3 Resonance Raman spectra of (PSO)$_2$Fe(II)TPP in binary solvent taken with 416 nm radiation. Solid line is the ground-state species, the dashed line is the excited-state species. * indicates solvent peaks.
Figure 5.4 Resonance Raman spectrum of (TMSO)$_2$Fe(II)TPP in binary solvent with 416 nm radiation. Solid line is the ground-state species, the dashed line is the excited-state species. * indicates solvent peak.
Figure 5.5 Resonance Raman Spectra of (DMSO)$_2$Fe(II)TPP obtained with 416 nm radiation in binary solvent. Solid line is the ground-state species, the dashed line is the excited-state species.
Chapter 6

Discussion and Conclusions

The UV-vis spectra of the bis-sulfoxide TPP complexes in the neat solvents (DMSO and TMSO) are very similar to each other (refer to Figures 4.1 – 4.3). There is a 3 nm red-shift in the Soret band of (TMSO)$_2$Fe(II)TPP as compared to (DMSO)$_2$Fe(II)TPP. The same 3 nm red shift seen in the bis-TMSO complex was also reported by Wheeler in a study of the PPIX bis-sulfoxide complexes. The shift was attributed to nonplanar distortions in the porphyrin ring.$^{48}$

The bis-sulfoxide TPP complexes in the binary solvent systems PSO/benzene and TMSO/benzene, (PSO)$_2$Fe(II)TPP and (TMSO)$_2$Fe(II)TPP, are observed to have Soret bands that are 5 and 4 nm red-shifted, respectively, from the Soret of the (DMSO)$_2$Fe(II)TPP species. It is doubtful that the same nonplanar distortions seen above are solely responsible for this shift. Tetraphenyl porphyrins are generally known for being much more planar than PPIX. Any ruffling or planar distortions in the ring, caused by ligand sterics, are expected to be more pronounced in (PSO)$_2$Fe(II)TPP than in (TMSO)$_2$Fe(II)TPP.

Solvent effects are a possibility for the red shift. The influence of the solvent on the electronic spectrum of iron porphyrins is generally attributed to factors of the solvent such as polarity and polarizability. The red-shift in the Soret band of
(TMSO)$_2$Fe(II)TPP in neat TMSO (when compared its bis-DMSO analog in neat DMSO) could be attributed to the solvent polarizability. The effects of solvent polarizability was investigated by Ondrias, Findsen, and Nalliah.$^{40,47}$ To be specific, Ondrias and Findsen$^{47}$ showed a rough correlation between the solvent $E_T(30)$ parameter and the Soret band energies and $\alpha$ and $\beta$ intensity ratios of NiPPDME (Nickel Protoporphyrin Dimethyl Ester)(along with Raman modes). The $E_T(30)$ parameter is an empirical measure of solvent polarity that includes polarizability and hydrogen bonding effects.$^{50}$ Nalliah$^{40}$ examined the roles of specific solvent effects for free-base and metalloporphyrins. She came to the conclusion that solvent polarizability of the solute environment is the primary solvent effect on the porphyrin $\pi-\pi^*$ transition energies.

Despite the argument put forth by other authors,$^{42}$ it is very unlikely that solvent polarity would cause the red-shift seen by $(\text{TMSO})_2\text{Fe(II)}\text{TPP}$ in neat TMSO. The dipole moments of neat DMSO and neat TMSO are 5.3 and 4.2 D, respectively. A red-shift in absorption bands with decreasing solvent polarity would indicate that the ground state is more polar than the excited state,$^{50}$ which is not possible in TPP because of its symmetry.

In binary solvent systems (such as PSO, TMSO, and DMSO in benzene) the effects of the solvent system on the electronic structure are much more complicated. Aside from interactions between solute and solvent, the interaction between the different solvent molecules comes into play.$^{50}$ It is also possible that the solvent shell of the porphyrin may very well be different than that of the bulk solution. There is also the possibility of selective solubilization in such an environment. Without studying the solvent system itself, the influence of the solvent mixture on the electronic spectrum cannot be stated with any certainty.
Another possible cause for the Soret red-shift seen in the UV-VIS spectra is the sulfoxide ligands bound to the iron center. These ligands alter the gap between the HOMO and LUMO. This can be examined by looking at the $\alpha/\beta$ intensity ratios of the porphyrin complexes. When examining the porphyrins in this study, complexes with smaller $\alpha/\beta$ intensity ratios tended to have more blue-shifted Soret bands.

It is very likely that the red-shift seen in the UV-VIS spectra for the bis-TMSO and bis-PSO species is predominantly due to the different sulfoxide ligands altering the HOMO-LUMO gap. As was mentioned in Chapter 3, the larger the $\alpha/\beta$ intensity ratio the larger the energy gap between the $a_{1u}$ and the $a_{2u}$ orbital. The larger the energy gap between the $a_{1u}$ and $a_{2u}$ orbitals, the smaller the gap between the HOMO and LUMO. This effect should be easily observed in tetraphenylporphyrins as the $a_{2u}$ orbital is higher in energy than the $a_{1u}$ orbital and electron-donating ligands on metalloporphyrins cause the energy of the $a_{2u}$ orbital to increase relative to that of the $a_{1u}$ orbital. This increase in the $a_{2u}$ orbital energy will increase the gap between the $a_{1u}$ and $a_{2u}$ orbitals and decrease the energy gap between the HOMO and LUMO. As is seen from the UV-vis spectra the $\alpha$ band is much more intense in the bis-TMSO and bis-PSO complex than for the bis-DMSO complex.

The resonance Raman (RR) data presented for all five complexes, in all environments studied, suggest that they are low-spin, six coordinate complexes in the ground state. This correlates with the UV-vis spectra of these complexes as seen in Fig 4.1 and 4.2.

In the RR spectra, the $\nu_4$ band is sensitive to the $\pi$-delocalization between the axial ligands and the iron, among other things. The peak position of $\nu_4$ for
(TMSO)$_2$Fe(II)TPP in neat TMSO is two wavenumbers from the position of $\nu_4$ in
(DMSO)$_2$Fe(II)TPP in neat DMSO. In the case of the transient five-coordinate, high spin
states, the position of $\nu_4$ for (TMSO)Fe(II)TPP* in neat TMSO is one wavenumber from
the position of $\nu_4$ for (DMSO)Fe(II)TPP* in neat DMSO. This suggests that there is no
significant difference in the $\pi$-accepting ability between the two sulfoxide species.

In the low power RR spectra of the three bis-sulfoxide complexes, $\nu_4$ does not
shift more than one wavenumber. In the high power RR spectrum of (PSO)$_2$Fe(II)TPP*,
$\nu_4$ does shift 2 cm$^{-1}$ from (DMSO)$_2$Fe(II)TPP* and (TMSO)$_2$Fe(II)TPP*. This data
suggests that there is little difference in the $\pi$-accepting ability of the three ligands.

These same experiments were done by Wheeler$^{48}$ on (TMSO)$_2$Fe(II)PPIX and
(DMSO)$_2$Fe(II)PPIX in their respective neat solvents. He found the position for $\nu_4$ was
the same for both ground state species in neat solvent. When examining the RR spectra
for the transient photoproducts, the position of $\nu_4$ for the (TMSO)Fe(II)PPIX* transient
complex in neat TMSO was 2 cm$^{-1}$ lower than the position of $\nu_4$ for the
(DMSO)Fe(II)PPIX* species in neat DMSO. He concluded that TMSO was a stronger $\pi$-
acceptor ligand than DMSO. After examining his data and the data presented here, his
conclusion may have been premature. Any significant difference in $\pi$-acidity would
accompany a larger shift in $\nu_4$.

The RR data for all bis-sulfoxide complexes point toward the formation of a
transient five-coordinate, high spin species at high laser power. All Raman bands of
interest (i.e. $\nu_2$, $\nu_3$, $\nu_4$, and $\nu_{11}$) see a decrease in frequency upon formation of this
transient photoproduct. Upon formation of the photoproduct, the iron is removed from
the porphyrin plane toward the ligand in the fifth position. It cannot be ascertained
directly from the data whether or not the porphyrin ring is “doming” or “ruffling” during the lifetime of the photoprodut as $\nu_2$, $\nu_3$, and $\nu_{11}$ are all insensitive to doming of the porphyrin.\textsuperscript{58} The vibrational mode $\nu_3$ should be sensitive to ruffling of the porphyrin but the intensity of $\nu_3$ for three of the TPP complexes was so low the band could not be assigned. In the instances where $\nu_3$ could be assigned a peak, its high or low power analog could not be assigned. However, some doming is expected in the transient complex as the geometry of the ring changes and the iron moves out of the porphyrin plane.

It is well known that the high frequency Raman modes of metalloporphyrins have strong correlation with the porphyrin geometry. To be more specific, there is an inverse correlation between the high frequency Raman modes (above 1400 cm$^{-1}$) and the core size of the porphyrin macrocycle. The core sizes of all of the TPP complexes were calculated from the Raman peak positions using linear trend analysis.\textsuperscript{59,39}

For (DMSO)$_2$Fe(II)TPP and (TMSO)$_2$Fe(II)TPP in neat solvent, the ground-state species possessed Raman modes that were consistent with core sizes of 2.00 Angstroms and 1.99 Angstroms, respectively. The (DMSO)$_2$Fe(II)TPP and (TMSO)$_2$Fe(II)TPP ground state species in the binary solvent possessed core sizes of 1.99 and 1.98 Angstroms. The (PSO)$_2$Fe(II)TPP species in the binary solvent was found to have a calculated core size of 2.01 Angstroms. The slightly larger core-size for the bis-PSO species was expected due to the bulkiness of the ligand.

The core size of the transient photoprodut can also be calculated from its Raman peak positions. For (DMSO)$_2$Fe(II)TPP and (TMSO)$_2$Fe(II)TPP in neat solvent, the core size of the transient photoprodut was calculated to be 2.05 and 2.04 Angstroms,
respectively. The core size for the transient photoproducts of (DMSO)$_2$Fe(II)TPP, 
(TMSO)$_2$Fe(II)TPP, and (PSO)$_2$Fe(II)TPP were calculated to be 2.05 Angstroms.

From observing the Resonance Raman spectra of the ground-state and excited state complexes a basic dynamic scheme can be suggested; applying to all the species studied in this paper, in both solvent environments. The low-spin, six-coordinate species seen in the ground-state has an electron on the porphyrin ring promoted to the excited state ($\pi$$-$$\pi^*$) with the absorption of the 416 nm radiation. The excited electron is then transferred to the central metal creating a (d,d) state. This (d,d) state is responsible for the photodissocation seen in the spectra of the transient photoproduct. This transient photoproduct then relaxes to a five-coordinate complex ground-state which then binds a sulfoxide to the sixth position on the iron. The process is summarized on Figure 6.1.

Figure 6.1 Photodynamics scheme suggested from Resonance Raman data and literature. DMSO is used in the diagram to represent all of the sulfoxides studied in this paper.
Figure 6.1 contains one concept not mentioned above and it involves the competition between rapid deactivation of the excited state and photodissociation. Rapid deactivation is expected to be the dominant route of relaxation for iron porphyrins. The excited state deactivation is believed to occur via a ligand state because the decay from the excited π* state to the ground π state is radiative as is seen in metalloporphyrins with closed shells and free-base porphyrins. As the laser power is increased the probability of photodissociation increases and the resulting species is seen in the high power spectra.

To gain more insight on these systems in the future, transient absorption studies should be carried out. Sulfoxide porphyrin systems are unique among the porphyrin systems (involved in photolysis studies) studied to date in the fact that after photolysis, recombination is extremely slow. Larsen and Findsen showed that (DMSO)\textsubscript{2}Fe(II)PPIX and (TMSO)\textsubscript{2}Fe(II)PPIX are both photolabile and that after photolysis recombination occurs with a rate constant of \( \sim 2 \times 10^6 \) s\textsuperscript{-1}. For comparison, measured rate constants for ligand recombination of various isocyanides and 1-methylimidazole to PPIXDME (protoporphyrin dimethyl ester) are on the order of \( 10^9 \) s\textsuperscript{-1}. The recombination of PSO is expected to be much slower than either of the other two sulfoxides involved in the study due to the ligand’s bulk.

It was postulated by Findsen that the unique kinetic properties of these porphyrin systems might have more to do with the solvent cage than the actual porphyrin structure. Neat DMSO is fairly viscous and TMSO is almost four times as viscous as DMSO. It is known that DMSO (in the bulk solvent) forms a chain-like aggregate where the dipoles align themselves. This has been used to explain DMSO’s viscosity. TMSO can be expected to behave in the same manner plus there is TMSO’s ring
structure which increases the force exerted between parallel layers of fluid. This viscosity might be the cause of the slow recombination as the association of the photo-dissociated sulfoxide to the bulk solvent would provide another energy barrier to recombination. Transient absorption studies on the three bis-sulfoxide porphyrin complexes in this study in the binary solvent would provide some insight to this postulation.
Bibliography


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