

**Exploring Ligand Field Effects on Fe(IV)-oxo Reactivity
Channels for Versatility as a Potential Catalyst for
Strong C-H Bond Activation**

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ABSTRACT

The non-heme iron(IV)-oxo enzyme intermediates can perform a variety of oxidation reactions in various mononuclear and dinuclear enzymatic systems. These species have generated a large amount of interest due to their potential to catalyze C-H bonds, specifically the sought-after conversion of methane to methanol. Various biomimetic model complexes with $S = 2$ spin have been synthesized allowing a much more detailed analysis of these high spin systems. Advanced spectroscopic analysis indicates the existence of three pathways for the oxyl radical to form. For the $S = 2$ complexes, one reactivity pathway occurs through the σ [sigma] channel arising from an electron excitation from the σ [sigma] to σ^* [sigma star] orbital, and two degenerate pathways occur through the π [pi] channel arising from an electron excitation going from the π [pi] to the π^* [pi star] channel. In molecular complexes that have hydrogen atoms in close proximity to the iron(IV)-oxo site, the π [pi] channel can cause a self-oxidation of ligand C-H bonds that will eventually lead to the self-decay of the catalyst. This distinction means in some cases it would be beneficial to prefer one channel over the other depending on if the π [pi] is contributing to a self-decay pathway. Using density functional theory and multireference wave function theory, we are able to gain an understanding of the characteristics of these reaction channels and how different ligand fields affect them. We benchmarked a Fe(IV)-oxo system to find the most appropriate level of theory to create the model systems. Model systems will allow the understanding of the reactive oxyl intermediate, which is the species responsible for the oxidation reaction. Finding trends of reactivity and understanding the development of the oxyl character will allow the best optimization of these systems and aid in the design of novel catalysts. By considering the reactivity of these systems under the influence of varying ligand field strengths, we can gain a better understanding of how these iron-oxo species can be tuned in order to obtain a desired level of reactivity. We are offering new insight with the use of multireference methods at the CASSCF/CASPT2 level in order to perform an examination of an array of strong and weak field ligand systems.

TABLE OF CONTENTS

Chapter One Introduction and Review of the Literature	1
Introduction.....	1
Recent Efforts	3
Reactivity Channels.....	7
Experiment and MCD Spectroscopy	12
Electronic Structure Theory.....	16
Chapter Two Benchmark Study.....	20
Software and Methods.....	20
Results and Discussion	22
Chapter Three Examination of Reactive Channels with Multireference Methods	26
Computational Details	26
Results and Discussion	29
Reactivity Channels in Quintet Complexes	31
Reactivity Channels in Triplet States	40
Chapter Four Conclusions and Recommendations	42
List of References	45
Appendix	53
Quintet Complexes	54
Triplet Complexes	61
Benchmarking Tables	66
Vita.....	68

LIST OF TABLES

Table 1. Contains the deviations of the bond lengths from their corresponding crystal structures.	25
Table 2. Shows the formation of the oxyl for both of the reactivity channels in the presence of the different ligand fields and the trigonal bipyramidal geometry.	34
Table 3. Shows the bond distance at which the pseudo octahedral complexes reactivity channels develop dominant oxyl configurations.	34
Table 4. Contains the Fe-O bond distance at which the σ and π channel potential energy surfaces cross over with one another.	35
Table 5. Benchmarking information comparing size of basis set and average difference in bond lengths from crystal structure.	66
Table 6. Complete list of benchmark calculations run.	67

LIST OF FIGURES

Figure 1. Shows structure for the active site of the enzyme intermediate TauDJ.	4
Figure 2. A qualitative molecular orbital diagram showing the difference between the a) low spin and the high spin b) molecular orbital configurations.....	6
Figure 3. Molecular orbital diagram with the ground state spin of a high spin species included for $[\text{FeO(IV)(H}_2\text{O)}_5]^{2+}$. Red atoms are oxygens. White atoms are hydrogens.....	8
Figure 4. The various reaction pathways present in the high spin Fe(IV)-oxo species. 4a shows a σ to σ^* transition yielding a Fe(IV) with a spin of 5/2. 4b shows a π to π^* transition yielding a Fe(IV) with a spin of 5/2. 4c shows a σ to σ^* transition yielding a Fe(IV) with a spin of 3/2. 4d shows a π to π^* transition yielding a Fe(IV) with a spin of 3/2. Dashed vertical lines depict excitation pathways.	10
Figure 5. spectra taken from a paper showing the clarification that MCD and variable MCD spectroscopy can offer. From Ref. 68.....	14
Figure 6. This includes the MCD Mechanisms for the (a) A-term , (b) B-term, and (c) C- term K denotes the intermediate state close in energy. J denotes an excited state and A denotes the ground state. The population of the lower state in the C-term is higher at lower temperatures making it so the states no longer cancel out with one another and provide significant peak intensity. This C-term intensity is very important because it contains complete information about the properties of the ground state.	15
Figure 7. Contains the $[\text{FeO(IV)(H}_3\text{buea)}]^{1-}$ complex.....	21
Figure 8. Illustrates the breaking up of the molecule into different coordination spheres so as to partition up the levels of theory adequately.....	22
Figure 9. Illustrates the difference seen in the various optimizations between the Fe atom and the highlighted atoms.	24
Figure 10. Contains the model compounds which were investigated using the CASSCF/CASPT2 methods. The bottom model complex has a charge of -1.....	28
Figure 11. Potential energy curves for the ground and first fourteen excited states for the $[\text{Fe(IV)O(H}_2\text{O)}_5]^{2+}$ species completed at the CASSCF(10,8) level.....	30
Figure 12. The potential energy curves of the $[\text{FeO(H}_2\text{O)}_5]^{2+}$ complex resulting from a CASPT2 (10,8) calculation. The black dashed line represents the point at which the π channels (represented by the black lines) develop dominant oxyl character that is indicative of the oxyl (radical) formation. The red dash line is the same thing for the σ channel (represented by the orange line).....	32
Figure 13. Illustrates the upward trend in the energy gap between the σ and π reactivity channels as it was computed for the pseudo octahedral geometries.	36
Figure 14. Illustrates the upward trend in the energy gap between the σ and π reactivity channels it was computed for the trigonal bipyramidal geometries.	36
Figure 15. This figure shows the percentage of configurations which are that of the radical oxygen for the σ and π channels for the trigonal bipyramidal species. Orange is the percentage of oxyl in the π channel. Blue is the percentage of oxyl in the σ channel.	38

Figure 16. This figure includes the percentage of configurations which are that of the radical oxygen for the σ and π channels for the pseudo octahedral complexes. orange is the percentage of oxyl in the π channel. blue is the percentage of oxyl in the σ channel.	39
Figure 17. Triplet CASPT2 (10,8) for $[\text{FeO}(\text{H}_2\text{O})_5]^{2+}$ species for the four lowest states..	41
Figure 18. Contains the potential energy surfaces calculated at the CASPT2 (10,8) level of theory for the states which are involved in the σ and π reactivity channels for the $[\text{FeO}(\text{NH}_3)_5]^{2+}$ complex. The dashed lines (red σ channel; black π channel) show the distance where the oxyl configuration becomes the dominant configuration.....	54
Figure 19. Contains the potential energy surfaces calculated at the CASPT2 (10,8) level of theory for the states which are involved in the σ and π reactivity channels for the $[\text{FeO}(\text{H}_2\text{O})_4]^{2+}$ complex. The dashed lines (red σ channel; black π channel) show the distance where the oxyl configuration becomes the dominant configuration.....	55
Figure 20. Contains the potential energy surfaces calculated at the CASPT2 (10,8) level of theory for the states which are involved in the σ and π reactivity channels for the $[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_3]^{2+}$ complex. The dashed lines (red σ channel; black π channel) show the distance where the oxyl configuration becomes the dominant configuration.	56
Figure 21. Contains the potential energy surfaces calculated at the CASPT2 (10,8) level of theory for the states which are involved in the σ and π reactivity channels for the $[\text{FeO}(\text{NH}_3)_4]^{2+}$ complex. The dashed lines (red σ channel; black π channel) show the distance where the oxyl configuration becomes the dominant configuration.....	57
Figure 22. Contains the potential energy surfaces calculated at the CASPT2 (10,8) level of theory for the states which are involved in the σ and π reactivity channels for the $[\text{FeO}(\text{NH}_3)_{\text{ax}}(\text{NH}_2)_3]^{-1}$ complex. The dashed lines (red σ channel; black π channel) show the distance where the oxyl configuration becomes the dominant configuration.	58
Figure 23. Shows increasing oxyl character and decreasing oxo character for σ channel of the $[\text{FeO}(\text{NH}_3)_{\text{ax}}(\text{NH}_2)_3]^{1-}$ species.	59
Figure 24. Shows increasing oxyl character and decreasing oxo character for π channel.	60
Figure 25. $[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_4]^{2+}$ Triplet CASPT2 (10,8) potential energy curves with the five lowest states.	61
Figure 26. $[\text{FeO}(\text{H}_2\text{O})_4]^{2+}$ Triplet CASPT2 (10,8) potential energy curves with the four lowest states.	62
Figure 27. $[\text{FeO}(\text{NH}_3)_4]^{2+}$ Triplet CASPT2 (10,8) potential energy curves with the seven lowest states.	63
Figure 28. $[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_3]^{2+}$ Triplet CASPT2 (10,8) potential energy curves with the four lowest states.	64
Figure 29. $[\text{FeO}(\text{NH}_3)_5]^{2+}$ Triplet CASPT2 (10,8) potential energy curves with the four lowest states.	65

CHAPTER ONE

INTRODUCTION AND REVIEW OF THE LITERATURE

Introduction

The design and synthesis of efficient catalysts for various chemical processes is greatly aided by the use of computational tools and methods and new chemical insight. computational chemistry can be a valuable field for understanding chemical systems and their electronic structure by complementing experimental results. We seek to use computational analyses to determine beneficial and desired characteristics of a new catalyst prior to the initiation of synthetic efforts. As such, the goal of this study is to determine the effect of ligand field structures on the reactivity of the Fe(IV)-oxo. This information is a stepping stone in the assistance of the design of a Fe(IV)-oxo homogeneous catalysts to activate relatively strong C-H bonds (with respect to the varying C-H bond strengths) followed by oxidation. This could prove to be an extremely beneficial reaction for the conversion of methane to methanol due to their unique ability to perform oxidation reactions.¹

Methane comprises 70-90% of the natural gas reserves.² It proves to be an important source of energy as it accounts for roughly 31% of the energy produced in the United States.³ Unfortunately, with modern limitations imposed by transporting volatile substances like methane and the risks and hazards associated with the uses of natural gas pipelines, a safer and more efficient way to gather and use our natural gas supply should be explored. In addition to the problems introduced from pipelines, another issue with large

implications is the wasted gas resources in the process of fracking. It is not financially efficient to collect and transport the natural gas when companies find reservoirs while fracking. As such the natural gas discovered while fracking is not collected due to the need for specialized equipment.⁴

Methane is a more potent greenhouse gas (about 34 times better at capturing heat) than carbon dioxide, so precautions are taken in order to prevent it from leaking into the atmosphere.⁴ A fracking flare is set up over the natural gas site where most of the escaping natural gas is burned and converted into carbon dioxide.⁵ This has become such a large problem in places like North Dakota, where the fracking flares can be seen from space. This of course is always introducing a lot of carbon dioxide into the atmosphere. It is also estimated that a third of all of the natural gas resources in the area are wasted due to this practice of setting up the flares and burning them.⁶

Two alternative approaches to the aforementioned issues are the liquification of methane or the chemical conversion to methanol. If converted to methanol, the collection and transportation process becomes greatly simplified. Industrially methane is converted to methanol through the production of synthesis gas but this is not a direct conversion and requires harsh reaction conditions as well as large industrial facilities.⁷ The process is neither easily performed in the field on a fracking site to capture the wasted natural gas nor is it an economical use of the natural gas supply due to the energy consumed in converting methane to methanol. Methanol is a valuable chemical resource for laboratories across the world.⁸

Recent Efforts

Currently, very few synthetic chemical systems exist that can perform the single step oxidation of methane to methanol.⁹ The iron containing ZSM-5 zeolite is proposed to be capable of performing single step oxidation.⁹ This zeolite has also recently been characterized,¹⁰ but still leaves room for more desirable materials. It is very important then to find and study homogeneous catalyst species capable of performing this direct conversion of methane to methanol. Homogeneous catalysis offers two main benefits. Firstly, is easier to understand and develop in the research stage and secondly, it needs less atoms to perform a reaction compared to a surface which needs an entire scaffold made up of several magnitudes greater of atoms to perform similar reactions. The efficient use of natural gas resources is an issue of growing importance, with the growing energy demands. Various avenues are being explored for potential homogeneous catalysts that can perform this reaction.

One class of species considered for the oxidation of methane is the Fe(IV)-oxo suite of complexes modeled after intermediate active sites of heme and non-heme enzymes. The non-heme enzymes in particular are of great interest for the synthesis of homogeneous catalysts. In nature, these Fe(IV)-oxo are found to be enzymatic intermediates with a high spin ($S = 2$) active site capable of activating strong C-H bonds for subsequent oxidation or the formation of a variety of other products.¹¹ The $S = 2$ spin is deemed to be of importance because of it is evolving into a Fe(III)-oxyl species which, as a radical can lead to hydrogen abstraction. Though $S = 1$ is capable of also forming this species, it is typically much less

reactive due to the necessity of a spin crossover since the abstraction will still have to take place on the $S = 2$ spin surface.

The active site of these non-heme enzymes have been isolated and characterized, where their unique high spin ground states were first discovered and analyzed. Such non-heme enzymes include taurine/ α -ketoglutarate dioxygenase (TauD), tyrosine hydroxylase (TyrH), syringomycin halogenase (SyrB2), (4-hydroxy)mendelate synthase (Hmas), and (4-hydroxyphenyl)pyruvate dioxygenase (HPPD).^{12,13,14-15,16} The TauD intermediate (TauDJ) is pictured in figure 1. Due to the fine-tuned nature of the reactions of these enzymes from the evolutionary process, they are capable of performing difficult to achieve reactions.¹⁴ One such reaction is the activation of strong C-H bonds in order to form a variety of desired products.

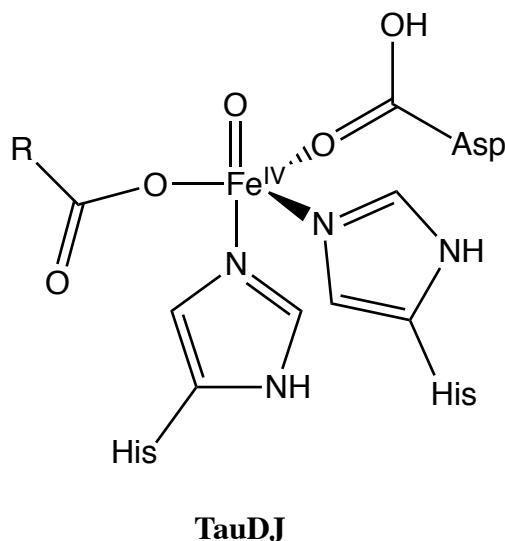


Figure 1. Shows structure for the active site of the enzyme intermediate TauDJ.

Some intermediate reactive species of enzymatic species have been characterized though a universal reaction mechanism for every Fe(IV)-oxo system is difficult to derive. This is due to the unique ligands of the enzyme taking part in important pieces of the mechanism as well as the near impossibility of developing a scaffold as complex as a protein.¹⁴ The same is true in the case of understanding the general reaction mechanism based off of a metal-organic framework (MOF). There is literature present for a mechanism in the case for the conversion of ethane to ethanol on the surface of a MOF with an Fe(IV)-oxo site.¹⁷

Additionally, it should be noted that there is another group of iron-based enzymes known as methane monooxygenases which are capable of the direct conversion of methane to methanol in nature which possess a Fe_2O_2 reactive site.¹⁸ In addition to these di-iron species there are also di-copper species methane monooxygenases.¹⁹ These complexes have two iron centers with a more complicated electronic structure.

Taking inspiration from the non-heme Fe(IV)-oxo enzymatic sites, synthetic chemists have made successful attempts to synthesize model compounds in a biomimetic approach.²⁰⁻⁵⁷ Most of the model compounds created contained a low spin ($S = 1$) ground state. There has been a handful of compounds however that do exhibit a high spin ground state. Developing a stable compound with a high spin ground state proves difficult as they tend to be reactive and thus hard to trap and characterize.⁵⁸ Typically two symmetries are considered when synthesizing Fe(IV)-oxo compounds; either one can be effective in synthesizing a compound with a high spin ground state. The first of which involves designing the ligand scaffolding in such a way as to promote a trigonal bipyramidal

geometry. This allows the d_{xy} orbital and the $d_{x^2-y^2}$ orbitals to become degenerate, stabilizing the high spin.⁵⁸ The second method is the use a pseudo octahedral geometry and surround the Fe(IV)-oxo center with weak field ligands. Due to the Jahn-Teller effect, the d_{xy} orbital and $d_{x^2-y^2}$ orbital become closer in energy and can stabilize a high spin ground state.⁵⁸ This is illustrated in figure 2.

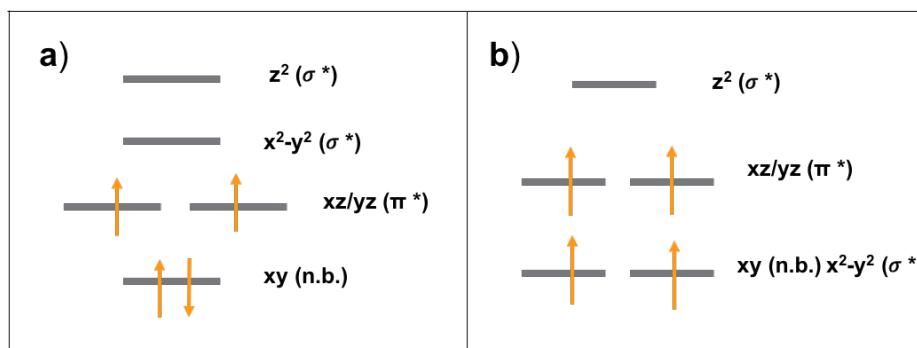


Figure 2. A qualitative molecular orbital diagram showing the difference between the **a)** low spin and the high spin **b)** molecular orbital configurations.

Successful attempts at forming high spin compounds through each of these methods have been achieved.^{52, 59} An example of the pseudo octahedral field complex with a weak ligand field is the hydrated case of $[\text{Fe(IV)O}(\text{H}_2\text{O})_5]^{2+}$. This complex was the first successfully synthesized with a high spin ground state.⁵² An example of the trigonal bipyramidal geometry is the case of $[\text{Fe(IV)OTMG}_3(\text{tren})]^{2+}$.⁶⁰ TMG_3tren stands for 1,1,1-tris{2-[N2-(1,1,3,3-tetramethylguanidino)]ethyl}amine), where tren is tris(2-aminoethyl)amine and TMG_3 is the rest of the name mentioned prior.⁵⁵

Reactivity Channels

The standard molecular orbital diagram for the high spin species is included in figure 3. In addition, it is important to note that the σ and π molecular orbitals for the system are primarily polarized on the oxygen comprising the Fe(IV)-oxo bond. The remainder of the molecular orbitals are mostly polarized on the iron atom. The σ orbital is comprised of the p_z orbital on the oxygen atom and the d_{z^2} orbital on the iron atom and is polarized towards the oxygen atom. The π orbitals are comprised of the p_x and p_y orbitals on the oxygen atom and the d_{xz} and d_{yz} atoms on the iron atom. Similarly, the π orbitals are polarized towards the oxygen atom. With respect to the oxygen atom the d_{xy} and $d_{x^2-y^2}$ atoms are bonding with respect to the equatorial ligands, but non-bonding with respect to the oxo bond. The π^* orbitals are the antibonding orbitals between the p_x and p_y on the oxygen with the same iron atom d_{xz} and d_{yz} orbitals. The σ^* orbital again consists of the p_z from the oxygen and the d_{z^2} from the iron atom. The σ^* and π^* orbitals are polarized towards the Fe center.

The desired transition state that leads to the C-H abstraction occurs on the high spin surface.⁵⁸ Even most of the low spin ground state compounds crossover to the high spin surface in order to perform the C-H abstraction.^{11, 61} This spin crossover hinders the reactivity of these low spin ground state complexes. This process is called Two State Reactivity (TSR) and is observed for Fe(IV)-oxo systems.⁶¹⁻⁶⁵ The formation of the Fe(III)-oxyl compound is an important component in the reactivity and C-H abstraction. A Single State Reactivity (SSR) complex was recently published where the reaction takes place

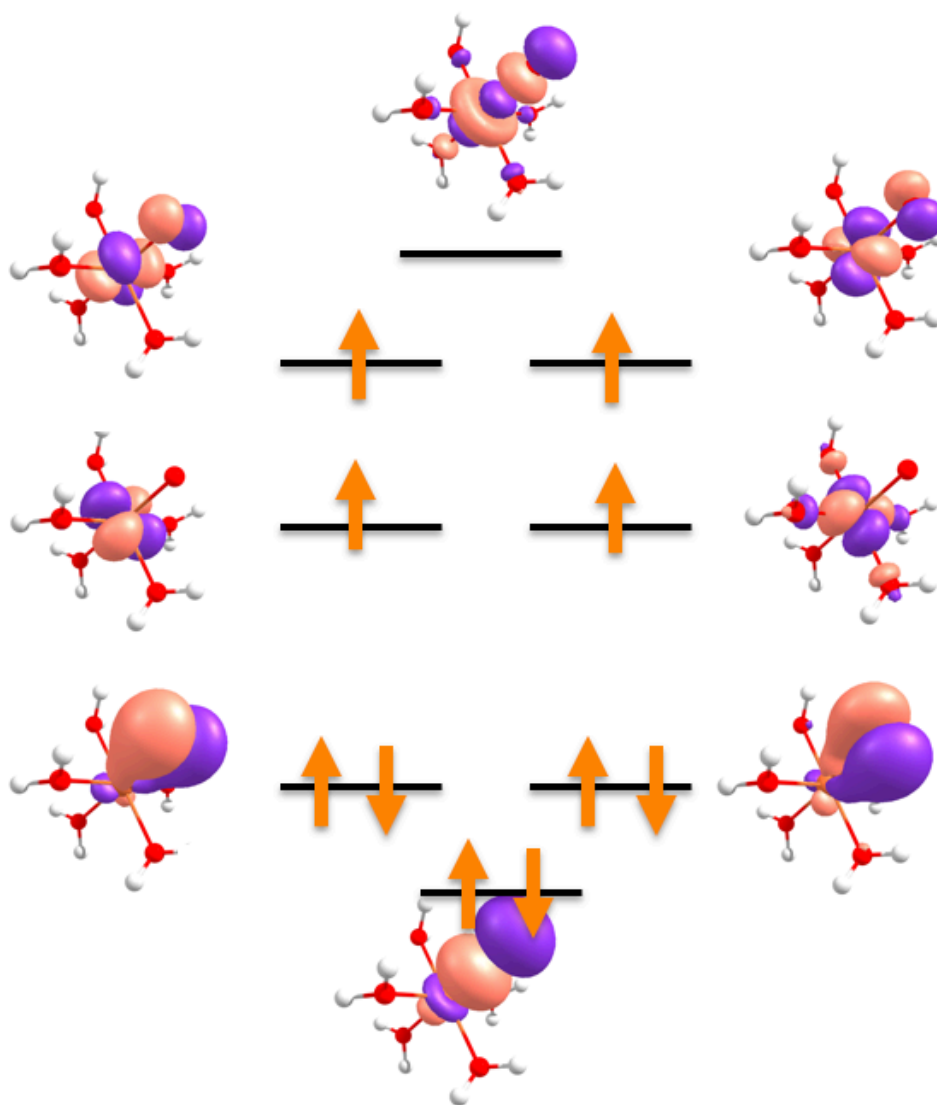


Figure 3. Molecular orbital diagram with the ground state spin of a high spin species included for $[\text{FeO(IV)}(\text{H}_2\text{O})_5]^{2+}$. Red atoms are oxygens. White atoms are hydrogens.

entirely on the $S = 1$ spin surface.⁶⁶ This is of particular interest because the principle of single state reactivity with an Fe(IV)-oxo can be translated over to an $S = 2$ complex for improved reactivity.

There are four distinct reactivity channels that must be discussed when examining the Fe(IV)-oxo species. The major difference between these is the resulting spin on the iron atom after an electronic transition has occurred. Figure 4 contains each of these reactivity channels illustrating their transitions when the formation of the oxyl occurs. Figure 4a demonstrates the promotion of an electron from a σ to a σ^* orbital. Since the σ orbital is polarized on the oxygen atom, the resulting electron promotion can be considered as an electron excitation from the oxygen to Fe(IV). Therefore, iron is reduced to Fe(III) with a $S = 5/2$ spin, while the oxygen evolves a radical (oxyl) character with $S = 1/2$, keeping the resulting total spin as $S = 2$. This is the previously mentioned σ channel where the resulting C-H abstraction occurs from the excitation from a σ orbital. This channel is present in the ground state electronic configuration of the Fe(IV)-oxo high spin complex. Figure 4b exhibits a similar excitation between the π and π^* orbitals from the dominant electronic configuration of the excited states. Two degenerate excited states arise from this transition between the π orbitals. The resulting excitation yields a spin on the iron atom of $S = 5/2$ and a spin on the oxygen atom of $S = 1/2$ again. This channel is what has been previously referred to as the π channel. These are the channels which have been looked at in the present study, as these are the channels which are the biggest factors in the reactivity of these Fe(IV)-oxo complexes. For the sake of completeness, two additional pathways are shown in figure 4c and figure 4d, respectively. These channels resulting in the $S = 3/2$ spin on the

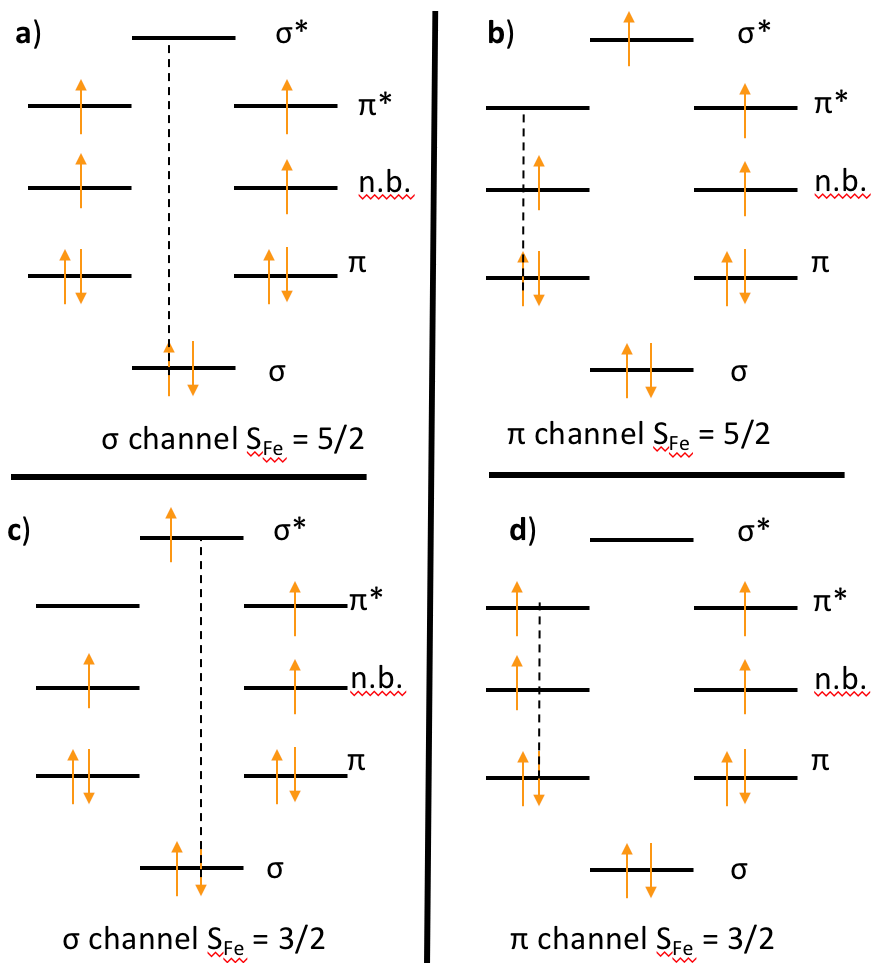


Figure 4. The various reaction pathways present in the high spin Fe(IV)-oxo species. 4a shows a σ to σ^* transition yielding a Fe(IV) with a spin of 5/2. 4b shows a π to π^* transition yielding a Fe(IV) with a spin of 5/2. 4c shows a σ to σ^* transition yielding a Fe(IV) with a spin of 3/2. 4d shows a π to π^* transition yielding a Fe(IV) with a spin of 3/2. Dashed vertical lines depict excitation pathways.

iron do not show the same reactive character even though they show similar behavior in the generation of the radical species on the oxygen.

A major factor in the determination of which channel will be responsible for the C-H activation is the orientation of the approaching substrate. There are several examples in the literature which illustrate the importance of the orientation.^{11, 14, 59} One such example is with respect to the enzymatic species SyrB2 and its non-heme Fe(IV)-oxo active site. The enzyme controls the approach of the substrate and directs the substrate to one of the two channels in order to produce one of the desired products. In the case of SyrB2, this means the difference between a halogenated product or an alcohol product.¹⁴

Magnetic Circular Dichroism (MCD) studies (*vide infra*) probing the σ and π channels have illustrated their importance in reactivity and substrate orientation. In the case of the $[\text{Fe(IV)(O)TMG}_3(\text{tren})]^{2+}$ complex, these channels yielded very different outcomes for a C-H abstraction reaction. The orientation of the hydrogen atoms on the ligands surrounding the molecule's Fe(IV)-oxo center is such that it is adjacent to the π channel resulting in the decomposition of the complex. The σ channel does not suffer from the same effect; this channel does not lead to self-degradation and can instead can perform C-H abstraction on a substrate.⁵⁹

It is these channels and their effect on reactivity that is the focus of this thesis. The σ and π channels have exceptionally important implications in reactivity and as such, we decided to investigate these channels. It may be beneficial to promote one reaction channel over the other. One way of doing this is by modifying the ligand field strength. Changing the strength of the ligand field would change the electronic structure of the complex,

reactivity of the complexes can be improved. This improvement in the reactivity could come in one of two paths. The first is that if the energy gap between the σ and the π channels can be made smaller; more channels are made accessible upon approaching the transition state geometry. This would increase the overall reactivity. Secondly, the energy gap could be increased favoring only the ground state's σ channel for reaction. This would be particularly beneficial since the π channel leads to a self-degradation pathway.

Experiment and MCD Spectroscopy

With the synthesis of the $[\text{Fe(IV)(O)TMG}_3\text{tren}]]^{2+}$ species, the improved stability of this $S = 2$ ground state is of significant importance because its reactivity channels were able to be extensively probed.⁵⁹ The σ and π reactivity channels by which the Fe(IV)-oxo becomes an Fe(III)-oxyl were rigorously characterized through the use of MCD spectroscopy. Both of these channels are present for species containing the high spin ground state and low spin ground state through the previously mentioned concept of TSR. Since these channels lead to the formation of a radical oxygen species they have large implications for reactivity.

MCD spectroscopy is a variation of Circular Dichroism (CD) spectroscopy. CD spectroscopy allows for the distinction between chiral molecules using Left Circularly Polarized Light (L-CPL) and Right Circularly Polarized Light (R-CPL). The chiral chromophore will absorb different amounts of L-CPL and R-CPL. The challenge with this spectroscopy, is that it is only useful when dealing with molecules that have chiral centers.

CD generates this L-CPL and R-CPL by using both vertically polarized light and horizontally polarized light with the same amplitude. Using a quarter wave plate to shift the phase of either the horizontal or vertically polarized light makes it, so the amplitude is maintained as the phase is changed and will thus generate circularly polarized light. CD spectroscopy actively measures the difference between the left and right circularly polarized light that is absorbed. See equation 1.⁶⁷

$$\Delta A(\lambda) = A(\lambda)_{LCPL} - A(\lambda)_{RCPL} \quad (1)$$

MCD spectroscopy remedies this with the introduction of magnetic field with distinctions in excitations beyond electronic excitations of chiral molecules.

In practice, what MCD spectroscopy is able to entirely uncover the electronic transitions seen in UV-Spectroscopy. MCD spectroscopy takes advantage of the Zeeman effect by which the spectral lines of an atom in a strong magnetic field undergo splitting, caused by the distortion of electron orbitals from the magnetic field. While only molecules with stereocenters will have active CD spectrums a wider variety of molecules will have MCD spectrums, but the molecule must be able to absorb at the wavelength being studied. An example of new features are shown in figure 5¹⁴ coming from several different effects denoted as terms. To further elucidate the features shown something known as Variable Temperature Magnetic Circular Dichroism spectroscopy is used (VT-MCD). Using low temperatures (LT-MCD) the features become clearer and the transitions are more readily visible.⁶⁸

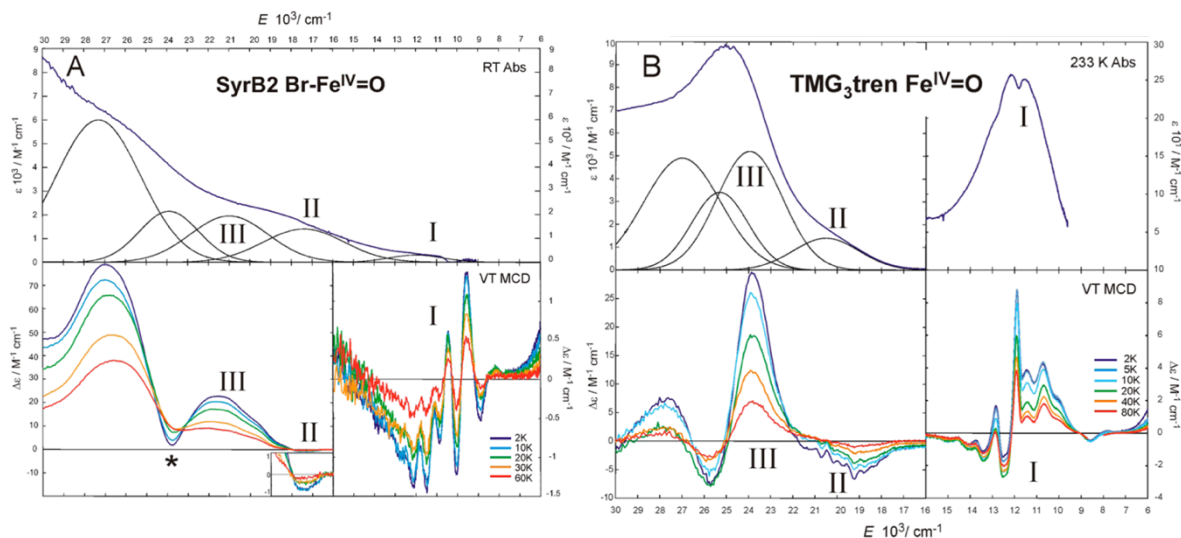


Figure 5. spectra taken from a paper showing the clarification that MCD and variable MCD spectroscopy can offer. From Ref. 14.

Each of the terms can be distinguished by the band shape observed. The A-term arises when the molecule contains degenerate excited states. These transitions from the degenerate excited state are split from the induced magnetic field which allows the visibility of previously degenerate transitions in the form of two separate transitions. These transitions arising from A-term character are only a few wavenumbers, therefore the transitions are typically fairly small.

The B-term arises from mixing between an excited state and an energetically close intermediate state which is caused by the introduction of the magnetic field. Mixing can also occur with an intermediate state near to the ground state. Significant B-term intensity will only be seen in cases where this intermediate state lies close to an excited state or the ground state.⁶⁸

The C-term is the most important term for low temperature MCD. This term arises from a degenerate ground state which splits in the magnetic field. This means that only paramagnetic compounds exhibit C-term character. A chart including the general character for each of the term transitions is included as figure 6.⁶⁸ For full understanding of the C-term, variable temperature measurements are needed.

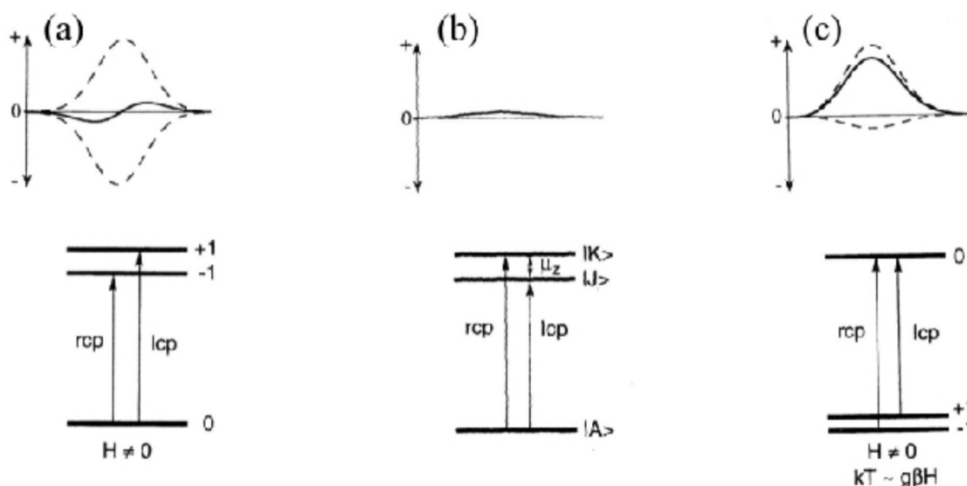


Figure 6. This includes the MCD Mechanisms for the (a) A-term , (b) B-term, and (c) C-term $|K\rangle$ denotes the intermediate state close in energy. $|J\rangle$ denotes an excited state and $|A\rangle$ denotes the ground state. The population of the lower state in the C-term is higher at lower temperatures making it so the states no longer cancel out with one another and provide significant peak intensity. This C-term intensity is very important because it contains complete information about the properties of the ground state. From Ref. 68.

Electronic Structure Theory

In order to gain better understanding of these structures, both Density Functional Theory (DFT) and Multi-Configurational Self-Consistent-Field (MCSCF) method were used. DFT could not be used for this project due to the presence of multiple degenerate electronic configurations of the Fe(IV)-oxo. DFT is concerned with solving the many-body Schrödinger equation and because of the many configurations DFT cannot solve for them individually. In DFT, the multidimensional problem is reduced from one that is $3N$ dimensional to one that is a 3-dimensional problem. Electron density can be defined by all of the single electron wavefunctions, allowing for the simplification of the $3N$ problem. DFT is based on two fundamental theorems: the Hohenberg–Kohn theorems. The first demonstrates that the ground state properties of a many-electron system are uniquely determined by an electron density that depends on only three spatial coordinates. The second theorem defines an energy functional for the system and proves that the correct ground state electron density minimizes this energy functional. An exchange correlation functional calculates all of the quantum mechanical interactions between electrons. In this work, the Kohn-Sham DFT scheme is used where as the Self-Consistent-Field (SCF) method is applied for solving the Kohn-Sham equations.⁶⁹

DFT uses a single Slater determinant but it accounts for the electron correlation via a parametrized exchange-correlation potential. On the other hand, wave function theory methods are including electron correlation in a more precise and systematic manner. Starting point of wave function theory methods is the Hartree-Fock (HF) theory. In HF, electrons interact with a mean charge field created by all the other electrons. In actual

quantum mechanical systems, electrons are constantly moving around interacting with one another, attempting to avoid other electrons. The HF method cannot accurately reproduce the correlated motion of the electrons. This results in the loss of electron correlation energy. Electron correlation can be divided in dynamic and static (non-dynamic) correlation. Static correlation occurs between close in energy electron configurations, while dynamic correlation takes into consideration the interactions of electrons over shorter inter-electronic distances. One Slater determinant can often be an insufficient choice for a system containing many degenerate electronic configurations. This is the reason for the loss of static correlation. HF theory does not include any electron correlation. The difference between the exact energy, which contains electron-electron interactions, and the HF energy can be given as equation (2).

$$E_{corr} = E_{exact} - E_{HF} \quad (2)$$

In MCSCF theory, the wave function is constructed from a linear combination of configuration state functions (CSFs). This expression for the zeroth-order wave function introduces the static correlation energy. The MCSFC wave function is presented in equation (3).

$$|\Psi_{MCSCF}\rangle = \sum_I c_I |\Psi_I\rangle \quad (3)$$

Here c_I are the expansion coefficients and $|\Psi_I\rangle$ represents a CSF or a Slater determinant, which allow the determination of the distinct electronic configurations. When only one determinant in equation (3) is considered it would be identical to the Hartree-Fock method. Now the orbitals can be optimized for a combination of near degenerate electronic configurations. For example, a situation illustrated in figure 4a and 4b where both of these electronic states are present simultaneously. Instead of the average electronic configuration, we are looking at multiple electronic configurations of our species.

Complete Active Space Self Consistent Field (CASSCF) is a type of MCSCF where the linear combination of CSFs is formulated from a set number of electrons in a set number of orbitals. In the molecular orbital diagram there are 10 active electrons in 8 present orbitals (figure 3). Thus, CASSCF(10,8) calculations are used to understand the desired electrons and orbitals. These orbitals are selected because they contain the reactivity pathway of interest. N (number of singlet CSFs) with m electrons in n orbitals is shown in equation (4).

$$N = \frac{n!(n+1)!}{\left(\frac{m}{2}\right)!\left(\frac{m}{2}+1\right)!\left(n-\frac{m}{2}\right)!\left(n-\frac{m}{2}+1\right)!} \quad (4)$$

CASSCF allows for the arrangement of electrons in all possible configurations. The total wavefunction consists of all these configurations for a given N-electron space, obeying given symmetry and spin. When more active electrons and orbitals are being investigated, a larger total number of CSFs will be used in the wave function. As more CSFs are included, the computational cost also increases, making it a very difficult and time-

consuming calculation with the introduction of more electrons and orbitals into the active spaces.

Perturbation theory is used to include dynamic correlation energy using the Complete-Active-Space-Second-Order Perturbation-Theory (CASPT2) method. The CASPT2 method adds to the CASSCF method by applying second-order perturbation theory in order to find the missing dynamic correlation energy. Instead of the choice of the previously mentioned RHF or UHF wavefunction, the MCSCF wavefunction was employed because this inclusion will allow more accurate energies. Additionally, CASPT2 can offer more accurate and precise energies when dealing with incomplete active spaces.

CHAPTER TWO

BENCHMARK STUDY

Software and Methods

DFT is a valuable tool for assessing properties about chemical systems and their electronic structures with a high efficiency and accuracy. The performance of DFT heavily depends on the choice of the functional and basis sets. Due to the selection of these parameters, the results may vary greatly from one functional to another. This is especially true for the cases involving transition metals and heavier atoms making selection of an appropriate functional very important for accurate descriptions of electronic structure. In consideration of these limitations, it is necessary to benchmark the quality of the chosen functional and basis sets against either a more accurate computational method or experimental results. A DFT benchmarking study was conducted to predict the bond lengths of model Fe(IV)-oxo complexes between the Fe atom and the ligand field surrounding it. When searching for functionals it is desirable to find the best level of theory that can be both accurate and quick in the acquisition of chemical structures for Fe(IV)-oxo model compounds. A level of theory was sought with acceptable accuracy (deviations with less than 0.02 Angstrom from the crystal structure, with the most accurate functionals providing values less than 0.05 Å) in order to have the potential of optimizing many Fe(IV)-oxo complexes quickly.

Benchmarking calculations were performed on the crystal structure of the $[\text{FeO(IV)}(\text{H}_3\text{buea})]^{1-}$ model system (figure 7). $[\text{H}_3\text{buea}]^{3-}$ is abbreviated for tris(*tert*-

butylureaylethylene)aminato.⁵⁵ This structure was chosen as it held a $S = 2$ ground state with readily available crystal structure information to compare optimized structures to. Functionals and basis sets that provide values close to those of the crystal structure yield reasonable level of theory to employ. The functionals considered in this benchmarking test were B3LYP⁷⁰⁻⁷², M06⁷³, BHLYP⁷⁴, M06-2X⁷³, BP86⁷⁰, BLYP^{70, 72}, PBE⁷⁵, PBE0⁷⁶⁻⁷⁷, TPSS⁷⁸, and TPSSh⁷⁹. In addition to the variation of the functionals, several different combinations of basis sets were considered. The basis sets include def2-TZVPP⁸⁰⁻⁸², def2-TZVP⁸⁰⁻⁸², and def2-SV(P)⁸². The complete list of the combinations of different basis sets and functionals are included in Table 5 in the appendix.

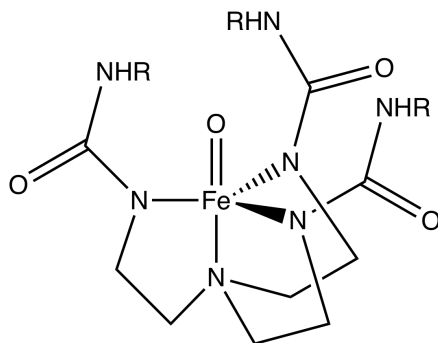


Figure 7. Contains the $[\text{FeO(IV)}(\text{H}_3\text{buea})]^{1-}$ complex.

For the $[\text{Fe(IV)}(\text{O})(\text{H}_3\text{buea})]^{1-}$ model compound, basis sets were applied over four segmented parts of the molecule illustrated in figure 8. These pieces were the Fe atom, the first coordination sphere, the second coordination sphere, and the remainder of the molecule. DFT calculations on these systems were applied using the TURBOMOLE⁸³ version 7.2 program package.

The first coordination sphere was comprised of the atoms directly connected to the Fe atom. For the chosen model compound, this included the oxygen in the oxo bond, the axial Nitrogen atom, and the equatorial Nitrogen atoms bonded to the Fe atom. The second coordination sphere included the carbons directly bonded to the axial and equatorial nitrogen atoms, as well as the hydrogen atoms bonded to the nitrogen atoms that are further out.

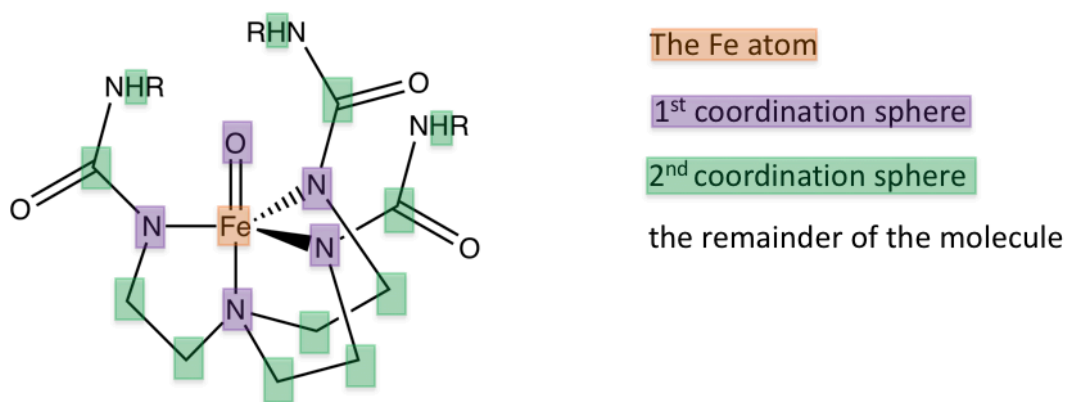


Figure 8. Illustrates the breaking up of the molecule into different coordination spheres so as to partition up the levels of theory adequately.

Results and Discussion

Benchmarking is an important step in the understanding of the electronic structure of complex species because it ensures the computational results can reflect the experimental reality of the complex. Some skepticism exists of the quality of B3LYP functional for optimizing Fe(IV)-ox complexes.⁸⁴ In this thesis, B3LYP showed bond

lengths in the optimized geometry to have significantly different lengths from the crystal structure reference data. The examination of how these different functionals affected the basis set was studied in order to determine a functional that could be optimized quickly and accurately according to crystal structure bond lengths with respect to the Fe-X bonds, where X is N or O.

We found the most accurate functionals, for obtaining geometries similar to that of the crystal structure, to be TPSS, TPSSh, PBE and PBE0. This is in the chart provided in Figure 9, and the chart shows the deviation in various bond lengths from the crystal structure of $[\text{Fe(IV)O}(\text{H}_3\text{buea})]^{1-}$ with respect to the oxo bond, the axial ligand, and the average of the equatorial ligands bond distance.

Basis set sizes were compared using the B3LYP functional with the lowest amount of basis functionals ranging from 846 to 1644. More basis functions affected the computational time significantly without any benefit to the accuracy of the calculation. These results can be seen in table 5 included in the Appendix. We compared functionals using the basis set size consisting of 846 basis functions because larger basis sets offered no more accurate computed geometrical values. A complete table for each of the benchmark calculations run, including the basis set applied to each atom sphere, is included in the appendix as table 6. When considering the amount of time each calculation used, the most computationally economical functionals based on our results were TPSS and PBE. Due to the accuracy they offered with very small amounts of computational time compared to their hybrid functional counter parts.

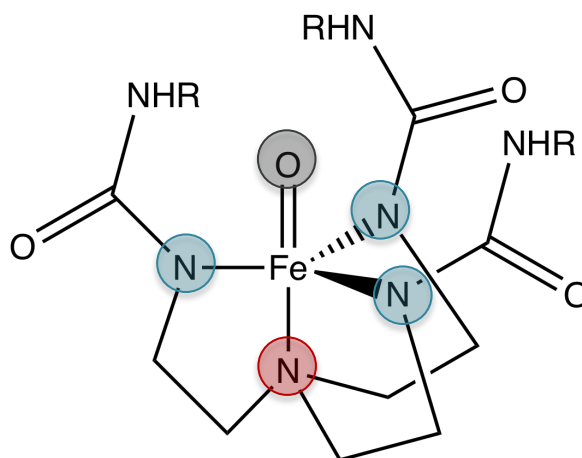
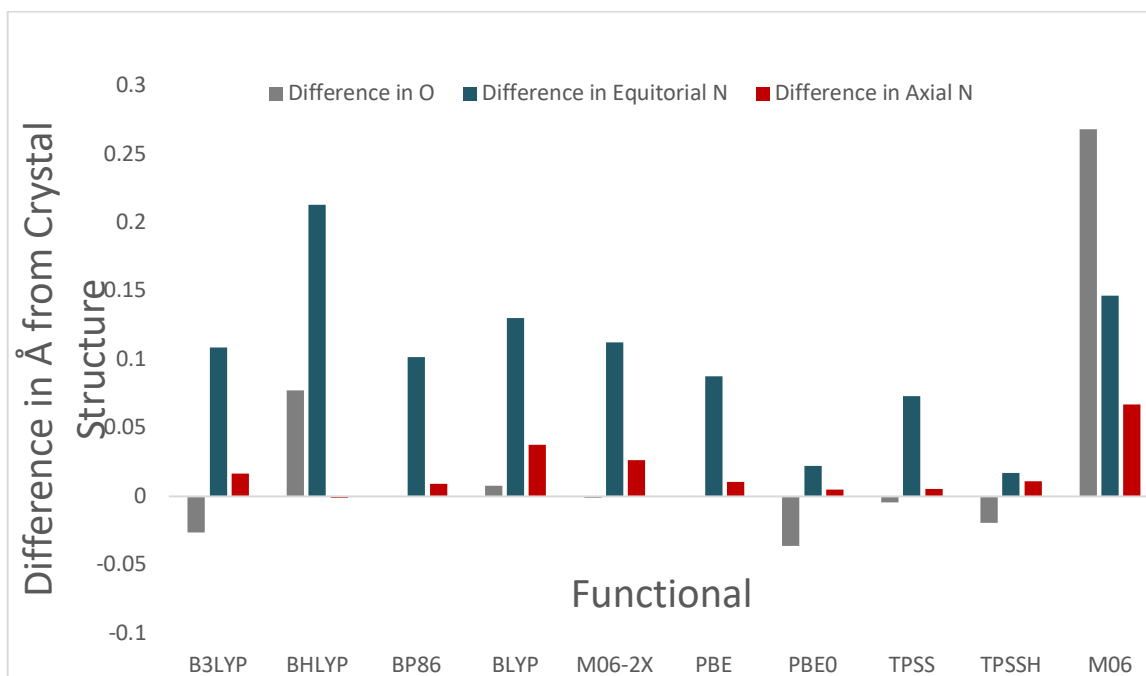


Figure 9. Illustrates the difference seen in the various optimizations between the Fe atom and the highlighted atoms.

The benchmark calculations could be generalized to three more model compounds including the $[\text{Fe(IV)(O)(TMG}_2\text{dienX)}]^{2+/1+}$ species where X is Cl, N₃, or NCH₃. The results showing the deviation in the bond distances from the crystal structures are included in table 1. This is an accurate functional for correctly determining bond distances in several Fe(IV)-oxo model complexes because it is able to quickly determine many optimized structures in a very short amount of time. These model complexes contain ligands similar to those of the TMG₃tren except one of the equatorial TMGen ligands are replaced by one of the previously mentioned molecules or atoms. It is expected that the large variation in the calculated value for the N₃ species could be due to interactions involving stronger π backbonding.

Table 1. Contains the deviations of the bond lengths from their corresponding crystal structures.

Complex	Fe-O (Δ in Å)	Fe-Ax (Δ in Å)	Fe-Equatorial (Δ in Å)	Fe-X (Δ in Å)
Cl	0.002	0.000	-0.001	-0.008
NCH₃	0.024	0.025	-0.095	0.041
N₃	0.023	0.084	-0.029	-0.153

CHAPTER THREE

EXAMINATION OF REACTIVE CHANNELS WITH MULTIREFERENCE METHODS

Computational Details

Model compounds were constructed to thoroughly examine the reaction channels in the presence of the weak and the strong ligand fields. These model compounds were examined by the CASSCF method. Additionally, for quantitative results, the use of the complete active space second perturbation theory (CASPT2) method was also employed. These methods will allow the monitoring of how the different electronic states evolve upon the elongation of the Fe(IV)-oxo bond. Therefore analyzing these characteristics at bond lengths corresponding to the transition state geometry of the Fe(IV)-oxo molecule will allow for better understanding regarding the reactivity at the transition state.

A couple modifications were made to the structures in order to simplify the calculations. These modifications were chosen in order to have a suite of model complexes that were completely identical, with the only difference being the changing ligands. The 2.1 Å bond distance was chosen due to it being the average bond distance found between the equatorial ligands and the iron atom in the crystal structure. In addition to bond lengths bond angles were frozen for both of the geometries where the octahedral angles were kept at 90 degrees, and the trigonal bipyramidal geometries were kept at 120 and 90 degrees.

A previous paper examined the effect of weak and strong ligands on the spin state of the Fe(IV)-oxo complex.⁸⁴ In this work, two model complexes were examined. These include a $[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_4]^{2+}$ for the strong ligand field complex and a $[\text{FeO}(\text{H}_2\text{O})_5]^{2+}$ complex for the weak ligand field complex. The study highlights that importance the spin state has on the reactivity of the Fe(IV)-oxo.⁸⁴ The weak and strong ligand fields were simulated by considering different coordination environments. Additionally, we examined the effect of charged ligands present in the molecule to better replicate some of the model compounds in the literature. Water was chosen as a representative of weak field ligand, while ammonia was selected as the strong field ligand. Charged ligands were also considered in the form of NH_2^- molecules. A variety of model compounds were made from combinations of the weak and strong ligand fields, and the effect of the ligand field strength on the reaction channels could be observed for both the low and high spin species. Figure 8 contains the model compounds that were created and observed in this study.

Both the low spin species and the high spin species were examined using a CASSCF and CASPT2(10,8). These eight orbitals involved in the active space are the ones previously shown in figure 5 and are directly accountable in the reactivity channels of interest for the Fe(IV)-oxo complexes. The occupations at the equilibrium geometry of this system lead to both the σ and π channels shown below.

Dominant configuration of the ground state (equilibrium geometry):

$$(\sigma)^2(\pi_x)^2(\pi_y)^2(d_{xy})^1(d_x^2-y^2)^1(\pi_x^*)^1(\pi_y^*)^1(\sigma^*)^0 \quad 72\%$$

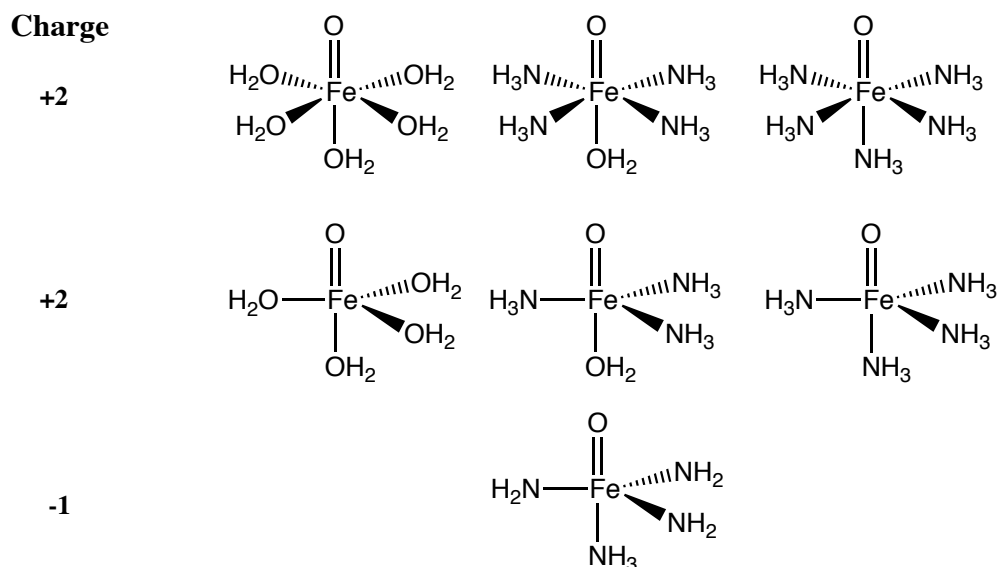


Figure 10. Contains the model compounds which were investigated using the CASSCF/CASPT2 methods. The bottom model complex has a charge of -1.

Dominant configurations of the doubly degenerate excited states (equilibrium geometry):

$$(\sigma)^2(\pi_x)^2(\pi_y)^2(d_{xy})^1(d_{x^2-y^2})^1(\pi_x^*)^0(\pi_y^*)^1(\sigma^*)^1 \quad 27\%$$

$$(\sigma)^2(\pi_x)^2(\pi_y)^2(d_{xy})^1(d_{x^2-y^2})^1(\pi_x^*)^1(\pi_y^*)^0(\sigma^*)^1 \quad 27\%$$

As is shown for the case of the doubly degenerate excited state, this electronic state is described by a portion of individual electronic configurations yielding the majority of the total electronic configurations. Thus, the application of multi-configurational theory was mandatory in order to accurately describe the chemical nature of the low-lying states. Three roots were examined by computing potential energy curves with multireference for the ground and doubly degenerate quintet states. The ground state is indicative of the σ channel while the two doubly degenerate excited states are indicative of the π channel. These

calculations were run using the MOLCAS⁸⁵ version 8.0 program with the ANO-RCC-VTZP basis set.⁸⁶⁻⁸⁹

Results and Discussion

Analysis of each of the potential energy curves was carried out for each of the molecules pictured in figure 10. The typical Fe(IV)-oxo bond length at the equilibrium is between 1.60-1.66 Å. Initially, a less computationally taxing CASSCF calculation was performed yielding potential energy curves shown in figure 11.

We determined from the results that it is only necessary to look at the three lowest states when probing from the distance of 1.5-2.0 Å. This stems from the distances in which the species is reactive which is approximately 1.5 Å to 2.0 Å.⁵⁹ There are only three low energy roots within these bond distances so no other electronic states was considered.

A noted feature from this is calculations, a second well in the potential can be seen at the distance around 2.8 Å to 3 Å. There are 6 electronic states that dissociate at similar energies. The energy gap between the six lowest states is large enough that the energy gap between the three lowest states need to be accounted for. The three lowest roots were calculated at the CASPT2 level. This is consistent with previous literature.⁵⁹

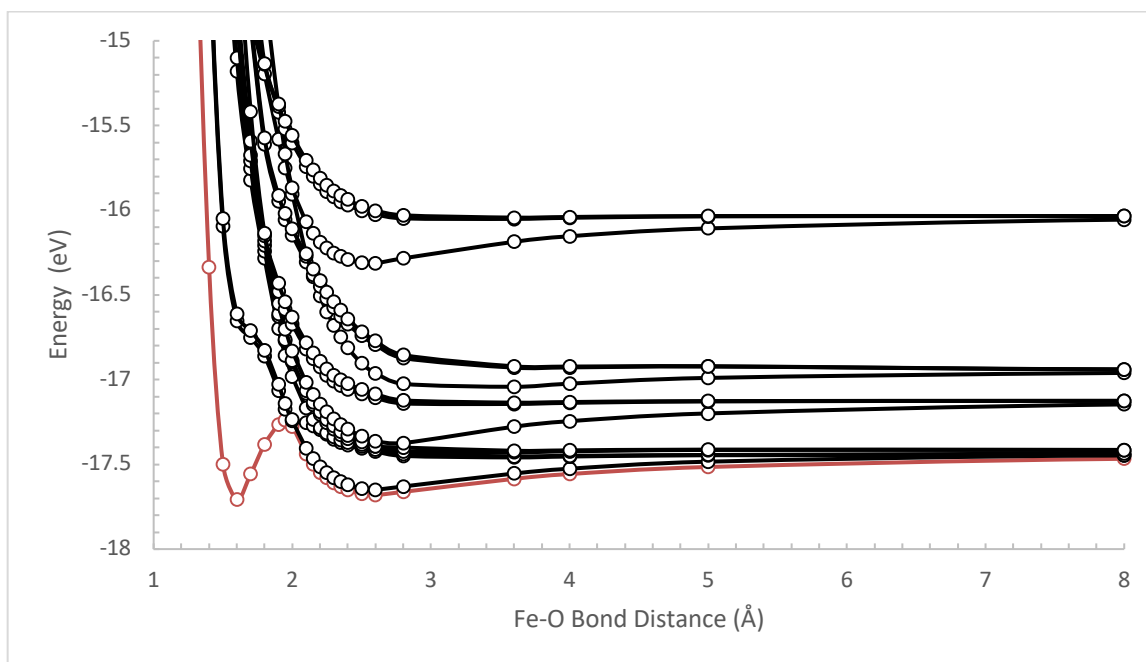


Figure 11. Potential energy curves for the ground and first fourteen excited states for the $[\text{Fe(IV)O}(\text{H}_2\text{O})_5]^{2+}$ species completed at the CASSCF(10,8) level.

There are four features of interest in the potential energy curves which are potential indications of the potential reactivity of the complexes. Figure 12 shows the potential energy curves generated by the CASPT2(10,8) calculation. Several features within these curves can elucidate potential reactivity. One feature is the bond distance where dominant electronic configuration converts to that of the radical oxygen for each of the reactivity channels. This means the majority of the electronic configurations are that of the oxyl species. These are denoted by the black and red dashed lines in figure 12. The second feature is the energy gap between the σ channel and the π channels at the distance of the most stable geometry. For this structure, this distance was determined to be 1.6 Å. The third feature is the percentage of oxyl character configurations at the transition state bond distance of roughly 1.86 Å. The final feature is the distance where the σ channel and the π channels intersect with one another for each of the quintet systems. The point of intersection is important because an intersection closer to the transition state geometry will lead to increased reactivity, whereas an intersection after the transition state geometry will lead to decreased reactivity. For the $[\text{Fe(IV)O}(\text{H}_2\text{O})_5]^{2+}$ complex in figure 12, the crossing occurs at roughly 1.88 Å. This bond distance is very near experimental transition state geometries reportedly around 1.86 Å being a potential indicator for a more reactive species.

Reactivity Channels in Quintet Complexes

The potential energy surfaces for each of the species in the quintet state are shown in figures 16 - 20 in the Appendix. The orange potential energy curve for each of the species represents the ground state of the σ channel.

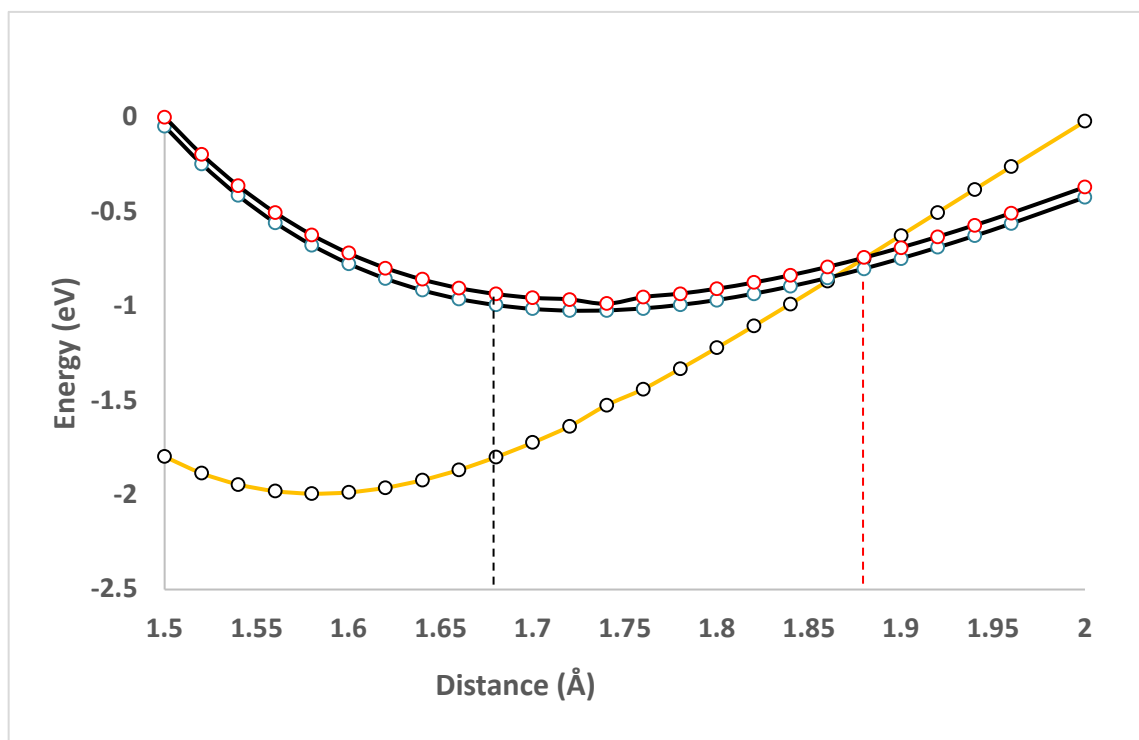


Figure 12. The potential energy curves of the $[\text{FeO}(\text{H}_2\text{O})_5]^{2+}$ complex resulting from a CASPT2 (10,8) calculation. The black dashed line represents the point at which the π channels (represented by the black lines) develop dominant oxyl character that is indicative of the oxyl (radical) formation. The red dash line is the same thing for the σ channel (represented by the orange line).

The two black curves in Figure 12, distinguished by blue and red dots, are the potential energy surfaces for the doubly degenerate π channels. Figure 23 and 24 in the Appendix show that the oxyl character formed smoothly and continuously for both the σ and π channels.

Tables and charts summarizing the trends of the information that was observed can be seen in tables 1 - 3 and figures 13 - 14 and makes the data more interpretable. One detail that is notable is the bond distance at which each of the channels develops dominant oxyl character. These bond distances are important because a dominant oxyl configuration in the reactivity channels allows for the C-H abstraction when the complex approaches the transition state geometry at 1.86 Å.

Table 2 includes the results for the trigonal bipyramidal structures and table 3 for the pseudo octahedral complexes. We do not see a significant difference in the distance where the reactive oxyl species becomes the dominant configuration among the different geometries. We do observe that when a stronger ligand field is in place for the trigonal bipyramidal species that the σ channel develops its character slightly later and the π channels have no notable difference. For the pseudo octahedral species, a similar pattern can be noted where the strong ligands push the dominant oxyl configuration to further Fe(IV)-oxo bond distances in the sigma channel and the π channel recedes to shorter Fe(IV)-oxo bond distances for the development of the oxyl channel.

Table 2. Shows the formation of the oxyl for both of the reactivity channels in the presence of the different ligand fields and the trigonal bipyramidal geometry.

Complex	Oxyl formation in σ (Å)	Oxyl formation in π (Å)
$[\text{FeO}(\text{H}_2\text{O})_4]^{2+}$	1.90	1.70
$[\text{FeO}(\text{NH}_3)_4]^{2+}$	1.92	1.70
$[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_3]^{2+}$	1.92	1.70
$[\text{FeO}(\text{NH}_3)_{\text{ax}}(\text{NH}_2)_3]^{1-}$	1.88	1.64

Table 3. Shows the bond distance at which the pseudo octahedral complexes reactivity channels develop dominant oxyl configurations

Complex	Oxyl formation in σ (Å)	Oxyl formation in π (Å)
$[\text{FeO}(\text{H}_2\text{O})_5]^{2+}$	1.86	1.66
$[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_4]^{2+}$	1.86	1.66
$[\text{FeO}(\text{NH}_3)_5]^{2+}$	1.88	1.66

We can couple the information from these tables with the data in table 4 where the σ and π reactivity channels crossing with one another at various distances. Table 3 illustrates the different distances where the channels intersect for each of the complexes. For the case of the trigonal bipyramidal species, both the $[\text{FeO}(\text{H}_2\text{O})_4]^{2+}$ and $[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_3]^{2+}$ complexes have not achieved dominant oxyl character in their σ channels and this could hinder the reactivity of that particular channel. Having more

available oxyl character in the weak ligands in the trigonal bipyramidal geometry could increase reactivity in both of the channels capable of C-H abstraction.

Table 4. Contains the Fe-O bond distance at which the σ and π channel potential energy surfaces cross over with one another.

Complex	Fe-O Channel Intersection Dist. (Å)
$[\text{FeO}(\text{H}_2\text{O})_4]^{2+}$	1.87
$[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_3]^{2+}$	1.88
$[\text{FeO}(\text{NH}_3)_4]^{2+}$	1.97
$[\text{FeO}(\text{NH}_3)_{\text{ax}}(\text{NH}_2)_3]^{1-}$	1.99
$[\text{FeO}(\text{H}_2\text{O})_5]^{2+}$	1.87
$[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_4]^{2+}$	1.94
$[\text{FeO}(\text{NH}_3)_5]^{2+}$	1.96

The size of the energy gap is summarized in figures 13 and 14. These charts show an upwards trend in the difference in energy between the two reactivity channels when increasing the strength of the ligand field. This trend is true for both the trigonal bipyramidal structures and the pseudo octahedral structures.

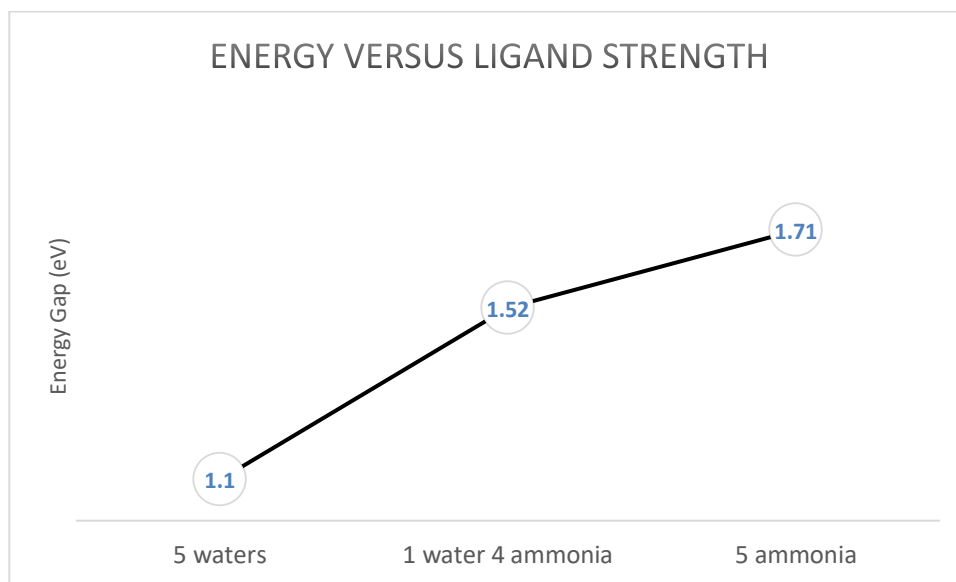


Figure 13. Illustrates the upward trend in the energy gap between the σ and π reactivity channels as it was computed for the pseudo octahedral geometries.

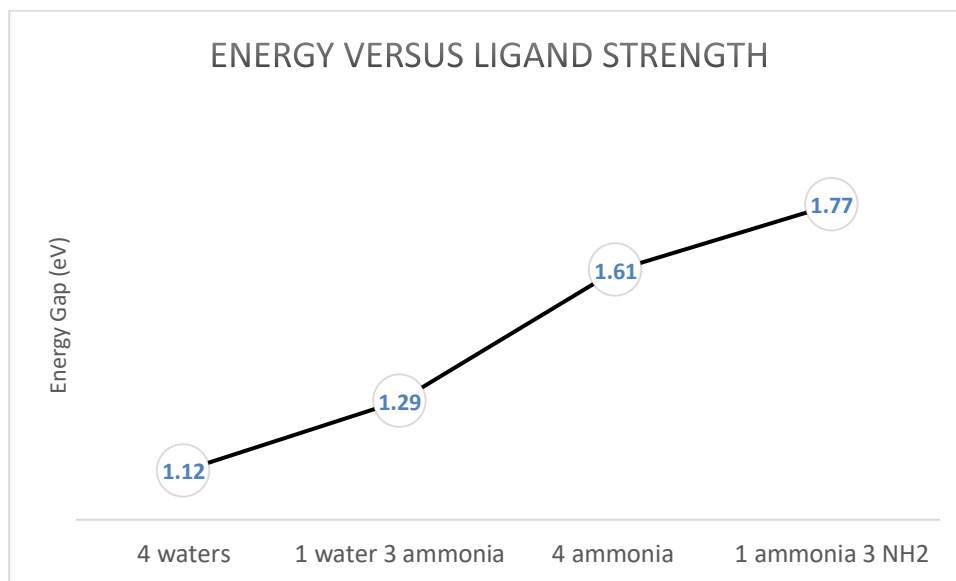


Figure 14. Illustrates the upward trend in the energy gap between the σ and π reactivity channels it was computed for the trigonal bipyramidal geometries.

A larger energy gap between the channels could give preference to one reactivity channel of the ground state over the excited states. It is important to note that the ground state for the pseudo octahedral complexes would not be in a quintet state when applying the stronger field ligands. In fact, the complexes would instead prefer to be in the triplet state. However, our results are of high importance since these species follow the two state reactivity scheme and they have a high spin $S = 2$ configuration at the TS geometry. These trends depict that a weak ligand field complex in either geometry configuration would favor higher reactivity due to the channels having a smaller energy gap making the excited state more accessible. These make both σ and π channels accessible for C-H activation. When discussing the trigonal bipyramidal species with strong field ligands, the energy gap between the states is much larger in the case of $[\text{FeO}(\text{NH}_3)_5]^{2+}$ which has a 0.6eV increase with respect to the weak ligand case where only water molecules are present. This indicates that the species would be more favorable in reacting through the σ channel rather than both the σ and π channels because the π channels will be higher in energy and less accessible from the ground state.

Finally, examination of the percentage of radical character that has been developed by each of the reactivity channels for each of the geometries around the transition state geometry Fe-O bond distance was undertaken. When looking at the trigonal bipyramidal species and the increasing strength of the ligand field (figure 15), the π channel exhibits a general upward trend in the amount of radical character present. The σ channel exhibits the opposite, a general downward trend in the amount of radical oxygen character formed.

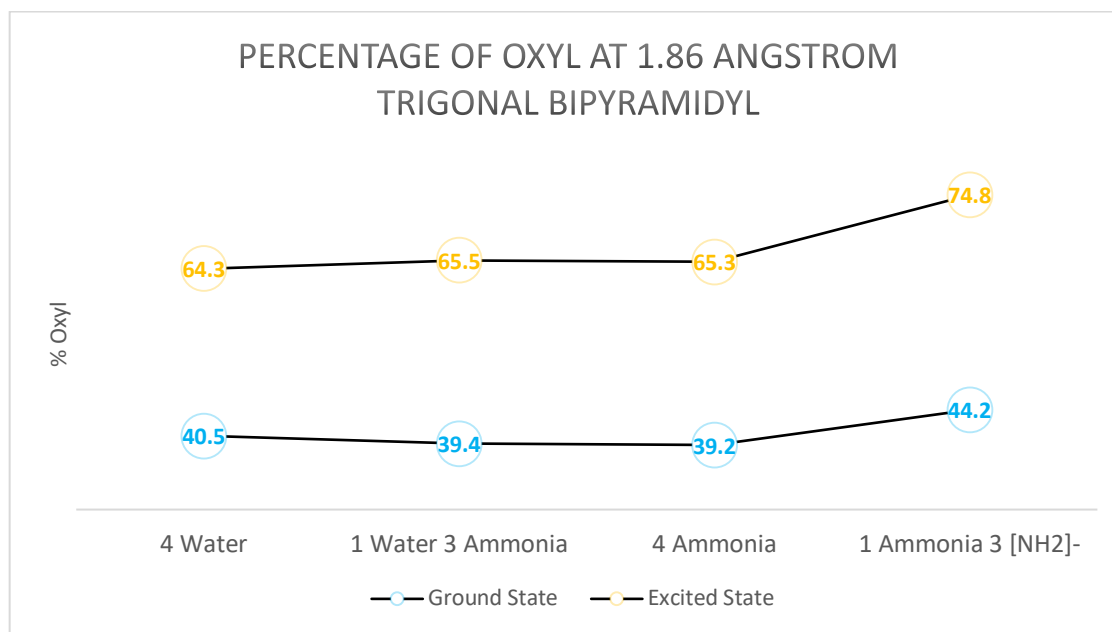


Figure 15. This figure shows the percentage of configurations which are that of the radical oxygen for the σ and π channels for the trigonal bipyramidal species. Orange is the percentage of oxyl in the π channel. Blue is the percentage of oxyl in the σ channel.

A similar pattern can be noted for the octahedral complexes (figure 16). Introduction of stronger ligand fields increases the amount of radical oxygen configurations present for the π channel and decreases the amount of radical oxygen configurations present for the σ channel. When the NH₂⁻ group is introduced, the π channel is dramatically increased in the amount of configurations present by 3.3%; however, the σ channel is not affected as drastically and only lowers 0.1% from the previous case.

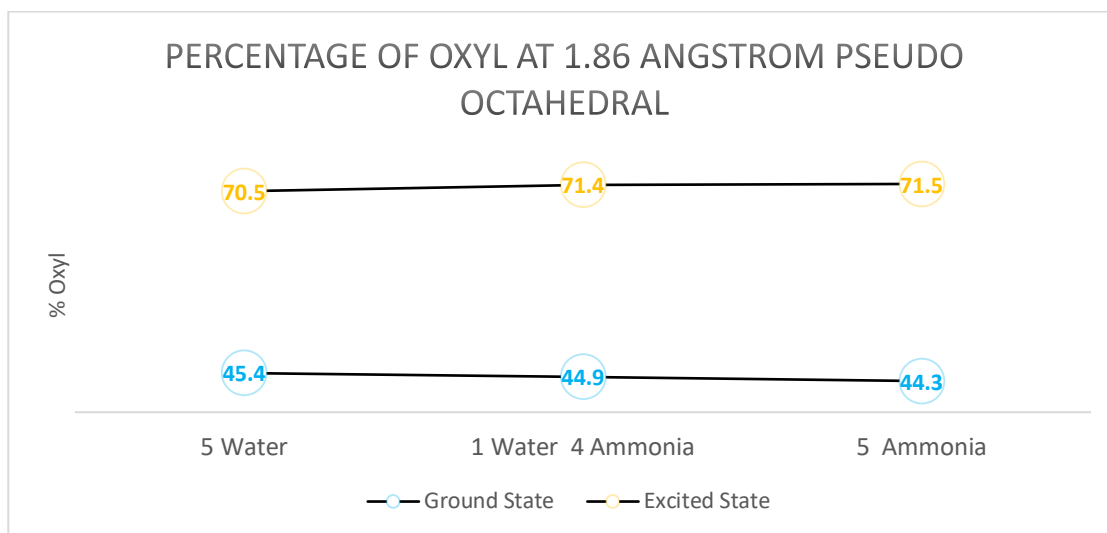


Figure 16. This figure includes the percentage of configurations which are that of the radical oxygen for the σ and π channels for the pseudo octahedral complexes. orange is the percentage of oxyl in the π channel. blue is the percentage of oxyl in the σ channel.

Reactivity Channels in Triplet States

These species were first investigated using CASSCF(10,8) methods, but the CASPT2 method was utilized to achieve more accurate calculations. CASPT2(10,8) calculations with triplet spin are shown in figure 17, 24-28. In the case of the triplet species, three roots is not a sufficient amount to probe the state and adequately understand the systems. The number of roots used vary from four through nine for each of the systems based off of what excitations are possible in the low spin electronic configuration because the amount of states examined for each of the cases changes at distances 1.9-2.0 Å where multiple states are crossing with one another. These several additional excitations come from a doubly degenerate ground state present as well as a doubly degenerate excited state. Examining the channels electronic configurations within the triplet species becomes more difficult in this species.

Issues with the active space cause these calculations on the triplet to be less precise. Since these rigid model systems were based off of the crystal structure of $[\text{Fe(IV)O}(\text{H}_3\text{buea})]^{1-}$, our model systems always predicted a ground state spin of quintet. This should not be the case for all of the species, which is the main reason we cannot comment on the triplet and quintet energy gaps, and this means the triplet calculations will also be incorrect and predict much higher energies than is expected.

Another issue with the triplet species arises from the choice of active space. A more accurate calculation requires the inclusion of additional ligand orbitals. These aforementioned issues prevent a reliable interpretation of the triplet curves as the expected π channels could not be determined for any of the curves.⁵⁹

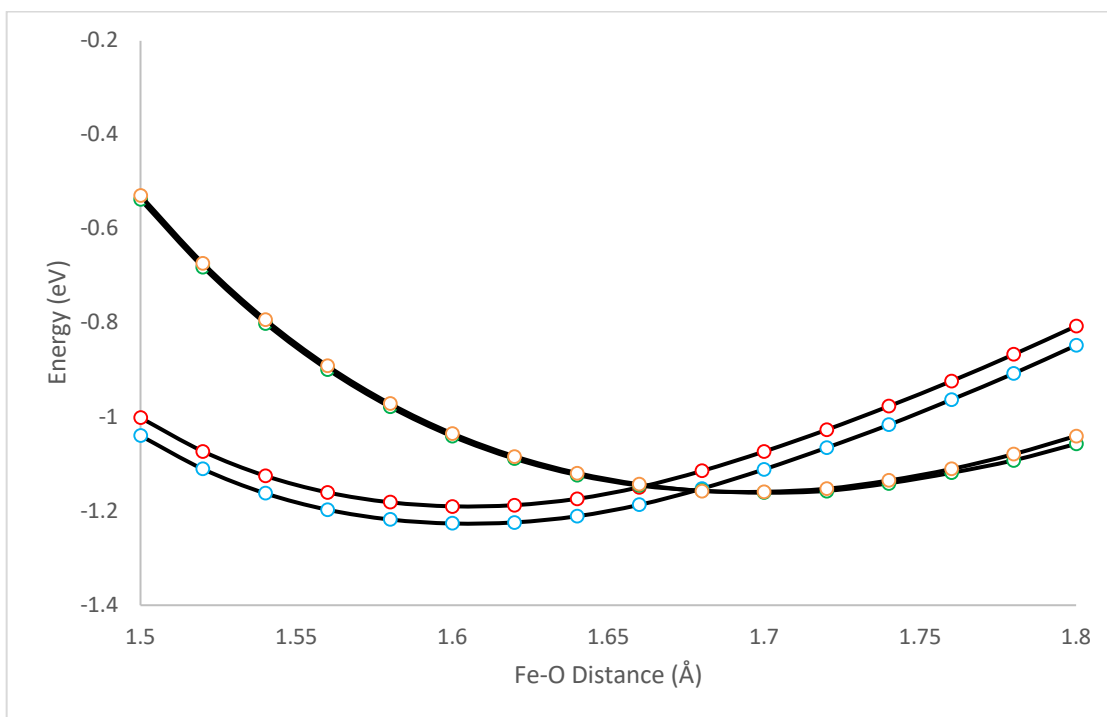


Figure 17. Triplet CASPT2 (10,8) for $[\text{FeO}(\text{H}_2\text{O})_5]^{2+}$ species for the four lowest states.

CHAPTER FOUR

CONCLUSIONS AND RECOMMENDATIONS

Computational tools can be efficiently used for the interpretation of experimental findings and contribute in the discovery of new molecules and materials. They are particularly useful in providing insight into potential characteristics about the electronic structure of many complexes. Here, we have shown the effect that ligand field strength has on the Fe(IV)-oxo effects the reactivity channels. For both pseudo octahedral and trigonal bipyramidal geometries, stronger ligand fields have larger energy gaps at equilibrium geometries than the weaker ligands, and stronger ligand fields have longer intersection distances between σ/π reactivity channels. The oxyl character of the π channel increases with increasing ligand strength while oxyl character of the σ channel decreased with increasing ligand strength.

The strength of the ligand field has various affects not only on the spin as is previously noted but also on the reactivity of the σ and π channels which can either hinder or promote a certain kind of reactivity. Some reactivity channels may be more beneficial than others for various circumstances as in the previously mentioned example of SyrB2. In the case of achieving a compound that is highly reactive, the reactivity channels should intersect at shorter bond distances, have a smaller energy gap between the channels, and develop their oxyl character more rapidly.

In the case for choosing a species which favors the σ channel over the π channel it would be beneficial to have larger energy gaps and a longer distance for intersection of the

reactivity channels. Likely meaning an increase in the formation of the oxyl character in the sigma channel would be beneficial.

The triplet species require a more careful inspection, and a revision to the methods to fully understand the underlying phenomena that affect the reactivity. The problems with the triplet also include issues with the active space. While the case of the weak ligands depicts the expected states, upon the increasing ligand field strength additional orbitals involving the equatorial ligands are necessary due to the skewing of the electronic states. The revision will also allow the ability to distinguish energy gaps between the quintet and triplet species. Thus, an accurate description of the ground state of the model compounds can be achieved as well as how these channels appear with respect to one another. This relationship elucidates potential crossover with the quintet and triplet potential energy surfaces.

The characteristics mentioned above can be taken into consideration when examining a ligand field for a specific synthetic purpose. In cases where a ligand field is being considered for metal organic frameworks or similar structures, where both channels are open to C-H abstraction, there is opportunity to make the gap smaller for increased reactivity. When taking into consideration species such as homogenous catalysts, where competing pathways are important, the energy gap between the two channels should be pushed further apart for a selective preference for the ground state channel.

Future insight into this project could be gained by looking at the various C-H activation barriers for each of the complexes allowing for a complete picture of reactivity between the species and the ligand spheres. In addition to this a better understanding of the

triplets is necessary. Understanding the complex nature of these reactivity channels completely can allow for the guidance of developing smarter materials for strong C-H bond activation. These materials are extremely important for using our natural resources to their fullest potential.

LIST OF REFERENCES

1. Costas, M.; Mehn, M. P.; Jensen, M. P.; Que, L., Dioxygen Activation at Mononuclear Nonheme Iron Active Sites: Enzymes, Models, and Intermediates. *Chemical Reviews* **2004**, *104* (2), 939-986.
2. Administration, U. S. E. I. Natural Gas Explained. https://www.eia.gov/energyexplained/index.php?page=natural_gas_home.
3. Administration, U. S. E. I. U.S. Energy Facts Explained. https://www.eia.gov/energyexplained/?page=us_energy_home.
4. Scientist, U. o. C., Environmental Impacts of Natural Gas. **2018**.
5. Scientists, U. o. C., Natural Gas Flaring, Processing, and Transportation. **2018**.
6. News, N., Fracking Boom Waste: Flares Light Prairie With Unused Natural Gas. **2014**.
7. Aasberg-Petersen, K.; Dybkjær, I.; Ovesen, C. V.; Schjødt, N. C.; Sehested, J.; Thomsen, S. G., Natural gas to synthesis gas – Catalysts and catalytic processes. *Journal of Natural Gas Science and Engineering* **2011**, *3* (2), 423-459.
8. Yoneda, N.; Kusano, S.; Yasui, M.; Pujado, P.; Wilcher, S., Recent advances in processes and catalysts for the production of acetic acid. *Applied Catalysis A: General* **2001**, *221* (1), 253-265.
9. Panov, G. I.; Sobolev, V. I.; Dubkov, K. A.; Parmon, V. N.; Ovanesyan, N. S.; Shilov, A. E.; Shteinman, A. A., Iron complexes in zeolites as a new model of methane monooxygenase. *Reaction Kinetics and Catalysis Letters* **1997**, *61* (2), 251-258.
10. Snyder, B. E. R.; Vanelderen, P.; Bols, M. L.; Hallaert, S. D.; Böttger, L. H.; Ungur, L.; Pierloot, K.; Schoonheydt, R. A.; Sels, B. F.; Solomon, E. I., The active site of low-temperature methane hydroxylation in iron-containing zeolites. *Nature* **2016**, *536*, 317.
11. Ye, S.; Neese, F., Nonheme oxo-iron(IV) intermediates form an oxyl radical upon approaching the C–H bond activation transition state. *Proceedings of the National Academy of Sciences* **2011**, *108* (4), 1228.
12. Jonathan M. Elkins, M. J. R., Ian J. Clifton, Julie C. Dunning Hotoppl, John S. Lloyd, Nicolai I. Burzlaff, Jack E. Baldwin, Robert P. Hausinger, and Peter L. Roach, X-ray Crystal Structure of Escherichia coli Taurine/ α -Ketoglutarate Dioxygenase Complexed to Ferrous Iron and Substrate. *Biochemistry* **2002**, *41* (16), 5185-5192.
13. Bekir E. Eser, E. W. B., Patrick A. Frantom, Lana Saleh, J. Martin Bollinger Jr., Carsten Krebs, and Paul F. Fitzpatrick, Direct Spectroscopic Evidence for a High-Spin Fe(IV) Intermediate in Tyrosine Hydroxylase. *J. Am. Chem. Soc.* **2007**, *129* (37), 11334-11335.
14. Martin Srnec, S. D. W., Megan L. Matthews, Carsten Krebs, J. Martin Bollinger Jr., and Edward I. Solomon, Electronic Structure of the Ferryl Intermediate in the α -Ketoglutarate Dependent Non-Heme Iron Halogenase SyrB2: Contributions to H Atom Abstraction Reactivity. *J. Am. Chem. Soc.* **2016**, *138* (15), 5110-5122.
15. Neidig, M. L.; Decker, A.; Choroba, O. W.; Huang, F.; Kavana, M.; Moran, G. R.; Spencer, J. B.; Solomon, E. I., Spectroscopic and electronic structure studies of aromatic electrophilic attack and hydrogen-atom abstraction by non-heme iron enzymes. *Proceedings of the National Academy of Sciences* **2006**, *103* (35), 12966.

16. Grant, J. L.; Mitchell, M. E.; Makris, T. M., Catalytic strategy for carbon–carbon bond scission by the cytochrome P450 OleT. *Proceedings of the National Academy of Sciences* **2016**, *113* (36), 10049.
17. Verma, P.; Vogiatzis, K. D.; Planas, N.; Borycz, J.; Xiao, D. J.; Long, J. R.; Gagliardi, L.; Truhlar, D. G., Mechanism of Oxidation of Ethane to Ethanol at Iron(IV)-Oxo Sites in Magnesium-Diluted Fe₂(dobdc). *J Am Chem Soc* **2015**, *137* (17), 5770-81.
18. Shu, L.; Nesheim, J. C.; Kauffmann, K.; Münck, E.; Lipscomb, J. D.; Que, L., An Fe^₂IV^₂O^₂; Diamond Core Structure for the Key Intermediate Q of Methane Monooxygenase. *Science* **1997**, *275* (5299), 515.
19. Sazinsky, M. H.; Lippard, S. J., Methane monooxygenase: functionalizing methane at iron and copper. *Met Ions Life Sci* **2015**, *15*, 205-56.
20. Grapperhaus, C. A.; Mienert, B.; Bill, E.; Weyhermüller, T.; Wieghardt, K., Mononuclear (Nitrido)iron(V) and (Oxo)iron(IV) Complexes via Photolysis of [(cyclam-acetato)FeIII(N3)]⁺ and Ozonolysis of [(cyclam-acetato)FeIII(O₃SCF₃)]⁺ in Water/Acetone Mixtures[‡]. *Inorganic Chemistry* **2000**, *39* (23), 5306-5317.
21. Rohde, J. U.; In, J. H.; Lim, M. H.; Brennessel, W. W.; Bukowski, M. R.; Stubna, A.; Munck, E.; Nam, W.; Que, L., Jr., Crystallographic and spectroscopic characterization of a nonheme Fe(IV)-O complex. *Science* **2003**, *299* (5609), 1037-9.
22. Bukowski, M. R.; Koehntop, K. D.; Stubna, A.; Bominaar, E. L.; Halfen, J. A.; Münck, E.; Nam, W.; Que, L., A Thiolate-Ligated Nonheme Oxoiron(IV) Complex Relevant to Cytochrome P450. *Science* **2005**, *310* (5750), 1000.
23. Jackson, T. A.; Rohde, J. U.; Seo, M. S.; Sastri, C. V.; DeHont, R.; Stubna, A.; Ohta, T.; Kitagawa, T.; Munck, E.; Nam, W.; Que, L., Jr., Axial ligand effects on the geometric and electronic structures of nonheme oxoiron(IV) complexes. *J Am Chem Soc* **2008**, *130* (37), 12394-407.
24. Rohde, J. U.; Que, L., Jr., Axial coordination of carboxylate activates the non-heme FeIV=O unit. *Angew Chem Int Ed Engl* **2005**, *44* (15), 2255-8.
25. Sastri, C. V.; Park, M. J.; Ohta, T.; Jackson, T. A.; Stubna, A.; Seo, M. S.; Lee, J.; Kim, J.; Kitagawa, T.; Munck, E.; Que, L., Jr.; Nam, W., Axial ligand substituted nonheme FeIV=O complexes: observation of near-UV LMCT bands and Fe=O Raman vibrations. *J Am Chem Soc* **2005**, *127* (36), 12494-5.
26. Bigi, J. P.; Harman, W. H.; Lassalle-Kaiser, B.; Robles, D. M.; Stich, T. A.; Yano, J.; Britt, R. D.; Chang, C. J., A high-spin iron(IV)-oxo complex supported by a trigonal nonheme pyrrolide platform. *J Am Chem Soc* **2012**, *134* (3), 1536-42.
27. Thibon, A.; England, J.; Martinho, M.; Young, V. G., Jr.; Frisch, J. R.; Guillot, R.; Girerd, J. J.; Munck, E.; Que, L., Jr.; Banse, F., Proton- and reductant-assisted dioxygen activation by a nonheme iron(II) complex to form an oxoiron(IV) intermediate. *Angew Chem Int Ed Engl* **2008**, *47* (37), 7064-7.
28. McDonald, A. R.; Bukowski, M. R.; Farquhar, E. R.; Jackson, T. A.; Koehntop, K. D.; Seo, M. S.; De Hont, R. F.; Stubna, A.; Halfen, J. A.; Munck, E.; Nam, W.; Que, L., Jr., Sulfur versus iron oxidation in an iron-thiolate model complex. *J Am Chem Soc* **2010**, *132* (48), 17118-29.

29. Ray, K.; England, J.; Fiedler, A. T.; Martinho, M.; Munck, E.; Que, L., Jr., An inverted and more oxidizing isomer of $[\text{Fe}(\text{IV})(\text{O})(\text{tmc})(\text{NCCH}_3)]^{2+}$. *Angew Chem Int Ed Engl* **2008**, 47 (42), 8068-71.
30. Fukuzumi, S.; Morimoto, Y.; Kotani, H.; Naumov, P.; Lee, Y. M.; Nam, W., Crystal structure of a metal ion-bound oxoiron(IV) complex and implications for biological electron transfer. *Nat Chem* **2010**, 2 (9), 756-9.
31. Suh, Y.; Seo, M. S.; Kim, K. M.; Kim, Y. S.; Jang, H. G.; Tosha, T.; Kitagawa, T.; Kim, J.; Nam, W., Nonheme iron(II) complexes of macrocyclic ligands in the generation of oxoiron(IV) complexes and the catalytic epoxidation of olefins. *Journal of Inorganic Biochemistry* **2006**, 100 (4), 627-633.
32. Chanda, A.; Shan, X.; Chakrabarti, M.; Ellis, W. C.; Popescu, D. L.; Tiago de Oliveira, F.; Wang, D.; Que, L., Jr.; Collins, T. J.; Munck, E.; Bominaar, E. L., (TAML)FeIV O complex in aqueous solution: synthesis and spectroscopic and computational characterization. *Inorg Chem* **2008**, 47 (9), 3669-78.
33. Popescu, D. L.; Vrabel, M.; Brausam, A.; Madsen, P.; Lente, G.; Fabian, I.; Ryabov, A. D.; van Eldik, R.; Collins, T. J., Thermodynamic, electrochemical, high-pressure kinetic, and mechanistic studies of the formation of oxo Fe(IV)-TAML species in water. *Inorg Chem* **2010**, 49 (24), 11439-48.
34. Kaizer, J.; Klinker, E. J.; Oh, N. Y.; Rohde, J. U.; Song, W. J.; Stubna, A.; Kim, J.; Munck, E.; Nam, W.; Que, L., Jr., Nonheme FeIVO complexes that can oxidize the C-H bonds of cyclohexane at room temperature. *J Am Chem Soc* **2004**, 126 (2), 472-3.
35. Klinker, E. J.; Kaizer, J.; Brennessel, W. W.; Woodrum, N. L.; Cramer, C. J.; Que, L., Jr., Structures of nonheme oxoiron(IV) complexes from X-ray crystallography, NMR spectroscopy, and DFT calculations. *Angew Chem Int Ed Engl* **2005**, 44 (24), 3690-4.
36. Bell, C. B., 3rd; Wong, S. D.; Xiao, Y.; Klinker, E. J.; Tenderholt, A. L.; Smith, M. C.; Rohde, J. U.; Que, L., Jr.; Cramer, S. P.; Solomon, E. I., A combined NRVs and DFT study of $\text{Fe}(\text{IV})=\text{O}$ model complexes: a diagnostic method for the elucidation of non-heme iron enzyme intermediates. *Angew Chem Int Ed Engl* **2008**, 47 (47), 9071-4.
37. Groger, H.; Chamouveau, F.; Orolagos, N.; Rollmann, C.; Drauz, K.; Hummel, W.; Weckbecker, A.; May, O., Enantioselective reduction of ketones with "designer cells" at high substrate concentrations: highly efficient access to functionalized optically active alcohols. *Angew Chem Int Ed Engl* **2006**, 45 (34), 5677-81.
38. Comba, P.; Fukuzumi, S.; Kotani, H.; Wunderlich, S., Electron-transfer properties of an efficient nonheme iron oxidation catalyst with a tetradentate bispidine ligand. *Angew Chem Int Ed Engl* **2010**, 49 (14), 2622-5.
39. Balland, V.; Charlot, M.-F.; Banse, F.; Girerd, J.-J.; Mattioli, Tony A.; Bill, E.; Bartoli, J.-F.; Battioni, P.; Mansuy, D., Spectroscopic Characterization of an FeIV Intermediate Generated by Reaction of XO^- ($\text{X} = \text{Cl}, \text{Br}$) with an FeII Complex Bearing a Pentadentate Non-Porphyrinic Ligand—Hydroxylation and Epoxidation Activity. *European Journal of Inorganic Chemistry* **2004**, 2004 (2), 301-308.
40. Martinho, M.; Banse, F.; Bartoli, J. F.; Mattioli, T. A.; Battioni, P.; Horner, O.; Bourcier, S.; Girerd, J. J., New example of a non-heme mononuclear iron(IV) oxo complex. Spectroscopic data and oxidation activity. *Inorg Chem* **2005**, 44 (25), 9592-6.

41. McDonald, A. R.; Guo, Y.; Vu, V. V.; Bominaar, E. L.; Munck, E.; Que, L., Jr., A Mononuclear Carboxylate-Rich Oxoiron(IV) Complex: a Structural and Functional Mimic of TauD Intermediate 'J'. *Chem Sci* **2012**, *3*, 1680-1693.
42. Annaraj, J.; Kim, S.; Seo, M. S.; Lee, Y.-M.; Kim, Y.; Kim, S.-J.; Choi, Y. S.; Jang, H. G.; Nam, W., An iron(II) complex with a N3S2 thioether ligand in the generation of an iron(IV)-oxo complex and its reactivity in olefin epoxidation. *Inorganica Chimica Acta* **2009**, *362* (3), 1031-1034.
43. Badiei, Y. M.; Siegler, M. A.; Goldberg, D. P., O₂ activation by bis(imino)pyridine iron(II)-thiolate complexes. *J Am Chem Soc* **2011**, *133* (5), 1274-7.
44. Lim, M. H.; Rohde, J.-U.; Stubna, A.; Bukowski, M. R.; Costas, M.; Ho, R. Y. N.; Münck, E.; Nam, W.; Que, L., An Fe=O complex of a tetradentate tripodal nonheme ligand. *Proceedings of the National Academy of Sciences* **2003**, *100* (7), 3665.
45. Rohde, J. U.; Stubna, A.; Bominaar, E. L.; Munck, E.; Nam, W.; Que, L., Jr., Nonheme oxoiron(IV) complexes of tris(2-pyridylmethyl)amine with cis-monoanionic ligands. *Inorg Chem* **2006**, *45* (16), 6435-45.
46. Paine, T. K.; Costas, M.; Kaizer, J.; Que, L., Jr., Oxoiron(IV) complexes of the tris(2-pyridylmethyl)amine ligand family: effect of pyridine alpha-substituents. *J Biol Inorg Chem* **2006**, *11* (3), 272-6.
47. Company, A.; Prat, I.; Frisch, J. R.; Mas-Balleste, R.; Guell, M.; Juhasz, G.; Ribas, X.; Munck, E.; Luis, J. M.; Que, L., Jr.; Costas, M., Modeling the cis-oxo-labile binding site motif of non-heme iron oxygenases: water exchange and oxidation reactivity of a non-heme iron(IV)-oxo compound bearing a tripodal tetradentate ligand. *Chemistry* **2011**, *17* (5), 1622-34.
48. Seo, M. S.; Kim, N. H.; Cho, K.-B.; So, J. E.; Park, S. K.; Clémancey, M.; Garcia-Serres, R.; Latour, J.-M.; Shaik, S.; Nam, W., A mononuclear nonheme iron(iv)-oxo complex which is more reactive than cytochrome P450 model compound I. *Chemical Science* **2011**, *2* (6).
49. Makhlynets, O. V.; Rybak-Akimova, E. V., Aromatic hydroxylation at a non-heme iron center: observed intermediates and insights into the nature of the active species. *Chemistry* **2010**, *16* (47), 13995-4006.
50. Jensen, M. P.; Costas, M.; Ho, R. Y.; Kaizer, J.; Mairata i Payeras, A.; Munck, E.; Que, L., Jr.; Rohde, J. U.; Stubna, A., High-valent nonheme iron. Two distinct iron(IV) species derived from a common iron(II) precursor. *J Am Chem Soc* **2005**, *127* (30), 10512-25.
51. Zhou, Y.; Shan, X.; Mas-Balleste, R.; Bukowski, M. R.; Stubna, A.; Chakrabarti, M.; Slominski, L.; Halfen, J. A.; Munck, E.; Que, L., Jr., Contrasting cis and trans effects on the reactivity of nonheme oxoiron(IV) complexes. *Angew Chem Int Ed Engl* **2008**, *47* (10), 1896-9.
52. Pestovsky, O.; Stoian, S.; Bominaar, E. L.; Shan, X.; Munck, E.; Que, L., Jr.; Bakac, A., Aqueous FeIV=O: spectroscopic identification and oxo-group exchange. *Angew Chem Int Ed Engl* **2005**, *44* (42), 6871-4.
53. England, J.; Martinho, M.; Farquhar, E. R.; Frisch, J. R.; Bominaar, E. L.; Munck, E.; Que, L., Jr., A synthetic high-spin oxoiron(IV) complex: generation, spectroscopic characterization, and reactivity. *Angew Chem Int Ed Engl* **2009**, *48* (20), 3622-6.

54. England, J.; Guo, Y.; Farquhar, E. R.; Young, V. G., Jr.; Munck, E.; Que, L., Jr., The crystal structure of a high-spin oxoiron(IV) complex and characterization of its self-decay pathway. *J Am Chem Soc* **2010**, *132* (25), 8635-44.
55. Lacy, D. C.; Gupta, R.; Stone, K. L.; Greaves, J.; Ziller, J. W.; Hendrich, M. P.; Borovik, A. S., Formation, structure, and EPR detection of a high spin Fe(IV)-oxo species derived from either an Fe(III)-oxo or Fe(III)-OH complex. *J Am Chem Soc* **2010**, *132* (35), 12188-90.
56. England, J.; Guo, Y.; Van Heuvelen, K. M.; Cranswick, M. A.; Rohde, G. T.; Bominaar, E. L.; Munck, E.; Que, L., Jr., A more reactive trigonal-bipyramidal high-spin oxoiron(IV) complex with a cis-labile site. *J Am Chem Soc* **2011**, *133* (31), 11880-3.
57. Ye, W.; Ho, D. M.; Friedle, S.; Palluccio, T. D.; Rybak-Akimova, E. V., Role of Fe(IV)-oxo intermediates in stoichiometric and catalytic oxidations mediated by iron pyridine-azamacrocycles. *Inorg Chem* **2012**, *51* (9), 5006-21.
58. Que, L., Jr., The road to non-heme oxoferryls and beyond. *Acc Chem Res* **2007**, *40* (7), 493-500.
59. Srnc, M.; Wong, S. D.; England, J.; Que, L.; Solomon, E. I., π -Frontier molecular orbitals in Fe(IV)=O = 2 ferryl species and elucidation of their contributions to reactivity. *Proceedings of the National Academy of Sciences* **2012**, *109* (36), 14326.
60. England, J.; Martinho, M.; Farquhar Erik, R.; Frisch Jonathan, R.; Bominaar Emile, L.; Münck, E.; Que, L., A Synthetic High-Spin Oxoiron(IV) Complex: Generation, Spectroscopic Characterization, and Reactivity. *Angewandte Chemie International Edition* **2009**, *48* (20), 3622-3626.
61. Hirao, H.; Kumar, D.; Que, L., Jr.; Shaik, S., Two-state reactivity in alkane hydroxylation by non-heme iron-oxo complexes. *J Am Chem Soc* **2006**, *128* (26), 8590-606.
62. Dhuri, S. N.; Seo, M. S.; Lee, Y. M.; Hirao, H.; Wang, Y.; Nam, W.; Shaik, S., Experiment and theory reveal the fundamental difference between two-state and single-state reactivity patterns in nonheme Fe(IV)=O versus Ru(IV)=O oxidants. *Angew Chem Int Ed Engl* **2008**, *47* (18), 3356-9.
63. Hirao, H.; Que, L., Jr.; Nam, W.; Shaik, S., A two-state reactivity rationale for counterintuitive axial ligand effects on the C-H activation reactivity of nonheme FeIV=O oxidants. *Chemistry* **2008**, *14* (6), 1740-56.
64. Schröder, D.; Shaik, S.; Schwarz, H., Two-State Reactivity as a New Concept in Organometallic Chemistry. *Accounts of Chemical Research* **2000**, *33* (3), 139-145.
65. Shaik, S., An anatomy of the two-state reactivity concept: Personal reminiscences in memoriam of Detlef Schröder. *International Journal of Mass Spectrometry* **2013**, *354*, 5-14.
66. Kupper, C.; Mondal, B.; Serrano-Plana, J.; Klawitter, I.; Neese, F.; Costas, M.; Ye, S.; Meyer, F., Nonclassical Single-State Reactivity of an Oxo-Iron(IV) Complex Confined to Triplet Pathways. *J Am Chem Soc* **2017**, *139* (26), 8939-8949.
67. Department of Chemistry, U. o. C. I., An introduction to circular dichroism spectroscopy.
68. University of Michigan, T. L. G., Magnetic Circular Dichroism (MCD).

69. Wolfram Koch, M. C. H., *A Chemist's Guide to Density Functional Theory*. Second ed.; WILEY-VCH: 2007.
70. Becke, A. D., Density-functional exchange-energy approximation with correct asymptotic behavior. *Physical Review A* **1988**, 38 (6), 3098-3100.
71. Becke, A. D., Density-functional thermochemistry. III. The role of exact exchange. *The Journal of Chemical Physics* **1993**, 98 (7), 5648-5652.
72. Lee, C.; Yang, W.; Parr, R. G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Physical Review B* **1988**, 37 (2), 785-789.
73. Zhao, Y.; Truhlar, D. G., The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theoretical Chemistry Accounts* **2008**, 120 (1), 215-241.
74. Becke, A. D., A new mixing of Hartree-Fock and local density-functional theories. *The Journal of Chemical Physics* **1993**, 98 (2), 1372-1377.
75. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, 77 (18), 3865-3868.
76. Adamo, C.; Barone, V., Toward reliable density functional methods without adjustable parameters: The PBE0 model. *The Journal of Chemical Physics* **1999**, 110 (13), 6158-6170.
77. Perdew, J. P.; Ernzerhof, M.; Burke, K., Rationale for mixing exact exchange with density functional approximations. *The Journal of Chemical Physics* **1996**, 105 (22), 9982-9985.
78. Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E., Climbing the Density Functional Ladder: Nonempirical Meta-Generalized Gradient Approximation Designed for Molecules and Solids. *Physical Review Letters* **2003**, 91 (14), 146401.
79. Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P., Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. *The Journal of Chemical Physics* **2003**, 119 (23), 12129-12137.
80. Schäfer, A.; Horn, H.; Ahlrichs, R., Fully optimized contracted Gaussian basis sets for atoms Li to Kr. *The Journal of Chemical Physics* **1992**, 97 (4), 2571-2577.
81. Schäfer, A.; Huber, C.; Ahlrichs, R., Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *The Journal of Chemical Physics* **1994**, 100 (8), 5829-5835.
82. Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys Chem Chem Phys* **2005**, 7 (18), 3297-305.
83. and, A. D. o. U. o. K.; GmbH, F. K. *TURBOMOLE V7.2* 2018.
84. Kazaryan, A.; Baerends, E. J., Ligand Field Effects and the High Spin-High Reactivity Correlation in the H Abstraction by Non-Heme Iron(IV)-Oxo Complexes: A DFT Frontier Orbital Perspective. *ACS Catalysis* **2015**, 5 (3), 1475-1488.
85. Aquilante, F.; Autschbach, J.; Carlson, R. K.; Chibotaru, L. F.; Delcey, M. G.; De Vico, L.; Fdez Galvan, I.; Ferre, N.; Frutos, L. M.; Gagliardi, L.; Garavelli, M.; Giussani,

- A.; Hoyer, C. E.; Li Manni, G.; Lischka, H.; Ma, D.; Malmqvist, P. A.; Muller, T.; Nenov, A.; Olivucci, M.; Pedersen, T. B.; Peng, D.; Plasser, F.; Pritchard, B.; Reiher, M.; Rivalta, I.; Schapiro, I.; Segarra-Marti, J.; Stenrup, M.; Truhlar, D. G.; Ungur, L.; Valentini, A.; Vancoillie, S.; Veryazov, V.; Vysotskiy, V. P.; Weingart, O.; Zapata, F.; Lindh, R., Molcas 8: New capabilities for multiconfigurational quantum chemical calculations across the periodic table. *J Comput Chem* **2016**, *37* (5), 506-41.
86. List, N. H.; Kauczor, J.; Saue, T.; Jensen, H. J.; Norman, P., Beyond the electric-dipole approximation: A formulation and implementation of molecular response theory for the description of absorption of electromagnetic field radiation. *J Chem Phys* **2015**, *142* (24), 244111.
87. Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O., Main Group Atoms and Dimers Studied with a New Relativistic ANO Basis Set. *The Journal of Physical Chemistry A* **2004**, *108* (15), 2851-2858.
88. Roos, B. O.; Lindh, R.; Malmqvist, P. A.; Veryazov, V.; Widmark, P. O., New relativistic ANO basis sets for transition metal atoms. *J Phys Chem A* **2005**, *109* (29), 6575-9.
89. Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O., New relativistic ANO basis sets for actinide atoms. *Chemical Physics Letters* **2005**, *409* (4), 295-299.

APPENDIX

Quintet Complexes

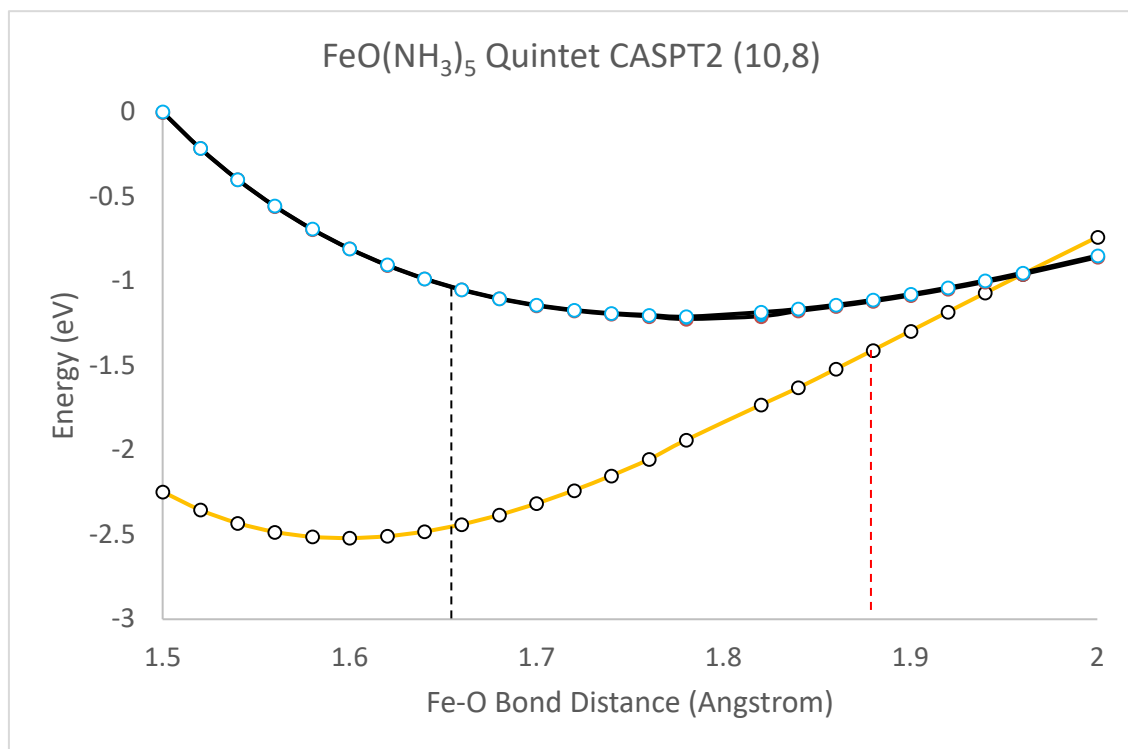


Figure 18. Contains the potential energy surfaces calculated at the CASPT2 (10,8) level of theory for the states which are involved in the σ and π reactivity channels for the $[\text{FeO}(\text{NH}_3)_5]^{2+}$ complex. The dashed lines (red σ channel; black π channel) show the distance where the oxyl configuration becomes the dominant configuration

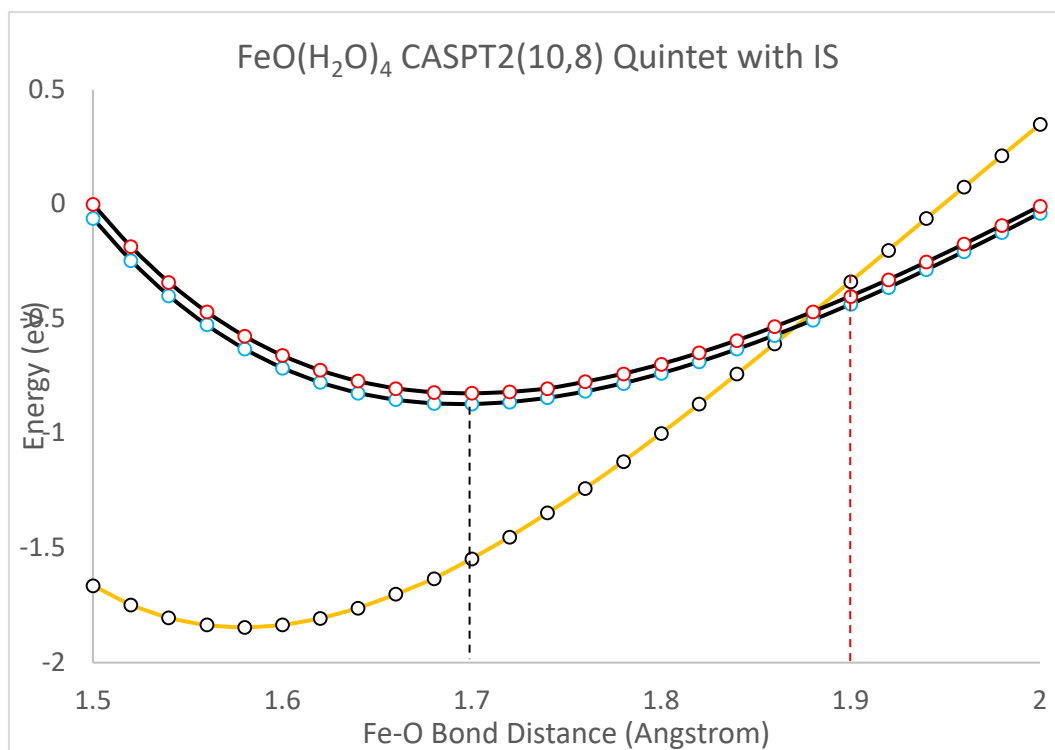


Figure 19. Contains the potential energy surfaces calculated at the CASPT2 (10,8) level of theory for the states which are involved in the σ and π reactivity channels for the $[\text{FeO}(\text{H}_2\text{O})_4]^{2+}$ complex. The dashed lines (red σ channel; black π channel) show the distance where the oxyl configuration becomes the dominant configuration.

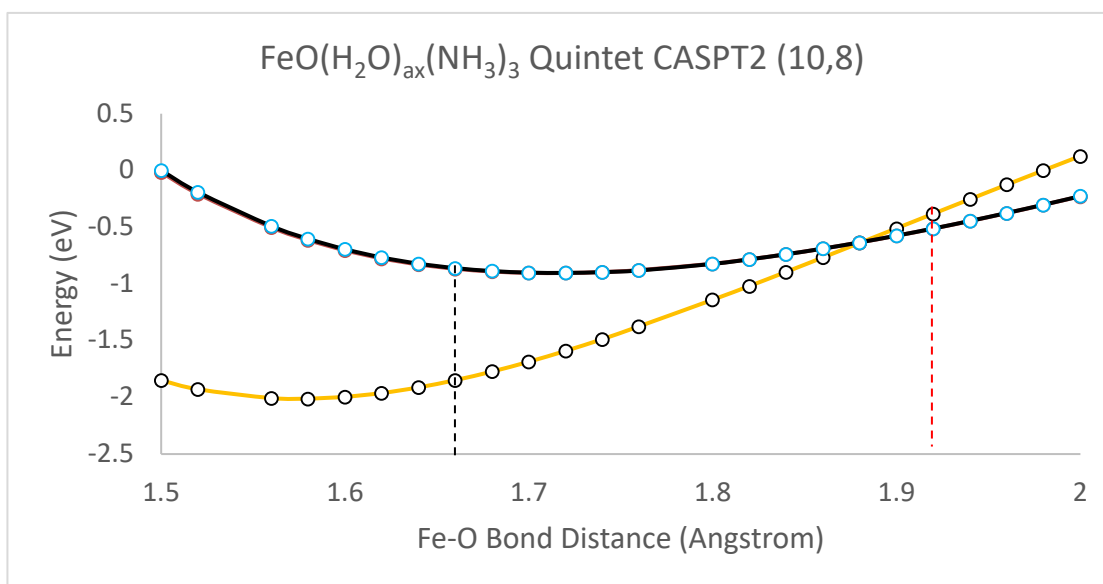


Figure 20. Contains the potential energy surfaces calculated at the CASPT2 (10,8) level of theory for the states which are involved in the σ and π reactivity channels for the $[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_3]^{2+}$ complex. The dashed lines (red σ channel; black π channel) show the distance where the oxyl configuration becomes the dominant configuration.

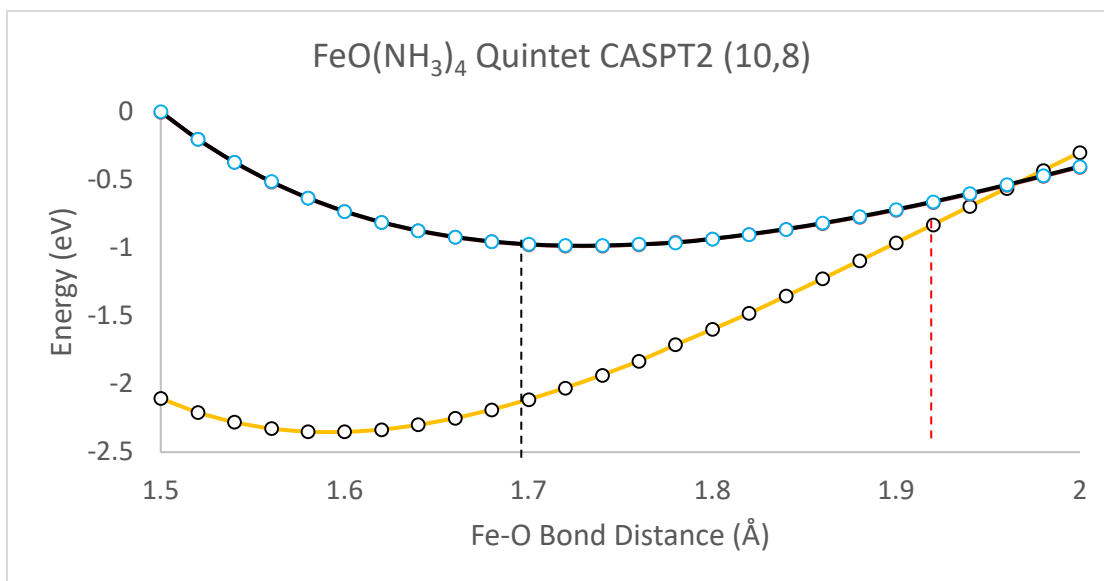


Figure 21. Contains the potential energy surfaces calculated at the CASPT2 (10,8) level of theory for the states which are involved in the σ and π reactivity channels for the $[\text{FeO}(\text{NH}_3)_4]^{2+}$ complex. The dashed lines (red σ channel; black π channel) show the distance where the oxyl configuration becomes the dominant configuration.

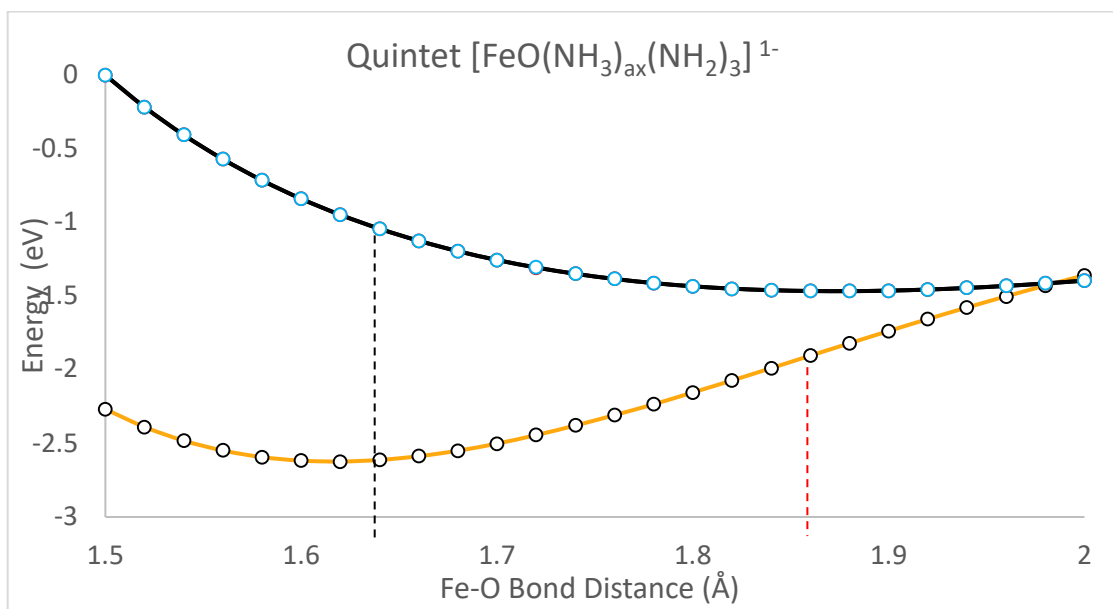


Figure 22. Contains the potential energy surfaces calculated at the CASPT2 (10,8) level of theory for the states which are involved in the σ and π reactivity channels for the $[\text{FeO}(\text{NH}_3)_{\text{ax}}(\text{NH}_2)_3]^{1-}$ complex. The dashed lines (red σ channel; black π channel) show the distance where the oxyl configuration becomes the dominant configuration.

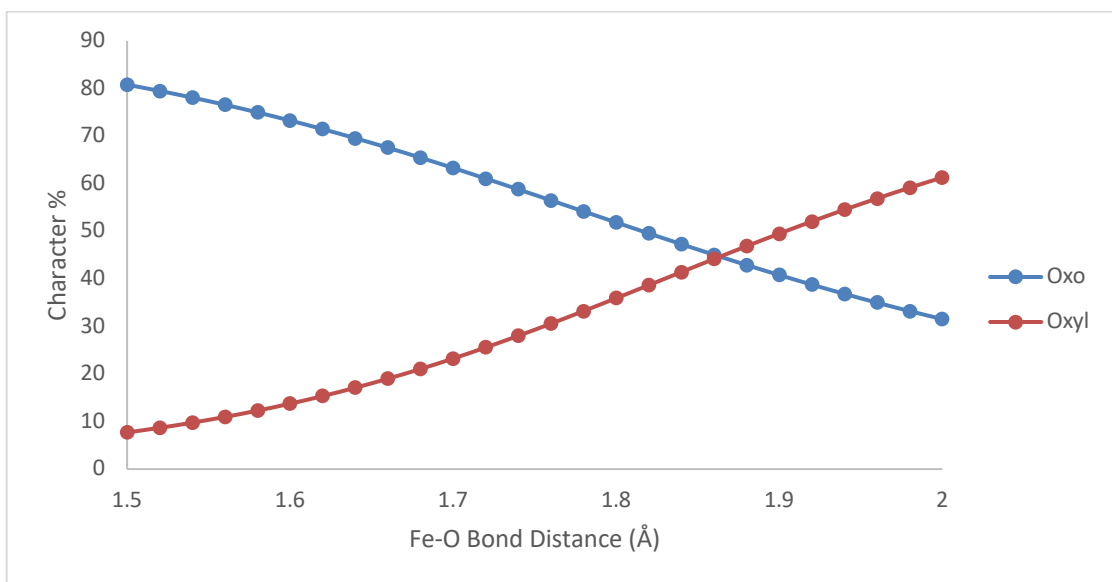


Figure 23. Shows increasing oxyl character and decreasing oxo character for σ channel of the $[\text{FeO}(\text{NH}_3)_{\text{ax}}(\text{NH}_2)_3]^{1-}$ species.

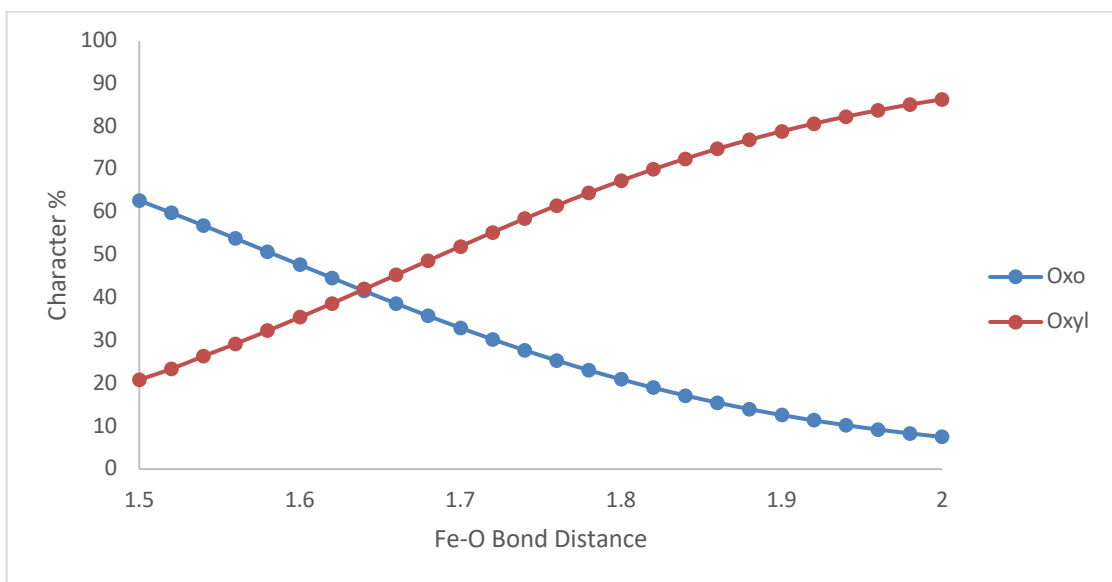


Figure 24. Shows increasing oxyl character and decreasing oxo character for π channel.

Triplet Complexes

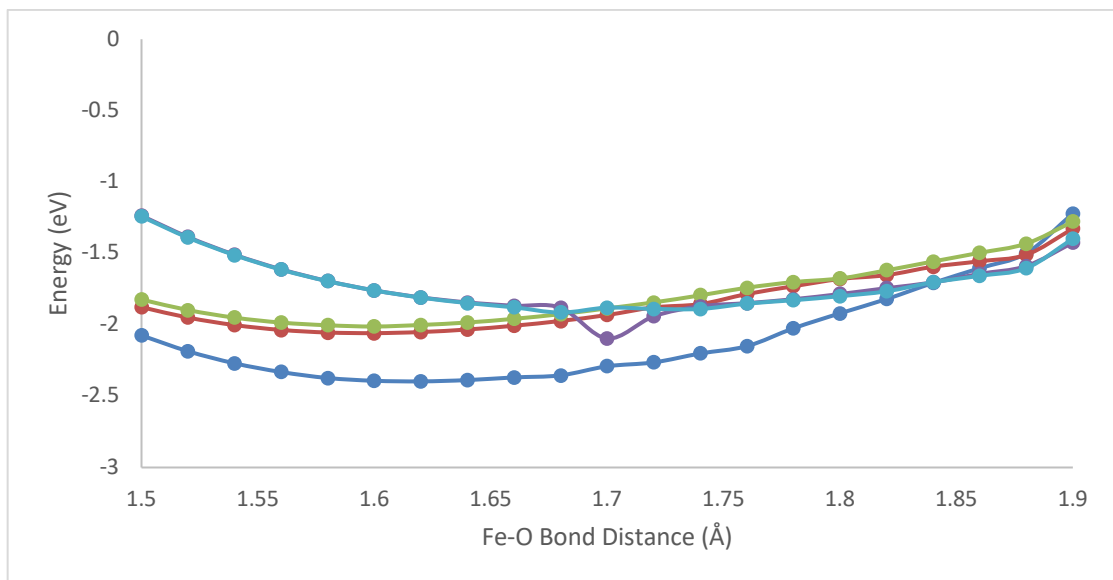


Figure 25. $[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_4]^{2+}$ Triplet CASPT2 (10,8) potential energy curves with the five lowest states.

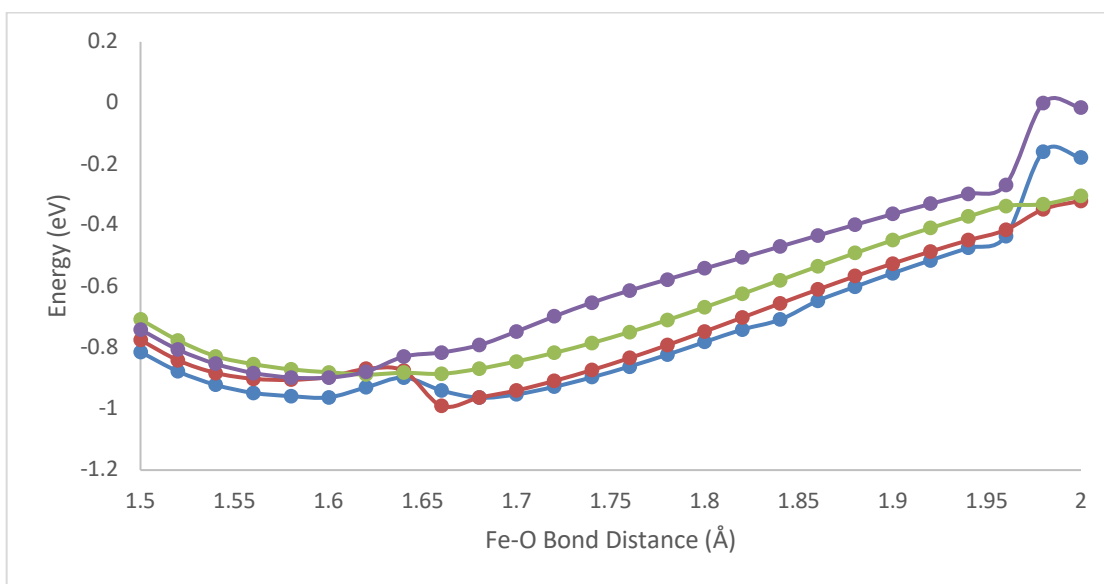


Figure 26. $[\text{FeO}(\text{H}_2\text{O})_4]^{2+}$ Triplet CASPT2 (10,8) potential energy curves with the four lowest states.

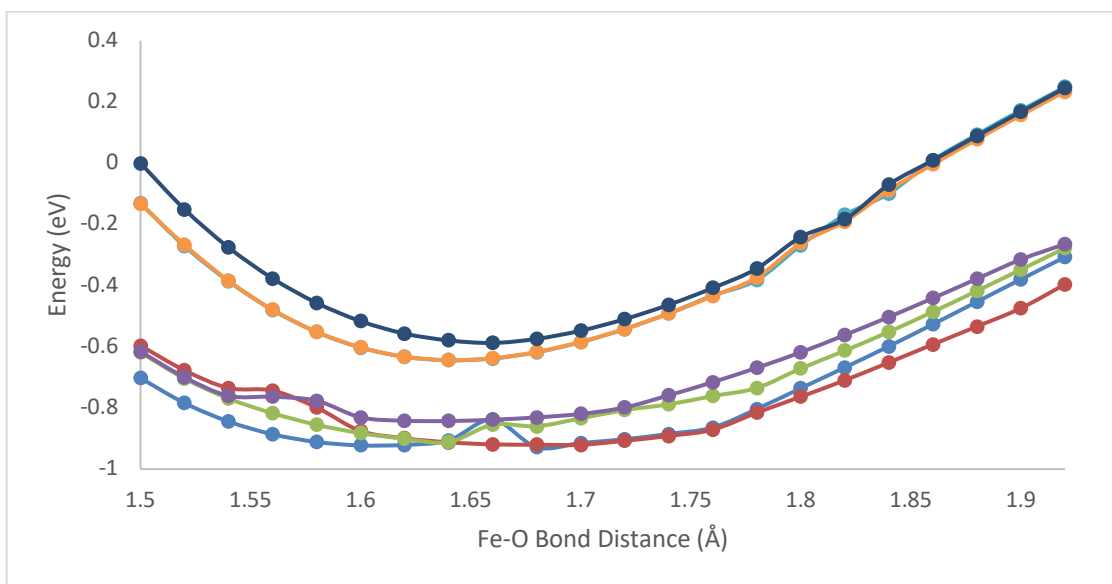


Figure 27. $[\text{FeO}(\text{NH}_3)_4]^{2+}$ Triplet CASPT2 (10,8) potential energy curves with the seven lowest states.

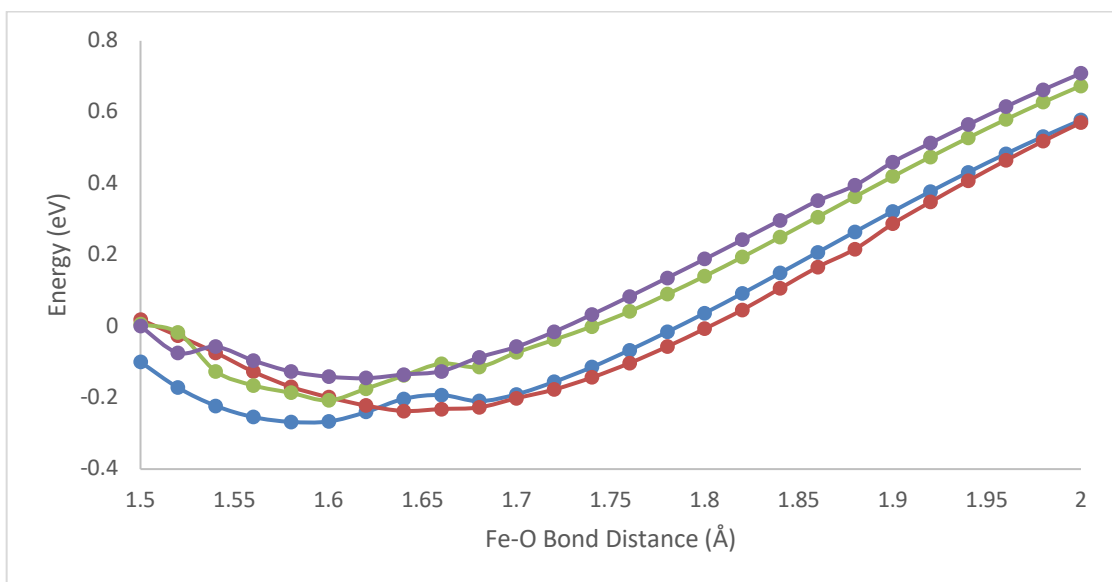


Figure 28. $[\text{FeO}(\text{H}_2\text{O})_{\text{ax}}(\text{NH}_3)_3]^{2+}$ Triplet CASPT2 (10,8) potential energy curves with the four lowest states.

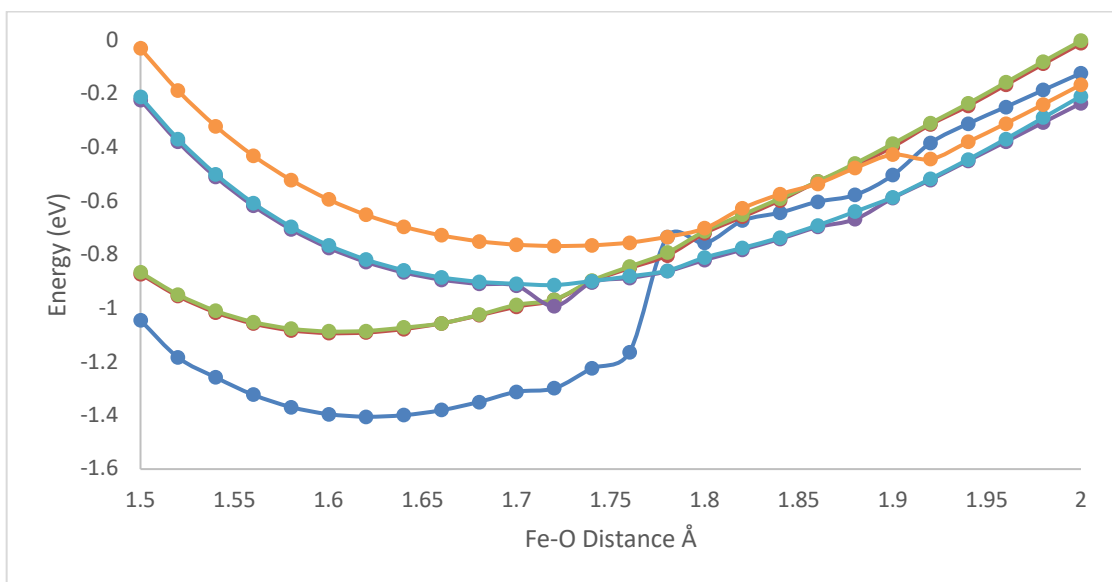


Figure 29. $[\text{FeO}(\text{NH}_3)_5]^{2+}$ Triplet CASPT2 (10,8) potential energy curves with the four lowest states.

Benchmarking Tables

Table 5. Benchmarking information comparing size of basis set and average difference in bond lengths from crystal structure

Iron	1st Coordination Sphere	2nd Coordination Sphere	Other	Functional	Number of Basis Sets	Average Difference (Å)
def2-TZVPP	def2-TZVP	def2-TZVP	def2-TZVP	B3-lyp	1308	0.034
def2-TZVPP	def2-TZVPP	def2-TZVP	def2-TZVP	B3-lyp	1308	0.034
def2-TZVPP	def2-TZVPP	def2-TZVPP	def2-TZVPP	B3-lyp	1644	0.032
def2-TZVPP	def2-TZVPP	def2-TZVP	def-SV(P)	B3-lyp	846	0.033

Table 6. Complete list of benchmark calculations run.

Iron	1st Coordination Sphere	2nd Coordination Sphere	Other	Functional	Average Difference (Å)
def2-TZVPP	def2-TZVP	def2-TZVP	def2-TZVP	B3-lyp	0.034216667
def2-TZVPP	def2-TZVPP	def2-TZVP	def2-TZVP	B3-lyp	0.034666667
def2-TZVPP	def2-TZVPP	def2-TZVPP	def2-TZVPP	B3-lyp	0.032886667
def2-TZVPP	def2-TZVPP	def2-TZVP	def-SV(P)	B3-lyp	0.033186667
def2-TZVPP	def2-TZVPP	def2-TZVP	def2-TZVP	m06	0.011066667
def2-TZVPP	def2-TZVPP	def2-TZVP	def2-TZVP	bh-lyp	0.095196667
def2-TZVP	def2-TZVP	def2-TZVP	def2-TZVP	bh-lyp	0.096896667
def2-TZVPP	def2-TZVPP	def2-TZVP	def2-TZVP	m06	0.045616667
def2-TZVPP	def2-TZVPP	def-SV(P)	def-SV(P)	m06-2x	0.03797
def2-TZVPP	def2-TZVPP	def2-TZVP	def-SV(P)	bh-lyp	0.09647
def2-TZVPP	def2-TZVPP	def2-TZVP	def-SV(P)	b-p	0.037226667
def2-TZVPP	def2-TZVPP	def2-TZVP	def-SV(P)	b-lyp	0.058613333
def2-TZVPP	def2-TZVPP	def2-TZVP	def-SV(P)	m06-2x	0.045836667
def2-TZVPP	def2-TZVPP	def2-TZVP	def-SV(P)	pbe	0.032713333
def2-TZVPP	def2-TZVPP	def2-TZVP	def-SV(P)	pbe0	-0.00296
def2-TZVPP	def2-TZVPP	def2-TZVP	def-SV(P)	tpss	0.02491
def2-TZVPP	def2-TZVPP	def2-TZVP	def-SV(P)	tpssh	0.003086667
def2-TZVPP	def2-TZVPP	def-SV(P)	def-SV(P)	bh-lyp	0.060366667
def2-TZVPP	def2-TZVPP	def-SV(P)	def-SV(P)	B3-lyp	0.01793
def2-TZVPP	def2-TZVPP	def2-TZVP	def-SV(P)	m06	0.160593333

VITA

Bryan Casale was born in Highpoint, North Carolina. He attended Jesuit High School in Tampa Florida where he graduated in 2011. He moved to Tallahassee Florida to pursue a B.S. in Chemistry, graduating in Summer 2016.