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X-ray spectroscopy of geometrically constrained systems

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X-RAY SPECTROSCOPY OF GEOMETRICALLY CONSTRAINED SYSTEMS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

In

The Department of Chemistry

by

Edward E. Doomes
BS, Morehouse College, 1993
August 2002
DEDICATION

This thesis is dedicated to my family.
“The path of the righteous man is beset on all sides by the inequities of the selfish and the tyranny of evil men. Blessed is he who in the name of charity and goodwill shepherds the weak through the valley of darkness, for he is truly his brother’s keeper and the finder of lost children...” Ezekiel 25:17 monologue by Jules (Samuel L. Jackson) in Quentin Tarantino’s Pulp Fiction
EED gratefully acknowledges support from the Huel D. Perkins Fellowship for the first four years of his graduate studies.
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ABSTRACT

Hard X-rays (2 KeV or greater) are used as spectroscopic tools in the characterization of chemical systems. X-ray absorption near edge structure (XANES) spectroscopy is used to characterize multiple groups of chemicals in a systematic fashion. This thesis focuses on chemical systems that in some context have geometrical constraints on their structure. They include self-assembled \( n \)-alkanethiol monolayers that are tethered to silver substrates, cyclic sulfides, and \((\text{Bis(diphenylphosphino) alkane tetracarbonyl metal complexes.})\) The study of \( n \)-alkanethiol monolayers on Ag(111) contains the first observation in the literature of an anomalous resonance in the 18 carbon monolayer. A new interpretation of a subthreshold feature and spectra of improved quality versus previously published work are reported for cyclic polymethylene sulfides. X-ray reflectivity is used to make qualitative assessments of differences in the surface morphology of \( n \)-alkanethiol monolayers on silver substrates. The first inner shell excitation spectra of \( \text{Bis(diphenylphosphino) alkane chromium complexes (alkane=methane, ethane, propane)} \) are presented in addition to the first spectra of \( \text{Bis(diphenylphosphino) ethane molybdenum and Bis(diphenylphosphino) ethane tungsten.} \) All of these \( \text{(Bis(diphenylphosphino) alkane tetracarbonyl metal complexes are examined in two ways, at both an inner shell orbital of the metal and at the phosphorus K-edge of the bridging ligand. These studies show that the inner shell X-ray spectra are sensitive to molecular geometry, bond angle, and molecular symmetry over a wide spectral range.} \)
1. INTRODUCTION

1.1 Motivation and Overview

This body of work is the latest chapter in the ongoing greater body of research conducted by this research group\textsuperscript{1-15} and many other experimenters who use inner and/or outer shell excitation to probe novel molecular systems. The research in the included projects varies somewhat; several systems are examined – they include \( n \)-alkanethiol monolayers, cyclic sulfides, and (Bis(diphenylphosphino) alkane tetracarbonyl metal complexes. Although at a glance, the systems appear dissimilar, and in many ways they are, they are unified by the spectroscopy that is used to characterize them and the opportunity that is presented to correlate X-ray spectroscopic structure with previously unexplored changes in molecular structure. In each case, a core electron is ejected by synchrotron radiation and the subsequent events that accompany this photoejection give information on the target system.

The primary spectroscopic technique\textsuperscript{16,17} used in this work is X-ray Absorption Near Edge Spectroscopy (XANES), and the specific kinds of information available from this technique includes and is not limited to oxidation state, electronic state, local structure, extended structure, and orientation. In the context of this work, X-ray reflectivity is used as an ancillary technique for surface-based systems of alkanethiols on silver, and provides general information on the overall order and feature height of surfaces. The molecular systems included in this work have been chosen carefully, because one of the key objectives is to characterize spectroscopic
trends that will allow for a greater understanding of the properties of useful materials and subsequently aid in the design of materials that have specific properties.

One of the motivations for this work is derived from recent valence-shell photoionization studies of CO$_2$. In that work, the continuum resonances were found to be strongly dependent on bond angle, and the result was that transitions with one quantum of bending excitation were observed, and such electronic transitions are forbidden. Because there are strong connections between valence and core-shell spectroscopies, it is reasonable to assume that connections between bond angle and photoexcitation dynamics will persist as one shifts from the VUV region to the X-ray.

A recurring theme in the research performed in the Poliakoff group has been the study of the effects of changes in molecular degrees of freedom on photoionization dynamics in the vacuum ultraviolet region. While these studies have been fruitful, there is a fairly high level of difficulty in performing the experiments, as the effects are usually subtle. This body of work takes a complementary approach, utilizing hard X-rays (energies on the order of KeV) to probe core shell electrons from systems that are geometrically fixed. There are two significant paths in this particular branch of research. The first system is self-assembled monolayers of $n$-alkanethiols on coinage metal (gold, silver, copper) surfaces. The goal of this study is to better determine the hotly debated structure of these types of systems. XANES spectroscopy is used to support and extend the results obtained in previous Extended X-ray Absorption Fine Structure (EXAFS) studies. The extension of these studies is the examination of ring systems with known geometry. By choosing ring
systems where it is possible to tailor the bond angle, we are able to quantitatively vary the absorbers’ environment and search for a change in the photoionization dynamics.

A previous study forms the foundation for much of the work presented in this dissertation. The sulfur K-edge XANES of $n$-alkanethiols on coinage metals was obtained at grazing incidence. This study was significant for multiple reasons. First, it included the first report of such a system on a gold substrate. Second, and equally if not more significant, was the fact that there was a chain length dependence on the spectra that were obtained on silver substrates. Specifically, the 18-carbon thiol was determined to have a unique adsorption structure that was not seen in shorter chain lengths. This structure is made apparent by the following figure that displays the fourier transform of the EXAFS function for three thiol chain lengths. A model was constructed and fit to the data. This model indicated that for C$_{18}$, the thiols adsorbed on atop sites in addition to the three-fold hollow sites where adsorption occurred exclusively for the other chain lengths.

The chain length dependence of the radial distribution function led to more careful analysis of the XANES region, as the sulfur is the point of attachment between the alkane portion of the system and the metallic substrate. It follows that the chemical state of the sulfur head group should be a direct indicator of the state of the overall system. This result led to the subsequent studies of systems with geometrical constraints.
After preliminary results from studies on self-assembled systems, cyclic polymethylene sulfides and ring-containing octahedral metal complexes were chosen as the target ring systems. The cyclic sulfides were chosen as an offshoot of surface work with alkanethiol monolayers. Our work with $n$-alkanethiol monolayers on coinage metal surfaces verified that with small changes in the sulfur absorber environment, dramatic differences are seen in the sulfur XANES spectra. However, because of uncertainty in the accuracy of our structural model, there is limited certainty in conclusions that correlate absorber environment with geometry. In the
cases of the cyclic sulfides, and the metal complexes, complimentary techniques such as electron diffraction and X-ray crystallography provide reliable structural information that allows us to effectively eliminate structural variables from the experiments and focus solely on the connection of spectroscopic features to structure. This approach allows an escape from the uncertainties inherent in EXAFS and XANES, in which structure is elucidated from spectra and spectra are reconciled partially, if not entirely from theoretical calculations that offer only approximations of the structure. The octahedral metal bidentate ligand complexes are particularly interesting because they allow us to obtain information from a strong backscatterer (the metal center) as well as its satellites (the phosphorous atoms).

One of the motivations for this work was to understand the relation between molecular structure and XANES structure better. The existence of XANES has been known for some time. Kossel presented the first explanation of near-edge structure in 1920. The structure that is now known as XANES initially was known as “Kossel structure.” It was known that the type of absorber, for example monatomic versus diatomic, affected the structure that was observed. However, for many years no substantial development in theory was advanced that led to greater understanding of XANES. This changed in 1966, when LaVilla and Deslattes reported the X-ray absorption spectrum of SF$_6$ at the sulfur K-edge. This study was the first extensive X-ray absorption study of a molecular gas with octahedral symmetry. At the time of their work, the available base of X-ray absorption spectra was small, consisting mainly of smaller two-coordinated, three-coordinated and four-coordinated gaseous molecules. Their goal was to find a molecule that would provide a stern test for the
theory of Hartree, Kronig, and Peterson.\textsuperscript{25} Hartree et al calculated the K-shell absorption of Ge in GeCl$_4$. This calculation was found to be in satisfactory agreement with experimental data published by Coster and Klamer.\textsuperscript{26} Lavilla and Deslattes’ SF$_6$ spectrum was shifted to higher energy relative to H$_2$S, and there was a large change in amplitude of the features that were observed. This result differed from previous measurements on gases of lower coordination in both the near edge region and far into the continuum. This result sparked interest in better explaining the near-edge structure of molecules. Shortly thereafter, Dehmer presented a comprehensive study of the X-ray absorption spectra of atomic centers with electronegative substituents\textsuperscript{27}. His work was the first to offer a full treatment of the near-edge structure with the concept of an effective potential barrier. In the area of the molecule close to the electropositive center, the photoelectron is subject to attractive forces from the partially screened nucleus. Attractive forces also affect the photoelectron at large distances from the nucleus in the region where the electron interacts only with the Coulomb attraction of the molecular ion. In the region of intermediate distance, in the vicinity of the electronegative atoms, the potential may be repulsive and the photoelectron can be quasi-bound momentarily by the competition between the opposing potentials. This is the genesis of the modern concept of the shape resonance in XANES spectra.

There are several models used to interpret XANES spectra. The following discussion focuses on the two prevalent schools of thought in the interpretation of XANES spectra. This discussion is not comprehensive, but it is reflective of the current debate in the literature.
Stöhr derived empirical rules that establish a linear relationship between carbon-carbon bond length and resonance position in chemisorbed hydrocarbons. The premise of this supposition is that once the linear relationship is established for a chemically similar series of molecules, the resonance position of a related molecule can be placed on the linear plot and the bond length can be determined by its position. It should be pointed out that in the original work by Stöhr, the empirical rule was applied only to the specific case of simple hydrocarbons adsorbed on substrates, and was not applied to other systems. An obvious question is whether in fact this empirical rule has general applicability beyond the initial systems that were examined.

Another school of thought on the interpretation of XANES spectra disagrees with Stöhr’s hypothesis on “bond length with a ruler.” This group believes that if such a relationship exists at all, it is an extremely loose correlation that is subject to other molecular considerations. Beyond disputing the validity of the assertion that bond lengths may be interpreted with linear fits, Piancastelli challenges the thinking of many authors who assign any above-threshold modulation in the absorption coefficient as a shape resonance. She presents the argument that shape-resonant phenomena depend on the molecular potential barrier, which requires a much more sophisticated interpretation than a simple linear relationship between the appearance of the shape resonance and the position of the absorption edge. The primary factors that determine the energetic position of a shape resonance are the shape, height, and width of the potential barrier. It is obvious that other structural changes might exert leverage on the X-ray spectra, and a major theme of this research is to search
for other structure-spectra correlations that are overlooked in the previous debates that have encompassed XANES spectroscopy.

1.2 Outline

The contents of this dissertation are as follows. Chapter one serves as an introduction and overview of the included work. In chapter two, a review of the theoretical and experimental background for the experiments performed is presented. Grazing incidence XANES studies of self-assembled monolayers of $n$-alkanethiols on silver are discussed in detail in section 3.1. The relation between geometry and photoabsorption in the sulfur K-edge near edge spectra of cyclic sulfides in the region below the ionization potential is explored in section 3.2. Section 3.3 details a series of XANES experiments on [Bis]-diphenylphosphino alkane chromium tetracarbonyl complexes, where the relation between fixed molecular geometry and the XANES structure of a series of ring compounds is revisited. A related study on tungsten and molybdenum tetracarbonyl ethane complexes is described in section 3.4. Section 3.5 summarizes the results to date of characterization of $n$-alkanethiol monolayers with reflectivity. Conclusions about the results obtained and the outlook for future study are summarized in chapter 4.
2. REVIEW OF SPECTROSCOPY AND EXPERIMENTAL TECHNIQUES

2.1 Background Information

This chapter serves as an introduction to the basic principles used in conducting the research in this thesis. It provides a cursory review of the types of radiation facilities used, the experimental infrastructure, and the spectroscopic techniques used to complete the experiments.

2.1.1 Synchrotron Radiation

This research is made possible by the high value of \( I \), the incident radiation provided by synchrotron radiation. The figure below offers a simplified view of a synchrotron.

![Schematic depiction of a synchrotron](image)

Figure 2, Schematic depiction of a synchrotron, showing storage ring, bending magnets (black), rf accelerators (blue), linear accelerator (red), and emitted radiation (yellow).

A synchrotron is comprised of four major components along with many other parts. The essential parts of the facility are the injector that provides a large number
of high-energy electrons, a storage ring that circulates the electrons, bending magnets that steer the electron bunches in the circular orbit, and beamlines that select the energy of interest from the full range of radiation provided by the source. Synchrotron radiation is characterized by its flux - overall intensity and equally if not more significantly, by brilliance - its intensity coupled with directionality, which defines how small a spot and how small a solid angle on which the beam may be focused. The number of photons per second per unit area defines both quantities. The overall intensity of the emitted radiation depends on beam energy and beam radius as will be shown below.

Once an unwanted side effect of accelerator physics experiments, synchrotron radiation has become a vital part of spectroscopic analysis for a growing body of researchers. Synchrotron radiation results from the relativistic acceleration of charged particles. The charged particles emit radiation in a narrow beam that is tangent to the particles' circular path. This beam contains a continuous spectrum that extends from the far-infrared through the X-ray region. The first generation synchrotron radiation sources were particle physics machines (e.g., accelerators that studied high-energy collisions of electrons and positrons) and the synchrotron radiation generated by such instruments was exploited by other types of scientists who wanted the tunable radiation primarily in the X-ray and vacuum ultraviolet (VUV) regions of the spectrum. This use of particle physics accelerators was termed “parasitic operation,” and gave rise to a new class of machines, second-generation sources, which were designed specifically to exploit the radiation that was previously an unwanted energy loss mechanism in the particle physics instrumentation. Third
generation synchrotrons are similar to second generation machines, being built for the sole purpose of providing synchrotron radiation, but with the additional conditions that they are designed around insertion devices (particularly undulators) rather than the bending magnets as the source of the radiation, with the goal that the radiation have higher brightness. Wigglers and undulators are periodic arrays of magnets that induce oscillations in the trajectory of accelerated electrons. Wigglers act as wavelength shifters, while undulators function as intensity amplifiers via interference. The length of the array and the strength of the magnetic field of the array determine the magnitude of the induced oscillations and the increase in photon flux. These devices are placed in straight sections of storage rings and thus are referred to as insertion devices. Examples of these third generation sources are the Advanced Photon Source at Argonne National Laboratory and the Advanced Light Source at Lawrence Berkeley National Laboratory. These facilities provide radiation that is several orders of magnitude brighter than that provided by second-generation sources. Currently, there are approximately 8 storage-ring based synchrotron radiation sources in the United States and about 75 in the world. The bulk of this work was performed at the J. Bennett Johnston, Sr. Center for Advanced Microstructures and Devices (CAMD) synchrotron.31

The decision as to which synchrotron radiation facility is best for a particular experiment is determined in large part by the power of the synchrotron and the critical photon energy at the facility. The power radiated by any particle that is relativistically accelerated in a circular orbit is defined in the following equation.
\[ P = \frac{2e^2 c \gamma^4}{3\rho^2} \]

Equation 1, The power radiated by a synchrotron.

In this expression, \( \rho = \frac{CE}{B} \), where \( E \) is the electron energy and \( B \) is the magnetic field of the dipole bending magnets of the synchrotron. Using the substitution \( E = mc^2 \), \( \gamma = \frac{E}{(m_0 c^2)^2} \), we arrive at the following expression for the power of a synchrotron.

\[ P = \frac{2e^2 c E^4}{3\rho^2 (m_0 c^2)^4} \]

Equation 2, The dependence of the power of a synchrotron on the mass of the accelerated particle.

The previous equation shows that the power of the emitted radiation is proportional to the inverse of the mass of the accelerated particle to the fourth power. This is why electrons are chosen for synchrotrons, as they are the lightest, most readily available subatomic particle. The universal curve for the spectral distribution of the CAMD synchrotron is presented in the following figure.\(^{32,33}\) The curve is characterized by the critical energy, \( h\nu_c \).

The critical energy, \( h\nu_c \), gives an estimate of the range of emitted radiation provided by a synchrotron. This value is not a cut off in the energy, but a guidepost indicating the general range of radiation that is available. Half of the radiated power is above this value and half is below. The upper limit of the usable flux is typically estimated to be a photon energy of four to five times the critical photon energy. The critical energy is defined as follows in equation 3.
Figure 3, Plot of intensity versus photon energy provided by the CAMD source\textsuperscript{31,34,35}

\[ h\nu_c = \frac{3hc\gamma^3}{4\pi p} \]

Equation 3, The critical photon energy of a synchrotron.

The critical energy of the bending magnet radiation from the CAMD storage ring is 1.66 keV at a beam energy of 1.3 GeV and 2.56 keV at a beam energy of 1.5 GeV. This allows for reasonable radiation intensity over the energies of interest for the studies that will be presented in this thesis. For a higher range of photon energies at high flux, a facility such as the NSLS X-ray ring which has a critical energy of 5.6 keV from its bending magnets may be used. At any facility, using an insertion device such as a wiggler or an undulator may increase the critical energy. These devices provide several orders of magnitude higher photon flux versus bending magnet radiation. No such device was used during the course of this work, so they will not be discussed. The CAMD storage ring contains eight bending
magnets with a radius of 2.928 meters. The electron storage ring is operated at either 1.3 GeV or 1.5 GeV. The ring provides high-intensity ($\approx 10^{10}$ photons/mrad/s at 0.1% bandwidth) radiation over the energy range from $\approx 100$ eV to $>10$ KeV. All experiments were performed between $\approx 2$ KeV and $\approx 10$ KeV. The X-ray reflectivity experiments also fell within this energetic range, but required a highly collimated beam and a specialized endstation that were not available at the LSU CAMD facility.

Other synchrotron sources provide a greater energetic range at the high intensity needed for successful X-ray absorption studies. The National Synchrotron Light Source at Brookhaven National Laboratory is a second generation light source of higher intensity and was used in X-ray reflectivity studies that will be discussed later. The NSLS X-ray synchrotron ring is significantly larger than the CAMD ring, with a radius of 85 meters.

One clear implication of the plot of the photon flux versus photon energy above is the scope of experiment that may be performed at the CAMD synchrotron. The upper energy limit of the radiation provided precludes the experimenter from examining the core orbitals (K-edges) of elements beyond $\approx Z=30$ (zinc), on the order of about 10 KeV. As will be shown, this range is adequate for all of the spectroscopy experiments described in this thesis.

### 2.1.2 Monochromators and Beamlines

The full spectrum of synchrotron radiation must be monochromatized into narrow target excitation energies for the purposes of this work. This target energy is selected with the monochromator, which is the principal component of a beamline used for spectroscopic measurements. This is achieved with either crystal or grating
monochromators. The result is a tunable source of high-energy photons that is available to provide access to many experimental arenas that were previously unattainable in a reasonable time frame. Double crystal monochromators produce the energy-selected radiation used in this work. Bragg’s law describes the conditions under which these monochromators work. Incident light striking a crystal with interplanar spacing \( d \) at incident angle \( \theta \) is diffracted according to the following equation.

\[
2d \sin \theta = n\lambda ,
\]

Equation 4, Bragg’s Law for diffraction of radiation. \( n \) must have an integral value. 36

The previous Bragg’s law description where monochromatic radiation is provided with a double crystal monochromator is an idealized scenario. The only factors taken into consideration are the incident angle and the crystal spacing. In practice, the closeness of the atoms in the crystal lattice contributes to loss in the intensity of the refracted radiation by scattering processes. Thus, in a real crystal system, the same crystal spacing that provides the monochromatic light influences the intensity of the radiation that is provided. This limits the range of monochromatized radiation that can be provided at high intensity. In a real crystal set, there is a finite angular width, \( \omega \), that reflection can occur in. This angular range, \( \omega \), is called the rocking curve.

The rocking curve for a given crystal set defines the range of energies and the intensity of the reflected radiation that is provided. The photon flux for the experiments performed at CAMD was on the order of \( 10^8 \) photons/sec. At low energy, bandwidth was at least 0.5 eV for experiments at low energy (sulfur,
phosphorus, and chromium K-edges; molybdenum L_{III}-edge) and 2 eV for experiments at high energy (chromium K-edge, Tungsten L_{III}-edge). This level of resolution is more than adequate for the studies presented, because the lifetime of the core-shell electrons induces Heisenberg broadening that is greater than these values.

Figure 4, Bragg's law; theta is the angle of the incident radiation; d is the interplanar spacing of the crystal; O, P, and R are the positions of atoms in the lattice.
The primary beamline used in this work is depicted in the following figure.

![Schematic view of the double crystal monochromator (DCM) beamline at CAMD.](image)

Figure 5, Schematic view of the double crystal monochromator (DCM) beamline at CAMD.

\[
\omega = \frac{2}{\sin 2\theta_B} \frac{r_0 \lambda^2}{\pi V} C |F_h| e^{-M}
\]

Equation 5, \(\omega\), the rocking curve of a double crystal monochromator. \(r_0 = \frac{e^2}{mc^2}\), \(V\) is the unit cell volume of the crystal, \(\lambda\) is the reflected monochromatic wavelength, \(\theta_B\) is the Bragg angle, \(C\) is a polarization factor, and \(e^{-M}\) is the Debye Waller factor for the crystal.

### 2.1.3 Experimental Considerations and Signal Intensity

Before one attempts to perform an experiment, it is wise to assess what information is desired, and what experimental technique is best suited to provide this information. The experiment that is planned is contingent on some observable physical phenomenon and the experimenter’s ability to record it. Also, the magnitude of the signal intensity needs to be defined (e.g. the number of photons produced that
can be collected in a reasonable experimental time frame). The fraction of events which can be detected with the chosen method must also be considered. Other significant concerns are the amount of data that should be taken and the precision that is required. After addressing these issues, the experiment should be set up with everything except the light source. How far in advance this preparation should occur should be assessed in terms of which component of the experiment takes longest to repair or replace in the event of failure.

For EXAFS and XANES experiments, there are several experimental strategies that are readily available, namely fluorescence yield, electron yield, and photoabsorption. First, the best type of experiment must be determined, detecting a fluorescent photon, an ejected electron, or photoabsorption of incident radiation. The number of both fluorescent photons and Auger electrons is proportional to the number of core holes created by X-ray absorption. The relative yields of fluorescence decay versus Auger decay are strongly dependent on the atomic number of the absorber. For light atoms (e.g. C, N, O), Auger processes dominate. As atomic number increases, the rate of fluorescence yield relative to Auger increases exponentially. To determine the rate of production for an optically thin sample, we can use a modified form of the Beer-Lambert law.

\[ I_{\text{exc}} = I_0 \rho n \sigma \ell \]
Equation 6, Beer-Lambert law applied to photoabsorption.

The number of excitations is equal to the product of the intensity of the incident radiation (photons/s), the number density of the sample (cm\(^{-3}\)), the molecular cross section (cm\(^2\)) of the sample and the path length (cm). By doing this relatively simple
calculation it is possible to immediately determine whether the intensity of the
radiation source is sufficient to perform a viable experiment, and it is possible to
determine approximately how long it will take to collect data.

Fluorescence intensity may be approximated as follows.

\[ I_{\beta} = I_{\text{exc}} f_{\beta} f_{\text{coll}} E_{\text{det}} \]

Equation 7, approximation of the fluorescence intensity for a XANES or EXAFS
experiment.\(^{39}\)

The number of excitations, \( I_{\text{exc}} \) equals the product of the incident intensity, \( I_0 \), the
number of target atoms, \( n \), the atomic cross-section, \( \sigma \); and \( l \) is the path length in cm.

The observed fluorescence, \( I_{\text{fl}} \) equals the product of \( I_{\text{exc}} \), the fraction of molecules that
fluoresce, \( f_{\text{fl}} \); the fraction that are collected, \( f_{\text{coll}} \), and the efficiency of the detector,
\( E_{\text{det}} \).

We can also go into greater detail in determining the expected signal for an electron
yield experiment. The following expression represents the total electron yield signal\(^{39}\)

\[ I_{\tau}(h\nu) = \frac{\Omega}{4\pi} I_0 A_0 \sigma(h\nu) \rho \omega \]

Equation 8, approximation of electron yield signal

The total electron yield signal, \( I_{\tau}(\theta, h\nu) \) is the product of the solid angle fraction, \( \frac{\Omega}{4\pi} \),
the incident photon flux, \( I_0 \), the area exposed to the beam, \( A_0 \), the absorption cross-
section, \( \sigma \), the atomic density, \( \rho \), and the nonradiative Auger yield, \( \omega \).
2.1.4 Ion Chambers

Gas-phase photoabsorption experiments in this work employ ionization chambers, which measure current generated by incident radiation striking and photoejecting electrons from the gas that is present. This current is related to the absorption cross-section of the gas in the chamber. The Beer-Lambert law for photoionization in a single ion chamber is as follows.

\[ I = I_0 e^{-\mu d} \]

Equation 9, Beer-Lambert law for photoionization in a single ion chamber.

\[ I_0 = \frac{i_1}{e^{\left(1 - e^{\mu d}\right)}} \]

Equation 10, Incident beam intensity for a single ion chamber.

\[ I_0 = \frac{i_1}{e^{\left(1 - e^{-2\mu d}\right)}} \]

Equation 11, Incident beam intensity for a double ion chamber.

The following two equations are expressions for the intensity of the incident radiation and the absorption coefficient of the sample.

\[ I_0 = \frac{i_1^2}{e(i_1 - i_2)} \]

Equation 12, Absorbed beam as a function of currents from ion chambers.

\[ \mu = \frac{1}{d} \ln \left( \frac{i_1}{i_2} \right) \]

Equation 13, Absorption coefficient as determined with ion currents.

Thus, the absolute intensity and the absorption coefficient may be determined with the currents from the two ion chambers. These values for the ion currents, \( i_1 \) and \( i_2 \) are insensitive to variations in pressure, temperature, and source intensity allowing for measurement of the absorption cross-section without separate ion
chambers. This construct is extremely useful for noxious samples that must be isolated from as many beamline components as possible.

2.1.5 Fluorescence Detectors and Multichannel Analyzers

A Ge fluorescence detector of the p-i-n type was employed to detect fluorescent photons from \( n \)-alkanethiol monolayers on silver substrates examined at the XMP beamline. The detector consists of three layers; a p-type region; an intrinsic, or depleted region; and an electron rich n-type region. Incident photons strike the p-type region and a highly energetic photoelectron is emitted that elevates thousands of electrons into the conduction band. The n-type region is attached to a biased contact. The resistivity gradient across the three layers allows a current to be measured that is proportional to the energy and the number of photons that strike the detector surface. The current that is measured is then amplified and converted to digital pulses that form a spectrum.

![Diagram of Pulse Height vs Channel Number](image)

Figure 6, Simplified depiction of the output of a dispersive element semiconductor detector.

The output spectrum is then windowed about the desired fluorescence and the integrated area the peak is plotted against the photon energy.
2.2 On the Origin of K, L, and M Edges

XANES and EXAFS are techniques that study fine details in the vicinity of X-ray absorption edges. An absorption edge arises when energy of an incident photon interacting with an atom is equal to the energy necessary to eject an electron from a specific core subshell of the atom. The initial intense peak that is seen in XANES and EXAFS is commonly referred to as the “white line” peak. This designation comes from early spectra that relied on X-ray film, where the emissions were detected as exposures, and the white line was a very strong exposure. In the vicinity of the white line peak, the kinetic energy of the excited electron goes through a zero in energy and an outer electron fills the vacancy that is created by ejecting this core electron. The most commonly used absorption edges are the K and L edges. The designations K and L are from the German “Kurtz” and “Lang”, referring respectively to short and long wavelengths. These arise from inner shell vacancies and the emission of energy (or absorption of incident radiation) that accompanies the transition of higher energy electrons to fill these vacancies. There is one K-edge that results from ejecting the degenerate 1s electrons, which have a principal quantum number of 1. The L_I, L_II, and L_III edges are respectively from transitions to the non-degenerate 2s, 2p^{1/2}, and 2p^{3/2} vacancies. The photoabsorption and fluorescence excitation spectra presented may be divided into two distinct regions, subthreshold (bound states) and the continuum (where the electron of interest is no longer attached to molecular orbitals). All of these transitions are governed by selection rules. The absorbing center is struck by a photon, and the photon’s angular
momentum is completely transferred to an electron. Because a photon has a single unit of angular momentum, the change in angular momentum for the excited electron must be \( \Delta \ell = \pm 1 \),\(^{41}\) which is the Laporte rule and is true for dipole transitions. This interpretation is sufficient for describing the relevant subthreshold resonances in the spectra presented. (The situation is more complex for the continuum electron in molecular systems, because the electron can rescatter multiple times in the anisotropic molecular environment\(^ {27}\).) The overall selection rules for \( 1s \rightarrow \) bound-state electronic transitions are as follows, \( \Delta \ell = \pm 1, \Delta m = 0, \pm 1; \) and \( \Delta n \) may have any value (restricted only by cross-section and symmetry considerations).

### 2.3 X-Ray Absorption Spectroscopy

X-ray absorption spectra are the result of electronic transitions between initial and final states \( \Psi_i \) and \( \Psi_f \). The X-ray absorption coefficient, \( \mu \), may be described by the following equation. The X-ray absorption, \( \mu \) is shown to be a function of \( p \), the momentum operator, and \( A(r) \), the vector potential of the incident electromagnetic field.

\[
\mu \propto \sum_f \left| \langle \Psi_f | p \cdot A(R) | \Psi_i \rangle \right|^2 \delta \left( E_f - E_i - \hbar \omega \right)
\]

Equation 14, Absorption coefficient for an X-ray transition.\(^ {42}\)

Historically, transitions from core orbitals were viewed as being atomic-like, and insensitive to the chemical state of the absorbing molecule. It was commonly believed that the valence shell electrons and the core potential were the only bellwethers to the chemical state of the molecule. However, a wealth of work has been done that contradicts this early view that core electrons were distant and
unaffected by the chemical state of the molecule. A.P. Hitchcock’s “Bibliography of Atomic and Molecular Inner-Shell Excitation Studies,” is an excellent reference that provides a voluminous listing of studies that use photon impact, electron impact, and theory to describe X-ray transitions of inner-shell electrons in various atomic and chemical systems. In light of the sensitivity of core electrons to chemical state and molecular structure, this work attempts to further develop systematic relationships between the inner-shell electron, molecular structure, and electronic structure. These X-ray transitions are governed by selection rules and expressions that define the probability of transition.

![Figure 7](image.png)

Figure 7, Illustration of the Franck-Condon principle. Black curve is ground state, red and green curves represent states of higher potential energy.

The probability of a transition may be described by the Franck-Condon principle. In simplest terms, the Franck-Condon principle states that on the time scale that electronic transitions occur in, the motion of the nucleus is negligible. Transitions of
interest go from ground state to states of higher potential energy. Excited states that have overlapping internuclear separation may be reached by vertical transitions from the ground state. The verticality of a transition is defined by the absence of change in the internuclear distance within the time frame of the transition. Two closely related facets of X-ray absorption spectroscopy are discussed in the following sub-sections (2.3.1 and 2.3.2). An overview of EXAFS spectroscopy is presented in 2.3.1. This technique was used in preliminary studies that were precursors to the work presented in this thesis. Both XANES and EXAFS spectroscopy are the result of scattering processes. EXAFS is the simpler of the two processes, as it is the result of single-scattering processes, so it will be discussed first. The XANES region is taken by default in acquiring EXAFS data, although generally not at the resolution required for a XANES specific experiment. The two techniques are closely related and provide complimentary information. Section 2.3.2 is dedicated to XANES spectroscopy, the primary technique used in the studies discussed in the results and discussion chapter (chapter three).

2.3.1 Extended X-ray Absorption Fine Structure Spectroscopy

EXAFS is the oscillatory structure found in the post-edge region of X-ray absorption spectra. Monochromatic X-rays allow for selective excitation of core electrons, which makes it possible to obtain molecular information via Extended X-ray Absorption Fine Structure (EXAFS). An incident X-ray strikes the target atom, ejecting a photoelectron that is backscattered into the target atom’s environment
Figure 8, X-ray absorption spectrum of a copper foil.  The inset graph shows the XANES region.

Figure 9, Simplified depiction of EXAFS backscattering.

Constructive and destructive interference between the outgoing photoelectron wave and the backscattered photoelectron wave causes a modulation in the absorption spectrum, seen as wiggles or “EXAFS.” This may be viewed as a
modulation in the transition probability $\langle \psi_i | \hat{\mu} | \psi_f \rangle$. Interference between the ejected photoelectron and its backscattering, which is a function of the local environment, creates a modulation in the final states. The overlap between the initial and final states is modified by the locally determined influence on $\psi_f$. The region from about 50 eV below the absorption edge to about 200 eV above the edge is known as the XANES region. The region from just below the absorption edge to approximately 1000 eV above the edge is the EXAFS region. A Fourier transform of the EXAFS function with respect to the photoelectron wave number provides the peak corresponding to the nearest neighbor interatomic distance.\(^\text{17}\)

In order to understand the EXAFS interaction, a review of the photoelectric effect and the particle-wave duality of the electron is helpful. The Einstein relation states that

$$E = h\nu = hc / \lambda$$
Equation 15, the Einstein relation.

This equation defines the relationship between a photon’s energy and its wavelength. Additionally, the DeBroglie equation relates an electron’s wavelength to its momentum.

The wave vector is defined as follows.

$$k = 2\pi / \lambda$$
Equation 16, the DeBroglie wave vector.
Table 1, Schematic depiction of several backscattering scenarios. The red sphere labeled “A” is the absorption center. The green sphere labeled “B” and the blue sphere labeled “C” are neighboring atoms with unique identities. The summing of the outgoing and backscattered wave is illustrated to be a function of distance, geometry, number and identity of the neighboring atoms.
The kinetic energy of the electron is given as follows.

\[ K.E. = \frac{p^2}{2m} = \frac{h^2k^2}{2m_e} \]

Equation 17, the kinetic energy of an electron.

Consequently, for a photoelectron with kinetic energy \((E - E_0)\), we can write

\[ k = \left[ \frac{2m}{h^2} (E - E_0) \right]^{1/2} \]

Equation 18, Expression relating the wave vector \(k\) to \(E_0\).

This equation relates the photoelectron wave vector \(k\) to the threshold energy of the electronic shell of interest in the target atom. It is the transformation of the spherical photoelectron wave vector \(k\) that allows the measurement of the “EXAFS.” The EXAFS function is defined as the modulation in the X-ray absorption rate normalized to the background.\(^{45}\)

\[ \chi(E) = \frac{\mu_e - \mu_0(E)}{\mu_0(E)} \]

Equation 19, the energy-dependent EXAFS function.

\(\chi\) represents the EXAFS function, \(\mu_e\) represents the absorption, and \(\mu_0\) represents the background absorption. The expression for \(\chi(k)\) is where the distance information of backscatterers is obtained. The expression is the sum of the backscattering contributions of the \(j^{th}\) atom.

\[ \chi(k) = \sum_j N_j S_j(k) F_j(k) e^{-2\sigma_j 2k^2} e^{-2r_j \lambda_j(k)} \sin(2kr_j + \phi_j(k) / kr_j) \]

Equation 20, the EXAFS function in terms of \(k\)-space

Fundamental parts of this equation\(^{17}\) are the backscattering amplitude \(N_j F_j(k)\); reduction factors \(S_j(k), e^{-2\sigma_j 2k^2}, e^{-2r_j \lambda_j(k)}\); the \(1/kr_j^2\) distance dependence, the
sinusoidal oscillation that is a function of the interatomic distance \((2kr_j^2)\) and the phase shift \([\phi_k(k)]\).

Well-established procedures for data analysis are used to elucidate interatomic distances from raw EXAFS data.\(^{16,46}\) Energy calibration, pre-edge and post-edge background subtraction, deglitching (removal of anomalous spikes in the raw data) and normalization are performed before transformation of the spectra to \(k\)-space and the subsequent Fourier transform to real space. Fitting of theoretical EXAFS functions to real data is done with the FEFF\(^{45}\) or FEFF\(^{47}\) code in conjunction with the WINXAS\(^{48,49}\) program. The algorithm used for fitting the data employs a least-squares minimization procedure wherein the input parameters are varied incrementally until a minimum in the difference between the theoretical EXAFS function and the real EXAFS data is reached.

### 2.3.2 X-ray Absorption Near-Edge Structure Spectroscopy

The near-edge region requires different treatment than the EXAFS region because the kinetic energy of the photoelectron is small and multiple scattering processes dominate versus the single-scattering events in the EXAFS region. It will be shown that multiple-scattering processes in the XANES region require a sophisticated model of the molecular potential. In XANES spectroscopy, a core electron is excited with X-ray photons, enters bound state(s), is quasi-bound in the continuum and is then completely ejected. At the most basic level, XANES spectra are analyzed by “fingerprinting”, or pattern recognition. Features seen in a well characterized system are cataloged and assigned. The similarity of spectral features
in an alternative system leads to the conclusion that the two systems share some physical feature. Although this approach is useful in many cases, its empirical nature is extremely subjective and often leads to errors in the interpretation of the spectra. This work will use a systematic approach to vary structure and establish unambiguous relationships with the spectroscopic data from the molecules. The spectra are signatures of the chemical state of the absorbing molecule. The threshold for trapping an electron in a quasibound shape resonance state near the ionization threshold of a core absorber is an extremely sensitive probe of molecular and electronic structure. The resonances seen in the XANES region may be ascribed to several entities, which may include vacant molecular orbitals, Rydberg levels, shake-up, shake off, and/or shape resonances. Shake-up refers to exciting another electron to a higher state as a result of transfer of kinetic energy from the outgoing electron. Shake-off refers to ejection of another electron as a result of transfer of kinetic energy from the outgoing electron. Shape resonances are quasibound states in which a photoelectron is temporarily trapped by a centrifugal barrier in the molecular potential.

XANES spectra give us a wealth of information on the absorbing atom; the presence or absence of specific bonds, the oxidation state of the absorber and in some cases, the length of the bonds and the orientation about the absorbing atom. To use this analysis technique, a large database of XANES spectra of known molecules is needed. It is also necessary to have as accurate a model of the target molecule’s molecular orbitals as is possible. It is then possible to systematically identify peak positions and intensities for the molecule of interest, match them with
known spectra and then make assignments. It is also possible to identify bound state transitions by correlating them with peaks below the ionization potential.

The XANES region is dominated by strong resonances that originate from transitions to unoccupied molecular orbitals and scattering of the photoelectron within the molecular framework. At low kinetic energy, the photoelectron is typically scattered by atoms at extended distances and/or scattered multiple times within the molecular framework. This is the underlying principle behind the multiple scattering interpretation of XANES structure. The oscillations are not as regular as is the case for EXAFS structure. On the other hand, the excursions in the cross section can be much more pronounced and the sensitivity to local structure can also be very strong.

The transition probability in the XANES region may be written in terms of the initial and final states, a Hamiltonian operator, and the energies of the initial state, \(|i\rangle\) at energy \(E_i\), and the final state \(\langle f|\) at energy \(E_f\). The following equation describes the transition probability.

\[
\Gamma_{i,f} = \frac{2\pi}{\hbar} \left| \langle f | H_{m} | i \rangle \right|^2 \delta(\hbar \nu - E_f + E_i)
\]

Equation 21, Transition probability between an initial and final state in the XANES region.

The quantity that is measured in the XANES spectra presented in this work is the photoabsorption cross-section\(^{53}\). The absorption cross-section is the summation of all the final states in the previously defined transition probability.

\[
\sigma(\omega) = 4\pi \alpha \varepsilon \sum_j \left| \langle f | \vec{r} \rangle | i \rangle \right|^2 \delta(\hbar \omega - \Delta E_{j-i})
\]

Equation 22, The absorption cross-section.
The quantity $\mathcal{F}$ is the electric dipole operator, and $\alpha$ is the fine structure constant ($1/137$).

The absorption cross-section has been defined, but the relative energetic position of the absorption edge has not been addressed. Each edge appears in a limited range of energies that are specific to the orbital that the photoelectron is excited from and the atomic number of the core that it is associated with. Within this general range of energies, the position of the white line in a XANES spectrum is dependent on the oxidation state of the absorber. As is the case in X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA), the binding of the photoelectron in XANES is related to the effective charge associated with the core absorber. An example is sulfur, which exists in oxidation states $-2$, $0$, $+2$, $+4$, and $+6$. The position of the white line ranges from $\approx 2472$ to $\approx 2490$ for these oxidation states. This allows for easy identification of the oxidation state of absorbers.

Stöhr used aromatic hydrocarbons in an early example of fingerprinting with XANES spectroscopy. The spectrum of a similar simple system, benzene, is used to make peak assignments by inspection and comparison. The benzene XANES spectrum is marked by several strong, well-separated resonances. By carefully examining and making assignments to the spectra of benzene as a gas sample, a multilayer sample on a metallic substrate, and as a monolayer on a metallic substrate, it is possible to make assignments and qualitative assessment of the character of related molecules. More recently, ab initio calculations using full-multiple scattering have been used to assign shape resonances and relate their position to
The relative intensities of features may be used to determine the molecular orientation and/or level of hybridization. In addition, it is possible to use simulations to model the systems. The primary objective in the XANES studies presented here is to identify spectroscopic trends in simple systems, laying the groundwork for future characterization of novel materials and unknown systems. It is also important to test the prevailing models that are used, often incorrectly, to draw conclusions about XANES data.

2.4 Quantum Mechanical Modeling

The experimental work conducted within the scope of this thesis was supplemented with quantum mechanical calculations of selected systems. Although the focus of the work is firmly entrenched in the experiments, these calculations provide useful insights that aid in interpretation of the spectra. There are two approaches, ab initio calculations and semi empirical calculations. Each approach has its merits and limitations, which will be discussed briefly. Ab initio calculations rely solely on an accurate Hamiltonian and fundamental physical constants. Conversely, semiempirical calculations use a simplified Hamiltonian and adjustable parameters that are set based on experimental data and the results of ab initio calculations. Both methods have shortcomings that affect their accuracy. Ab initio calculations approximate the molecular wavefunction as a product of the wavefunctions of the individual electronic spin-orbitals. This imposes a finite basis set that cannot fully describe the overall electronic structure. Semiempirical calculations simplify the Hamiltonian, which imposes inaccuracy on any result from the outset. Semiempirical calculations also rely on experimental results and the
results of *ab initio* calculations, each of which may not be appropriate for the molecular system of interest. Each type of quantum mechanical calculation depends strongly on the basis set, the representation of the atomic orbitals that is chosen. There are several approximations of atomic and molecular orbitals, including but not limited to Slater-type orbitals and Gaussian-type functions, which may be used. The basis sets that are formed from the chosen orbital types vary in how the functions that represent the orbitals are combined. This work uses standard basis sets from the literature.

The specific calculations that are included in this work are FEFF 8.10 calculations\(^47\) and HyperChem Pro 6 calculations.\(^60\) The HyperChem calculations provide several important pieces of information on the molecular systems that are simulated. The molecular orbital simulation provides the relative energies of the highest energy-occupied molecular orbital (HOMO) and the relative energies of unoccupied levels (LUMOS). The HyperChem calculations also identify orbital symmetries and provide three-dimensional renderings of the potential energy surfaces of the orbitals. These calculations may be performed at the semiempirical or *ab initio* level and may include any of a number of basis sets for the molecular orbitals. At the *ab initio level* the orbitals used are Gaussian-type, while at the semiempirical level Slater-type orbitals are used. The calculations are Hartree-Fock Self-Consistent Field type, which minimize the integral of the antisymmetric product of the one-electron functions that make up the orbitals evaluated with the Hamiltonian of the system.
\[ \int \phi^* \mathcal{H} \phi \, d\tau \]

Equation 23, Hartree-Fock transition probability integral

Although extremely useful, the HyperChem calculations do not allow for the simulation of the continuum wavefunctions that are central to the XANES investigation. The simulated X-ray spectra presented in this work were created with the FEFF 8.10 code. All spectra simulated with the FEFF 8.10 code were constructed with a muffin-tin type approximation using overlapping atomic potentials. Spherical scattering potentials approximate the absorber and its neighbors. The individual muffin tins are described by atomic phase shifts, which are calculated from spherically symmetric atomic-like potentials inside the muffin tins. The scattering centers are connected with Green’s-function propagators. The interstitial region and the scattering potentials are significant for XANES calculations because the scattered electron has low kinetic energy and often requires sophisticated approximations of the interatomic potential. The model Hamiltonian simulates exchange interactions as local potentials. As described previously, the photoelectron in the XANES region is subject to multiple scattering and long-range scattering effects. It is also significant that the FEFF 8.10 creates model spectra strictly within the framework of multiple scattering. It excludes any effects that are due to multi-electron effects.

It will be shown in subsequent chapters that the way that the calculation is defined not only influences the magnitude of the energy splitting of features and orbitals, but may also be determinative of the relative positions of features and the absolute outcome of the calculation.
Figure 10, Illustrative view of muffin tin approximation with non-overlapping spherical potentials. The colored spheres (Q0-8) represent atomic potentials. The shaded gray region (Qi) represents the region of interstitial potential.

Figure 11, Representation of muffin-tin approximation with overlapping spheres. Note the reduced size of the interstitial region versus the previous figure without overlapping spheres.

The FEFF 8.10 calculations allow for simulation of X-ray absorption spectra of an absorber as a function of the positions of its neighbors. The code calculates XANES
spectra using the potentials of the atomic cores and the electronic potential. This
simulation allows for qualitative, and in some cases, quantitative evaluation of trends
in resonance positions and oscillator strength distributions.

2.5 X-ray Reflectivity

When an X-ray impinges upon a sample, three things may happen: The
incident X-ray may be reflected, refracted, or absorbed. By monitoring the
propagation of an X-ray between media of differing refractive index, it is possible to
determine the thickness and identity of the materials that are in the path of the X-ray.
The index of refraction in the X-ray region, \( \hat{n} \), may be written as follows.

\[
\hat{n} = 1 - \delta - i\beta
\]

Equation 24, the index of refraction in the X-ray region

In a case of a perfectly reflective surface, the real part of the dispersion, \( \delta \),
and the imaginary term, \(-i\beta\), are both zero and the incident wave is elastically
reflected. For real systems in the X-ray regime, \( \delta \) and \(-i\beta\) are small quantities and
can be approximated as the sums of contributions from the atoms that make up the
sample matrix.

\[
\delta = 4.1516 \times 10^{-4} \frac{\rho}{M\\sigma^2} \sum_{j=1}^{N} c_j f_{1j}
\]

Equation 25, \( \delta \), the real part of the dispersion of an X-ray

\[
\beta = 4.1516 \times 10^{-4} \frac{\rho}{M\\sigma^2} \sum_{j=1}^{N} c_j f_{2j}
\]

Equation 26, \( \beta \), the imaginary part of the refractive index
In these expressions\textsuperscript{63}, \( \rho \) is the density, \( E \) is the energy of the X-ray, \( M \) is the molar weight of a compound of \( N \) different atoms, and \( C \) is the number of atoms of type \( j \) per molecule. The indices \( f_{ij} \) and \( f_{2j} \) are the atomic scattering factors as described by Cromer\textsuperscript{64} for atoms of type \( j \).

The scattering vector of the incident X-ray is described by the following equation and figure.\textsuperscript{65}

\[
|q| = |k_r - k_i| = \left(\frac{4\pi}{\lambda}\right)\sin \alpha_r
\]

Equation 27 The scattering vector, \( q \)

Figure 12, Incident and reflected waves at the interface of two media with differing refractive indices. In this scenario, \( \alpha_i \neq \alpha_r \).
3. RESULTS AND DISCUSSION

3.1 Anomalous XANES Spectra of Octadecanethiol on Ag(111)

3.1.1 Introduction

Self-assembled systems have generated a great deal of interest because of their ability to impart selected chemical characteristics to surfaces, and the numerous applications that result (such as coatings and sensors). These systems of monolayers are defined by the substrate, the sulfur head group that attaches to the substrate, alkane chains of varying lengths, and a methyl end group. Another parameter that is significant to the structure of a self-assembled monolayer is the tilt angle, or the angle between the alkane chain and the surface normal. This geometrical factor provided the impetus for the study of these monolayer systems in the XANES region. The possibility to make connections between spectroscopic structure and geometrical factors, including bond length and bond angle is evident in the case that monolayer assembly is a function of the alkane chain length. A key to the usefulness of alkanethiol monolayers is the ability to fashion specific chemical properties over a large area. The application of alkanethiol-based systems for devices relies on adsorbate layers with well-characterized, reproducible chemical properties. As a result, it is important to understand how monolayers form in such systems, and in particular, how the adsorbed layers are tethered to the underlying substrate. We report sulfur K-edge XANES spectra for a series of $n$-alkanethiols adsorbed on Ag (111) surfaces. XANES spectroscopy is extremely useful for providing information on the oxidation state and local structure of a specific atom in a
molecule.\textsuperscript{68} Even in the case of a monolayer, XANES is a sensitive indicator of the local environment and electronic character of an adsorbed species.\textsuperscript{69}

A central motivation for this study is to determine how the octadecanethiol (C\textsubscript{18}) XANES spectrum compares to the spectra resulting from other thiols. In a previous EXAFS study of alkanethiols adsorbed on metallic surfaces,\textsuperscript{11} the results for C\textsubscript{18} adsorbed on Ag(111) were qualitatively different from those obtained from the shorter chain length thiols (C\textsubscript{5} and C\textsubscript{10}, in that study). Specifically, the Fourier transforms of the EXAFS functions were very different for C\textsubscript{18}, and they suggested that the C\textsubscript{18} adsorbate is bound not only on the hollow surface sites, but also at the atop surface sites. This result was surprising, so in an effort to probe these observations further, the current study focuses on XANES spectra which have been generated on several alkanethiols adsorbed on Ag(111). One expects that the XANES spectra for the C\textsubscript{18} adsorbates would be different from those of other chain lengths, as the near-edge structure is a sensitive indicator of local structure. In the course of performing these experiments, it was noted that the angular dependence of the XANES spectra for the C\textsubscript{18} adsorbates was markedly different from those of the other thiols, so measurements are also presented on the angular dependence for C\textsubscript{18}. In addition, XANES spectra are presented for non-adsorbed alkanethiols for comparison purposes.

\textbf{3.1.2 Sample Preparation and Experimental}

Experiments were performed at the X-ray microprobe (XMP) double crystal monochromator beamline at port 5A of the Center for Advanced Microstructures and Devices (CAMD) synchrotron radiation source at Louisiana State University.\textsuperscript{31,70} The
storage ring was operated at an electron beam energy of 1.3 GeV. The injection current was \textit{ca.} 200 mA and injections were typically done before the beam decayed below 100 mA. The beamline monochromator was calibrated with the strong absorption resonances observed for zinc sulfate\textsuperscript{71} Si(111) crystals provided monochromatic X-rays in the region of interest. The energy bandwidth for the excitation radiation was approximately 0.5 eV over the range of energies examined. The samples were all prepared in the same manner. A Si(100) wafer was cleaned in a piranha solution (1 to 3 ratio of H\textsubscript{2}O\textsubscript{2} to H\textsubscript{2}SO\textsubscript{4}) at 75\degree C for at least 30 minutes. A 2000 Å thick layer of 99.99\% Ag was thermally evaporated onto the freshly cleaned wafers as previously reported.\textsuperscript{11} All alkanethiol samples were determined to be greater than 99\% pure using gas chromatography. The Ag substrate was immersed in 1 mM ethanolic solution of the alkanethiol of interest for at least 12 hours. The adsorption was done in a nitrogen-purged box. A self-assembled monolayer of the alkanethiol forms on the substrate under these conditions.\textsuperscript{72-74} After the assembly process, the samples were rinsed with absolute ethanol and dried under a stream of argon immediately prior to performing the XANES measurements. The endstation consisted of an I\textsubscript{0} monitor, a goniometer, a single element germanium detector, and a photodiode, and was enclosed within a Plexiglas box, Figure 13. For these experiments, an inert atmosphere was maintained inside the box by flowing helium gas through inlet and outlet valves. The silicon wafer substrate was placed on a goniometer and the zero angle was determined by monitoring the current with ionization chambers placed before and after the sample stage. The beam was collimated with two four-jaw apertures, one before the window of the sample box, and
one immediately before the $I_o$ ionization chamber. Samples were placed on a motorized goniometric sample stage assembly consisting of two translation stages (Newport model UTM25PE.1 and MVN80) and two rotation stages (Newport model URM80PE and BGM50PE). This sample positioner had 0.001″ precision in the x, y, and z directions, and a precision of 0.01° for the pitch and yaw. The absolute zero angle and zero height were determined by elevating the sample until the beam intensity behind the sample stage was reduced by 50%, as measured by a photodiode. The stage position was adjusted until the photodiode signal was reduced, regardless of the angle that it was adjusted by. The stage was withdrawn from the beam and the process was performed iteratively until there was good reproduction of the zero angle. All measurements were taken below the critical angle of the silver substrate (1.33°) reducing the penetration of incident X-rays into the bulk, suppressing elastic scattering, and reducing background signal.75 Fluorescence photons were detected at the S-Kα peak (2307 eV) with a single element Ge semiconductor detector (Canberra, model GUL01110P). A multichannel analyzer was used to window the signal about the sulfur K-alpha fluorescence transition with a bandwidth $\Delta E \approx 150$ eV. The Ge detector was perpendicular to the sample on an xyz translator.

For comparison purposes, fluorescence excitation spectra were obtained for thiols that were not adsorbed on substrates. These spectra were taken to determine which features emerged from interactions following adsorption, and which are intrinsic to the thiol molecules. Spectra were taken for shorter chain thiols (C$_5$ and C$_{12}$) in solution, and for C$_{18}$ as a powder. A Lytle-detector$^{76}$ was used as a fluorescence-
yield detector for these measurements, and the solutions were prepared in ethanol at 0.5 M concentrations. It was not possible to make a sufficiently concentrated solution of the C$_{18}$ compound, so it was studied as a powder.

Figure 13, Schematic of endstation used to obtain grazing incidence X-ray spectra.$^{77}$

3.1.3 Results and Discussion

The spectra of all of the samples exhibited angular dependence over a narrow range of shallow angles (0.2 – 1.0°). In the following figure, some representative spectra are shown for incidence angles of 0.2° and 0.6°. The spectra are normalized to the integrated cross section at the midpoint of the oscillatory structure in the continuum at approximately 2510 eV, where effects due to local structural changes will be relatively small. With the exception of the C$_{18}$ sample, all of the XANES
spectra are similar to one another. While the relative intensities of the features varied somewhat for different thiols, the basic patterns were consistent. The spectra for the chain lengths not shown in the following figure (C₈, C₁₀, C₁₄, C₁₆, and C₂₂) are consistent with the spectra of the C₆ and C₁₂ monolayers.

Figure 14, Fluorescence excitation spectra of C₆, C₁₂, and C₁₈ monolayers on silver substrate at incidence angles of 0.2° and 0.6°.
In the following figure, the data for the $1^\circ$ incidence angle are shown. In this figure, spectra are shown for all of the thiols, and they are not offset. The results underscore the point that the spectra for all of the thiols other than $C_{18}$ coincide closely.

Figure 15, Fluorescence excitation spectra of a larger subset of the $n$-alkanethiols examined at $1.0^\circ$ incidence angle. The isolated symbols are for all of the compounds other than $C_{18}$, while the solid line is the $C_{18}$ spectrum. All of the thiol spectra track one another except for the $C_{18}$ spectrum.
Among the adsorbate results, the C\textsubscript{18} data exhibit four noticeable differences from the other samples, and these differences are visible in both of the preceding figures. First, there is a peak observed at \( h\nu_{\text{exc}} \approx 2487 \) eV which is absent in all of the other thiol spectra (although there may be a hint of this feature in the C\textsubscript{12} spectrum). Secondly, there is a high energy shoulder (\( h\nu_{\text{exc}} \approx 2477 \) eV) on the white line transition which is absent for the other thiols. Thirdly, the plot shows that there is a low energy shoulder on the white line feature (\( h\nu_{\text{exc}} \approx 2469 \) eV) for all of the thiols other than C\textsubscript{18}. Fourthly, the peak observed at 2480.8 eV for the other thiols are absent for C\textsubscript{18}.

It was noticed that the angular dependence of the C\textsubscript{18} results was different than those of the other thiols studied, so a more detailed angular dependence was determined for the C\textsubscript{18} adsorbate. The C\textsubscript{18} results are shown with an expanded scale in Fig. 4. It is striking that both the 2487 eV resonance and the shoulder at 2477 eV are grouped into two distinct families of curves.

Table 2 and figure 18 further demonstrate the differences between the octadecanethiol spectrum and the other chain lengths examined. In addition to the anomalous feature at 2486.6 eV, there is an additional low-intensity resonance (feature IV) at 2478.8 that is absent in the other systems. The pre-absorption edge resonance (feature I) is absent for octadecanethiol. Also, the white line features (labeled II and III) are shifted for the octadecanethiol sample. What is clear is that there is a strong spectral signature in the case of the octadecanethiol system and to a lesser extent in the other adsorbed thiols. Future work may lead to even higher
resolution spectra that will allow for better separation of peaks, determination of absolute energetic position, and assignment of all observed spectral features.

Figure 16. Comparison of sulfur K-edge XANES for octadecanethiol-deposited layers on Ag(111) at angles of incidence ranging from 0.05° to 1.0°. The data sets bifurcate into two groups, suggestive of 2 alternative adsorption sites.
Figure 17, Spectra taken for non-adsorbate systems. The C\textsubscript{5} and C\textsubscript{12} molecules were in solution, and the C\textsubscript{18} compound was a powder. The reference lines indicate the positions of strong resonances observed for the adsorbate systems that are largely or completely absent here.

Table 2, Energies of features in the Sulfur K-edge spectra of \textit{n}-alkanethiols adsorbed on Ag taken at 0.2°.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Hexanethiol</th>
<th>Dodecanethiol</th>
<th>Octadecanethiol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feature I</td>
<td>2469.1</td>
<td>2469</td>
<td>2471.6</td>
</tr>
<tr>
<td>Feature II</td>
<td>2471.8</td>
<td>2472</td>
<td>2472.5</td>
</tr>
<tr>
<td>Feature III</td>
<td>2480.2</td>
<td>2480.2</td>
<td>2476.5</td>
</tr>
<tr>
<td>Feature IV</td>
<td></td>
<td></td>
<td>2478.8</td>
</tr>
<tr>
<td>Feature V</td>
<td></td>
<td></td>
<td>2486.6</td>
</tr>
</tbody>
</table>
Previous work has shown that the ionization potential of similar sulfur containing compounds is on the order of 2476-2478 eV. This bolsters our assertion that the anomalous feature is an above threshold feature.

3.1.4 Conclusions

We have obtained XANES spectra at the sulfur K-edge of n-alkanethiol monolayers on Ag(111) using fluorescence excitation at grazing incidence. The results show that such spectra are sensitive to changes in bonding between the adsorbed n-alkanethiol and the silver substrate. These experiments indicate the presence of an anomalous...
spectrum for the eighteen-carbon chain length. Previous EXAFS results indicated that the monolayer structure was of octadecanethiol adsorbate was inconsistent with that of shorter chain lengths.\textsuperscript{11} Within the scope of the previous study, it was unclear whether the spectrum of the 18-carbon thiol was the beginning of a trend. This study determined that this was in fact not the onset of a trend, but rather a local extremum, as a longer chain length adsorbate (C\textsubscript{22}) was consistent with the spectra of the shorter chain thiols (< C\textsubscript{18}). The C\textsubscript{18} spectra exhibit an anomalous resonance at 2487 eV assigned as a shape resonance which is enhanced by the anomalous binding geometry for C\textsubscript{18}. The underlying conclusion to these results is that XANES spectroscopy can be a useful probe of the detailed nature of self-assembled monolayer structure, and that chain-length dependent measurements provide insights into the formation and stability of such adsorbate systems. While this project provided extremely useful and surprising insights into the surface binding of thiol self-assembled monolayers, it did not provide information on correlations between bond angle and XANES spectra. For this reason, I began experiments on another class of compounds – heterocyclic ring systems – that varied the bond angle about the absorbing atom using an alternative strategy, i.e., by altering the heterocycle ring size. These experiments are described in the following section and they provide a useful pathway towards understanding the spectral/structure correlations that are at the heart of this dissertation.
3.2 The Effect of Changes in Bond Angle on X-Ray Spectra of Cyclic Sulfides

The threshold for trapping an electron in both bound states and quasibound states near the absorption edge energy of a core absorber is an extremely sensitive probe of molecular and electronic structure. The research described in this chapter and subsequent chapters on organometallic ring compounds involves investigating the evolution of the binding of outgoing photoelectrons in series of chemical analogues that allow chemical manipulation of the bond angle and local environment of the absorbing atom. Also, one attempt is made to test the relationship between resonance position and bond length. Further, it is desirable to unambiguously correlate observed resonances with the physical and chemical properties of the chemical series.

3.2.1 Introduction

X-ray absorption near-edge structure (XANES) spectroscopy is a sensitive tool for chemical fingerprinting, but there have not been many studies that have investigated how the spectroscopic features evolve as the geometries of larger polyatomic systems are altered in a systematic fashion. In this study, how the XANES region of a spectrum changes as the bond angle is varied over a wide range is investigated. Both the sub-threshold region and the continuum portion of the excitation channel can be investigated in such spectra. This chapter describes both the sub-threshold region and the above-threshold (continuum) region. Studies have attempted to correlate changes in molecular geometry with spectroscopic shifts of XANES features, but most of the attention has been focused on how changes in
bond lengths correlate with resonance positions.\textsuperscript{28,39,80-86} There has been comparatively little effort focused on how other geometrical changes might affect the XANES spectra. While there is a consensus that above threshold shape resonance features should be sensitive to the geometry changes (based on valence-shell diatomic photoionization \textsuperscript{9,87-91}) there are disagreements about the general applicability of simple correlations.

For example, there has been a detailed XANES study of basket porphyrins,\textsuperscript{92} molecules with ligands that extend from the periphery of the nominally planar porphyrin structure to the metallic center. The planarity of the molecules can be distorted by adjusting the length of the “basket handle” complexing ligand. In that investigation, it was found that the puckering of the ring structure modulated the intensities of the XANES resonances. However, the effects were muted because the geometric distortions of the ring were comparitively small.\textsuperscript{92} In another study, investigators attempted to establish a relationship between XANES line shapes and changes in bonding and geometry in chromium silicide crystals with differing ratios of chromium and silicon.\textsuperscript{93} They found that solid-state theory accounted well for observed line shapes in valence-band studies of chromium silicides of varying structural and chemical composition. XANES spectroscopy has also been used in a study similar to this work where the intensity of multiple scattering features in a series of aluminosilicate sodalites were shown to be a function of bond angle at the Al K-edge and Si K-edge\textsuperscript{94}. However, in all of the previous studies, it has been difficult to control the geometric changes over a wide range in a systematic fashion, and the current use of chemical heterocycles accomplishes this readily.
Sulfur K-edge XANES spectra have recently been obtained for the cyclic polymethylene sulfides.\textsuperscript{95} That study focused primarily on the subthreshold features in the spectrum. Based on that study and the results from the present investigation, calculations have been performed on all of the cyclic sulfides presented here, and those detailed calculational results will be presented elsewhere.\textsuperscript{96} The results from the present study will be compared to those from the previous investigation.\textsuperscript{95} The current investigation, in combination with previous studies which illuminate correlations between XANES structure and molecular geometry,\textsuperscript{28,85,86,94,95} demonstrate the utility of investigating how XANES spectra respond to systematic structural changes. Moreover, the cyclic compounds studied here provide a particularly useful template, as we can test (primarily) how bond angle changes affect the continuum resonances in XANES spectra. This allows us to probe the sensitivity of continuum resonance to bond angles first observed for valence-shell photoionization, and in so doing, develop a clear qualitative and predictive framework for interpreting molecular X-ray spectra.

In order to obtain a clearer picture of how XANES spectra respond to changes in molecular geometry, it is useful to employ "tailored" molecular systems that permit more systematic control over molecular geometry. As mentioned previously, there have been some studies that have investigated novel types of correlation between structure and spectroscopic characteristics, but this is still not a large enough body of work to provide an unambiguous picture of how general such effects may be. The cyclic sulfides studied in the present investigation provide a means of probing such
effects, and the current results show clear evidence of correlations between bond angle and sub-threshold XANES features.

Another method for testing the effect of geometry and absorber environment on X-ray spectra is to perform quantum calculations. FEFF 8.10 calculations are used. These \textit{ab initio} calculations predict that X-ray absorption spectra will demonstrate sensitivity to bond angle in the below threshold region. The following figure displays the absorption spectrum of a model C-S-C system wherein the bond angle is varied and the bond length is held constant. The ultimate result of the calculation is extremely sensitive to how the model molecular potential is constructed with the parameters that define the calculation. The oscillator strength of the white line features changes dramatically with the change of bond angle from a bent configuration to a linear configuration. This is indicative of a change in the character of the white line feature. Without speculating on the origin of the features, there are two features in the white line of the bent configuration and there is no discernible shoulder resonance in the linear configuration. This indicates an angular dependence for the shoulder feature. As the bond length is increased, there is more head-on overlap as the resonances increase in intensity and become degenerate in the linear configuration.

The conclusion to be drawn from figure 19 is that the calculations are extremely sensitive to the bond angle about the absorbing atom – even for the relatively light elements, sulfur and carbon.
FEFF 8.10 Calculation of Sulfur K-edge XANES Spectra as a function of bond-angle

Figure 19. Calculated spectra of a model system with a sulfur molecule between two carbon atoms. The carbon-sulfur distance is held constant and the bond length is varied.

The experimental results presented here agree well with those obtained by the previous investigators. However, this work proposes alternative spectroscopic assignments that alter some of the main conclusions of the previous work. In fact, a primary focus of the previous study (as well as the present one) was to search for
trends in the X-ray spectra accompanying bond angle changes. While the previous study concluded that such trends may be nonexistent or too subtle to be useful, the current study suggests a much more hopeful outlook. All of the compounds studied display a shoulder on the strongest subthreshold peak (i.e., the X-ray "white line" transition). It will be demonstrated that if that shoulder is assigned to a $1s \rightarrow \sigma^*(C-S)$ transition, the pattern that emerges is markedly different than if the feature is assigned as $1s \rightarrow \pi^*(CH_2)$ transition (as was assumed in the previous investigation). Results from Hartree-Fock level calculations form the basis for this assignment. These experimental results, in combination with the calculations, demonstrate that the variation of the X-ray spectra with ring size exhibits understandable trends. Moreover, because resonances in the continuum can be affected strongly by geometrical changes, these results suggest that there is a positive outlook for mapping relationships between structure and spectra in the XANES regime.

The central point is that there are strong connections between X-ray absorption spectroscopy and parameters that define molecular geometry. As a result, it is possible to exploit variations in X-ray absorption features as guideposts to molecular structure parameters. The X-ray absorption spectra of cyclic polymethylene sulfides at the sulfur K-edge are reported. The influence of ring size and bond angle on continuum resonances is documented. This study helps to illuminate how the ring size affects the spectra, and the analysis of these results help to suggest future directions for such work, as well.
Table 3. Ball and stick representation of cyclic sulfide series. Bond angles and bond lengths are also presented.97-101

<table>
<thead>
<tr>
<th></th>
<th>(CH$_2$)$_2$S</th>
<th>(CH$_2$)$_3$S</th>
<th>(CH$_2$)$_4$S</th>
<th>(CH$_2$)$_5$S</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-S-C Bond Angle</td>
<td>48.3°</td>
<td>78.2°</td>
<td>94.6°</td>
<td>101°</td>
</tr>
<tr>
<td>C-S Bond length</td>
<td>1.82 Å</td>
<td>1.83 Å</td>
<td>1.82 Å</td>
<td>1.82 Å</td>
</tr>
</tbody>
</table>

3.2.2 Experimental

Experiments were performed at the double crystal monochromator (DCM) beamline$^{102}$ at the Center for Advanced Microstructures and Devices (CAMD) synchrotron radiation source$^{31,34}$ at Louisiana State University. The CAMD storage ring is typically operated at an electron beam energy of 1.3 GeV. The injection current is ca. 200 mA and injections are typically done before the beam decays below 100 mA. These experiments were performed in transmission mode using standard methods$^{40}$. The compounds were introduced into the absorption cell as low-pressure gas-phase samples ($P_{\text{gas}} < 10$ Mbar). A windowed double ion chamber$^{40}$ containing the sample gas was used to measure the absorption spectra. The windows were made of thin Kapton® sheets. A zinc sulfate standard was measured simultaneously with each spectrum for calibration purposes. The ion currents were read with Keithley picoameters (model #6512)$^{103}$, and the signals from the picoameters were recorded by a computer.
For these experiments, InSb(111) crystals with an interplanar spacing $2d = 7.48$ Å were used to transmit monochromatic photons in the region of the sulfur K-edge with a resolution of $\sim 0.1$ eV. The monochromator was calibrated with the strong white line absorption of ZnSO$_4$ at 2481.44 eV prior to taking XANES spectra. Liquid samples of the heterocycles were placed in a reservoir connected to the sample chamber. The pressure due to the sample vapor and background gas was approximately 50 millibar. Spectra were taken at various pressures, as well as with helium buffer gas to discern whether there were pressure dependent effects and/or background effects due to the atmosphere in the sample chamber. No such artifacts were observed. Transmission spectra (i.e., $\ln(I/I_0)$) were obtained over the region from 2460 eV to 2510 eV. The cyclic sulfide samples were obtained from Aldrich (>97%) purity and were used without further purification.

Figure 20, Schematic of double ion chamber experimental set up. Arrow indicates direction of incident radiation. The sample cell is isolated with Kapton windows. Two ionization chambers and the sample gas are in the cell. A zinc sulfate standard and a third ionization chamber are placed downstream from the sample cell.
3.2.3 Calculations

Initial calculations were performed by Zurales\textsuperscript{96} using the GAMESS\textsuperscript{104} package, and standard procedures were employed. The calculations were found to be suitable for reproducing the qualitative features in the spectra. Two alternative approaches were used. First, a Koopmans-type\textsuperscript{105,106} approach was used, where the same orbitals were used for the neutral molecule and the core-hole molecular ion. Second, the orbitals were allowed to relax upon ionization. Both approaches generated the same trends and corroborate the conclusions that are presented. The best quantitative agreement is achieved when the orbitals are allowed to relax upon ionization, i.e., the non-Koopmans approach. Both transition energies and transition strengths result from these calculations and both are reported in the following section. Alternatively, we used HyperChem Pro 6.0 to construct molecular orbital diagrams. The HyperChem calculation uses Polak-Ribiere\textsuperscript{107} conjugate gradient algorithm for both molecular mechanics and semi-empirical structural optimization. The semi-empirical calculation relies on the PM3 formalism\textsuperscript{108,109} to optimize molecular structure and calculate the molecular orbital energies and symmetries. PM3 is a quantum mechanical theory in which electrons are included explicitly. It is not an "ab initio" theory because many of the detailed integrals have been replaced by empirical parameters. The values of these parameters were adjusted to reproduce experimental data for a large set of molecules. Four gas-phase properties were used in the parameterization: enthalpy of formation, dipole moment, ionization energy, and molecular geometry (i.e., structure).\textsuperscript{60}
The relative energetic positions of the sub-threshold features depend on the ionization potential. The ionization potentials for the S 1s electron of these compounds are not available in the literature. The calculated peak positions for the sub-threshold features depend on the ionization threshold, and the ionization thresholds calculated by Zurales are used.\textsuperscript{96} The validity of the ionization potentials calculated by Zurales is pivotal, and it may be necessary to reexamine the analysis when experimental values become available. Values for the S 1s ionization potential reported in the previously published study\textsuperscript{95} are of unspecified accuracy and are not used.

### 3.2.4 Results and Discussion

The following figures display the sulfur K-edge XANES spectra of the cyclic polymethylene sulfides, ethylene sulfide [(CH\textsubscript{2})\textsubscript{2}S], trimethylene sulfide [(CH\textsubscript{2})\textsubscript{3}S], tetrahydrothiophene [(CH\textsubscript{2})\textsubscript{4}S], and pentamethylene sulfide [(CH\textsubscript{2})\textsubscript{5}S].

The spectra in the previous figure were aligned with the peak that is assigned to the ZnSO\textsubscript{4} reference compound at 2481.44 eV. The true absorption spectra of the cyclic sulfide series are displayed in the following figure.

A typical experimental spectrum is shown for trimethylene sulfide in the following figure, and it agrees well with the one recently obtained at Super-ACO.\textsuperscript{95} In each spectrum, the white line contains two resonances of equal width, and differing intensities. The high energy resonance is of significantly lower intensity. The spectrum of S(CH\textsubscript{2})\textsubscript{3} (trimethylene sulfide) is shown in the following figure. It is chosen for individual display because of the molecules in the series, it demonstrates the strongest resonances and the greatest separation of features.
Figure 21, Scaled comparison of cyclic sulfide spectra with ZnSO₄ reference. All spectra are aligned such that maximum in ZnSO₄ peak is at 2481.44 (Vertical line).
Figure 22, Scaled comparison of Sulfur K-edge photoabsorption spectra of cyclic sulfides. Each spectrum is aligned with its calibration spectrum. Vertical hatched lines indicate ionization potentials as calculated by Zurales.
Figure 23, Photoabsorption spectrum of trimethylene sulfide in the XANES region.
Again, all of the compounds exhibit the features shown by this compound, and trimethylene sulfide is useful for purposes of illustration because the features are most clearly evident for it. Vertical lines indicate calculated transition energies and relative amplitudes and the overall agreement with experiment is good. The vertical lines are not drawn to scale. They have been magnified for ease of viewing.

![Graph showing calculated transition energies and experimental data for trimethylene sulfide.](image)

Figure 24. Calculated transition energies and experimental data for trimethylene sulfide. Vertical lines indicate calculated transition energies and relative oscillator strengths. Inset shows full spectrum.

Initially, the subthreshold region is examined. This region of the spectrum was not the initial focus of this work, but the work of Dezarnaud-Dandine\textsuperscript{95} et al. made it essential to examine this area of the spectra carefully. The pertinent transitions are labeled, and it is important to discuss the assignments in some detail. At low energy, there is a strong peak that is assigned as a 1s $\rightarrow \sigma^*(S-C)$ and a weaker shoulder to
the blue which we also assign as a transition to a nondegenerate $\sigma^*(S-C)$ valence MO. This assignment is significant, as the previous investigation assigned this transition to a $\pi^*(CH_2)$ valence MO. It is important to emphasize this distinction, as it affects the trends that are observed. Both the Hartree-Fock calculations performed by Zurales$^{110}$ and the semiempirical HyperChem calculations indicate that the $\pi^*$ orbital is of slightly higher energy than two $\sigma^*$ orbitals that lie close in energy to one another. Specifically, in the HyperChem calculation, for ethylene sulfide, the simplest case, there are several closely spaced unoccupied molecular orbitals.

Two separate studies have been performed previously on both the full set of cyclic sulfides $(CH_2)_nS$ (n=2-5)$^95$ and on the $(CH_2)_4S$$^86$ (i.e., n=4) molecule. In both of these studies, assignments are made for subthreshold peaks as well as continuum features. The primary white line feature is assigned to a $\sigma^*$ (C-S) state and the shoulder to the high-energy side of the peak is assigned to a $\pi^*$ (CH$_2$) state. The energetic positions of the resonances in our spectra match both sets of previously published data (within error) for the $(CH_2)_4S$ molecule. The assignment of the shoulder feature on the white line in $(CH_2)_4S$ to a $\pi^*$ (CH$_2$) in each of the aforementioned studies is presumably based upon a determination made for the unsaturated analogue of $(CH_2)_4S$, thiophene. Newbury et al.$^{111}$ have presented an interpretation wherein transitions from a localized core level (2p) to a $\pi^*(CH_2)$ orbital are allowed for tetrahydrofuran and pyrrolidine, molecules where there is no low-lying $\sigma^*$ level and there is no overlap between the orbitals involved in the transition. However, in the case of $(CH_2)_nS$ ring systems, there is a low-lying $\sigma^*$ level and
according to the calculations that will be presented here it is of lower energy than the
π*(CH₂) orbital.

A symmetry argument is employed in conjunction with the calculational results
for the ethylene sulfide molecule. Ethylene sulfide is used as it is the simplest case,
belonging to C₂ᵥ, having a C₂ axis, and two mirror planes (σᵥ and σᵥ). The other
molecules are not true members of C₂ᵥ, and the condition that C-S-C portion is the
only part of the molecule relevant to the ejection of the S 1s electron must be
imposed in order to extend the argument to the full set of cyclic polymethylene
sulfides. This supposition is not trivial, as the other molecules in the series actually
transform as C₅. This discrepancy calls the results of the Dezarnaud-Dandine et al.
into question, as it is not implausible to extend the assignments for the C₂ᵥ molecule
in the series to those of much lower symmetry (C₅), but this extension does not
necessarily hold true. One-dimensional representations that are symmetric with
respect to rotation by 180° about the principal Cₙ axis are designated A and those
that are antisymmetric about the principal Cₙ axis are designated B.¹¹² The
subscripts 1 or 2 indicate whether the representation is symmetric or antisymmetric
with respect to a C₂ axis perpendicular to the principal axis. In the absence of a C₂
axis perpendicular to the principal axis, a vertical plane of symmetry may be used to
determine whether the representation is labeled 1 or 2. The σ* (C-S) orbitals have
positive and negative lobes separated by a nodal plane and transform as B₂. The
sigma star orbitals are antisymmetric to rotation by 180° and symmetric with respect
to a horizontal plane of symmetry, but not a vertical plane of symmetry. The π*(CH₂)
orbital transforms as $B_1$, anti-symmetric with respect to rotation by $180^\circ$, and symmetric with respect to a vertical plane of symmetry.

For demonstration purposes, the three-dimensional renderings of the pertinent molecular orbitals are presented in the following figures. These images serve as a graphic proof of the validity of the symmetry labels assigned by the HyperChem calculation to the orbitals in the case of S(CH$_2$)$_2$.

Figure 25, Image of the 3B$_2$ molecular orbital electron density. The green and violet icososurfaces represent positive and negative lobes of the molecular orbital, respectively.
Figure 26; Image of the \(5A_1\) molecular orbital electron density.

Figure 27; Image of the \(4B_2\) molecular orbital electron density.
Figure 28, Image of the 3B₁ molecular orbital electron density.

The lowest unoccupied molecular orbitals, as constructed in the simulation of ethylene sulfide, and their energies relative to the 1A₁ level are presented in the following table.

Table 4; Ethylene Sulfide molecular orbital energies and assignments calculated with Hyperchem Pro 6.0.

<table>
<thead>
<tr>
<th>LUMOs</th>
<th>Energy (eV)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>5B₂</td>
<td>40.67</td>
<td>σ⁺</td>
</tr>
<tr>
<td>6A₁</td>
<td>40.23</td>
<td>σ</td>
</tr>
<tr>
<td>3B₁</td>
<td>39.92</td>
<td>π⁺</td>
</tr>
<tr>
<td>4B₂</td>
<td>39.14</td>
<td>σ⁺</td>
</tr>
<tr>
<td>5A₁</td>
<td>36.83</td>
<td>σ</td>
</tr>
<tr>
<td>3B₂</td>
<td>37.58</td>
<td>σ⁺</td>
</tr>
</tbody>
</table>
Beyond the features that are described as $\sigma^*$ (C-S) resonances, at higher energy are two observable (albeit weaker) Rydberg transitions. These Rydberg states are located between the bound state orbitals and the shape resonant features in the continuum. The closeness of the energetic spacing between the Rydberg levels and the valence orbitals indicates that chemical and structural changes can shift the energies of the valence states, which affects the interpretations of the spectra. Finally, weaker resonances are visible above the ionization threshold. These are probably due to either shape resonances or multielectron transitions converging to satellite (e.g., shake-up) photoionization continua at still higher energy. Probably, they are shape resonances, based on the width and position of these features. However, high quality scattering calculations are required to verify this assumption. For the present purposes, it is useful to focus on the $1s \rightarrow \sigma^*(S-C)$ transitions at the lowest energy. Calculations and experimental data for these transitions are presented for all four compounds in Table 1. The trends observed in experiments are well reproduced by the theoretical calculations. The disagreement between this work and the previously reported data is relatively small, but the best peak-fits are obtained with the parameters used here. The data from the other study has been carefully compared with the data presented here, and the peak fitting that was used adequately fit those data as well. The peaks that comprised the white line structure were fit with Voigt profiles of equal width (1.6 eV). This method is reasonable based on S 1s core hole lifetime$^{113}$ and monochromator resolution. The results of these fits are presented in the following figure.
Figure 29, Summary of fitting of white line features of cyclic sulfides with Voigt profiles.
Figure 30, Plot of term values for C-S $\sigma^*$ resonances (and average value) versus bond angle.
Table 5, Peak positions used in fit of C-S $\sigma^*$ white line resonances.

<table>
<thead>
<tr>
<th></th>
<th>Peak 1 (eV)</th>
<th>Peak 2 (eV)</th>
<th>Ave. Position (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(\text{CH}_2)_2\text{S}$</td>
<td>2473.00</td>
<td>2474.00</td>
<td>2473.50</td>
</tr>
<tr>
<td>$(\text{CH}_2)_3\text{S}$</td>
<td>2472.63</td>
<td>2474.10</td>
<td>2473.37</td>
</tr>
<tr>
<td>$(\text{CH}_2)_4\text{S}$</td>
<td>2473.38</td>
<td>2474.85</td>
<td>2474.12</td>
</tr>
<tr>
<td>$(\text{CH}_2)_5\text{S}$</td>
<td>2473.50</td>
<td>2474.95</td>
<td>2474.23</td>
</tr>
</tbody>
</table>
Figure 31, Above-threshold portion of cyclic sulfide photoabsorption spectra.

The above threshold spectrum of the series is presented in the preceding figure. There are two significant resonances in the spectra. The first feature is near the calculated ionization threshold. In each case, excepting ethylene sulfide, the first resonance is likely due to the convergence of valence and Rydberg states based on
FEFF 8.10 calculations and previous work on similar compounds. The ethylene sulfide resonance at approximately 2477 eV is sufficiently weak that it may in fact be due to shake-up, shake-off, or other undetermined multi-electron processes. The second resonance (observed from approximately 2482-2486 eV) is clearly an above threshold feature, and based on its oscillator strength, calculations, and fingerprinting, it is a shape resonant effect. A plot of the resonance position (term value) versus ring size reveals a similar trend in the continuum as was seen in the average value of the subthreshold resonances. The curves are inverted due to the change of sign for the term values of above threshold and below threshold resonances.

Figure 32, Term values of above threshold resonances versus ring size
Figure 33, The relationship between subthreshold $\sigma^*$ (C-S) resonance term value and the carbon-sulfur bond length.

This figure contains linear fit plots of both of the $\text{S(CH}_2\text{)}_{n=3,4,5} \sigma^*$ (C-S) resonance positions. The experimental data points for $\text{S(CH}_2\text{)}_2$ are also included along with the values that are predicted based on the linear plots. The empty circle
with the x-strikethrough is the predicted value for resonance 1 in S(CH₂)₂ (Bond length 1.815 Å, term value 1.99585 eV). The empty diamond with the x-strikethrough is the predicted value for resonance 2 in S(CH₂)₂ (Bond length 1.815 Å, term value 0.65315 eV). The equation of the line for resonance 1 is \( y = 95.59x - 171.5 \) The equation of the line for resonance 2 is \( y = 89.01x - 160.9 \). With the exception of the strained S(CH₂)₂ ring, the below threshold resonances agree with the bond length with a ruler prediction of a linear relationship between bond length and term value. However, the failure of the prediction in the strained system indicates that bond length is not the sole determinative factor in the resonance position.

The following figure (figure 34) displays the lack of correlation between bond length and relative continuum resonance position in the cyclic sulfide series. The strong level of disagreement offers direct evidence of the lack of generality in the “bond lengths with a ruler” postulate. The approach used here where the molecules are very similar electronically and structurally allows for elimination of outside variables that might skew the result. In conclusion, the position of a resonance relative to the threshold is a function of the many variables that are part of the construction of the overall molecular potential and is not limited to the single variable of bond length.

3.2.5 Conclusions

These data demonstrate that for cyclic polymethylene sulfides, the spectroscopic center of gravity is shifted to higher energy as the bond angle is relaxed in a series of chemical analogues. Second, both the primary white line feature and the weak shoulder transitions of the white line feature are of \( \sigma^* \) character.
Bound-state resonances in XANES spectra are sensitive to bond strain and above-threshold features are also sensitive to bond strain. These data also provide strong evidence of the non-generality of the ability to predict bond distances with a ruler.

Figure 34, Plot of bond length versus the term value of continuum resonances for the cyclic sulfide series. The circle-X marks are the data points.
3.3 Angle-dependent Effects in the X-ray Spectra of Chromium Complexes

3.3.1 Introduction

X-ray absorption spectra are useful and direct probes of the bonding and overall electronic character of chemical species. These experiments are based upon the approach of using chemical means to direct the bond angle within a system of molecules. The molecules of interest are of the formula Cr(CO)$_4$PPh$_2$(CH$_2$)$_n$PPh$_2$; $n$ = 1-3). These bidentate organometallic compounds allow us multiple angles of experimental attack since the size of the alkane chain affects bond angles about both the metal center and the phosphorous atoms. Beyond providing information on the effect of bond-angle, we hope to add to existing work$^{71,114}$ that has characterized the chemical effect in chromium complexes and provide a comprehensive view of the molecular photoabsorption and photoionization dynamics by combining information from the individual absorbers. Another study of note was performed where an attempt to establish a relationship between the shapes of spectra and changes in bonding was attempted.$^{93}$ They found that solid-state theory accounted well for observed line shapes in valence-band studies of chromium silicides of varying structural and chemical composition. One of the goals of this work is to extend the general types of results obtained in the aforementioned study to the core-shell spectra of chromium tetracarbonyl bidentate ligands.
### 3.3.2 Sample Preparation and Experimental

<table>
<thead>
<tr>
<th>Bridge</th>
<th>In Plane</th>
<th>Perpendicular</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td><img src="image1" alt="HyperChem structure of chromium tetracarbonyl diphenylphosphino methane" /></td>
<td><img src="image2" alt="HyperChem structure of chromium tetracarbonyl diphenylphosphino methane" /></td>
</tr>
<tr>
<td>Ethane</td>
<td><img src="image3" alt="HyperChem structure of chromium tetracarbonyl diphenylphosphino ethane" /></td>
<td><img src="image4" alt="HyperChem structure of chromium tetracarbonyl diphenylphosphino ethane" /></td>
</tr>
<tr>
<td>Propane</td>
<td><img src="image5" alt="HyperChem structure of chromium tetracarbonyl diphenylphosphino propane" /></td>
<td><img src="image6" alt="HyperChem structure of chromium tetracarbonyl diphenylphosphino propane" /></td>
</tr>
</tbody>
</table>

Figure 35, HyperChem structures of chromium tetracarbonyl diphenylphosphino alkane compounds shown with chelating ring in the plane of the page and perpendicular to the page. Carbon atoms are represented by the light blue spheres, phosphorus atoms are represented by yellow spheres, oxygen atoms are represented by red spheres. The chromium center is eclipsed in each view, and hydrogen atoms are omitted for ease of viewing.

Standard Schlenk synthesis procedures from the literature\textsuperscript{115,116} were used in the preparation of the compounds. In a glove box with a dry nitrogen atmosphere,
equimolar amounts of the bridging ligand (diphenylphosphino alkane) and chromium hexacarbonyl were combined in a Schlenk flask with diethylene glycol dimethyl ether as a solvent. A mixture of hexacarbonyl chromium + (dppm, dppe, dppp, or dppb) + diethylene glycol dimethyl ether (diglyme) (15 mmol + 15 mmol in 25 ml) was heated under nitrogen. Each reaction mixture was refluxed for at least 3 hours. After cooling and addition of 25 ml methanol, the crystals that formed were removed by filtration. The samples were characterized with melting point analysis and agreed well with literature values.

Table 6: Bisdiphenylphosphino tetracarbonyl chromium complexes and bond angles.

<table>
<thead>
<tr>
<th></th>
<th>P-Cr-P Bond Angle (°)</th>
<th>C-P-Cr Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>70</td>
<td>96.3</td>
</tr>
<tr>
<td></td>
<td>83.4</td>
<td>108.6</td>
</tr>
<tr>
<td></td>
<td>89.7</td>
<td>109</td>
</tr>
</tbody>
</table>

A portion of the $^{13}$C NMR data taken for Cr(CO)$_4$dppe is presented in the following figure.
Figure 36. $^{13}$C NMR spectrum of methane bridged complex

The spectrum includes the peak for the benzene rings (128-138 ppm), unassigned (99 ppm), diglyme (75-78 ppm), (CH$_2$)$_2$ (28 ppm). The CO groups (not shown in this spectrum) are expected to appear from 210-220 ppm. The observed peaks assigned to the complex and the other molecules (not shown) agree well with literature values.$^{117}$

A thin uniform layer of each powdered diphenylphosphino alkane chromium hexacarbonyl complex was placed on a piece of Kapton tape. Several layers of the tape were used to achieve an optimal absorption. The samples were then run in transmission mode at the CAMD DCM beamline using standard techniques.$^{16,17,39}$ All samples are air stable due to their 18 electron configurations.
All experiments were performed using synchrotron radiation generated at the Louisiana State University Center for Advanced Microstructures and Devices (CAMD). Spectra were taken at the Double Crystal Monochromator beamline at port 5A of CAMD. Si(311) crystals were installed in the monochromator and the beamline was calibrated using the strong absorption spectrum of a chromium foil standard. Several other well-characterized reference compounds were also used to ensure the calibration of the beamline. For phosphorus K-edge measurements, InSb(111) crystals were installed in the monochromator, and the beamline was calibrated with the absorption spectrum of AlPO₄. XANES scans were performed from ≈10 eV below each absorption edge to ≈70 eV above each absorption edge. Standard procedures were used in the analysis of raw XANES spectra.

3.3.3 Results and Discussion

The pre-edge region of the chromium K-edge spectrum of chromium hexacarbonyl contains several well-defined features; the dipole forbidden but quadrupole allowed \(1s \rightarrow 3d^{5/2}\) and \(1s \rightarrow 3d^{3/2}\) transitions, the white line feature which is attributed to a \(1s \rightarrow \gamma_{2g}\) transition, a very intense \(\sigma^*\) shape resonance feature due to the CO and diphenylphosphino ligands and a final resonance that is assigned to EXAFS. The breaking of \(O_h\) symmetry in Bis Cr(CO)₄ dpp alkanes is accompanied with decreased white line height and the absence of the \(1s \rightarrow 3d^{3/2}\) feature observed in Cr(CO)₆. Reduction of white line height is indicative of decreased electron density about the chromium center due to ability of the diphenylphosphino groups to donate electron density and fill available orbitals. In the K-edge spectra of the substituted
ligand series, effects that are a function of chromium bond angle are muted, as the symmetry of the center and the four carbonyl groups is the dominant factor in the scattering environment. However, the phosphorus K-edge spectra prove to be extremely sensitive to small changes in bond angle, as shown in the following two figures. Phosphorus 1s ionization potentials for the compounds are not available, but they are estimated to be on the order of 2150 eV based on measurements by Sodhi and Cavel. These spectra exhibit both shifting and broadening of above-threshold resonances as the bond-angle is changed. The effect is amplified by subtracting the nonresonant portion of the background in the second figure.

Figure 37, Chromium K-edge XANES spectra of reference compounds.

Figure 38, Chromium K-edge XANES spectra of (Bis) Diphenylphosphino alkane tetracarbonylchromium series. Graph legend indicates bridge compound.
3.3.4 Calculations

For all of the compounds examined, the FEFF 8.10 \textit{ab initio} self-consistent real space Green's function code for simultaneous multiple-scattering calculations of X-ray absorption spectra and electronic structure was used to create model XANES spectra. For the chromium K-edge and phosphorus K-edge, full multiple-scattering calculations on a sphere of the molecular size were performed. All multiple scattering events within the molecular sphere were considered. The interstitial potential was determined locally about the absorbing atom. The interstitial volume is calculated using the estimation, \( V_{\text{tor}} = \frac{V_{\text{mol}}}{n_{\text{atoms}}} \frac{n_{\text{atoms}}}{r_{\text{min}}^3} \) where \( V_{\text{mol}} \) is the molecular volume, \( n_{\text{atoms}} \) is the number of atoms in the molecule, and \( r_{\text{min}} \) is the shortest bond distance of the
absorbing atom. The energy dependent exchange correlation potential was
calculated with a Hedin-Lundquist self-energy potential.

The results of the FEFF 8.10 calculations are presented in the following figures.

Figure 41, Calculated and experimental spectra of methane-bridged organochromium complex.
Figure 42, Example of comparison between experimental phosphorus K-edge spectra and FEFF 8.10 calculation.
Figure 43, Expanded view of continuum portion of comparison between experimental and theoretical phosphorus K-edge spectra.

Only a sampling of the full range of spectra from the calculations performed is presented in the preceding figures. The experimental trend wherein the observed resonance is shifted to higher energy as the bond angle is relaxed is borne out in the calculations, specifically in the case of the resonance at approximately 2160 eV.

3.3.5 Conclusions

The chromium K-edge XANES spectra of the series were largely insensitive to changes in bond angle. The compounds maintain a distorted octahedral symmetry, which causes deviation from the spectrum of the parent compound, Cr(CO)₆ (O₅) to be minimal. However, the phosphorus K-edge spectra show high sensitivity to the effects of bond angle. The near threshold resonances above the ionization potential are affected both in intensity and energetic position. The calculations performed
qualitatively reproduced the line shapes for the chromium complexes. The relative intensities of the pre-edge features and the intense bound-state resonances were slightly skewed, but the relative energetic positions were correct. It was necessary to adjust the absolute energy scale of the calculated chromium K-edge spectra by ≈5 eV to match the resonance positions of the experimentally observed spectra. The assignments of the character of the resonances agree well with literature work on these compounds. For the phosphorus complexes, the calculations failed to confirm the relative positions of the below threshold resonances and shape resonant features far into the continuum. However, for the features far into the continuum, the calculations agreed very well without adjustment of position or intensity. The vapor pressure of this class of compounds, which is sufficient to sublime them, should be exploited in further studies to determine whether there are solid-state effects present in the spectra presented in this work.

3.4 Inner Shell X-ray Absorption Spectra of Organometallic Ring Compounds

3.4.1 Introduction

Transition metal carbonyl compounds are an important class of compounds and are extremely useful in many applications including catalysis\textsuperscript{122} and biological processes. Molybdenum is an important part of biological processes such as nitrogen fixation\textsuperscript{123} and enzymes involved in the reduction of sulfur\textsuperscript{124}. Molybdenum also functions as a catalyst in petrochemical processes. Tungsten's primary application is in light bulb filaments and it also has the highest melting point of all metals.\textsuperscript{125} Tungsten also has applications in reduction of sulfur\textsuperscript{126} and catalytic
The coordination compounds of interest of each of these metals are in oxidation state 0, with d⁶ configurations (Mo – (Kr)⁴d⁵5s¹, W – (Xe)⁴f¹⁴5d⁴6s²). These metals accept six ligands, and in this context, these ML₆ complexes may be viewed as having six σ bonds. These compounds with heterocyclic chelating rings provide an excellent opportunity to examine the contributions of several types of bonding to inner-shell X-ray absorption spectra. XANES acts as a powerful probe of the electronic states of molecular systems. The systems of interest are derivatives of the well-known hexacarbonyl metal complexes. These compounds have a bridging ligand that creates a ring structure at the two of the equatorial ligand positions. The two systems are tailored such that the molecular geometry is relatively rigid due to the bulky diphenylphosphino groups.

Further, the diphenylphosphino groups donate electron density to the metal center, affecting the ratio of σ and π bonding in the M-L, axial M-CO bonds, and equatorial M-CO bonds. Much has been made of the relationship between bond

![Figure 44](image-url)
length, bond angle and X-ray absorption spectra.\textsuperscript{28,95,127,128} This study probes the function of absorber size and bond angle on the local electronic structure of the central metal atom and the peripheral phosphorus atoms.

3.4.2 Sample Preparation and Experimental

1,2-diphenylphosphino)-ethane tetracarbonyl tungsten (97%) and 1,2-Bidiphenylphosphino)-ethane tetracarbonyl molybdenum (97%) were purchased from Aldrich Chemical and used without further purification. A thin uniform layer of each complex was placed on a piece of Kapton\textregistered tape. The tape was folded over as necessary to achieve the thickness necessary for an optimal absorption edge. The samples were run in transmission mode at the CAMD DCM beamline using standard techniques. All samples are air stable during their minimal exposure to air due to their 18 electron configurations.

XANES experiments were performed at the tungsten and molybdenum L\textsubscript{III} edges and at the phosphorus K-edge of each sample. For tungsten L\textsubscript{III} XANES experiments, Si(311) crystals were installed in the monochromator and the beamline was calibrated using the strong absorption spectrum of a chromium foil standard. The resolution of the beamline is approximately 5 eV in the vicinity of the tungsten L\textsubscript{III}-edge. Several other well-characterized reference compounds were also used to ensure the calibration of the beamline. For phosphorus K-edge spectra and molybdenum L\textsubscript{III}-edge spectra, InSb (111) crystals were installed in the monochromator, and the beamline was roughly calibrated with the absorption spectrum of AlPO\textsubscript{4}. XANES scans were performed from \(\approx 10\) eV below each absorption edge to \(\approx 70\) eV above each absorption edge. The resolution of the
beamline was approximately 0.5 eV in each scenario. Standard procedures were used in the analysis of raw XANES spectra.  

3.4.3 Results and Discussion

The white lines of L_{III} absorption edges are due to transitions of 2p electrons to unoccupied d states in the absorbing atom. The intensity of the white line feature is related to the number of vacancies in the d-band of the absorber. For the molybdenum and tungsten complexes examined in this work, the electronic configurations are (Kr)4d^{5}5s^{1} and (Xe)4f^{14}5d^{4}6s^{2}, respectively. The intensity of the white line in each complex is a function of both the number of allowed transitions that obey the dipole selection rule $\Delta \ell = \pm 1$, and the overlap integral between these states. Molybdenum (z=42, 2p^{3/2}→4d) has a sharper white line than tungsten (z=74, 2p^{3/2}→5d) because as the atomic number becomes higher and the excitation energy is higher, lifetime-effects and increased excitation bandwidth come into play and broadening occurs. The core hole lifetime is shortened and final states become more diffuse. Although the molybdenum white line is greater in absolute intensity, the integrated areas of the molybdenum and white lines differ by only 4 percent. In cis-M(CO_{4})L_{2} complexes, two axial carbonyl groups are in competition with the L groups for both metal dπ orbitals with which they can interact as π acceptors as well as with the two equatorial carbonyl groups which compete mainly with each other for dπ electrons. The spectra in the following figures contain assignments for features based in part upon literature assignments from the spectra of the molybdenum parent hexacarbonyl compound. Ionization potentials are assigned based on estimates in the previous references.
The white line features in the phosphorus K-edge spectra the metal complexes show a reversal of the trend seen in the metal L_{III}-edge spectra, i.e. there is decreased intensity in the molybdenum tetracarbonyl dppe complex relative to the tungsten tetracarbonyl dppe complex. This change in intensity is a result of the electron-donating properties of the diphenylphosphino ligand and metal center’s relative ability to accept electron density from the ligand.\textsuperscript{131} The phosphorus ligand in the tungsten complex has a higher density of accessible “p-like” states than the lower-z molybdenum complex.

The relative contributions of single scattering and multiple scattering to metals in octahedral environments have been examined previously.\textsuperscript{119,130}

In the spectra of the molybdenum hexacarbonyl, the white line (feature one) is assigned to bound state transitions, feature two is assigned to a double excitation, feature three is assigned to a $\sigma^*$ shape resonance, and feature four is assigned to EXAFS. The literature indicates that the feature three is a sigma shape resonance and feature four is due to EXAFS.

The absorption spectrum of Mo(CO)$_4$dppe (presented in figures 49 and 50) is similar to that of the parent compound (Mo(CO)$_6$), with two significant exceptions. First, the white line of the sample is broader than that of the parent compound, and secondly, the feature attributed to a double-excitation is either absent or absorbed within the first peak assigned to EXAFS. Some degree of the spectral broadening may be ascribed to non-monochromaticity of incident radiation at the energies of interest. Also, these differences may be ascribed in part to the presence of the
diphenylphosphino ligand, which introduces electron density and changes the overall density of bound states available to the outgoing electron. Although there are clear similarities between the spectrum of the parent compound and the ethane-bridged complex examined here, a different interpretation for the origin of feature four is used. The relative large intensities of features three and four indicates that both of the peaks are sigma shape resonances. The proximity to the ionization potential and the large intensity make it unlikely that peak four is due to a single-scattering phenomenon. Allowing that peak four is within the XANES regime, it is seen that the relative intensity of peak four is nearly identical to that seen in the hexacarbonyl parent compound, indicating that with respect to the multiple scattering, the distortion of the octahedron resulting from substitution of the bridging ligand is not significant. The absorption spectrum of W(CO)₄dppe (presented in figures 46 and 47) is similar to that of Mo(CO)₄dppe, and the assignments are made in similar fashion.

Figure 45, Molybdenum L_{III}-edge XANES spectrum of Mo(CO)₆.
Fits of the XANES spectra are presented in figures 47 and 49. These fits were performed by summing an arctangent function with a linewidth that approximates the core-hole lifetime with a series of Voigt (Gaussian/Lorentzian) functions that represent the white line and resonances.\textsuperscript{132} The Gaussian and Lorentzian parameters were adjusted to fit the widths of the strong resonances. The energetic position of the arctangent function was then varied to reach a best fit of the data, as previous literature values did not allow for a fit that approximates the experimental data. The white line resonances are also slightly broader than the core hole lifetimes would indicate. It has been determined previously that inhomogeneous broadening in white line features can be ascribed to extensive vibrational excitations in the final state.\textsuperscript{133}

Quantum calculations on these systems will aid in the assignments of the resonances. However, even semiempirical calculations for molecules of this size are computationally prohibitive due to the large number of electrons and the corresponding large number of integrals that must be evaluated to construct an accurate molecular orbital diagram.

Experiments at improved monochromator resolution are possible and highly desirable. The molybdenum L\textsubscript{III}-edge spectra taken in this work are significantly broader than the natural linewidth of the transition. This shortcoming of the work can easily be overcome with either a higher flux beamline where the beam can be better collimated or longer counting times and narrower slits for the CAMD DCM beamline.
Figure 46, Tungsten L_{III}-edge XANES of tungsten tetracarbonyl dppe.
Figure 47, Fit of L_{III}-edge XANES spectrum of tungsten tetracarbonyl dppe. The fit is the sum of Gaussian/Lorentzian peaks with an arctangent function that approximates the continuum absorption. The arctangent function is the integral of a Lorentzian function with a FWHM of 4.4 eV.

L_{III}-edge XANES spectrum of tungsten tetracarbonyl dppe is shown in a preceding figures. The fit is the sum of Gaussian/Lorentzian peaks with an arctangent function that approximates the continuum absorption. The arctangent function is the integral of a Lorentzian function with a FWHM of 4.4 eV. The ionization potential in this case is based on best fit of the data.
Table 7, Summary of Peak types, positions, and intensities used in fit of tungsten L_{III}-edge XANES spectrum of tungsten tetracarbonyl dppe.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Peak Type</th>
<th>Energy, FWHM</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Voigt (40% Gaussian 60% Lorentzian)</td>
<td>10207.5 eV, 6 eV</td>
<td>3.65</td>
</tr>
<tr>
<td>2</td>
<td>Gaussian</td>
<td>10212.5 eV, 5 eV</td>
<td>0.44</td>
</tr>
<tr>
<td>3</td>
<td>Gaussian</td>
<td>10223 eV, 10 eV</td>
<td>0.38</td>
</tr>
<tr>
<td>4</td>
<td>Asymmetric Gaussian</td>
<td>10258 eV LFWHM 12.4 eV RFWHM 15 eV</td>
<td>0.44</td>
</tr>
</tbody>
</table>

Figure 48, Phosphorus K-edge XANES of W(CO)$_4$dppe complex.
Figure 49, Mo L_{III} XANES spectrum of molybdenum tetracarbonyl dppe.
Figure 50, Fit of molybdenum L$_{III}$-edge XANES spectrum of molybdenum tetracarbonyl dppe.

Table 8, Summary of peak types, positions, and intensities used in fit of Molybdenum tetracarbonyl dppe spectrum.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Peak Type</th>
<th>Energy, FWHM</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>75% Gaussian, 25% Lorentzian</td>
<td>2524.8 eV, 5 eV</td>
<td>4.42</td>
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<tr>
<td>2</td>
<td>Gaussian</td>
<td>2530.2, 5 eV</td>
<td>0.56</td>
</tr>
<tr>
<td>3</td>
<td>Gaussian</td>
<td>2541.3, 10 eV</td>
<td>0.45</td>
</tr>
<tr>
<td>4</td>
<td>Asymmetric Gaussian</td>
<td>2571.6 eV, LFWHM 11 eV, RFWHM 15 eV</td>
<td>0.45</td>
</tr>
</tbody>
</table>
Figure 51, Phosphorus K-edge XANES of Mo(CO)$_4$dppe complex.
Figure 52, Comparison of continuum portion of Phosphorus K-edge XANES spectra of W and Mo complexes.
The ionization potential for the L_{III}-edge excitation of the molybdenum complex (≈2533 eV) is an estimate based on literature values for the parent compound and best fit of the data. The fit is the sum of Gaussian/Lorentzian peaks with an arctangent function that approximates the continuum absorption. The arctangent function is the integral of a Lorentzian function with a FWHM of 1.3 eV.

Figure 52 contains above threshold portions of the Phosphorus K-edge XANES spectrum of Mo(CO)_{4}dppe and W(CO)_{4}dppe complexes. What is apparent is that for both complexes, the XANES features mirror one another, with a shift to higher energy in the higher molecular weight complex (Tungsten). In the absence of usable EXAFS data, this z-dependent quantification of the spectral shift may prove helpful in resolving the structure of mixed metal clusters where there is a common neighboring species for a light element such as phosphorus.

3.4.4 Conclusions

Spectra of the bidentate transition metal complexes, molybdenum tetracarbonyl diphenylphosphino ethane and tungsten tetracarbonyl diphenylphosphino ethane have been taken at the L_{III} metal edge and the phosphorus k-edge. This is the first report of XANES spectra of these compounds. These data provide evidence of the z-dependent electronic behavior of this class of compounds.
3.5 X-ray Reflectivity of \( n \)-Alkanethiol Monolayers on Ag(111)

3.5.1 Introduction

Self-assembled monolayers of short and long chain \( n \)-alkanethiols on silver(111) substrates were examined in an X-ray reflectivity study at the National Synchrotron Light Source at Brookhaven National Laboratory. The samples were of interest because of the anomalous grazing incidence X-ray absorption spectra obtained by our group\(^{11,134} \) and others\(^{135-142} \) that probed the sulfur-silver interface of these systems. There is no consensus as to the overall structure of these monolayer systems, and we hope to clarify the origins of the anomalous GIXAFS spectral features found only in the octadecanethiol monolayer. There have been several proposed structures of the sulfur-silver interface, including dialkyl disulfides\(^{137} \), adsorption at multiple sites\(^{143} \), and binding that is directed by substrate preparation\(^{22} \).

The simplest model for assembly of an \( n \)-alkanethiol – silver interface is presented in the following figure.

In the following Drude interface model (figure 53), the silver substrate, sulfur monolayer, hydrocarbon tail and vacuum layers have different indices of refraction. By dividing the sample into differentially thin slabs whose refractive indices are computed with Equation 25 and Equation 26, and creating a model that is the summation of the contributions of each refractive index to the overall reflected wave, it is possible to make a determination of the gross surface structure of the \( n \)-alkanethiol systems.
Figure 53, Schematic of a “step” Drude\textsuperscript{144} interface with a uniform alkanethiol monolayer atop it.

### 3.5.2 Experimental

Experiments were carried out at beamline X-10A of the National Synchrotron Light Source at Brookhaven National Laboratory. The beamline contains a platinum coated fused silica toroidal mirror for 1:1 focusing on a sample located 24 meters from the source. The X10-A monochromator contained a channel cut Si(220) crystal configured for double bounce Bragg reflection. The monochromator was used to select a beam energy of 8 KeV, along with higher-energy harmonics. The incident beam had a height and width of 0.5 and 7 mm, respectively. The vertical and
horizontal beam divergences were 0.2 and 2 mrad, respectively. The X-ray flux incident on the sample was on the order of $10^9$-$10^{10}$ photons/second, as measured with an ionization detector. Samples were placed on a goniometric plate on a six-circle Huber diffractometer. A set of six attenuators was available for insertion in the path of the beam at small angles. A Bicron scintillation detector was used to measure the reflected beam.

Self assembled monolayers of pentanethiol and octadecanethiol were prepared on Ag(111) substrates. Ag substrates for monolayer synthesis were made by thermal evaporation of 99.99% Ag onto Si(100) wafers. The Si(100) wafers were thoroughly cleaned in a piranha solution (H$_2$SO$_4$ and H$_2$O$_2$ (3:1 v/v) at 100° C for 30 minutes) then rinsed with copious amounts of ultrapure water prior to the deposition of the silver. An adhesion layer of 60 Å chromium was deposited on the wafers followed by 2000 Å Ag. The metal-coated substrates were annealed at 350° C for 3-4 hours and then cleaned by exposure to ultra-violet light. Under these experimental conditions, the predominance of the (111) character of the metal surface has been established.$^{145-147}$ The freshly cleaned substrates were then placed in $1 \times 10^{-3}$ M thiol solutions (absolute ethanol) for at least 12 h. Immediately prior to reflectivity experiment, the samples were rinsed with absolute ethanol and dried under a stream of nitrogen.
3.5.3 Results

In the following figure, plots of reflectivity versus the magnitude of the scattering vector, \(|q| = |k_r - k_i| \frac{4\pi}{\lambda} \sin (\alpha, )\), are displayed.

Creating a model that adequately fits the data will provide a better picture of the true structure of the self-assembled systems. The following figure shows the surprising evidence of the presence of dissimilar surface structure in the \(n\)-hexanethiol monolayers and \(n\)-octadecanethiol monolayers.

Figure 54, Log of the reflectivity of \(n\)-hexanethiol and \(n\)-octadecanethiol monolayers versus the magnitude of the scattering vector \(|q|\)
3.5.4 Discussion

X-ray reflectivity data is not invertible, so the measured reflectivity must be compared to predicted results from models. Within physically reasonable parameters, the model may be iteratively refined to better fit the data. In this sense, X-ray reflectivity is used as a probe that can eliminate possible profiles rather than directly determine the true profile.

Because X-ray reflectivity is sensitive to the overall electron density normal to the surface, the general approach is to assign the absorption and dispersion coefficients $\beta$ and $\delta$ from equation 24 as a function of height from the interface. This may be done using a local approximation in which the local $\beta$ and $\delta$ are averages of the local components’ bulk values. For example, in the region of the surface where the sulfur density is only a fraction of the bulk value, $\beta$ and $\delta$ are reduced accordingly. For multi-component layers, an average is arrived at through the sum of the individual components.

The general strategy used is to first postulate the extent of the monolayer coverage, assign a tilt angle to the alkane chain, use the local approximation to compute values for $\beta$ and $\delta$, and then compute the X-ray reflectivity.

The reflectivities of the monolayers serve as signatures of the gross characteristics of the surface structure. This result indicates that the source of the anomalous behavior of $n$-alkanethiol monolayer thiol spectroscopic behavior is due to
a significant difference in the overall surface structure of the adsorbate-monolayer system for the two molecules. Although the extent of the overall difference in the surface morphology of the two systems is indeterminable without a complete model of the refractive indices, it is clear that there is a separation in the features exhibited by the samples.

3.5.5 Conclusions

Careful construction of a model of the interface will allow for determination of the surface structure of the \( n \)-octadecanethiol-silver(111) system. The possibility exists that the surface is of sub-monolayer, monolayer, or multilayer character. The model, when calculated, will provide strong supporting evidence for any interpretation of the structure of \( n \)-alkanethiol interfaces.
4. CONCLUSIONS AND OUTLOOK

The work presented in this dissertation is unified by the theme of correlation of molecular structure to spectroscopic behavior. The excitation of inner shell electrons and monitoring of subsequent events comprise the basis of each experiment. Using synchrotrons to provide high intensity X-rays allows for systematic characterization of chemical systems over a wide spectral ranges. These experiments are building blocks for the future creation of general relationships between molecular structure, chemical composition and photoabsorption dynamics in the hard X-ray regime.

As is always the case, there are many experiments that can be performed to increase the base of knowledge obtained in this work. In the case of the cyclic sulfides, examining the analogous oxygen heterocycles at the oxygen K-edge as well as performing XANES at the carbon K-edge would provide a more comprehensive view of the overall electronic character of the molecules while providing a truly global view of the molecular photoabsorption. An obvious follow-up to the work on the chromium complexes would be to examine them at the chromium L_{III}-edge as well as in gas phase at both the chromium K-edge, L_{III}-edge and phosphorus K-edge. The surface studies in this work would be greatly enhanced by performing experiments on a full range of $n$-alkanethiols, even and odd from $n=1$ to $n=30$, allowing for a full range of data points to fully explore the relationships that develop between chain length and spectroscopic behavior. Additionally, performing the surface studies on single crystals of Ag(111) would provide undisputable evidence of the composition of the substrate, allowing for clearer characterization of the relationship of the
alkanethiol adsorbate and the metal surface. Finally, creating a working qualitative model of the alkanethiol interface for the reflectivity studies will bolster the conclusions made in other areas of the surface work on \textit{n}-alkanethiols on silver.
BIBLIOGRAPHY


(103) Keithley-Instruments. Model 6512 Programmable electrometer.


(110) Zurales, R. W., Private communication - Calculated sulfur 1s ionization potentials for cyclic polymethylene sulfides.


(120) Joos, G.; Peter, K. H. Zeitschrift fur Physikalische Chemie Neue Folge 1958, 18, 74.


APPENDIX, ABSORBER PROPERTIES AND X-RAY DATA

Sulfur, [Ne]3s^23p^4

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<th>Value</th>
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Absorption Edges

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Cross-Section

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<th>σ = µ/ρ (cm^2/g)</th>
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Oxidation States: -2, 2, 4, 6
Phosphorus, \([\text{Ne}]^2\text{3s}^2\text{3p}^3\)

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**Absorption Edges**

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**Cross-Section**

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<td>2156</td>
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Oxidation States: -3, 3, 4, 5
Chromium, [Ar]3d⁵4s¹

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Absorption Edges

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Cross-Section

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Oxidation States: 6, 3, 2
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Absorption Edges

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Cross-Section

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Oxidation States: 6, 3, 2
**Tungsten, [Xe]4f^{14}5d^{4}6s^{2}**

<table>
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<td>Density</td>
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**Absorption Edges**

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<th>Edge</th>
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Oxidation States: 6, 5, 4, 3, 2

Compilation of X-Ray Cross Sections based on the tables of W. H. McMaster, N. Kerr Del Grande, J. H. Mallett, and J. H. Hubbell National Bureau of Standards UCRL-50174 Section II Revision I available from National Technical Information Services L-3,
VITA

Edward E. Doomes was born on September 25th, 1971, in Minneapolis, Minnesota. He grew up in Baker, Louisiana, and graduated from Baker High School. Edward matriculated at Morehouse College in Atlanta where he took a Bachelor of Science degree in chemistry in 1993. He entered graduate school at Louisiana State University in 1995. After an arduous scientific journey, he took the degree of Doctor of Philosophy from Louisiana State University in August 2002. Edward belongs to several organizations, including the American Chemical Society, the National Organization for the Professional Advancement of Black Chemists and Chemical Engineers, Phi Lambda Upsilon, and Alpha Phi Alpha Fraternity, Inc. He continues a tradition of chemistry in his immediate family, with his father, mother, sister and brother all possessing at least one degree in chemistry. At the time of this writing, Edward is married to Erin J. Wilder-Doomes and has one son, Evan Edward Doomes.