Investigations of Uranium Hexafluoride Chemistry on Organic Surfaces

Kristin Nicole Knight

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INVESTIGATIONS OF URANIUM HEXAFLUORIDE CHEMISTRY ON ORGANIC SURFACES

by

Kristin Nicole Knight

A Dissertation

Submitted in Partial Fulfillment of the

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As I sat down to write this section, I was simply moved at just the thought of how many people have been there along my journey. There were people who were there every day who cheered me on, people who have come and gone but still offered sage wisdom and support, and people who may have just entered into the scene, but have mentored me, supported me, and taught me things that I only hoped to know.

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For I know the plans I have for you,” declares the LORD, “plans to prosper you and not to harm you, plans to give you hope and a future. – Jeremiah 29:11
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Abstract

Currently, the process of determining the enrichment levels of uranium for enrichment processing plant is a long and involved process, requiring samples to be collected, shipped, and then processed at a separate facility. This system takes weeks to get results about a critical process. Lowly enriched uranium is used to make fuel rods for nuclear energy, but highly enriched uranium is used to make nuclear weapons. To reduce the time it takes to determine enrichment, we explore creating an alpha detector that is able to connect on-line at the enrichment plant and determine enrichment from the source gas. To enrich uranium, it is processed to uranium hexafluoride (UF₆), which when heated, transforms to a gas, and is pumped through a series of gas centrifuges. UF₆ is known to be very corrosive so any alpha detector would have to be passivated to protect it from attack. We proposed protecting the detector with a self-assembled monolayer (SAM) chemisorbed to gold. However, there is not much literature available on how UF₆ reacts with different functional groups.

To investigate this, we used reflection absorption infrared spectroscopy (RAIRS) to monitor a SAM surface while it was exposed to UF₆ gas. We exposed three different surfaces to UF₆ gas: a hydrocarbon, a fluorocarbon, and an amine surface. All three surfaces showed a high degree of disorganization post-exposure, resulting from UF₆ oxidizing the thiol bond of the SAM. The amine surface showed the most reaction with UF₆ due to the attraction between UF₆ and the lone pair on the terminal amine group. Both the hydrocarbon and fluorocarbon surface had UF₆ adsorb to the surface, but it did not appear to react with either surface.
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List of Abbreviations

AASI = Advanced AlphaSpectrometric Simulations
ALD = Atomic Layer Deposition
AlF$_3$ = Aluminum Fluoride
HEU = Highly Enriched Uranium
HF = Hydrogen Fluoride
IAEA = International Atomic Energy Agency
IBE = Intermolecular Binding Energy
L = Langmuir (unit)
LEU = Low Enriched Uranium
MCA = Multichannel Analyzer
MCT = Mercury Cadmium Tellurium
MFP = Mean Free Path
PIPS = Passivated Implanted Planar Silicon
QCM = Quartz Crystal Microbalance
RAIRS = Reflection-Absorption Infrared Spectroscopy
RGA = Residual Gas Analyzer
SA = Specific Activity
SAM = Self-Assembled Monolayer
SRIM = The Stopping and Range of Ions in Matter
SSD = Sample-Detector Distance
TEA = Triethylamine
TM = Turbomolecular
TOF = Time-of-Flight
TRIM = Transport of Ions in Matter
UHV = Ultra-High Vacuum
UF₆ = Uranium Hexafluoride
UO₂F₂ = Uranyl Fluoride
WF₆ = Tungsten Hexafluoride
WO₃ = Tungsten Oxide
XPS = X-ray Photoelectron Spectroscopy
XRF = X-ray Fluorescent Spectroscopy
CHAPTER 1: Introduction

1.1 Thesis Statement

The purpose of this work was to study the interactions between organic monolayer surfaces and hexafluoride gases. In doing this work, we hope to add to the scientific knowledge more information about the gas-surface interactions between hexafluoride gas and organic surfaces.

1.2 Motivating Factors

The motivation behind this work was to create an on-site near-real-time detector for uranium hexafluoride enrichment. The International Atomic Energy Agency (IAEA) listed as a high priority the timely detection of highly enriched materials in low enrichment facilities.\(^1\) This is important to monitor because highly enriched uranium can be used for nuclear weapons.

Uranium is naturally found in the earth crust. When uranium is mined, it is mined in its ore form. The ore form contains three naturally occurring isotopes: U-238, U-235, and U-234. Of these three isotopes, U-235 is the only isotope that is fissile. This means that this isotope can sustain a fission chain reaction with neutrons of thermal energy. For example, when a U-235 atom decays and releases neutrons, a neighboring U-235 atom has high probability of capturing that neutron and splitting into smaller atoms, releasing more neutrons. A byproduct of fission is heat. This byproduct, heat, is what is used in nuclear power plants to produce steam. Fuel rods, which contain uranium in the form of uranium oxide pellets, are lowered into a pool of water. The water acts to cool the reactor by absorbing heat released from the fuel rods. The water absorbs so much heat that it turns to steam, which spins turbines and converts heat to electrical energy.
The uranium that is mined cannot be used directly for fuel because the enrichment level is too low. Enrichment refers to the concentration of the U-235 isotope as compared to the others. While uranium is mined from the ground in its ore form, it is processed to become uranium hexafluoride (UF$_6$). UF$_6$ is used during the enrichment process for a couple reasons. The first is that fluorine only has one naturally occurring isotope. Therefore, during the enrichment process, which involves a cascade of several gas centrifuges, any separation of weight is based only on the uranium isotope. The second is that UF$_6$ exists as a solid at room temperature and pressure, but when it is heated slightly or pulled under vacuum, it converts to the gas phase.

Naturally, the composition of uranium is 99.26% U-238, 0.7% U-235, and 0.004% U-234. The natural abundance of U-235 is insufficient for power production. To increase productivity, the uranium undergoes the enrichment process to increase the abundance from 0.7% to 3-5% U-235, which is considered low enriched uranium (LEU). This concentration is deemed to be acceptable in both terms of safety and productivity. Once the concentration of U-235 reaches over 20%, this is considered highly enriched uranium (HEU) and can be incredibly dangerous. At high levels of enrichment, the fission chain reaction is harder to be controlled. Large amounts of energy get released very quickly if the chain reaction is not controlled. This is the general concept of nuclear weapons. It is for this reason that the IAEA cares so much about tracking the production of HEU materials.

The current methods for determining enrichment levels are slow, laborious, and time-consuming. Currently, to determine the enrichment level of uranium, a sample is collected at the enrichment facility. An IAEA employee collects samples on cotton swipes from around different parts of the facility. The samples are then shipped off to an IAEA laboratory and undergo an initial characterization with a gamma spectrometer. Then, samples are analyzed by X-ray
fluorescence for the presence of uranium to determine if further analysis is needed. If uranium is detected, then the samples get electrodeposited on a filament and get analyzed by mass spectrometry.\(^2\) This process is slow considering the numerous analysis tools that are used to determine enrichment levels. Also, very few IAEA labs exist in the world so adding the time it takes for the samples to be collected, shipped off, and received to be analyzed can be several weeks. Ideally, determining enrichment levels would only take a couple hours and up to a couple days. Our proposed method would improve the current design by having detection be on-site and in near-real-time.

### 1.3 Detector Design

Our proposed method involves using passivated implanted planar silicon (PIPS) detectors. PIPS alpha detectors are commonly used and are available off the shelf. However, UF\(_6\) is known to be very corrosive to silicon, which makes up the active area material, so these detectors would have to be protected in some way.\(^3\) Previous thermogravimetric studies have shown that these detectors can be used to select single isotopes using PIPS detectors that have been coated in gold. In this method, the different radioisotopes are selected based off their thermal temperature. Instead of selecting radioisotopes based on temperature, we propose modifying these detectors further with an organic monolayer on top of the gold layer to capture UF\(_6\) molecules. Self-assembled monolayers are commonly used as a model organic monolayer. The terminal functional group can be chosen in a way that increases selectivity while also making the alpha detector reusable.
1.4 Reactions of Uranium Hexafluoride and Organic Material

UF₆ was first prepared in 1911 by Otto Ruff. In Ruff’s work, he mainly focused on identifying the physical properties of the molecule. However, he also studied a few reactions of UF₆ with organic materials. Then, UF₆ was largely ignored until the 1940’s when it was found that it can be used in the process of making nuclear energy. The ability of UF₆ to sublime at slightly elevated temperatures and the single isotope of fluorine makes it a molecule that can be separated based on the different isotopic weights of uranium. In the process of making nuclear fuel, tons of depleted UF₆, which are composed of primarily U-238, are produced that currently have no use except to be stored away in barrels. While Ruff did show some interest in using UF₆ as a fluorinating agent, it wasn’t until tons of this depleted byproduct was produced and wasted that more interest in using UF₆ was created.

One of the first reviews of the existing reactions between UF₆ and organic materials was published in 1941. This book summarizes the work of Ruff and several technical reports. They report that UF₆ is stable in oxygen, nitrogen, and dry air. The distinction for dry air is made because UF₆ is known to react rapidly with water to form uranyl fluoride (UO₂F₂) and hydrogen fluoride (HF). They showed that UF₆ acts as a strong fluorinating agent when mixed and dissolved in organic solvents. The resulting products are HF and carbon fluorides. This was shown to hold true for alcohols, ethers, benzene, toluene, and xylene. Alkane hydrocarbons did not dissolve in UF₆, but still were shown to react. Fluorinated hydrocarbons were the only organic material that was shown to be stable in a solution with UF₆.

While the culmination of Ruff’s work and these technical documents claimed that UF₆ acts a strong fluorinating agent, they provide no explanations for reaction mechanisms to explain
these reactions. However, a few years later, work was published that seemed to show that UF₆ might not act as strongly as a fluorinating agent as previously thought. In this work, the researchers were interested in the reaction between hydrogen sulfide (H₂S) and carbon disulfide (C₂S) with UF₆. In an excess of carbon sulfide, the solid product that is formed is uranium tetrafluoride (UF₄). When CS₂ is reacted with a known strong fluorinating agent, cobalt trifluoride, the main product is CF₃SF₅. Instead, UF₆ forms similar products to weak fluorinating agents. This data seems to counteract the previously reported data, but still so little is known about the reaction pathways and how products form. The differences in their conclusions could come down to the difference in their methods.

The difference of methods and results is shown in a paper published several years later that shows that not only does the temperature of the experiment factor into product formation, but reagent quantity heavily factors in as well. For example, when UF₆ is reacted with excess ammonia at temperatures between -50 to 30°C, the products UF₅, NH₄F, and N₂ are formed. However, when this experiment was done at higher temperatures and with less UF₆, between 100 and 125°C, the products NH₄F and N₂ are still produced, but also NH₄UF₅ is produced. This paper also comments on the argument of the strength of UF₆ as a fluorinating agent. They recognize the work by Trevorrow and come to the same conclusion when UF₆ and CS₂ react, UF₆ is acting as a mild fluorinating agent. However, when comparing the reactivity of UF₆ with the transition element fluorides, it was shown that UF₆ has a higher reactivity. While it is the least reactive of the actinide hexafluorides, they conclude that it should be considered a moderate fluorinating agent.

The first works that were published that tried to use UF₆ as an oxidizing agent and determine a reaction scheme for different functional groups were a few papers published by
In these papers, they perform all their reactions with UF$_6$ in a solution of chlorofluorocarbons or chlorohydrocarbons. This makes a stable solution of UF$_6$, which makes it easier to work with. They react UF$_6$ with several different functional groups, including ethers, alcohols, aldehydes, hydrazones, carboxylic acid hydrazides, oximes, amines, benzylic bromides, and adamantanone. For these groups, they reported that UF$_6$ was highly effective as an oxidizing agent. They also reported that UF$_6$ also acts a fluorinating agent for aldehydes and adamantanone. However, there was no reaction seen between UF$_6$ and ketone, esters, amides, nitriles, and nitro groups.

Several years after Olah’s works, another paper came out in 1986 by Goosen that also attempted to determine products from UF$_6$ reacting with different functional groups. While Olah reported no reaction with ketones, in Goosen’s work, when they mixed gas phase cyclohexanone with frozen UF$_6$, they reported a reaction. A peak at 1840 cm$^{-1}$ was seen in the IR spectrum that could belong to acyl fluoride functionality. While this contradicts Olah’s original findings, it is likely due to a difference in method. Olah mixed inert solutions of UF$_6$ with different ketone groups, while Goosen mixed gas phase cyclohexanone with solid UF$_6$. This difference in procedure and corresponding results highlights the complexity of these UF$_6$ reactions based on their chemical environment. However, their reactions with UF$_6$ and aldehydes confirms what Olah saw, in that aldehydes react with UF$_6$ to form acyl fluorides. Goosen was unable to repeat the fluorination of adamantanone, suggesting that fluorination may not actually occur.

To further illustrate the lack of research into UF$_6$ reactions with organic material and the need for more insight into these specific reactions, a report came out in 1986 detailing accidents of a few explosions of UF$_6$ holding tanks. The one common thing linking all the incidents
together is the fact that UF$_6$ came into contact with pump oil and the tanks were being heated during 3 of the 4 incidents. They concluded that all the explosions were a direct result of UF$_6$ coming into contact with the hydrocarbon pump oil. While engineering methods can be put in place to ensure that pump oil won’t have contact with the tanks to minimize the risk, knowing the chemistry behind the explosions minimizes the risk even further. Also, none of the reports up to this point have reported any reactions between UF$_6$ and alkane hydrocarbons. However, these incidents show that while in a lab setting no reaction was seen, something else in the holding tanks may have acted as a catalyst for these reactions to occur.

The interest in UF$_6$ chemistry seemed to die off for a stretch of time as indicated by the lack of articles published between 1986 and 2014. In 2014, an article came out that tried to clear up the discrepancies with the literature that had already been published. This review attempts to do what the articles before it did: use UF$_6$ as a fluorinating agent.

In this review, they go back through all the previously mentioned literature and attempt to rectify any discrepancies by performing their own experiments.$^{22}$ As previously studied, there was no reaction between UF$_6$ and primary alcohols, except when heated and both reagents were in the gas phase. However, at room temperature, they did see a reaction between UF$_6$ and bulkier, aromatic alcohols like 4-(biphenyl)methanol. They reported that the products were a complex mixture of fluorinated and oxidative species, with the fluorinated species being dominated by the oxidative ones. They hypothesize that the extent of fluorination was kept low due to the presence of the aromatic rings. The aromaticity allows a charge transfer complex between UF$_6$ and the ring to form, which stabilizes the intermediate. Then, the intermediate is too stable to react with the hindered fluorides.
It seems as if the stability of the intermediate is the main driver for whether UF₆ reacts as a Lewis acid and oxidizes the reagent or reacts as a fluorinating agent. Take for example two different secondary alcohols. When decan-2-ol reacts with UF₆ in a solution of chlorofluorohydrocarbons, the main product is a fluorinated hydrocarbon, with minimal dehydrated and oxidative products. However, when 4-phenyl-butan-2-ol with UF₆ in a solution of chlorofluorohydrocarbons, the main product was not the fluorinated species. As mentioned previously, this different in reaction products is likely due to the ability of the aromatic compounds to stabilize their intermediates.

There are two commonalities between all the previously published works that react UF₆ with different organic groups. The first is that most reactions are done with UF₆ in a solution of chlorofluorocarbons. While this solution is supposed to be inert, the presence of another reagent may help or hinder reactions that would not have behaved differently if not in solution. The second is that while papers report products, or mixtures of products, the pathways can only be guessed at. If UF₆ were to be used efficiently as a fluorinating or oxidative agent, then the reaction pathway should be known.

1.5 Reactions of Self-Assembled Monolayers and Gases

One way to gather information about the actual reaction pathway between UF₆ and different functional groups is to monitor the reaction while it is occurring. One way that this can be done is using a model organic surface and monitor the reaction during UF₆ exposure using in situ characterization techniques. An ideal model organic surface would be a SAM. The details of SAMs are discussed in the following chapter, Chapter 2. However, briefly, SAMs are an ideal candidate for studying reactions between molecules and surfaces because they act as crystalline
surfaces, and their terminal group can be tuned to different functional groups. Not only can they be used to model different reactions, but they can be used to determine the surface energetics, like attraction forces between the adsorbate and adsorbent.

Molecular beam scattering experiments with SAMs have been used to determine not only the energy of a gas interacting with a surface, but also how the surface reacts because of the gas. For example, by scattering Ar molecules with a set energy off different SAMs, the effect of the terminal group of the SAM and the interactions of the chains was determined. It was shown that chain length plays an important role in energy transfer between the surface and a gas. For a methyl terminal SAM, as the SAM chain got shorter, it became more rigid. The rigidness prevented as much energy transfer between the impinging gas and a surface made from a longer chain SAM. A chain made up of 6 or more carbons allows for long-range motions over the chains.

Molecular beam scattering experiments show that not only does the length of the chain determine the interactions with a gas, but so does the terminal functional group. As compared to a CH$_3$-SAM, energy is transferred less effectively to an OH-SAM. While the CH$_3$-SAM forms a periodic surface, the surface of the OH-SAM is more irregular due to the tendency of the surface to form hydrogen bonds between terminal groups. This causes the surface to be more rigid, therefore, the surface is less efficient at transferring energy through the chains. Other surfaces that form similar hydrogen bonding networks like NH$_2$- and COOH-SAMs also show more inelastic scattering of Ar molecules, further proving that the more rigid surfaces inhibit energy transfer along the chains.

The mass of the impinging molecule on the surface and the mass of the surface also influences the collision energy. When scattering several rare gases from a CH$_3$-SAM and CF$_3$-
SAM, it was shown that the heavier rare gas, Kr, has enough momentum to transfer energy to the chains on the CF₃-SAM. However, a light gas like Ne transfers more energy to the lighter surface. Not only does the mass and chain composition effect the energy transfer, so does the actual packing of the chains. SAMs chemisorbed to silver are more tightly packed than those chemisorbed to gold. The more loosely packed SAMs on gold allow for more thermal transfer between the chains due to Ar having a longer residence time on the surface.

Molecular beam studies can also be used with more complex molecules than inert noble gases. Gases like carbon monoxide, CO, have different rotational modes that interact with stronger or weaker surface forces depending on the impinging rotational mode. Not only does the appearance of different rotational modes affect the energetics, but the ability of CO to interact with the surface causes changes in the energetics that were not previously shown by atomic scattering experiments.

While molecular beam scattering studies use SAMs to get insight into the energetics between different organic surfaces and gases, it offers little insight into any reactions without additional characterization techniques. Because most alkane SAMs are chemisorbed to gold substrates, they can be characterized during the scattering experiments using in situ reflection absorption infrared spectroscopy (RAIRS). For example, by combining the molecular beam scattering with in situ RAIRS, the reaction of a SAM surface with ozone was determined. A vinyl terminated SAM was exposed to a steady stream of O₃ molecules. The time-of-flight (TOF) data from the molecular beam scattering showed that the extent of surface reaction was quite low. The flux of O₃ molecules was increased to gather RAIRS data, which showed that the vinyl terminal groups reacted with ozone. As seen previously, and this work, the first step of ozone reacting is the addition across the double bond to form an ozonide. The ozonide
decomposes and forms formaldehyde, which desorbs and leaves behind a diradical intermediate. The unstable intermediate rearranges to form carboxylic acid groups.

Outside of using a molecular beam to impinge a surface with gas molecules, using in situ RAIRS during gas exposure has been shown to determine reaction pathways as well as reactions rates. Again, looking at a vinyl terminated SAM, the surface was exposed to nitrate (NO$_3$) gas. The RAIRS data showed that over time of exposure, the surface modes for the terminal group, C=C modes, decreased and new modes assigned to O$_2$NO stretches appeared and increased. By integrating the area under the respective curves, a reaction rate and proposed mechanism was found.$^{34}$

1.6 Overview of Thesis

While the overall goal of this work is to build an on-site near-real-time alpha detector, in order to realize building this, we must first understand the science behind different aspects of the detector. This work will explore several different topics that lend themselves to understanding this science. In Chapter 2, we explain the experimental methods that were used throughout the entire work. Chapter 3 looks at modelling alpha spectroscopy to determine if even using gas phase UF$_6$ with an alpha detector is possible or not. Because we plan to modify a PIPS detector, we need to see how UF$_6$ adsorbs to different surfaces over time and its effect on an actual detector. Chapter 4 shows the results of such adsorption studies and proof-of-concept experimental alpha spectroscopy studies. While the two previous chapter focuses mainly on the detector, Chapter 5 is all about the chemistry between UF$_6$ molecules and organic surfaces. By the end of this work, we hope to show that this idea of an on-site detector is one that can and should come into fruition. But also, we show that this method of using in situ RAIRS to study
UF$_6$ gas molecules interacting with surfaces has offered new insights into reactions that were previously only guessed at.

1.7 References

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Chapter 2: Experimental Methodology

2.1 Background

We will discuss the theory and our experiment design for each characterization technique that we use to explore how hexafluoride gases interact with organic materials; a field that has only been minimally explored. In this chapter, the necessary tools to explore these reactions are discussed in detail. We use self-assembled monolayers (SAMs) in an ultra-high vacuum environment to minimize interactions between the surface and ambient gases. SAMs act as a model organic surface and can be tuned with different functional groups to explore a variety of reactions. They are also stable in ultra-high vacuum (UHV). The use of UHV is important because at atmosphere, a surface is constantly bombarded with molecules, while in UHV the surface can remain pristine for longer. Another system that is explored is using SAMs to passivate the surface of an alpha detector. Computational models are used to optimize not only the detector, but also the experimental set-up that is also explored.

2.2 Self-Assembled Monolayers

2.2.1 Introduction

The study of surface reactions requires that the surface be pristine and remain clean throughout the experiment. Maintaining the surface is accomplished by keeping the sample in a low-pressure environment. Before the experiments begins, we need to make a careful choice in what surface we use to study. Because one of the goals of this work is to coat an alpha detector with an organic material, the first choice for a surface is a self-assembled monolayer (SAM). Most polymers are too amorphous to characterize interactions that are happening at the surface.\textsuperscript{1} SAMs offer a more defined surface that can be functionalized, as compared to metal or metal
oxide surface, which is prone to contamination due to adsorbates lowering the free energy of the interface between the surface and the environment. These semicrystalline surfaces are easy to synthesize and characterize and are stable in UHV environments, further making them a great choice for an organic surface. Several of the characterization methods are discussed in detail later on.

In our work, we use gold as a substrate. Gold has historically been the most studied substrate for SAM's. This is because gold, although expensive, is easy to obtain as a thin film and is used as a common substrate for other existing spectroscopies and it is also inert. For SAM's, we use the Au (111) facet. The sulfur head groups bind to the gold to form a strong Au-S bond. This creates a $\sqrt{3} \times \sqrt{3}$ R30° overlayer on the gold. This overlayer creates a configuration with the sulfur heads having a nearest neighbor of ~21 Å²/molecule.

As shown in Figure 2.1 the sulfur head binds to the gold. Then, the carbon chains that make up the backbone of the SAM assemble and then align overtime by allowing for high degrees of van der Waals interactions between the chains, which minimizes the free energy of the surface. It has been shown that for optimal packing, and therefore lower energy, the chains should be longer than six methylene groups. These chains also offer protection of the Au-S bond from oxidation in the ambient environment.
Figure 2.1: Self-Assembled Monolayer (SAM) on gold substrate. The SAMs rotate and tilt to minimize the surface’s energy.

Another way the chains minimize their energy is by rotating ($\alpha$) and tilting ($\beta$) relative to the surface normal, as seen in Figure 2.1. While the process of SAM synthesis, which simply requires submerging a clean gold substrate into thiol solution, happens quickly, the process of the chains reordering and aligning happens much slower. Typically, we allow for $>18$ hours to let the surface optimize in solution.\textsuperscript{13}

The last part of the SAM is the terminal functional group. This is what forms the gas-surface interface and makes up the functionality of the SAM. The terminal group can be tuned after formation chemically to the desired group.

2.2.2 Materials for SAM Fabrication

All the alkanethiols used in this work for making SAMs were commercially available and were used without further purification. 1-octadecanethiol ($\text{HS(\text{CH}_2)_{17}\text{CH}_3}$) (98% purity), 16-
amino-1-hexadecanethiol hydrochloride (HSCH$_2$(CH$_2$)$_{14}$CH$_2$NH$_2$·HCl) (96% purity), and 1H,1H,2H,2H-perfluorodecanethiol (HSCH$_2$CH$_2$(CF$_2$)$_7$CF$_3$) (97% purity) were all purchased from Sigma-Aldrich. 200-proof ethanol and triethyl amine solvents used were obtained from Sigma-Aldrich. Gold substrates used in these experiments were purchased from Evaporated Metal Films (EMF). The 1 in x 1 in gold substrates consisted of float glass coated with a 50 Å chromium adhesion layer and topped with 1000 Å gold. QCM crystals were 6 MHz (14 mm) and were purchased from Inficon.

### 2.2.3 Formation of SAMs on Gold

Formation of SAMs on gold slides and QCM crystals was the same process. Prior to use, all gold substrates were cleaned with fresh piranha solution, made up of 70% concentrated sulfuric acid and 30% hydrogen peroxide. Piranha solution should be handled with care as it reacts violently with organic materials and releases great amounts of heat. Substrates were immersed in the piranha solution for 1 hour before being rinsed first with copious amounts of 18 MΩ water, then with pure ethanol. Cleaned substrates were immediately placed in the 1 mM ethanolic thiol solution. Each sample was in solution for at least 24 hours prior to use to achieve a well-ordered and densely packed monolayer. Surfaces made from 1-octadecanethiol and 1H,1H,2H,2H-perfluorodecanethiol were rinsed with copious amounts of pure ethanol to remove any unbound thiols. The surface made from 16-amino-1-hexadecanethiol hydrochloride was first rinsed with triethyl amine to remove the chloride ion and then rinsed with pure ethanol to remove any unbound thiols. After the substrates were rinsed, they were dried under a stream of UHP N$_2$. All glassware used was cleaned in a base bath and thoroughly rinsed with deionized water prior
to use. Plastic forceps were used to handle samples and were cleaned by sonicating in isopropyl alcohol for \(~30\) min prior to use.

### 2.2.4 Surface Characterization

#### 2.2.4.1 Reflection Absorption Infrared Spectroscopy

Reflection absorption infrared spectroscopy (RAIRS) is a surface technique that uses infrared spectroscopy to characterize thin films.\(^\text{14}\) In order to use transmission IR to study molecules adsorbed directly on a surface, the surface must be thin enough to allow for transmission. This presents challenges in characterizing these systems because enough adsorbed material is needed to produce useful spectra, but too much can lead to insufficient transmission of infrared light through the sample. One way that researchers have studied adsorption of molecules on metal surfaces is to use a metal oxide support that has been decorated with small metal particles. Instead of studying the adsorption of gases on metal oxides by transmission IR, a reflection technique would allow for the study of the adsorption of gases on bulk metal. This eliminates the interaction between the gas and the oxide support and also increases the spectral regions to beyond that which is just transparent by the oxide support.\(^\text{15}\)

For a metal surface, if the incoming light is perpendicular to the surface normal, the incident and reflected light combine to form a standing wave-field.\(^\text{14}\) This means that a node exists at the surface for the metal for the standing wave-field, therefore the amplitude of the electric field is zero. Because there would be no electric field, there is nothing for the adsorbed material to interact with. If the incident light was nonnormal to the surface, meaning the light hits the surface at an angle, then the phase change of light would depend on both the polarization of light and the angle of incidence. For polarized light that is parallel to the surface normal, which
we denote as s-polarized light, at any angle of incidence, the phase change of light is 180°. However, for polarized light that is perpendicular to the surface normal, which we denote as p-polarized, the phase change depends on the incident angle of light. When the angle of incidence is 90°, the phase change is 180° and the reflected light cancels the incident light. A high angle, yet not 90° should provide optimum absorbance for the carbon chains of a thin film.

RAIRS is a great technique to characterize surfaces like self-assembled monolayers (SAMs). Because the carbon backbone of the SAM orients itself almost perpendicular to the surface, the chains are sensitive to p-polarized light. Figure 2.2 demonstrates the dipole moment of a SAM chain chemisorbed to gold compared to the different polarizations of light. As this figure shows, the dipole moments of the CH\textsubscript{2} modes are angled in such a way to absorb the p-polarized light, while the s-polarized light does not interact with these dipole moments. Using s-polarized light as the background spectrum, p-polarized light can be used to characterize how well-ordered a surface is before, during, and after an experiment.
Figure 2.2: P-polarized light is reflected off the metal surface and excites the dipole moment of the carbon chain. S-polarized light cancels itself out due to the phase change of light as it reflects off the surface.

RAIRS was used to track in situ reaction products and surface changes of the SAM surface during exposure to hexafluoride gas. A Bruker 80v spectrometer was connected to a UHV chamber through a series of gold coated Harrick mirrors. Focused IR radiation from a SiC globar was reflected onto the gold surface at ~86° relative to the surface normal and directed to a liquid nitrogen cooled mercury cadmium tellurium (MCT) detector. This resulted in radiation that could be detected in the mid-range (400-4000 cm\(^{-1}\)). A polarizer was placed at the entrance window of the chamber so that the incoming light could be changed between p- and s-polarized light. For the in situ gas exposure studies, the p-polarized light spectrum of the original SAM was used as the background. Any positive modes in the difference spectrum are a result of new bonds forming in the system because of gas exposure, while any negative modes are the
disappearance of surface modes. All spectra shown for the in situ exposure studies were the average of 256 scans with a resolution of 2 cm\(^{-1}\), which took ~1 min/spectrum.

While the RAIRS set-up described above was used to collect a bulk of the RAIRS data that will be described later in this work, another RAIRS set-up was used to collect data on SAMs that have been chemisorbed to gold substrates with varying thicknesses of gold. This set-up and work are described below in section 2.2.5.

2.2.4.2 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface technique that can characterize not only the elements that are present in a sample, but also their oxidation state based on what they are bound to.\(^ {17–19} \) In our experiments, we use XPS to help identify any potential reaction products on the SAM after hexafluoride gas exposure.\(^ {17,20–22} \) In this technique, using an Al K\(\alpha\) source, X-rays bombard the surface of the sample, causing core electrons to eject. Figure 2.3 demonstrates the fundamental principle of XPS. The ejected core electrons then reach the detector, and the kinetic energy is measured. The number of electrons that reach the detector are directly proportional to the concentration in the sample. Equation 1 shows that based on the energy of the X-ray photon (for an Al K\(\alpha\) source, \(h\nu = 1486.7\) eVs), the binding energy can be found.\(^ {19} \)

\[
E_{binding} = h\nu - E_{\text{kinetic}} - \phi \\
\text{Eqn. 1}
\]
The term $\phi$ is the work function of the surface and this term corrects for the electrostatic environment of the electron. It is an instrumental correction factor that helps account for energy lost in the system.

**Figure 2.3:** Depiction of XPS scheme. A core electron absorbs an x-ray and ejects from the core.

The bulk of the XPS data presented in this work was performed on surfaces before and after they were exposed to tungsten hexafluoride (WF$_6$) gas at Argonne National Laboratory. Samples that were exposed to uranium hexafluoride (UF$_6$) were not allowed to be removed from the protective hood that housed the UHV chamber and therefore could not be analyzed by XPS. For the samples that could be analyzed, they were removed from the chamber and then had to be surveyed out of the hood before they could be transferred to the XPS. The process of surveying the samples involved using a Geiger counter above the surface of the sample and in no way
should affect the sample itself. Once the samples were cleared, they could be transferred into the vacuum chamber of the XPS instrument. This system was a K-Alpha system from ThermoFisher that used monochromatic radiation from Al K α to collect data. For our samples, the high-resolution spectra were acquired in the region of interest using the following parameters: standard lens mode, pass energy of 50.0 eV, and energy step size of 0.1 eV. The average time between removing samples from the chamber and installing them into the XPS was ~48 hours.

When using the XPS to collect data, the first scan taken is a survey scan, an example of which is shown in Figure 2.4. This example survey scan was taken after a 1-octadecanethiol surface was exposed to WF₆ gas. The survey scan scans the entire energy range (1350 – 0 eV) for a sample spot. This survey provides data about all the elements that are in the sample. In this survey scan, the W 4f, Au 5p, Au 4f, C 1s, Au 5d, Au 4p, and Au 4s peaks can be seen. It should be noted that a peak at ~643 eV is seen in the survey. The only possible assignment for this peak is Mn 2p. However, this peak is seen at the same position before and after exposure for this particle sample. Also, this peak is seen on all the survey scans for a 1-octadecaenthiol surface, regardless of exposure. This indicates that manganese is a possible impurity in the 1-octadecanethiol sample.
Figure 2.4: A XPS survey scan of a 1-octadecaenthiol surface after exposure to WF$_6$ gas.

To get better quantitative data, scans of an energy region of interest are taken after the survey scan. Just by looking at a smaller region of interest more scans can be taken in a short amount of time to provide higher resolution. This is important to do because typically only a small number of survey scans are taken since they take a long time to acquire. This means that some elements, which aren’t as sensitive to the x-rays, may not produce peaks in some survey scans. For example, the survey scan in Figure 2.4 does not show S 2p peaks, but when more scans are taken in the energy region for S 2p, peaks do appear. These regions of interest are selected prior to the XPS experiment. For the hexafluoride gas exposure studies, each surface had a long survey scan, followed by higher resolution scans for the Au 4f, C 1s, F 1s, O 1s, N 1s, S 2p, and W 4f regions.
Following data collection, the high-resolution spectra were fit using the program XPSPEAK41. First, a Shirley background was subtracted from each spectrum to account for the inelastic scattering of electrons that contribute to background broadening.\textsuperscript{23,24} The XPS signal is fit with a symmetric curve containing a Gaussian/Lorentzian sum with 70% Gaussian and 30% Lorentzian character. For elements with the 1s high-resolution region, for each chemical environment, a model with only one component was fit. However, elements with either the 2p or 4f high resolution regions, a model with 2 peaks was required for the fit. This is due to what is known as the spin-orbit splitting. The equation for total angular momentum, $j$, is shown below in Equation 2, where $l$ is the angular momentum and $s$ is the spin angular momentum. When the angular momentum, $l$, is 0, then the only possible value for $j$ is 1/2. However, for core levels where $l > 0$ (p, d, and f), then the total angular momentum number, $j$, will have 2 values. For example, when $l = 1$, as in the case of a p orbital, then $j = 3/2$ and 1/2. The ratio of the area for the two peaks is set based on the degeneracy of the energy for each $j$ value. For example, for a p orbital, when $j = 1/2$, the total angular momentum has 2 different orientations that it can have the same energy. For $j = 3/2$, this value is 4. This means that the ratio for the areas for $j = 1/2$ and $j = 3/2$ is 1 to 2. For the f-orbitals, the values of $j$ are 5/2 and 7/2 and their area ratios are 3 to 4.

$$j = l + s$$  \hspace{1cm} \text{Eqn. 2}

While the XPS system described above was used for a bulk of the XPS data collected in this work, another XPS system was used to collect data on SAMs that been chemisorbed to gold substrates with varying thicknesses of gold. This set-up and work are described below in section 2.2.5.
2.2.4.3 Quartz Crystal Microbalance

Quartz crystal microbalance (QCM) was used to characterize adsorption between the hexafluoride gas and the SAM surface.\textsuperscript{25,26} QCM measures the change in frequency as an adsorbate adsorbs to the surface.\textsuperscript{27} The principle behind QCM is the piezoelectric effect. The quartz vibrates at a certain frequency when voltage is applied and as a molecule adsorbs to the surface, the vibration frequency decreases due to an increase in mass on the surface. This change in frequency can be related to the change in mass by the Sauerbrey Equation, Equation 3, where \( f_0 \) is the resonance frequency, \( A \) is area, \( \rho_q \) is density of quartz, \( \mu_q \) is the shear modulus, and \( \Delta m \) is the change in mass.\textsuperscript{27}

\[
\Delta f = -\frac{2f_0^2}{A\sqrt{\rho_q\mu_q}} \Delta m
\]

Eqn. 3

The UHV system, which is described in detail in section 2.4, contains a QCM drawer so that RAIRS data and QCM data could be collected at the same time and in the same environment. The QCM was operated using a Inficon oscillator and a Kurt J Lesker Rate/Thickness monitor to measure any change in frequency of the QCM + SAM surface once it was exposed to hexafluoride gas.

While the QCM drawer in the chamber was used to directly compare RAIRS and QCM data, another system was used to collect more detailed data for WF\(_6\) exposed to SAMs. The pulsed WF\(_6\) QCM experiments were conducted in an atomic layer deposition (ALD) instrument. After the samples were installed, they were exposed to pulses of WF\(_6\) gas under a continuous purge of 1 torr argon. These experiments were performed at room temperature unless otherwise
noted. Also, these samples were only exposed to WF6 since the system was not rated for radioactive work.

2.2.5 Different Thicknesses of Gold for SAMs

2.2.5.1 Introduction

The focus of this work centers on building an alpha detector that is able to be brought into enrichment facilities and determine enrichment based on the signal from the alpha detector. We propose modifying the face of the detector first with a layer of gold, followed by the chemisorption of self-assembled monolayers. In order to maintain resolution for the alpha detector, the surface cannot be modified with thick layers of gold. The SAM, no matter which surface is chosen, is a very thin layer in its nature and is no more than a few nanometers thick. However, the SAMs that are made on store bought gold surfaces are usually made on 100 nm of gold that is deposited on either 10 nm of either chromium or titanium that acts as a binder layer for the gold to the glass substrate. SAMs of varying different functional groups and chain compositions have been used across countless studies and have been shown to make well-ordered monolayers using similar gold substrates. We don’t anticipate that using a thinner layer of gold should affect monolayer formation, as long as the gold layer covers the substrate uniformly. To test our hypothesis, we created SAMs on substrates of different thicknesses of gold and characterized the SAM using RAIRS and XPS.

2.2.5.2 Gold Surface Deposition

To create the custom gold slides, first microscope cover slips (Levenhuk G100 Cover Slips 0.94” x 0.94” x 0.005-0.006”) were cleaned in piranha solution (70% concentrated sulfuric
acid/30% hydrogen peroxide) for 30 min, and then rinsed thoroughly with 200 proof ethanol and
dried under a stream of UHP N₂. The cleaned substrates were then transferred to the UHV
chamber of the AJA Orion 5 deposition unit through a load lock transfer arm system. The
samples were allowed to pump down overnight to allow the chamber base pressure to reach
UHV. Metal layers were built by sputtering the source targets with the ionized argon gas. The
thickness of the metal layers was monitored with a QCM crystal. All the substrates were first
deposited with a 3.5 nm thick layer of titanium followed by either a 10, 20, or 100 nm layer of
gold.

2.2.5.3 Monolayer Quality of Different Gold Surfaces

SAMs made from 1-octadecanethiol were made on a clean 10, 20, and 100 nm surface of
Au that had a binding layer of 3.5 nm Ti. The three SAM surfaces made on different thicknesses
of gold were characterized by RAIRS and XPS. Figure 2.5 shows the RAIRS data for the three
different surfaces. This figure shows that the asymmetric and symmetric stretches for the CH₂
modes are at 2918 and 2848 cm⁻¹, respectively, for the 20 and 100 nm surfaces. This indicates
that the chains reside in a crystalline like environment and that monolayer quality is good.³,¹⁰
Because we do not see any change in the peak position or the FWHM of these peaks, we can
assume that the thinner layer of gold does not affect monolayer formation. However, the 10 nm
gold substrate spectrum shows no peaks. Visually, the sample contained very little metal on the
glass slide and was therefore not reflective. Even though RAIRS could not be performed on this
sample, XPS could.
Figure 2.5: RAIRS data of a 1-octadecaenthiol surface on 100 nm, 20 nm, and 10 nm on gold deposited on a glass slide first covered with 3.5 nm Ti. No peaks are seen for the 10 nm surface because not enough metal covers the surface to make it reflective.

Figure 2.6 shows the high-resolution XPS data for the C 1s and S 2p regions for all three surfaces. In the C 1s region, there is a peak at ~284.9 eV for all three surfaces, which corresponds to the C-C bond of the SAM backbone. While the 10 nm layer could not be analyzed with RAIRS to confirm monolayer quality, the XPS data shows a C 1s peak position that is consistent with the other two surfaces. The peak position of the S 2p 3/2 peak at ~162.0 eV indicates that sulfur is bound to gold. Just as with the C 1s data, there is no change in the peak
position of the S 2p 3/2 peak as the layers of gold get thinner. Another indication that the SAM surface is unaffected by the amount of gold is the C to S ratio of the area under each respective peak. After normalizing the ratios of carbon and sulfur to the area of the gold, all three surfaces showed a C/S ratio of ~16.5. This confirms that as long as there is sufficient coverage of gold, a well-ordered monolayer should form.

**Figure 2.6:** High-resolution XPS data of the C1s and S2p region of a 1-octadecanethiol surface on 100 nm, 20 nm, and 10 nm on gold deposited on a glass slide first covered with 3.5 nm Ti.
2.3 Alpha Spectroscopy

2.3.1 Introduction

In the United States, since 1990, ~20% of the electricity generated has come from nuclear power plants. We are not the only ones generating power this way with 31 other countries having commercial nuclear power plants. The most common fuel source comes from uranium. Once uranium is mined from the ground, it undergoes several chemical transformations to make it into UF$_6$, which is the form used to enrich the uranium. Enrichment refers to the process of increasing the concentration of the U-235 isotope, from the natural abundance of ~0.7% to ~5%. Naturally occurring uranium exists in three isotopes: U-238, U-235, and U-234. While the U-238 isotope makes up most of the uranium (>99%), the U-235 isotope is the isotope of interest since it is fissile, meaning that it can sustain a fission chain reaction.

Over time, the uranium atoms will decay because their nuclei are unstable. Uranium atoms decay by alpha decay, releasing an alpha particle (charged helium atom), daughter products, more neutrons, and heat. The U-235 isotope can capture neutrons with lower energy and then undergo fission, releasing more neutrons that are then captured by other U-235 isotopes, thus sustaining the fission chain reaction. At such a low natural abundance, this process does not produce a lot of heat and would be ineffective as an energy source. Therefore, uranium is enriched.

The process of enrichment is slow, but it must be carefully monitored because highly enriched uranium can be used to make nuclear weapons. Typically, an enrichment facility consists of a large warehouse with thousands of gas centrifuges, each one connected to the previous one. In a single centrifuge, a flow of UF$_6$ gas comes in, and the centripetal force of the centrifuges forces the heavier isotope, U-238, to the outer walls, while the lighter isotopes, U-
235 and U-234, concentrate towards the middle. Then, a line feeds the more enriched gas to the next centrifuge, where the process continues until the desired enrichment is met. It is at the enrichment facilities where enrichment is measured periodically by the International Atomic Energy Agency to ensure that enrichment levels are kept low. Each isotope releases an alpha particle with a specific energy so the characterization and concentration of each isotope can be found with an alpha detector.

2.3.2 Modelling Alpha Spectroscopy

2.3.2.1 Advanced Alpha-Spectrometric Simulations

Advanced Alpha-spectrometric Simulations (AASI) uses a Monte Carlo method to simulate an alpha particle energy spectra. This program can be used to find the most important factors in a system, which can lead to optimizing the whole counting system for the detector. For alpha particle counting, careful sample preparation is essential since alpha particles continuously lose their energy as they travel through matter. Modelling UF$_6$ gas as the sample is of particular interest to us since a gas sample is far from the more traditional samples and this program was designed to model non-traditional samples. Another challenge with the gas sample is the sample-detector distance (SSD). Typically, in a counting experiment, the SSD is kept relatively large (~ a couple mm) to minimize peak spreading due to energy loss. However, because we are measuring a gas, the source actually comes into contact with the detector face. By utilizing this program, we can verify if this method is feasible and optimize different conditions if it is.

The program starts by emitting a particle from a randomly selected point within the confines of the source parameters and with a certain energy. The emitted alpha particle is tracked, and the continuous energy loss is calculated as that particle interacts with other source
molecules or an absorbing layer. This movement is assumed to be linear. The energy loss is calculated using the stopping power parametrization. Once the particle energy is below the cut-off value, it is no longer tracked. If the alpha particle hits the active volume of the detector, all the remaining energy is assumed to be deposited and that alpha particle is counted in the resulting spectrum.

The program AASI was used to do complex alpha spectroscopy modelling. For our studies, we are interested in modifying a passivated implanted planar silicon (PIPS) detector with gold and exposing it to UF$_6$ gas. In this work, we modelled the PIPS detector after a detector from Mirion Technologies (Model No. A450-18AM), which was the model used in our experimental studies. This detector has a total area of 450 mm$^2$, which corresponds to a diameter of 12 mm. This model has an intrinsic resolution of 18 keV. For the series A detectors, Mirion claims that they have a minimum active area depth of 140 µm, which is more than enough to capture the uranium isotopes of interest, so a value of 140 µm was set for the active volume. They also claim that all their PIPS detectors have an entrance window that is <50 nm, so the value of the dead layer thickness was set to 0.05 µm. The dead layer material is silicon. The peak shape parameters were left as the default settings: total tailing 1.0, fast component 10.0 keV, intermediate component 66.0 keV, slow component 1000.0 keV, fast/intermediate area ratio 12.0, and slow/intermediate area ratio 0.25.

The three naturally occurring isotopes of uranium, U-238, U-235, and U-234, were set as the source for radionuclides. The number of decays was determined based on the decay constant and abundance of each isotope. The decay constant is found by taking the natural log of two divided by the isotopes naturally occurring half-life. The abundance of each isotope is based on the different enrichment levels. Enrichment refers specifically to the abundance of the U-235
isotope. Focusing on the U-235 isotope, we denote natural abundance as 0.7%, low enriched as 5%, and highly enriched as >20%. Because we know that U-234 is enriched alongside U-235, we can also calculate the U-234 abundance at higher enrichments. Finally, the amount of U-238 is found by simply adding the other two isotopes and subtracting from 100%.

The source was a homogenous source, representing a column composed of UF$_6$ gas on the detector face. The distance of the column of gas from the detector (SSD) was always set to 0.02 mm. Ideally, this value would be set to 0 mm to represent a column of gas that has direct contact with the surface of the detector. However, this value is the minimum distance the program allows to give stable conditions, while giving a detector efficiency >49%. The source diameter was set to 12 mm to match the detector diameter, which maximizes detector efficiency. The thickness of the column was changed based on the calculations being run, but the central and side thickness always matched and had 0 fluctuation. The density of the gas was also changed based on the calculations run. The density was found based on the volume of the column above the detector and on the number of molecules based on the pressure of gas simulated.

The absorbing layers were used to modify the surface of the detector with different materials. For each material, the density was set as well as the desired thickness of the layer. The fluctuations were always set to 0. Before starting the calculations, the emissions were set to emit to source detector cone only to maximize detector efficiency. The energy bin size was 4.0 keV and the integration step was 0.2 µm (AASI requires a value higher than 0.1). Figure 2.7 shows a model of the simulated column of UF$_6$ gas above an example modified surface.
2.3.2.2 Stopping and Range of Ions in Matter

The program SRIM (The Stopping and Range of Ions in Matter) is broken into two parts: SRIM and TRIM (Transport of Ions in Matter). For our work, we use the SRIM portion of the program. SRIM uses a quantum mechanical treatment of ion-atom collisions to calculate the stopping and range of ions into different materials. Because we are interested in uranium decay, the ion chosen is helium. As the helium ion travels through matter, it loses energy as it collides with molecules. As soon as scientists discovered this phenomenon of energetic particles losing energy, they tried measuring this energy loss to further study the atoms that were releasing them. From the work of Bragg and Kleeman testing different ions through various thin films, they were
able to establish Bragg’s rule, which states that the stopping power of a compound can be formed from the linear combination of the individual elements stopping powers.39

For our studies, we are interested in using SRIM to calculate the energy loss of an alpha particle through different materials. One of the goals of this project is to modify the surface of the PIPS detector to protect it from UF₆ gas. However, the resolution of the detector must be maintained so the choice of the material to modify with must not deteriorate the signal. The stopping power of a helium ion (alpha particle) through different materials was calculated. The output of the program is the distance that the helium ion can travel before losing all energy to the target material.

2.3.3 Experimental Alpha Spectroscopy

2.3.3.1 Experimental Setup

The experimental alpha spectroscopy experiments were performed in the UHV system that is discussed in detail in section 2.4. The alpha detector that was chosen was a series A (Model No. A450-18AM) PIPS detector from Mirion Technologies. When a uranium atom decays and releases an alpha particle, if that alpha particle hits the surface of the detector, it creates several electron-hole pairs in the active area of the detector. These electron-hole pairs are counted, and the number of pairs made corresponds to a specific energy, resulting in one count for that specific energy. Only one alpha particle can be counted at a time, meaning there is a “dead time” for the detector. More alpha particles may strike the detector but are not counted since the detector is still counting the first alpha particle. Therefore, it is important to minimize the activity of the sample.
In our sample, we can control the activity by changing the pressure in the chamber. Typical operating pressures in an enrichment facility are 1-80 torr so we want to stay in this range to ensure that our detector can work in that environment. To minimize the gas head space above the detector to help with resolution at these pressures, a puck was placed on the detector that covers all but a minimal space of a desired height above the surface. The PIPS detector was connected to a multichannel analyzer and the program Genie 2K was used to process any data.

2.3.3.2 Experimental Alpha Spectroscopy Issues

To our knowledge, using a PIPS detector with gas-phase UF$_6$ has not been documented before. Typically, a sample for alpha spectroscopy is thin and kept ~10 mm from the detector during counting. Both of these are done to achieve high resolution. While modelling experiments showed that gas-phase spectroscopy is possible, in practice, these experiments proved to be much harder to execute. During the experiment, it was difficult to get any peaks and the dead time of the detector remained near 100% even after evacuation. This indicates that during the experiment, radioactive material adsorbs to the surface of the detector and is not removed by vacuum. Each time after the experiment, once the chamber was opened to remove the detector, a red precipitate formed around the electrical end of the detector. X-ray fluorescent spectroscopy (XRF) analysis showed evidence for uranium in the precipitate. We hypothesize that while the surface of the detector was protected, it seems as if the electronics were not as well protected and the UF$_6$ gas began to destroy some components.
2.4 Ultra-High Vacuum Chamber

2.4.1 Preface

The following description of the UHV chamber used throughout this work was one that was custom built at Argonne National Laboratory. For future reference, the details and operation of the chamber are contained below. This information is of potential interest to future group members, but the chamber itself has been decommissioned at Argonne.

2.4.2 Chamber Description

2.4.2.1 Background

The UHV chamber was built at Argonne National Laboratory specifically for the project to develop a new approach for rapidly measuring UF$_6$ enrichment levels in UF$_6$ gas, as shown in Figure 2.8. By maintaining UHV conditions in the main chamber (~10$^{-8}$ torr), we can help ensure that any reactions observed are a result of the hexafluoride gas interacting with the surface and not a product of contaminants. The benefit of UHV is that it increases the mean free path (MFP) of molecules, which decreases the number of collisions between gas phase molecules and the chamber. A surface with the normal surface density of ~10$^{15}$ molecules/cm$^2$ at atmospheric pressure will have a flux, F, of molecules striking the surface as given by Equation 4, where m is the average molar weight of gaseous species, T is temperature, k is the Boltzmann constant, and p is pressure.$^{11}$

$$F = \frac{p}{(2\pi mkT)^{1/2}} \quad \text{Eqn. 4}$$
If we reduce the pressure to $10^{-6}$ torr at room temperature, the flux reduces to $\sim 10^{15}$ molecules/cm$^2$/sec, meaning that the surface is covered by ambient gas molecules within seconds, assuming a sticking probability of 1 for each incident gas molecule. This shows how the unit Langmuir (L) is derived. A 1 L exposure should cover the surface with a monolayer of gas molecules in one second, assuming that each gas molecule sticks. By maintaining UHV, which is a couple of magnitudes lower than $10^{-6}$ torr, in the main chamber where the surface is held, the surface can remain pristine and free of contamination for longer.

### 2.4.2.2 UHV Chamber Design

As mentioned, the UHV chamber used in this work was custom built to handle not only the toxic nature of hexafluoride gases, but also to maintain a safe work environment for the radioactive UF$_6$ gas. One of the main safeguards is housing the entire UHV chamber and pumps in a floor to ceiling fume hood, which is accessible only on two sides by a series of sliding plexiglass doors. While ensuring safety, a challenge of the fume hood is the limited space since anything that was brought into the hood had to remain until it could be surveyed out and transferred to a waste bin. With that in mind, the chamber was built according to the diagram shown in Figure 2.8A. A more detailed schematic of the workings of the chamber is shown in Figure 2.8B.
Figure 2.8: (A) A 3D rendering of the UHV system as it sits in the containment hood. (B) A detailed schematic of the UHV system.
The most prominent feature of the UHV system is the reaction chamber. The reaction chamber shares a backing scroll pump with the load lock chamber, which evacuates higher pressures of gas from each chamber. To pump down to UHV, each chamber has their own turbomolecular (TM) pump. The reaction chamber also contains an IR bake-out lamp and is surrounded by heat tape, which helps further evacuate any adsorbed gases on the chamber walls by heating the walls inside and outside the chamber. The temperature of the reaction chamber is monitored with a thermocouple feedthrough. On top of the reaction chamber is an XY and a rotary manipulator, which are used to align the sample with the infrared beam. Each manipulator contains a micrometer to help with alignment. The XY manipulator is also used to move the sample holder out of the way to install a QCM sample. The QCM drawer is housed in the reaction chamber so both RAIRS and QCM experiments can happen simultaneously and under the same conditions. A Bruker Vertex 80v was connected by a series of Harrick mirrors to direct IR through the chamber to a MCT detector. The QCM was operated using an Inficon oscillator and Kurt J. Lesker Rate/Thickness Monitor. Both QCM and RAIRS samples can be installed through the load lock chamber, using the linear transfer arm. A residual gas analyzer (RGA) off the reaction chamber is used to monitor the composition of gas in the reaction chamber prior to and after the experiment. Before an experiment, the chamber is checked for the concentration of water, and after the experiment, the concentration of hydrogen fluoride (HF) gas is monitored. To install the PIPS alpha detector, the load lock chamber had to be disconnected from the main chamber and the gate valve connecting both chambers was replaced with a special flange that allowed the connections for the alpha detector to feed through.

For experiments, hexafluoride gas is drawn into the main reaction chamber through an expansion chamber. The hexafluoride gas tanks are directly connected to an expansion chamber.
that is continuously pumped down to UHV when not in use. The expansion chamber is connected to the reaction chamber by a pneumatically controlled gate valve and flow into the chamber is controlled by a leak valve. The expansion chamber can be bypassed to flow inert gas to purge the reaction chamber or lines in the system. After an experiment, gas is evacuated through an alumina (Al₂O₃) filled polypropylene screw-top flash cartridge. The hydrated alumina reacts with the hexafluoride gas to produce tungsten oxide (WO₃ from WF₆) or uranyl fluoride (UO₂F₂ from UF₆) and HF gas. The HF gas is pumped out of the waste trap by a diaphragm pump.

2.4.3 Example Experiment Walkthrough

2.4.3.1 Preface

This is example walkthrough of an experiment using the UHV chamber as described above.

2.4.3.2 Pre-Job Briefing

It should be noted that working with hexafluoride gases can be dangerous and extra precautions should be taken. When hexafluoride gases interact with even a small amount of water, they produce HF gas, which is toxic. When opening the hexafluoride tanks, another person should always be present, and the fill status of the lines should be noted.

2.4.3.3 Sample Introduction

To install a sample using the load lock chamber, the chamber is brought up to atmosphere using inert gas and then is opened. First, a QCM sample is installed on the end of the transfer
arm by twisting the sample puck to lock it in. The load lock chamber is then closed and evacuated, first using the backing scroll pump to bring the pressure below 100 mtorr, and then with the TM pump. Once the load lock chamber has reached UHV, the gate valve connected to the reaction chamber can be opened and the QCM sample can be slid into place. This procedure is repeated for the RAIRS sample. If installing a sample without the load lock chamber, the reaction chamber is brought up to atmosphere using inert gas. The IR bake out lamp is turned on to minimize the amount of atmospheric gas that contaminates the chamber. Both samples are installed, and the chamber is closed by installing a new copper gasket and tightening the bolts to 15 ft. lbs.

2.4.3.4 Gas Introduction

If using tungsten hexafluoride, confirm that the chiller has reached the target temperature so that WF$_6$ is solid. Evacuate all the gas lines and charge tank, if not already. Close off each step of the lines so that each part can be opened individually. Open the hexafluoride tank momentarily and then close. Using the needle valve, slowly open the charged line to allow gas to fill the charge tank until pressure reads between 40-90 torr. Open the gate valve on the main chamber and using the leak valve, slowly let hexafluoride gas into the chamber until the desired pressure is reached.

2.4.3.5 Experiment

Before gas is introduced to the chamber, the QCM Rate/Thickness monitor is started to get a baseline for the sample. The TM pump gate valve is closed, and the chamber is backfilled with hexafluoride gas. RAIRS spectra are taken to characterize the quality of the SAM. Once gas
is introduced, spectra are taken every minute to monitor the reaction between the gas and the surface.

### 2.4.3.6 Purge

Once the experiment is over, the chamber should be evacuated and purged to remove hexafluoride and HF gas. Turn on the diaphragm pump connected to the waste trap system. Allow the waste trap to pump down to -25 inHg before opening the inert gas to the chamber. Fill the chamber to 100 Torr with inert gas and then open the chamber to the waste trap to pump back down to -25 in Hg. Repeat this procedure 4 times. After the last backfill-purge cycle, close the chamber to the waste system and then open it the backing scroll pump. Once chamber pressure reaches below 100 mtorr, turn on the TM pump and allow that to reach the operating speed of 1500 rpms. Once the TM pump is back on, the cold cathode gauge can be switched on and when this reads $10^{-4}$ torr or less, the RGA filament can be turned on.

### 2.5 Summary

In this chapter, we have described the theory and our instrumentation for both XPS and RAIRS. In Chapter 5, we show how we used both of these surface techniques to characterize our organic surfaces. We also described the theory behind alpha spectroscopy and have shown in both Chapter 3 and 4 two alpha spectroscopy modelling programs that we used to optimize parameters for an alpha detector.
2.6 References


Chapter 3: Alpha Spectroscopy Modelling

3.1 Introduction

The current sampling method for determining the level of uranium enrichment being produced at enrichment facilities is laborious and time consuming. It involves collecting samples from around the facility and shipping them to an off-site lab where they undergo several steps of chemical processing before the enrichment level is eventually determined by mass spectrometry. The International Atomic Energy Agency (IAEA) is interested in exploring other methods to get faster results.¹

One way to speed up the process is an on-site detector system that can hook up to existing ports along the enrichment cascade of gas centrifuges. An on-site detector would offer near-real-time detection of the enrichment level directly from uranium hexafluoride (UF₆) gas with alpha spectroscopy. The detector system would consist of an array of passivated implanted planar silicon (PIPS) alpha detectors with a small gap between the two faces of the detector for the flow of UF₆ gas. Because hexafluorides are known to be corrosive to silicon, which makes up the active area of the detectors, the detector face will have to be modified with some kind of protective coating to ensure that the detectors aren’t destroyed.² The protective coating must be resistant to hexafluoride attack and unreactive with UF₆ gas. However, by covering the surface of detector with extra material, a longer path is created that an emitted alpha particle must travel through. This reduces the resolution of the peaks in the resulting alpha spectrum.

One way of modifying the detector for protection is with a layer of gold. A previous study modified a PIPS detector with a layer of gold that was used to capture single radionuclides for detection.³ Instead of just a layer of gold, we plan to further modify the detector with a model organic surface. We anticipate finding a surface that does not react with UF₆, but instead binds
reversibly with UF₆. By increasing the residence time of a UF₆ molecule on the surface, we hope to increase the chance of capturing a decay event, which reduces counting time. Chapter 5 shows the results of different model organic surfaces interacting with UF₆. A proof-of-concept study using modified PIPS detectors in contact with solution containing the radionuclide has shown that PIPS can be used without the ideal sample.⁴ Typical samples for alpha spectroscopy are necessarily very thin to prevent self-absorption and are kept ~10 mm from the detector face to improve resolution.⁵ We hope to extend this range of samples to include gas samples, specifically UF₆ gas.

The effect of the material choice on resolution can be compared by measuring the stopping power of different materials. When an alpha particle is emitted from UF₆, as it travels through the gas and additional materials on the surface, it loses energy. If the protective coating gets too thick or has too high a stopping power, the alpha particle could lose all its energy before it is counted. The protective coating material must be chosen carefully as to pick a material that is resistant to the gas but does not cause the alpha particle to lose too much energy. Before we proceed with building the detector, we can simulate different materials and see how they affect spectrum quality with various simulation tools. Then, we optimized these parameters and showed how we can determine enrichment based on the number of counts for each isotope that reaches the detector.

### 3.2 Simulation Methods

Stopping power simulations of different materials were preformed using the Stopping and Range of Ions in Matter (SRIM) code develop by James F. Ziegler.⁶ SRIM uses a quantum mechanical treatment of ion-atom collisions to calculate the stopping and range of ions into
different materials. More complex simulations of the alpha spectra and detector properties were accomplished using Advanced AlphaSpectrometric Simulations (AASI), which was developed and provided by STUK. AASI uses a Monte Carlo code to simulate energy loss in the source and any adsorbing layers to produce an alpha spectrum. The number of counts were found by summing up the counts over a range of interest.

3.3 Experimental

3.3.1 SRIM Simulations

Before moving on to more complex alpha spectroscopy simulations, the stopping power of the different modification materials was calculated. Figure 3.1 shows the SRIM data for the different materials that the detector would be modified with or that would adsorb to the surface. This figure shows that energy loss is most favorable in the gold layer. For an alpha particle with 5 MeV of energy, the predicted range through gold is ~8 μm. This means that an alpha particle of this energy would lose all of its energy in only an 8 μm layer of gold. In order to chemisorb a SAM to the surface of the detector, a layer of gold must be deposited onto the detector face first. Typically, SAMs are made on store bought gold surfaces that have a 100 nm layer thickness. If the detector was coated with 100 nm of gold, the SRIM data predicts that a resulting alpha spectrum would have broad peaks that are shifted from the expected energy due to energy loss through the layers. However, we have shown in Chapter 2 that SAM quality is not affected by being made on surfaces with gold as thin as 10 nm. While we would still expect some peak broadening at this thickness, it should be minimal.
Figure 3.1: SRIM data showing the stopping power as the projected range (μm) of a helium ion (alpha particle) through different target materials.

SAMs are necessarily thin in nature, with an 18-carbon length chain being ~3 nm thick. The addition of the model organic monolayer should have minimal effect on the resolution of an alpha spectrum, as predicted by the data in Figure 3.1. However, the choice of SAM could influence the amount of adsorbed UF₆ to the surface. A more repulsive surface should adsorb less UF₆ than an attractive surface. However, the adsorbed UF₆ would still decay and produce an alpha particle, therefore adding to the total count. Another material that could adsorb to the
surface is uranyl fluoride, \( \text{UO}_2\text{F}_2 \). \( \text{UF}_6 \) is known to undergo hydrolysis when in contact with water to produce \( \text{UO}_2\text{F}_2 \) and HF gas immediately.\(^8\) Like adsorbed \( \text{UF}_6 \), \( \text{UO}_2\text{F}_2 \) would also decay and release an alpha particle, adding to the overall counts. However, even if the alpha detector was exposed to 50 torr of \( \text{UF}_6 \) and either all \( \text{UF}_6 \) adsorbed to the surface or all \( \text{UF}_6 \) reacted with water to form \( \text{UO}_2\text{F}_2 \) on the surface, the total height of the adsorbed layers would be <2 \( \mu \text{m} \).

Assuming this worst-case scenario, an alpha particle emitted from the top layer would have minimal energy loss. Also shown in Figure 3.1 is the energy loss of an alpha particle through the operating pressure of \( \text{UF}_6 \) in a gas centrifuge. Because the density of gas is so low relative to the other materials, the projected range is much higher in comparison.

### 3.3.2 AASI Simulations

#### 3.3.2.1 AASI Parameters

Following the SRIM calculations, AASI was used for more complex detector simulations. As we have shown with the SRIM data, the alpha particle may lose a significant amount of energy through certain adsorbing layers, like gold. AASI allows us to simulate different adsorbing layers, and other experimental conditions such as gas pressures, and predict their effect on the resulting alpha spectrum. For the AASI simulations, the simulated detector is modelled after a Mirion Technologies series A detector (Model No. A450-18AM). The parameters in AASI were set to match this detector. The active area is 450 mm\(^2\) with an intrinsic resolution of 18 keV. The energy bin size is 4.0 keV and the integration step is 0.2 \( \mu \text{m} \) (AASI requires a value higher than 0.1). The source consists of a homogenous column of \( \text{UF}_6 \) gas with a source-detector distance (SSD) of 0.02 mm. This is the minimum distance to ensure stable simulation conditions and gives a >49% detector efficiency. The pressure of the simulated gas is
controlled by the height of the gas column and density of gas. To simplify and speed up the simulations, 100,000 decays of an alpha particle with the energy 5 MeV, the energy representative of the most energetic uranium isotope alpha particles, were simulated.

The AASI simulations were done in a series of steps. First, a pristine detector with no adsorbed layers was simulated. Then, a detector with different thicknesses of gold was simulated. Finally, we simulated a pristine detector with different pressures of UF$_6$ gas to determine the effect of pressure on FWHM and total counts. Figure 3.2 shows a model of the simulated set-up.

![Figure 3.2: AASI model set-up.](image)

First, a pristine detector was modelled to show how many counts reach the detector and the resolution of the resulting peak without adsorbing layers. For this simulation, and the
simulations with the modified detector, a pressure of 50 torr UF$_6$ in a 1 mm gas headspace was modelled. Figure 3.3 shows the resulting alpha spectrum of the pristine detector. Out of 100,000 simulated decays with 5 MeV, 44.4% of the decays are counted by the detector. The anticipated peak would have a maximum at 5 MeV and then a low-energy tail. However, the pristine detector in Figure 3.2 has a peak maximum at 4.9 MeV. The small shift of 0.1 MeV is from the emitted alpha particle losing energy after colliding with UF$_6$ molecules. Figure 3.2 also shows the resulting alpha spectrum of a detector modified with different thicknesses of gold. As predicted by the SRIM data, energy will be lost through thick layers of gold.
Figure 3.3: Simulated spectrum from AASI with a model detector modified with different thicknesses of gold.

Table 3.1 sums up the data from Figure 3.3. SAMs are typically made on gold samples with 100 nm gold. From the simulated data, the peak for a gold modified surface with 100 nm of gold captured 44.3% of the alpha decays. While the number of counts captured is not different from that of the pristine detector, the FWHM and tailing of the modified detector peak is much greater than that of the pristine detector. For the pristine detector, the FWHM was 57.1 keV. Once the detector was modified with 100 nm gold, the FWHM increased to 80.7 keV. With the
increased tailing and broader peak, peaks that are closer together will be difficult to resolve. In a UF$_6$ sample, the U-234 isotope releases an alpha particle with an energy of 4.77 MeV and the U-235 isotope releases an alpha particle with an energy of 4.40 MeV. The difference between these two isotopes is 0.37 MeV, or 370 keV. While the difference between these two peaks is larger than the 81 keV FWHM seen with the modified detector, the large tailing factor would likely conceal any small peaks at this amount of separation.

**Table 3.1: Influence of gold layers and adsorbed uranium species on alpha spectrum of a 5 MeV alpha particle.**

<table>
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<tr>
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<th>Counts</th>
<th>Count %</th>
<th>Peak Position</th>
<th>Peak Shift (keV)</th>
<th>FWHM (keV)</th>
</tr>
</thead>
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<td>44.4</td>
<td>4.904</td>
<td>-96.4</td>
<td>57</td>
</tr>
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<td>4.888</td>
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<td>62</td>
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<td>4.869</td>
<td>-131.2</td>
<td>63</td>
</tr>
<tr>
<td>50 nm Au</td>
<td>44452</td>
<td>44.5</td>
<td>4.836</td>
<td>-163.9</td>
<td>68</td>
</tr>
<tr>
<td>100 nm Au</td>
<td>44252</td>
<td>44.3</td>
<td>4.780</td>
<td>-220.4</td>
<td>81</td>
</tr>
<tr>
<td>250 nm Au</td>
<td>44100</td>
<td>44.1</td>
<td>4.638</td>
<td>-362.3</td>
<td>115</td>
</tr>
<tr>
<td>500 nm Au</td>
<td>43431</td>
<td>43.4</td>
<td>4.461</td>
<td>-539.5</td>
<td>165</td>
</tr>
<tr>
<td>1000 nm Au</td>
<td>41444</td>
<td>41.4</td>
<td>4.195</td>
<td>-805.0</td>
<td>277</td>
</tr>
<tr>
<td>0.186 um UF6</td>
<td>44403</td>
<td>44.4</td>
<td>4.804</td>
<td>-196.1</td>
<td>73</td>
</tr>
<tr>
<td>1.86 um UF6</td>
<td>41777</td>
<td>41.8</td>
<td>4.309</td>
<td>-691.5</td>
<td>231</td>
</tr>
<tr>
<td>0.168 um UO2F2</td>
<td>44145</td>
<td>44.1</td>
<td>4.802</td>
<td>-197.6</td>
<td>75</td>
</tr>
<tr>
<td>1.68 um UO2F2</td>
<td>41935</td>
<td>41.9</td>
<td>4.298</td>
<td>-702.1</td>
<td>228</td>
</tr>
</tbody>
</table>
However, Figure 3.2 and Table 3.1 shows that a coating of 10 nm of gold should only minimally affect the resolution of the resulting alpha spectrum. Compared to the pristine detector, the 10 nm gold coated detector has almost the same number of counts and the same FWHM of the peak. Even though 10 nm of gold causes a shift of ~112 keV, because this shift would be consistent across all experiments, the experimental detector could be calibrated to account for the shift. Also, from the data in Figure 3.1, a monolayer of any model SAM on only 10 nm of gold should form a well-ordered monolayer on the surface of the detector, while the minimal layer of gold and organic material should not affect the resolution of the resulting alpha spectrum.

While any shift in peaks or attenuation of signal for the SAM and gold modification on a detector can be calibrated for experimentally, we anticipate that some amount of different uranium species will be adsorbed to the surface. Figure 3.4 shows a model detector with different amounts of both adsorbed UF₆ or UO₂F₂. If a detector is exposed to 50 torr UF₆ gas in 1 mm headspace and assuming a worst-case scenario where all 50 torr gas adsorbs to the surface, this would form a 1.86 μm layer of adsorbed UF₆. This much adsorbed UF₆ causes only 41.8% of the counts to reach the detector and the resulting peak has a FWHM of 231 keV. However, if we assume that only 10% of the gas adsorbs to the surface and forms a 0.186 μm layer of UF₆, then 44.7% of the counts reach the surface with the resulting peak having a FWHM of 73 keV. We anticipate that based on the choice of which SAM is used some amount of UF₆ will adsorb.
Another uranium species that we anticipate forming is UO$_2$F$_2$. UF$_6$ is known to react with water quickly, even with the low amounts of moisture in atmospheric air. However, if we assume that there is enough water to react with all 50 torr UF$_6$ gas to form UO$_2$F$_2$, then a maximum of a 1.68 μm layer of UO$_2$F$_2$ would adsorb to the surface of the detector. Like the adsorbed UF$_6$ layer, this reduces the absorbed counts to 41.9% and the resulting peak has a
FWHM of 228 keV. However, if only 10% of UF₆ reacts and forms UO₂F₂ that adsorbs, the number of absorbed counts increases to 44.1% and the FWHM decreases to 75 keV.

While we anticipate that some mixture of UF₆ and UO₂F₂ will adsorb to the SAM surface, depending on the SAM surface and how much water is available to react, it is unknown how much material will adsorb. For the SAM and gold layers, because the effect on peak position is consistent, we can calibrate the detector. However, because any amount of each uranium species may adsorb to the surface, the peak position shift cannot be account for. For example, assuming that only 10% of the UF₆ exposed to the detector adsorbs, the resulting peak is shifted 196 keV, but if all UF₆ adsorbs, the peak shift 691 keV. While we don’t anticipate a thick layer of either material to form immediately, if detection time takes several days, multilayers of UF₆ or UO₂F₂ would form on the detector surface over time. The growth of these layers would slowly shift the peak to lower energies and make the peaks broader.

3.3.2.2 Simulating Different Enrichments

The previous section of simulations focused on each parameter and their effect on the simulated alpha spectrum. This next section focuses on the different levels of enrichment and how we can determine enrichment from an alpha spectrum. The term enrichment refers to the concentration of the U-235 isotope in the sample. Naturally, uranium has three isotopes: U-238, U-235, and U-234. The U-235 isotope is the isotope of interest because it is fissile, meaning that it sustains a fission chain reaction. Because of this property, for nuclear fuel, we increase the concentration of U-235 from ~0.7%, the concentration found in nature, to 5%. The process of enrichment occurs in a cascade of gas centrifuges. While the U-235 isotope concentration increases along the cascade, the U-234 isotope also increases. This is because the gas
centrifuge concentrates the lighter isotopes towards the center of the centrifuges. Then, the feed lines direct the more concentrated gas to the next centrifuge where the process repeats.

We denote low-enriched uranium as 5% U-235 and highly enriched as anything >20%. Over time, the uranium atoms in UF₆ decay by an alpha particle. Each isotope decays at a different rate, which is related to the half-life of the isotope. The term half-life refers to the time it takes for half of the sample to decay. Table 3.2 shows the half-lives for each of the naturally occurring uranium isotopes. U-238, which is the most abundant uranium isotope, has the longest half-life, while U-234 has the shortest. Inversely proportional to half-life is the decay constant, which is shown in Eq. 1. From the decay constant, the specific activity of an isotope can be found. Specific activity (SA), shown in Eq. 2, is number of decays per second and per quantity of molecules in a sample. We use the activity of the sample for each isotope at each enrichment to simulate the number of decays. Table 3.2 shows the half-lives, decay constants, and number of decays for 50 torr UF₆ in a 1 mm gas headspace for a 1-hour span.

\[
\lambda = \frac{\ln(2)}{t_{1/2}} \quad \text{Eq. 1}
\]

\[
SA = \lambda \times N \quad \text{Eq. 2}
\]
Table 3.2: Decay properties of the naturally occurring uranium isotopes.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Half-Life (s)</th>
<th>Decay Constant (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U-238</td>
<td>1.41E+17</td>
<td>4.92E-18</td>
</tr>
<tr>
<td>U-235</td>
<td>2.22E+16</td>
<td>3.12E-17</td>
</tr>
<tr>
<td>U-234</td>
<td>7.75E+12</td>
<td>8.95E-14</td>
</tr>
</tbody>
</table>

Figure 3.5 shows a simulation of 50 torr UF₆ in a 1 mm headspace for 1 hour for three different enrichments. This figure shows that as enrichment increases, the height of the U-235 and U-234 peak increase, as expected. The U-234 peak is more intense than either the U-238 or U-235 peak because of the shorter half-life, which corresponds to higher activity. Even for the pristine detector, the tailing in the peaks increases as the enrichment increases. From the spectra, we get the counts associated for each peak at the different enrichments. We can use the ratio of the U234/U238 counts to build a calibration curve that can be used to determine the enrichment of UF₆ by just knowing the counts of these two peaks.
Figure 3.5: Simulated spectrum from AASI with a model detector showing naturally occurring, low, and high enrichment of UF$_6$ gas.

Figure 3.6 shows a calibration curve made from the simulated data of the different enrichments. This curve can used for a spectrum of a sample with an unknown enrichment to determine the enrichment level. The curve was fit with a logarithmic line with the equation, Eq. 3. By inputting the ratio of U234/U238 counts from a resulting alpha spectrum as x, the corresponding enrichment is given as a percentage as y.
Figure 3.6: Calibration curve calculated from simulated spectra. Used to determine the enrichment of UF$_6$ from the ratio of U234/U238 counts.

$$y = -17.9 \times (1 - e^{(0.031 \times x)})$$

3.3.2.3 Optimized Detector

Because AASI is able to perform complex simulations of a modified detector in different environments, we can use this program to optimize different parameters before beginning experiments. There are several parameters that we can change experimentally, including: gas
pressure, gas headspace above the detector, and amount of gold adsorbed. By optimizing these parameters, we can minimize the time it takes to collect a sufficient number of counts, while maximizing the resolution of the resulting peaks. We have already shown in Figure 3.3 the effects of adding too much gold to the surface. However, as mentioned previously in Chapter 2, a 10 nm layer of gold is sufficient for SAM formation. So, for the optimized detector, 10 nm of gold will be enough to chemisorb a SAM while minimizing the effect on the resulting resolution.

Therefore, the other parameters that we can control experimentally are the gas pressure exposed to the detector and the gas headspace above the surface of the detector. Experimentally, the gas head space is controlled by the distance in between the two surfaces of the detector. In the simulations, we represent this space as a column of gas sitting on the detector surface. Figure 3.7 shows effect of the height of the gas head space on the alpha spectrum. For these simulations, the pressure is kept the same. However, because the pressure is kept the same while the volume changes, that means that the total number of UF$_6$ molecules is different between the different gas head spaces. To account for this, the number of decays is changed. For all the spectrum, alpha particles with an energy of 5 MeV were simulated. For the 0.5, 1, and 2 mm head spaces, 50,000, 100,000, and 200,000 decays were simulated, respectively. While the number of counts increases due to more molecules in the system at the larger head spaces, the resolution also decreases. This is due to both the longer path that some of the alpha particles take as they travel from the top of the head space to the detector and the more molecules causing more collisions with the alpha particles which cause them to lose energy. So, while the larger headspace provides more counts in a shorter amount of time, and the smaller head spaces gives better resolution, the 1 mm gas head space provides a comprise between these two spectrum features.
Finally, we examined the alpha signal from gas-phase UF$_6$ versus a monolayer of UF$_6$ on the surface. Our original hypothesis was that the signal from a UF$_6$ monolayer would be much higher and provide better resolution than that of the gas phase. However, as we have shown with the previous data, the most determining factor in capturing more counts for the sample is having enough molecules in the sample. Because all the uranium isotopes have such a long half-life, this means that there is activity is very low. The number of molecules in a monolayer of UF$_6$ is so
low that no decay would be seen for a very long time. Table 3.3 shows the calculated number of
decays for a monolayer of UF₆ of natural enrichment and the number of molecules. As this table
shows, because the number of molecules is so low, there is no appreciable number of decays,
even after a year. Therefore, we have shown that gas-phase UF₆ provides much more signal than
a monolayer would.

Table 3.3: Decay properties of a monolayer of UF₆.

<table>
<thead>
<tr>
<th>Activity (decay/(s*g))</th>
<th>Natural Abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Isotope</td>
</tr>
<tr>
<td>U-238</td>
<td>4.48E-06</td>
</tr>
<tr>
<td>U-235</td>
<td>2.00E-07</td>
</tr>
<tr>
<td>U-234</td>
<td>4.99E-06</td>
</tr>
</tbody>
</table>

3.4 Summary

Typically, samples for alpha spectroscopy are required to be thin, homogenous sources
that are kept at a distance from the detector. However, we have shown using an alpha
spectroscopy modelling program, that performing gas phase alpha spectroscopy with a PIPS
detector is possible. While additional passivation of the surface is necessary to protect the
detector from the corrosive gas, we have shown that as long as the protective material is kept
thin, it should have minimal effect on the resolution. Also, to keep the resolution high, the
amount of adsorbed UF₆ and UO₂F₂ should be minimized as much as possible. Originally, we
thought this adsorbed layer of UF$_6$ would provide more signal at a higher resolution than gas phase UF$_6$, but we have shown that it would have minimal activity. A sample at the operating pressure of UF$_6$ (50 torr) should result in an alpha spectrum with high resolution and a significant number of counts in a relatively short amount of time.

3.5 References

(1) IAEA. Research and Development Plan; 2018.


(9) Handling, S. Uranium Hexafluoride — Safe Handling, Processing, and Transporting. **1988**.

CHAPTER 4: Hexafluoride Adsorption Studies

4.1 Introduction

One of the overall goals of this project was to build an alpha detector that can produce near-real-time data on the enrichment levels of uranium hexafluoride (UF₆) gas in a processing plant. To have the detector be reusable and protected, a suitable coating must be found. As we have shown in Chapter 3, far more alpha signal comes from gas-phase UF₆ than adsorbed UF₆. Ideally, this coating would have irreversible binding with UF₆, while not hindering the resolution of the resulting alpha spectrum. In this chapter, we will test out different organic surfaces made from self-assembled monolayers (SAMs) by exposing them to first tungsten hexafluoride (WF₆), which can act as a surrogate gas, before moving on to UF₆ gas. To determine the adsorption/desorption of both gases on the model surfaces, we will use the quartz crystal microbalance (QCM) technique. After we have tested different surfaces, we moved on to alpha spectroscopy experiments and determining enrichment levels from exposing passivated implanted planar silicon (PIPS) alpha detectors to UF₆ gas.

4.2 Methods

4.2.1 SAM Preparation

All the model organic surfaces were created in the same manner. The 1-octadecanethiol (98%), 16-amino-1-hexadecanethiol hydrochloride (96%), and 1H,1H,2H,2H-perfluorodecanethiol (97%) were purchased from Sigma-Aldrich and used without further purification. For brevity, these surfaces will be referred to as C18, NH2, and F8H2, respectively. The gold QCM crystals were 6 MHz (14 mm) and were purchased from Inficon. Prior to use, the gold crystals were cleaned with fresh piranha solution (70%/30% ratio concentrated sulfuric
acid/30% H$_2$O$_2$) for ~ 1 hour. The cleaned crystals were first rinsed with copious amounts of 18 MΩ water, and then pure ethanol, before being placed in a 1 mM ethanolic thiol solution. The substrates remained in the thiol solution for a minimum of 24 hours to ensure well-ordered and closely packed surfaces. The amine terminated crystal needed an additional step and was first rinsed with triethylamine (TEA) to remove the chloride ion. All other samples needed only to be rinsed with ethanol. After rinsing all the crystals with ethanol and drying under a stream of UHP N$_2$, the SAMs were directly placed into the reaction chamber.

4.2.2 Quartz Crystal Microbalance

The pulsed tungsten hexafluoride (WF$_6$) QCM experiments were conducted in an atomic layer deposition (ALD) instrument. After the samples were installed, they were exposed to pulses of WF$_6$ gas under a continuous purge of 1 torr argon. These experiments were performed at room temperature unless otherwise noted. Also, these samples were only exposed to WF$_6$ since the system was not rated for radioactive work. It should be noted that the pulse experiments were performed by Anil Mane at Argonne National Laboratory. However, we provided the samples, and the analysis was performed by us.

The long-term exposure experiments were performed in a UHV vacuum chamber. The chamber was continuously pumped down by a turbomolecular (TM) pump when not in use. The modified QCM crystals were placed in a QCM drawer and operated with an Inficon oscillator. The chamber was backfilled with hexafluoride gas. Upon exposure to hexafluoride gas, a Kurt J Lesker Rate/Thickness monitor was used to measure the change in frequency of the QCM plate. After exposure, the chamber was evacuated through the waste trap and was flushed several times with inert gas. These experiments were performed at room temperature.
4.2.3 Alpha Spectroscopy Experimental

The alpha spectroscopy experiments were performed with a passivated implanted planar silicon (PIPS) alpha detector. The specific PIPS detector was a model No. A450-18AM from Mirion Technologies. This detector has a total detector area of 450 mm$^2$ with an active layer thickness of 140 µm and an inherent resolution of 18 keV. To control the height of the gas headspace above the detector, a custom-made fixture with interchangeable pucks was housed around the detector, as shown in Figure 4.1.

![Picture showing the PIPS alpha detector (model No A450-18AM) and the custom-made fixture with interchangeable pucks.](image)

**Figure 4.1:** Picture showing the PIPS alpha detector (model No A450-18AM) and the custom-made fixture with interchangeable pucks.

To protect the detector from corrosive UF$_6$ gas, the surface of the detector was coated with 2.7 nm AlF$_3$ using an ALD instrument. For the experiment, the detector was exposed to 1 torr of 3.159% enriched UF$_6$ for a period of ~1 month, checking the counts at different times during the month. The detector was connected to a multichannel analyzer (MCA), which was
connected to the computer. The software for the MCA was Genie 2K. After exposure, the
chamber was evacuated through the waste trap and the chamber was purged by repeatedly filling
and evacuation the chamber with inert gas.

4.3 Results and Discussion
4.3.1 Quartz Crystal Microbalance Adsorption Studies
4.3.1.1 Pulsed Tungsten Hexafluoride Gas Adsorption

QCM studies were performed to determine chemical compatibility between hexafluoride
gas and the model organic surfaces. Preliminary studies used tungsten hexafluoride (WF₆) as a
surrogate gas for uranium hexafluoride (UF₆). In these initial studies, the surfaces were baked
prior to exposure to remove any surface water. WF₆ is known to react with small amounts of
water to form tungsten oxide (WO₃).²³ Figure 4.2 shows a gold surface that was exposed to
pulses of WF₆ gas at room temperature (28°C) (A) and 90°C (B). The left y-axis shows the mass
deposited on the surface as a result of the pulses of WF₆ gas, as shown by the right-axis. The
mass was calculated from the change in frequency by the Sauerbrey equation, as mentioned in
Chapter 2. Before beginning experiments, the instrument was calibrated to be able to determine
mass from this equation.

In Figure 4.2 A, after the first pulse of WF₆ gas, the mass deposited on the QCM is ~ 80
ng/cm², which is predicted to be the mass of a monolayer of WF₆ on the surface. Following the
initial pulse, the deposited mass continues to increase even with the continuous purge of argon
after each pulse. This means that as more gas is exposed to the surface, more WF₆ molecules
adsorb. However, on the surface that was exposed to pulses of WF₆ at 90°C, the same initial
mass deposition is seen after the first pulse, but the continuous deposition over time is not seen.
At room temperature, water is more likely to be condensed on the surface and thus react with WF$_6$ to form WO$_3$ than the surface at 90°C. This indicates that even under UHV conditions, the small amounts of water will react with WF$_6$ to form WO$_3$, which is irreversibly adsorbed at these conditions.

**Figure 4.2:** *QCM spectra of an unmodified gold QCM plate exposed to pulses of WF$_6$ gas at (a) room-temperature and (b) 90°C.*

Figure 4.3 shows the results of pulses of WF$_6$ gas on the NH$_2$, C18, and F8H2 surface. In Figure 4.3 A, which shows the data for the NH$_2$ surface, after the initial pulse of WF$_6$, a mass of ~190 ng/cm$^2$ was deposited on the surface, which is significantly more than a monolayer of gas of 80 ng/cm$^2$. With each successive pulse of gas, more and more mass is deposited on the surface. The large mass deposition from the first pulse of gas is indicative of the surface reacting with the gas, rather than just the gas adsorbing. The amine surface has a hydrogen network formed over the surface due to terminal functional group. These hydrogen bonds pull some of the terminal functional groups closer together, which can create holes where the terminal groups
would originally be. Because of these holes, the carbon chain, which is normally not exposed to WF₆ gas becomes exposed, creating sites for WF₆ to react with. This means that the initial mass may be due to surface fluorination, as well as WF₆ and WO₃ adsorption. The continued addition of mass over successive pulses could result from WO₃ formation from residual water. Also, because the chains are more exposed from these “holes” on the surface, WF₆ could get trapped in the chains. Therefore, more gas adsorbs to the NH₂ surface than to an unmodified gold surface.

In contrast to both the NH₂ and gold surface, in Figure 4.3 B after the initial pulse, the C18 surface showed no increase in the mass, meaning there was nothing deposited on the surface. However, over multiple pulses, the mass grew uniformly in a stepwise pattern. While the deposition appears to be irreversible under these conditions, the added mass likely comes from WO₃ forming on the surface and not WF₆ fluorinating the surface, or even adsorbing to the surface. The C18 surface was expected to be highly reactive with the hexafluoride gas since hydrocarbons are known to be highly reactive with UF₆.⁴⁻⁶ However, the methyl terminal group of the SAM likely provided protection from fluorination by WF₆ by creating a steric hindrance between the two molecules.
Figure 4.3: QCM spectra of gold QCM plates modified with NH$_2$, C18, and F8H2 surfaces exposed to pulses of WF$_6$ gas followed by flushes of inert gas.

Figure 4.3 C shows a mostly fluorinated surface exposed to pulses of WF$_6$ gas. This surface, due to the mostly fluorinated chain and fluorinated terminal group, is expected to be resistant to attack from WF$_6$ gas. After the first pulse of gas, $\sim 30$ ng/cm$^2$ is deposited on the surface. However, during the flush with argon, the mass grows to $\sim 75$ ng/cm$^2$. Then, with each successive pulse and flush, the mass stays the same at $\sim 75$ ng/cm$^2$. Due to the fluorine chains being repulsive to WF$_6$, a full monolayer of WF$_6$ does not adsorb to the surface after the initial
pulse. Instead, it isn’t until the surface is flushed with inert gas that we see a quick rise in adsorbed mass to what we predict to be a monolayer of WF\(_6\). As with the other surfaces, the added mass is likely due to WO\(_3\) forming on the surface. Any miniscule amount of water either in the inert gas tank or gas lines reacts with WF\(_6\) to form WO\(_3\). However, unlike the other surfaces, the mass does not increase over time and number of pulses. Instead, it remains covered in just a monolayer of oxide. Based on the composition of the chains, we expected the F8H2 surface to be the most inert surface. The fluorines on the carbon chain and the fluorines of the WF\(_6\) molecule would repel each other. Based on the data presented above, the F8H2 surface is the most inert. While a layer of oxide forms on the surface, the data does not indicate any multilayer formation.

4.3.1.2 Long-Term Hexafluoride Gas Adsorption

While the pulsed WF\(_6\) gives us an idea of adsorption/desorption of the gas from each surface, a long-term exposure is more indicative of actual working conditions that the detector will undergo. While the system used for these long-term experiments is different from the pulsed experiments, this system is still an UHV system. While this system could not be calibrated to determine the mass from the Sauerbrey equation, the change in frequency can still be used to compare the different surfaces with each gas. As shown in the previous experiments, even miniscule amounts of water results in WO\(_3\) depositing on the surface. This behavior should be the same for UF\(_6\), since UF\(_6\) has been shown to react quickly with water to form uranyl fluoride (UO\(_2\)F\(_2\)).\(^7,8\)

Figure 4.4 shows F8H2, C18, and NH\(_2\) surfaces exposed to WF\(_6\) and UF\(_6\) gas over time. For the surfaces exposed to WF\(_6\) gas, this figure shows that deposited mass, which is inversely
proportional to the change in frequency, follows the trend of F8H2 < C18 < NH2. This trend is indicative of the attraction of the WF6 molecule to each surface, which follows the predicted trend of UF6 molecules to dimers with the same functional groups. This figure also shows that the deposited mass for UF6 is much greater than that for WF6, which shows that UF6 has a higher overall attraction to the surfaces than WF6. While not shown, after evacuation, the frequency did not return to the original frequency. In most cases, the frequency continued to decrease. This is likely due to the presence of trace amounts of water in the waste evacuation system. However, this further proves to the theory that minute amounts will react with UF6 very quickly to form UO2F2 that is irreversible adsorbed to the surface, under these conditions.
Figure 4.4: QCM spectra of gold QCM plates modified with NH₂, C18, and F8H2 surfaces exposed to WF₆ and UF₆ gas for long-term exposure.

The shape of the NH₂ surface during exposure to UF₆ is very different from the other curves. The irregular curve suggests that multiple different processes might be occurring at one time. While the WF₆ data suggests that the NH₂ is reacting in some way with the gas, the shape of the long-term exposure is not irregular. However, as mentioned previously, the NH₂ surface has “holes” where the carbon chain is exposed. Some UF₆ molecules may be just reacting with the surface and fluorinating it, while others may actually be cleaving the chain since UF₆ has
been shown to be a strong oxidizer.\textsuperscript{10} The F8H2 surface exposed to UF\textsubscript{6} has a small irregularity in the curve towards the beginning of exposure. While the mostly fluorinated surface was expected to be resistant to attack by UF\textsubscript{6} gas, this small irregularity in the adsorption curve may suggest that the surface does experience some attack from UF\textsubscript{6} gas. However, like the pulse experiments showed, while the F8H2 surface experienced an initial uptake of mass, over time, the mass didn’t change very much. This data also confirms our theory that the F8H2 surface would be the most resistant to hexafluoride gas adsorption.

4.3.2 Alpha Spectroscopy

4.3.2.1 Passivated Implanted Planar Silicon Alpha Detector Exposure

Initial counting experiments with the Passivated Implanted Planar Silicon (PIPS) alpha detector were preformed using a detector coated in aluminum fluoride (AlF\textsubscript{3}) to protect the detector from corrosive UF\textsubscript{6}. AlF\textsubscript{3} has been shown to be resistant to UF\textsubscript{6} attack and is currently used in processes handling UF\textsubscript{6}.\textsuperscript{4} Typically, the samples used for alpha spectroscopy are very thin samples that undergo several processing steps to produce a uniform sample that eventually gets electroplated onto a disc to be analyzed. Then, the sample is kept several millimeters away (~10mm) from the detector face under vacuum conditions to maximize the resolution of the resulting spectra.\textsuperscript{11} By keeping a larger source-to-detector distance, only alpha particles that are emitted directly towards the detector face are counted. Alpha particles that are emitted at an angle, even a small angle, will lose more energy due to collisions with air molecules than alpha particles that are emitted straight to the detector face. This energy loss of the alpha particles to molecules in the air results in the characteristic low energy tailing seen in alpha spectroscopy.
While a larger source-to-detector distance improves resolution, too large of a distance result in a shift in energy for all the resulting peaks and a low number of counts. While the shift in energy can be accounted for by calibrating the detector with a known sample, the low number of counts can only be solved with longer counting times. To achieve a number of counts within an acceptable statistical uncertainty could take days at too large of a source-to-detector distance. However, our proposed detector design would have a source-to-detector distance of virtually zero since the UF\(_6\) being analyzed would be a gas. While this would decrease counting times, the very small distance could create poor resolution. To the best of our knowledge, using a PIPS detector to analyze a gaseous sample has not been done. However, using a modified PIPS detector to analyze a radioactive solution has been shown to produce resulting spectra with discernable peaks.\(^{12}\)
Figure 4.5: Alpha spectrum of a PIPS detector modified with 2.7 nm AlF$_3$ with a 1 mm gas headspace exposed to 1 torr of ~3% enriched UF$_6$ gas over a period of 1 month.

Figure 4.5 shows a 2.7 nm AlF$_3$ modified PIPS detector with a 1 mm gas headspace exposed to 1 torr of ~3% enriched UF$_6$ gas over a period of 1 month. It should be noted that while the x-axis is labelled as MeV, the actual MeV of the recorded counts are not accurate. Due to the set-up of the experiment in the UHV chamber, a known sample could not be used to calibrate the energy scale. Instead, initial experiments were used with higher enrichment values to set the largest expected peak, the U-234 peak, to be at its known alpha particle energy of 4.77
MeV. Therefore, the energy scale is likely not proportional to the actual energies and the data taken from this graph should only be viewed as a “proof of concept,” and not quantitative data. However, with that being said, a lot can still be gleaned from this data.

This figure shows two discernable peaks with a long low energy tail that appear after one day of counting. The more intense, higher energy peak is likely the U-234 peak, while the less intense lower energy peak is likely the U-238 peak. However, there is no peak seen for the U-235 isotope. This is not entirely unexpected based on the results shown in Chapter 3. At such a low enrichment level, the U-235 peak would be small as compared to the other two peaks. Combined with the large tailing effect from the U-234 peak, any U-235 would be lost in the spectrum.

Over time, the peaks don’t become more intense, but seems to lose some intensity while shifting to slightly lower energies. Based on the QCM data, UF₆ reacts with minute amounts of water in the chamber to create UO₂F₂ that gets plated out on the surface. We showed in Chapter 3, that any amount of adsorbed UF₆ or UO₂F₂ would cause the signal to be attenuated and the peak to shift to lower energies. This figure confirms that some amount of adsorbed uranium species does block the signal from the rest of the gas phase UF₆. Any alpha particle that is released then loses all its energy as it travels through adsorbed layers before reaching the detector. Like the QCM data shows, the deposited mass does not leave the surface when the chamber is evacuated. The alpha spectrum taken after evacuation shows that the signal does not change. This confirms that under these conditions, the adsorption onto the detector face is irreversible.
4.4 Summary

We first exposed three different modified QCMs crystals with self-assembled monolayers, as well as an unmodified gold QCM, to pulses of WF$_6$. This data shows that while the surfaces showed different affinities for WF$_6$, one of the main problems with exposing surfaces WF$_6$ is that it will react with small traces of water on the surface to produce WO$_3$, which is irreversibly bound under these conditions. That same behavior is seen over the long-term exposures as well. The long-term exposure also showed that the affinity of both hexafluoride gases for the surfaces is the same: NH$_2$ > C18 > F8H2. Also, UF$_6$ has a much greater affinity for all the surfaces as compared to WF$_6$. The issue with hexafluoride gas reacting with trace amounts of water extended to the alpha spectroscopy experiments as well. Once a detector was exposed to UF$_6$, the surface of the detector became contaminated with UO$_2$F$_2$. Any future experiments on this work would have to take great care to eliminate all traces of water.

4.5 References


Chapter 5: Hexafluoride Gas-Surface Interactions

5.1 Introduction

Currently, verification of uranium hexafluoride (UF₆) enrichment at a processing plant is a time-consuming and laborious process, involving the collection of samples on-site being sent off for analysis.¹ The International Atomic Energy Agency (IAEA) has listed the timely detection of highly enriched uranium (HEU) in low enriched (LEU) facilities as a high priority.² Based on previous work that modified a passivated implanted planar silicon (PIPS) detector with gold for the detection of single radionuclides, we have proposed building on that idea and further modifying the detector face with organic materials.³ The idea is a device that can withstand corrosive UF₆ gas, while not interfering with the resolution of the detector. As part of this goal, computational work has been done to study the interactions between UF₆ gas and small organic dimers to model how UF₆ will interact with an organic surface.⁴ While a gold coating could act as a sufficient passivation layer, the idea for the organic layer was to have a capture surface for UF₆ gas to adsorb to. Originally, we hypothesized that UF₆ would need to adsorb to the surface of the detector to increase resolution in the alpha spectrum and decrease the overall counting time. However, our work in Chapter 3 displays why a “sticky” detector coating isn’t necessary, but rather a repulsive coating would work better for our purposes. While the work in Chapter 3 changed the ending goal for a coating choice, the need for discovering the science behind UF₆ interactions did not. The chemistry of UF₆ with different organic materials remains to be determined, and this work provided a method for determining the science.

Because of the abundance of depleted UF₆ that is produced from the enrichment process, previous studies have attempted to utilize UF₆ as a fluorinating agent.⁵⁻¹⁶ However, while some of these studies offer some insight into product formation, to the best of our knowledge, no
previous works have studied in situ gas phase reactions of UF$_6$ with different organic materials. In past experiments, only the products were analyzed. However, to offer more insight into how products are formed, we monitored the surfaces during exposure. In this work, we intend to expose model organic surfaces to UF$_6$ gas to facilitate possible reaction pathways between the gas and the surface. Self-assembled monolayers (SAMs) act as a good model organic surface and have been shown previously to offer insight into how a gas reacts at an interface. Therefore, we exposed three different SAMs first to tungsten hexafluoride (WF$_6$) gas, which may act as a simulant gas. Then, we exposed pristine surfaces to UF$_6$ gas. WF$_6$ has the same molecular geometry as UF$_6$. While WF$_6$ has been shown to be a milder oxidizer, there has been conflicting reports on the strength of UF$_6$ as an oxidizer. The conflicting data between reports appears to stem from varying reaction conditions. By spectroscopically monitoring gas-surface reactions, we hope to offer more insight into unexplored reaction pathways.

In a series of different experiments, we monitored the reaction between WF$_6$ and UF$_6$ with three different surfaces. The first surface presented was a SAM made from 1-octadecanethiol. The methylene chains and terminal methyl group make this surface act as a model saturated hydrocarbon. The next surface presented was a SAM made from 1H,1H,2H,2H-perfluorodecanethiol. Since the whole carbon chain except for the two carbons closest to the thiol head are fluorinated, this surface should act as a model fluorinated surface. The last surface presented was a SAM made from 16-amino-1-hexadecane thiol hydrochloride. This surface is similar to the hydrocarbon surface, but it has an amine functional group as the terminal group. Since the terminal group is what makes up the interface, this difference in functional groups will affect the chemistry between UF$_6$ and the surface.
A computational study was done that investigated the intermolecular binding energies (IBEs) between UF$_6$ and several different functionalized small molecules. This work shows that the predicted IBE values for UF$_6$ with methane and ethane are 1.23 and 1.67 kcal/mol. While the molecules in the model are much shorter than the 18-carbon chain, we can predict that the IBEs of UF$_6$ with the hydrocarbon surface will be similar to the computational values. The predicted IBEs for UF$_6$ with small, partially fluorinated and fully fluorinated carbon chains are between 0.76 - 1.68 kcal/mol. This study predicts that UF$_6$ will interact in a similar way with the hydrocarbon and fluorocarbon surface. In contrast to the weak predicted IBEs, several different length carbon chains with a terminal amine group showed a much higher IBE with a range of 14.47 - 15.32 kcal/mol.

5.2 Materials and Methods

All experiments performed in this work were conducted in an ultra-high vacuum (UHV) system. Three different model organic surfaces were chosen: an 18-carbon methyl terminated SAM, a 12-carbon mostly fluorinated SAM, and a 16-carbon amine terminated SAM. For brevity, these surfaces will be referred to as C18, F8H2, and NH2 surface, respectively, throughout. Experiments were done on all model organic surfaces with WF$_6$ before using UF$_6$. Changes made to the surfaces during gas exposure were tracked via in situ reflection-absorption infrared spectroscopy (RAIRS). For the surfaces exposed to WF$_6$, surface changes were characterized post-exposure by x-ray photoelectron spectroscopy (XPS) as well. All the model organic surfaces were created and prepped for the UHV chamber in the same manner. This has been described in detail in Chapter 2.
RAIRS was used to track in situ reaction products and surface changes during exposure to hexafluoride gas. A Bruker 80v spectrometer was used to focus IR radiation onto the gold surfaces at ~86° relative to the surface normal and was directed to a liquid nitrogen cooled MCT detector. A polarizer was placed at the entrance window to the chamber. Light that is perpendicular to the surface and light that is parallel to the surface is denoted as p- and s-polarized light, respectively. For the background, s-polarized light was used, while p-polarized light was as the sample to characterize the SAM initially. Therefore, p-polarized light gives information about surface and gas modes, while s-polarized light gives information about just the gas modes. By using s-polarized light as the background, we subtract out any gas modes. However, for the in situ studies, p-polarized light of the pristine SAM pre-exposure was used as the background. This way we can track any differences in the surface due to the exposure of gas. Any positive bands indicate an increase in absorbance of an existing band or the development of new modes, while any negative features indicate the removal of modes from the surface or disordering of the carbon chains. All spectra shown here were the average of 256 scans with the resolution of 2 cm$^{-1}$, which took about one minute/spectrum.

XPS was only able to be performed on samples exposed to WF$_6$ gas. Because the XPS system is separate from the UHV system, the samples were removed from the chamber and consequently were exposed to atmosphere before being analyzed. Also, as a consequence of having to transfer samples, any sample exposed to the radioactive UF$_6$ gas could not be removed from the hood housing the UHV to ensure safe practices. The detailed fitting procedures of XPS peaks are discussed in Chapter 2.
5.3 Results and Discussions

5.3.1 Hydrocarbon Surface

5.3.1.1 Tungsten Hexafluoride

5.3.1.1.1 RAIRS

The first surface to be discussed is the C18 (hydrocarbon) surface. As mentioned, we first studied the interactions between WF$_6$ and organic surfaces to glean any information of reactions between a safer simulant gas and the surface before moving on to the more dangerous radioactive gas. As detailed earlier, the predicted binding energy for UF$_6$ and a hydrocarbon surface is weak. While the binding energy between a WF$_6$ molecule and a methane group is most likely different, we anticipate that the trend between the gas and different surfaces may be similar. Based on these calculations, a methyl terminated hydrocarbon surface should have minimal interactions with both WF$_6$ and UF$_6$ gas.

A C18 surface that has been exposed to 3.00 torr WF$_6$ gas over the span of a few hours is shown in Figure 5.1. The black spectrum is the SAM prior to exposure using s-polarization as the background for the spectrum. In this spectrum, the peaks that are associated with the SAM are at 2918 and 2849 cm$^{-1}$ and are assigned to the asymmetric ($\nu_a$) and symmetric ($\nu_s$) stretches, respectively, of the CH$_2$ modes of the carbon backbone. The peak position and FWHM of these peaks indicate that the chains of C18 surface reside in a crystalline environment.$^{23,24}$ Blue shifted peaks that are more broad would indicate a monolayer that is more heterogeneous and not as well ordered. The peaks at 2964 and 2877 cm$^{-1}$ are assigned to the CH$_3$ asymmetric and symmetric stretches, respectively, of the terminal methyl group.
**Figure 5.1:** Reflection-absorption infrared difference spectra of a C18 surface exposed to ~3.00 torr WF$_6$ gas. The spectrum shown at the top is the SAM prior to exposure. Each spectrum, starting from the bottom, increases by ~5 x 10$^8$ L up the figure.

Below the pristine SAM is a series of spectra taken during WF$_6$ exposure. Here the p-polarized light spectrum of the pristine SAM is used as background, while p-polarized light of the SAM during exposure is used as the sample. The amount of exposure increases from bottom to top of the figure, with each spectrum increasing in about 5 x 10$^8$ L (1 Langmuir (L) = 10$^6$ Torr s). During the experiment, a series of peaks appear as a result of gas exposure (Figure 5.1).
Several of these peaks are expected, and belong to different gas phase WF$_6$ vibrational modes.$^{25}$ These peaks are 712 ($\nu_3$), 810 ($\nu_2 + \nu_6$), 1028 ($\nu_3 + \nu_5$), and 1386 ($\nu_2 + \nu_3$). There is also a peak seen at 946 cm$^{-1}$, which is a documented WF$_6$ impurity peak.$^{26}$ A peak at 992 cm$^{-1}$ also appears. Based on the peak position, this band could belong to the W=O stretch in tungsten oxide (WO$_3$).$^{27,28}$ WF$_6$ is readily hydrolyzed by water to form WO$_3$ and hydrogen fluoride (HF).$^{29}$ Even though the chamber is kept under UHV, there are still trace amounts of water in the chamber and gas lines that could react, as seen by the ro-vibrational lines between 1700 - 1400 cm$^{-1}$. The lack of a feature around 4200-3900 cm$^{-1}$ indicative of the formation of HF suggests WF$_6$ did not undergo complete hydrolysis.$^{30}$ While we can't assign this peak with certainty yet, we will tentatively assign this band to a W=O stretch.

The goal of this experiment was to monitor the reaction of WF$_6$ with a C18 surface. We would expect to see negative peaks for those modes if the gas was interacting with the surface at all. The absence of any peaks in the spectra corresponding to the CH$_2$ or CH$_3$ stretches indicates that the surface does not react with the gas. WF$_6$ is a fluorinating agent, albeit a weak one, but the absence of any new peaks between 1500 - 1100 cm$^{-1}$ means that no fluorination reaction is happening.

While the surface did not seem to react with $\sim$3.00 torr of WF$_6$ over several hours, it is possible that the surface could react if exposed to more gas. Figure 5.2 shows a surface that was exposed to $\sim$8 torr of WF$_6$ gas over several hours. In this figure, each spectrum increases by $\sim$2.5 x $10^9$ L. Unlike the previous figure, Figure 5.2 shows a very small negative peak that appears at 2915 cm$^{-1}$ at the start of gas exposure. In the SAM spectrum prior to gas exposure, this peak is assigned to the asymmetric CH$_2$ of the carbon chain. A slight decrease in this peak could either mean the disappearance of the carbon chains of the SAM or that the SAM is rearranging.
Because we don’t see any change in the CH₃ modes, it is unlikely that the chain is desorbing and causing the decrease in the CH₂ mode. Also, no new peaks are seen between 1500-1100 cm⁻¹, which indicates that no surface fluorination has occurred. Rather it is more likely that the higher pressure of gas is causing WF₆ to adsorb to the surface and the interaction between the surface and gas is causing a slight rearrangement in the surface. However, a small peak appears at 655 cm⁻¹. Just like the negative asymmetric CH₂ band, this peak appears at the start of the experiment and doesn't change in intensity throughout the experiment. This peak could be adsorbed WF₆, red shifted from the gas phase WF₆ bands. Because this peak is not seen when the surface is exposed to lower pressures, the presence of this peak confirms the idea that the higher pressure of WF₆ causes a small number of WF₆ molecules to absorb to the surface, which slightly perturbs the order of the underlying chains. After the chamber has been evacuated, the small negative peak remains. This means that some WF₆ molecules remain trapped in the chains, even under vacuum.
**Figure 5.2:** Reflection-absorption infrared difference spectra of a C18 surface exposed to ~8.00 torr WF₆ gas. The spectrum shown at the top is the SAM prior to exposure. Each spectrum, starting from the bottom, increases by ~2.5 x 10⁹ L up the figure.

Just as with the C18 surface that was exposed to ~3.00 torr WF₆, this figure shows a peak at 992 cm⁻¹. To help determine if this peak was in the gas phase or surface bound, we looked at the s-polarized light spectrum during exposure. As previously mentioned, p-polarized light was used during the experiment to monitor the reaction between the gas and the surface because the light travels the same direction as the chains. However, the opposite is true for s-polarized light.
This means that p-polarized light provides information about the surface and gas modes, while s-polarized light only gives information about the gas phase mode. Figure 5.3 shows an s-polarized spectrum taken near the end of the exposure. A p-polarized light spectrum that was taken sequentially is shown for reference.

**Figure 5.3:** A s-polarized light spectrum taken while a C18 surface was exposed to ~8.00 torr WF$_6$. The s-polarized spectrum shows only gas-phase modes. A p-polarized spectrum taken consecutively is shown for reference.
This figure confirms that the peak at 992 cm\(^{-1}\) belongs to a gas phase species since it is present in in only the s-polarized spectrum. The peak has the same intensity in both spectra suggesting this species is solely in the gas phase and none of it is surface bound. This figure also confirms that the peak at 655 cm\(^{-1}\) belongs to a surface bound species since it is only present in p-polarized light spectrum.

While WF\(_6\) is a known fluorinating agent and oxidizer, the RAIRS spectra showed no evidence of WF\(_6\) fluorinating or oxidizing the C18 surface. At higher pressures, WF\(_6\) adsorbs to the surface and causes slight disordering of the methylene chains, but no reaction is seen. Because only the CH\(_2\) modes are affected, and not the CH\(_3\) modes, it appears that WF\(_6\) interacts with the underlying chains and not the terminal methyl groups. The only reaction observed is indicated by the appearance of a band at 992 cm\(^{-1}\). While we postulate that this band belongs to the W=O stretch of tungsten oxide, the absence of any HF bands suggests that complete hydrolysis is not occurring. By utilizing post-exposure XPS on these samples, we can gain insight into further characterization of the reaction between the gas and the C18 surface.

5.3.1.1.2 XPS

To help confirm our findings from the RAIRS data and clarify what is happening at the surface, XPS was performed on samples pre- and post-exposure to WF\(_6\) gas. It should be noted that prior to characterization with XPS, these surfaces were exposed to atmosphere after the experiment and before being pumped down to vacuum in the XPS chamber. Exposure to ambient conditions allows for WF\(_6\) remaining on the surface to react with water in the atmosphere and hydrolyze, forming WO\(_3\)\(^{51,32}\). Figure 5.4 shows the high-resolution XPS data for the C18 surface.
shown in Figure 5.1 that was exposed to 3.00 torr WF₆. In this figure, the C 1s, S 2p, F 1s, W 4f, and O 1s high-resolution regions are shown. The background and peak fittings are shown.
**Figure 5.4:** High-resolution x-ray photoelectron spectroscopy spectra of the C 1s, S 2p, F 1s, W 4f, and O 1s regions of a C18 surface before and after exposure to ~ 3.00 torr WF₆.

*Corresponding RAIRS data shown in Figure 5.1.*
Based on the RAIRS data from Figure 5.1, we concluded that WF$_6$ was not able to fluorinate the surface. The F 1s region in Figure 5.4 confirms that surface fluorination is not occurring due to the absence of a peak post-exposure. However, some tungsten does remain on the surface post-evacuation, which was not seen in the RAIRS data. The W 4f region has a j = 7/2 peak positioned at the 36.2 eV with a FWHM of 1.4 eV. This peak position is consistent with WO$_3$.\textsuperscript{33,34} This peak assignment is also confirmed by the O 1s region post-exposure. The peak post-exposure at 531.4 eV with a FWHM of 1.5 eV is consistent with oxygen in WO$_3$.\textsuperscript{34}

While the RAIRS data did not show evidence of any adsorbed WF$_6$ or WO$_3$, XPS confirmed that the surface was contaminated by some amount of tungsten. Likely, the amount was so small that it was below the limit of detection for the RAIRS data. However, even with some amount of WO$_3$ on the surface, the XPS data shows that the C18 monolayer remains unaffected, mirroring the conclusion reached using the RAIRS data.

To confirm that the SAM was not affected by WF$_6$ gas, we looked at the C 1s and S 2p regions. Pre-exposure, the C 1s region was best fit with a peak at 284.9 eV with a FWHM of 1.2 eV and a peak at 285.9 eV with a FWHM of 3.8 eV. These peaks are consistent with the C-C bonds of the SAM backbone and the C-S bond of the thiol, respectively.\textsuperscript{35–38} Post-exposure, the C 1s region was best fit with a peak at 284.9 eV with a FWHM of 1.3 eV and a peak at 286.2 eV with a FWHM of 3.4 eV. Pre-exposure, the S 2p region was fit with two pairs of peaks. The main peak had a j = 3/2 peak at 162.0 eV and the smaller pair had a j = 3/2 peak at 163.3 eV. These peaks are consistent with bound and unbound thiol. Post-exposure, two S 2p pairs have a j = 3/2 at 162.0 eV and j = 3/2 and 163.4 eV.

For both the C 1s and S 2p regions, the pre- and post-exposure both have consistencies with peak positions. However, the peaks in the post-exposure spectra for both regions are lower
in intensity. This could be due to a layer of WO$_3$ on the surface. To confirm that the WF$_6$ gas isn’t affecting the surface, we can look at the C/S area ratio. Ideally, the C/S area ratio would be 18 because of the ratio of 18 carbons to 1 sulfur in the 1-octadecanethiol that makes up the C18 surface. In practice, this ratio may be slightly higher due to the core electrons for the sulfur head not reaching the detector due to travelling through the carbon chains. For the pre-exposure surface, the C/S ratio is 18.2, nearly the ideal ratio. Post-exposure, the C/S ratio is 17.5. Although slightly lower than ideal, this ratio is still nearly ideal. The lack of fluorination in both the RAIRS and XPS data, combined with the XPS data for the C 1s and S 2p regions confirms that the C18 surface remains unaffected by WF$_6$ gas at this pressure.

Figure 5.5 shows the high-resolution XPS data for the C18 surface shown in Figure 5.2 that was exposed to ~8.00 torr WF$_6$. In this figure, the C 1s, S 2p, F 1s, W 4f, and O 1s high-resolution regions are shown. As with the previous XPS data, there is no evidence of surface fluorination since there is no peak in the F 1s region. Also, we see the same evidence for WO$_3$ on the surface with a $j = 7/2$ peak in the W 4f region post-exposure at 36.3 eV and a peak in the O 1s region post-exposure at 531.5 eV. In the C 1s region pre-exposure, the peak for the C-C bonds of the SAM backbone is at 284.9 eV and shifts slightly to 284.8 eV for post-exposure. Like the XPS data for the surface exposed to a lower pressure of WF$_6$, the peak position for the C 1s region pre- and post-exposure does not show any change for the SAM. However, we still see the decrease in intensity likely from WO$_3$ on the surface.
Figure 5.5: High-resolution x-ray photoelectron spectroscopy spectra of the C 1s, S 2p, F 1s, W 4f, and O 1s regions of a C18 surface before and after exposure to ~ 8.00 torr WF₆. Corresponding RAIRS data shown in Figure 5.2.
Pre-exposure, the S 2p region was fit with two pairs of peaks. The main feature, which corresponds to bound thiol, has a $j = 3/2$ peak at 161.9 eV and the smaller feature, which corresponds to unbound thiol, has a $j = 3/2$ peak at 163.2 eV. Post-exposure, the peak positions for both peaks does not change, but the intensity decreases. However, now a new peak is seen at 168.9 eV. This region corresponds to a more oxidized state of sulfur, similar to that of a sulfonate group.\(^{39}\)

The C/S ratio for the pre-exposed sample was slightly higher than ideal at 19.2. While this value is higher than ideal and higher than the previous sample, it is still in range for what is expected pre-exposure. For post-exposure, the C/S ratio increases to 25.2. This increase is due to some of the sulfur heads being oxidized, which lowers for the count of bound thiol heads, shifting the ratio to be higher.

Overall, at lower pressures of WF\(_6\), the C18 surface remains unaffected except for some WO\(_3\) that forms on the surface, likely from WF\(_6\) molecules trapped in the chains. However, at higher pressures, WF\(_6\) oxidizes some of the thiol heads, causing a slight chain rearrangement. However, this oxidation is weak since there is very little sulfur oxidation seen in XPS or chain rearrangement seen in RAIRS.

5.3.1.2 Uranium Hexafluoride

5.3.1.2.1 RAIRS

Now that we have shown that WF\(_6\) will oxidize the C18 surface at higher pressures, we looked at the reaction between UF\(_6\) gas and the C18 surface. We anticipate that the experiments with UF\(_6\) would be more reactive since UF\(_6\) is known to be a stronger oxidizer than WF\(_6\) and can
be a fluorinating agent. In the RAIRS spectra, the best way to monitor how the surface reacts to the gas is to monitor the CH modes of the SAM chains.
Figure 5.6: Reflection-absorption infrared difference spectra of a C18 surface exposed to different pressures of UF₆ gas. The spectrum shown at the top is the SAM prior to exposure. (A) 0.01 torr of gas with each spectrum increasing by ~ 2 x 10⁶ L (B) 0.05 - 0.12 torr of gas with
each spectrum increase by \( \sim 2.5 \times 10^7 \) L (C) 1.00 torr UF\(_6\) with each spectrum increasing by \( \sim 2 \times 10^8 \) L.

Figure 5.6 shows how the CH modes react to three different pressures of UF\(_6\) gas. At the top of all three figures is the SAM prior to exposure. All pristine SAM spectra have peaks at 2918 and 2850 cm\(^{-1}\) for the CH\(_2\) asymmetric and symmetric stretches, respectively, which confirms that the SAM is well-ordered prior to exposure. Figure 5.6A shows a C18 surface that was exposed to 0.01 torr UF\(_6\). This was the lowest pressure that could be read on the chamber pressure gauge. Each spectrum increases in exposure up the figure by \( \sim 2 \times 10^6 \) L. Starting at the bottom, at the initial exposure, a negative mode appears at 2918 cm\(^{-1}\). The decrease in the asymmetric CH\(_2\) stretch indicates that the monolayer became disordered once gas was introduced into the chamber. Figure 5.7 shows how the CH\(_2\) asymmetric stretch changes over time. Only an initial decrease in absorbance for this stretch is seen. When a C18 surface was exposed to higher pressure of WF\(_6\), a weaker oxidizer, a similar negative CH\(_2\) asymmetric stretch feature was seen. The XPS data showed that this feature was due to the sulfur head being oxidized. We can assume that negative CH\(_2\) asymmetric stretch feature seen in Figure 5.6A is due to UF\(_6\) oxidizing the sulfur head to a sulfonate group. Because UF\(_6\) is a much stronger oxidizer, oxidation is seen at a much lower pressure.
Figure 5.7: Integrated absorbance of the CH modes of a C18 surface that was exposed to 0.01 torr UF$_6$ vs exposure (in L).

While the extent of oxidation is low when the pressure of UF$_6$ is low, Figure 5.6B shows how surface oxidation increases as the pressure of UF$_6$ increases. In Figure 5.6B, the C18 surface is first exposed to 0.05 torr UF$_6$. After several minutes, more UF$_6$ is let into the chamber, bringing the total pressure in the chamber up to 0.12 torr. The addition of more gas is denoted by an * on the figure.
When additional gas is introduced to the system the asymmetric and symmetric modes of the CH\textsubscript{2} and CH\textsubscript{3} modes decrease greatly. Over the span of the experiment, the modes continue to decrease, but at a slower rate. The initial decrease is likely due to UF\textsubscript{6} oxidizing the sulfur heads. As some sulfur heads become oxidized, this affects the packing of the chains, which is reflected in the decrease of the CH modes. The intensity of the negative modes indicates that the extent of oxidation is greater than at the lower pressure. This is due to more UF\textsubscript{6} molecules in the system and the higher pressure of gas causing more reactions. Once more gas is introduced to the system, the intensity does not appear to change. This suggests that while the initial decrease is due to sulfur head oxidation, the continual decrease is likely due to the SAM chains rearranging to accommodate for the bulkier sulfonate head. The intensity of the CH modes does not show another drastic decrease once more gas is introduced, suggesting that the surface has reached the extent of possible oxidation.

The same drastic decrease is seen for 1.00 torr UF\textsubscript{6} with the C18 surface, as seen in Figure 5.6C. As with 0.05 - 0.12 torr UF\textsubscript{6}, the surface continues to rearrange over time of the experiment as the surface continues to rearrange to accommodate the sulfonate head groups. At this higher pressure of UF\textsubscript{6}, HF gas is produced. Figure 5.6C shows a series of ro-vibrational lines between 4250 – 3900 cm\textsuperscript{-1} that belong to HF. While HF could be reacting with and fluorinating hydrocarbons, we have already shown that UF\textsubscript{6} oxidizes the sulfur heads and is responsible for the drastic reordering of the monolayer.

While monitoring the SAM chains is one way to determine how the surface reacts with UF\textsubscript{6}, the RAIRS spectra also shows the appearance of other features. Figure 5.6A shows the RAIRS data between 1325 – 500 cm\textsuperscript{-1} for a C18 surface exposed to 0.01 torr UF\textsubscript{6}. The only notable peak of interest is centered at 630 cm\textsuperscript{-1}. The gas phase UF\textsubscript{6} is expected at 625 cm\textsuperscript{-1}.\textsuperscript{41,42}
However, this peak is not seen due to the low concentration of UF$_6$ in the chamber. The peak at 630 cm$^{-1}$ is too blue shifted to be gas phase UF$_6$ but could be adsorbed UF$_6$. Calculations have predicted a blue shift of about 40 cm$^{-1}$ for UF$_6$ interacting with an ethyl amine trimer. While these preliminary calculations are with a different model surface, we anticipate a blue shift for adsorbed UF$_6$ on all SAM surfaces. The small blue shift of ~5 cm$^{-1}$ could be due to low concentration of absorbed UF$_6$. In fact, as we expose a C18 surface to higher pressures of UF$_6$, we see the peak shift further. Figure 5.8 shows the effect of UF$_6$ pressure, which is directly related to coverage, on the peak position of adsorbed UF$_6$. The peak position shifting to higher wavenumbers as coverage increases implies that the bond between UF$_6$ and the C18 surface gets stronger with higher coverage.
Figure 5.8: Peak position (in wavenumbers) of adsorbed UF$_6$ vs exposure of UF$_6$ gas (in torr).

Figure 5.9A shows how the integrated absorbance of adsorbed UF$_6$ on a C18 surface exposed to 0.01 torr changes over time of exposure. This figure shows that no UF$_6$ adsorbed to the surface until several minutes into the experiment. Then, once UF$_6$ does start to adsorb to the surface, the integrated absorbance quickly decreases back down to zero. We have already shown that the surface rearranges due to exposure to UF$_6$ gas.
Figure 5.9: Integrated absorbance of adsorbed UF$_6$ and UO$_2$F$_2$ for C18 surface that was exposed to (A) 0.01 torr, (B) 0.05 - 0.12 torr, and (C) 1.00 torr UF$_6$ gas.

The delay in UF$_6$ adsorbing could be due to the lack of surface sites available. Once the surface rearranges and sites become available, UF$_6$ begins to adsorb. The decrease in adsorbed UF$_6$ could be due to a few different factors. One is that the adsorbed UF$_6$ reacts. However, there is no indication in the RAIRS data that any sort of reaction occurs since no other peaks are seen. Instead, it is more likely that as the surface continues rearranging, the surface sites for adsorbed UF$_6$ become less thermodynamically favorable, causing UF$_6$ to desorb from the surface.
This behavior of the integrated intensity of adsorbed UF$_6$ decreasing over time is also seen at the higher pressure, as seen in Figure 5.9B and 5.9C. However, at these higher pressures, the integrated absorbance does not go completely to zero. Instead, it reaches an equilibrium with the surface, indicating that some UF$_6$ remains on the surface and could be trapped in the chains. Something that could be blocking UF$_6$ from desorbing completely is uranyl fluoride, UO$_2$F$_2$, on the surface. UF$_6$ is known to react with water upon immediate contact and form UO$_2$F$_2$ and HF gas$^{43-46}$. At the lowest pressure, 0.01 torr, there is no HF gas seen in the RAIRS spectra, nor is there any indication of UO$_2$F$_2$ forming. This would explain why UF$_6$ is able to desorb from the chains easily. With 0.05 torr UF$_6$, a very small peak starts to grow in at 974 cm$^{-1}$ that could belong to the U=O stretch in UO$_2$F$_2$, based on the peak position and peak shape. The expected position for the U=O stretch in UO$_2$F$_2$ is an asymmetric peak between 1010 – 930 cm$^{-1}$.47–49 As more gas is introduced to the system, this peak grows in intensity. Figure 5.9B shows that once UO$_2$F$_2$ is absorbed to the surface, some adsorbed UF$_6$ remains on the surface. This is also seen in Figure 5.9C, a C18 surface exposed to 1 torr, but to a much greater extent. Because so much more UO$_2$F$_2$ adsorbs to the surface, more UF$_6$ stays absorbed on the surface.

In Figure 5.6C, a series of peaks appears corresponding to gas phase UF$_6$ and different combination bands. These peaks are 625 ($v_3$), 670 ($v_2 + v_6$), 820 ($v_3 + v_5$), 1157 ($v_2 + v_3$), and 1291 ($v_1 + v_3$).41 An impurity peak appears at 1031 cm$^{-1}$, and grows in over time that belongs to SiF$_4$, which is produced due to UF$_6$ etching the glass backing of the gold substrate.43 There are also two impurity peaks that appear and grow in intensity over the course of the experiment at 949 and 1272 cm$^{-1}$. These peaks have previously been attributed as impurity peaks in the system reporting on the hydrolysis of UF$_6$.43 Their system contained Viton O-rings, and once they remove these O-rings and continued exposure, these peaks disappeared. Therefore, they
concluded that UF₆ gas was attacking the Viton and producing these impurity peaks. The primary structure of Viton is a polymer of fluorocarbons. This means that UF₆ was attacking the polymer and cleaving it into smaller gas phase fluorocarbon chains. In our work, we see these peaks appear once UF₆ is introduced to the system and then grow over time of exposure. Our system is devoid of any Viton or a similar substance. If this was just an impurity in the gas tank, we would expect the concentration of this peak to stay the same over time or decrease as it adsorbed to the surface of the sample or the chamber walls. Because these peaks increase over time, we believe that UF₆ is fluorinating the only source of hydrocarbon in the chamber, the SAM. Since no C-F modes are seen, the first possible step is UF₆ oxidizing the sulfur head, then another UF₆ molecule cleaves and fluorinates the chain. While this is not seen at lower pressures of UF₆, this may be due to a low concentration in the system.

5.3.2 Fluorocarbon Surface

5.3.2.1 Tungsten Hexafluoride

The next surface that was analyzed was a fluorinated surface made from 1H,1H,2H,2H-perfluorodecanethiol adsorbed to a gold substrate. For brevity, this surface will be called F8H2, since it consists of 10 carbons, with two methylene linkers between the sulfur head group and the exterior “fluoroctane” chain. Thus the interface between the gas and the surface is fluorinated. The fluorocarbon SAM, an opposed to a hydrocarbon SAM, on gold adopts a more perpendicular orientation relative to the surface due to the tilt angle being only 11° as compared to 30° for the hydrocarbon SAM.⁵₀,⁵¹ The difference in tilt angle is a result of the larger van der Waals diameter of the fluorocarbon chain causing the spacing of the sulfur heads on gold to be spaced ~5.7 Å, which is larger than the ~4.9 Å for the hydrocarbon sulfur heads.⁵²,⁵₃ The larger van der
Waals diameter not only causes the spacing of the sulfur heads to change, it also makes the fluorinated monolayers form a c(7 x 7) or p(2 x 2) hexagonal lattice, which differs from the (√3 x √3)R30 hexagonal lattice commonly seen in hydrocarbon SAMs.\textsuperscript{54,55} Not only is the terminal functional group and chain different between these monolayers, but the ordering and packing of the layers differ as well. While the terminal functional groups differ, the fluorinated functional group is predicated to have a similar intermolecular binding energy to the hydrocarbon surface. The predicted intermolecular binding energy between a fluoroethane molecule and a UF\textsubscript{6} molecule is 1.68 kcal/mol, just slightly higher than that of a methane and UF\textsubscript{6} pair. Any changes seen between how the hydrocarbon surface and fluorocarbon surface responds to UF\textsubscript{6} gas could be a result of the orientation of the chain as well as the chemical composition of the chain.

Before exposing the F8H2 surface to UF\textsubscript{6} gas, we exposed a pristine surface to ~6 torr WF\textsubscript{6} gas, as shown in Figure 5.10. At the top of the figure is the surface prior to any gas exposure, using s-polarized light as the background. Starting from the bottom spectrum, each spectrum increases in exposure by ~1.5 x 10\textsuperscript{9} L. In the original F8H2 SAM at the top, the peaks at 1373 and 1335 cm\textsuperscript{-1} are bands for the asymmetric and symmetric vibrational modes for CF\textsubscript{2} with a transition dipole parallel to the perfluorohelical axis.\textsuperscript{56,57} The broad band at 1206 cm\textsuperscript{-1} could be the vibrational modes for CF\textsubscript{2} with a transition dipole more perpendicular to the perfluorohelical axis.\textsuperscript{56,57} The presence of this peak suggests that some disordered regions may exist, however the peak position and FWHM of the parallel peaks suggest a well-ordered monolayer overall. Due to the short alkyl linker chain, the only CH\textsubscript{2} mode seen is a small band for the asymmetric CH\textsubscript{2} stretch. Because we are aiming to characterize how the surface reacts to the gas, we can track any surface changes with the CF\textsubscript{2} modes in the same manner as the CH\textsubscript{2} modes of the C18 surface discussed previously.
Figure 5.10: Reflection-absorption infrared difference spectra of a F8H2 surface exposed to ~6.00 torr WF₆ gas. The spectrum shown at the top is the SAM prior to exposure. Each spectrum, starting from the bottom, increases by ~1.5 x 10⁹ L up the figure.

Figure 5.10 shows a slight decrease in the CF₂ modes with a transition dipole perpendicular to the perfluorohelical axis at 1206 cm⁻¹, followed by a new broad peak appearing ~1278 cm⁻¹. However, no change is seen in the peaks for the parallel modes. While a new gas phase WF₆ peak at 1387 cm⁻¹ could be covering any small changes for the band at 1373 cm⁻¹ for
the parallel modes, we would anticipate a negative peak at both 1373 and 1335 cm\(^{-1}\) peaks, which is not seen. This data suggests that while WF\(_6\) may interact with the disordered regions of the monolayer in some way, it does not affect the ordered regions. A small broad peak appears at 635 cm\(^{-1}\) and grows over time, which could be WF\(_6\) adsorbing to the surface, likely causing the disordered regions of the SAM to rearrange. As compared to the adsorbed WF\(_6\) peak for the C18 surface at 655 cm\(^{-1}\), WF\(_6\) would have a weaker attraction to the F8H2 surface. The lower wavenumber indicates a less energetic bond. This is due to the repulsive nature between the fluorines of WF\(_6\) and the fluorinated surface.

5.3.2.2 Uranium Hexafluoride

In contrast to WF\(_6\), we exposed a pristine F8H2 surface to a continuous 1.00 torr UF\(_6\) gas, as shown in Figure 5.11. Starting from the bottom spectrum and moving up, each spectrum increases exposure by \(\sim 5 \times 10^8\) L. In the F8H2 SAM prior to exposure at the top, the peaks at 1373 and 1336 cm\(^{-1}\) are bands for the vibrational modes for CF\(_2\) with a transition dipole parallel to the perfluorohelical axis. This indicates that the perfluoro chains all exist in the same manner. The lack of any bands between 1200 to 1300 cm\(^{-1}\), which is the vibrational modes for CF\(_2\) with a transition dipole perpendicular to the perfluorohelical axis, also indicates that the perfluoro chains that make up the monolayer are all in the same orientation.\(^{56,57}\)
Figure 5.11: Reflection-absorption infrared difference spectra of a F8H2 surface exposed to 1.00 torr UF₆ gas. The spectrum shown at the top is the SAM prior to exposure. Each spectrum, starting from the bottom, increases by ~5 x 10⁸ L up the figure.

Figure 5.11 shows that upon introduction of the gas, the peaks at 1373 and 1336 cm⁻¹ decrease almost completely as compared to the pristine surface, while a new set of peaks appear at 1252 and 1223 cm⁻¹. This new set of peaks likely belongs to the vibrational modes for CF₂ with a transition dipole perpendicular to the perfluorohelical axis. This simultaneous decrease and increase in the parallel and perpendicular modes, respectively, could indicate that upon
exposure to UF₆ gas, the surface undergoes a massive rearrangement. Fully fluorinated species are known to be resistant to UF₆ fluorination, so any reaction must come from the Au-S-C bond of the thiol.¹³,⁵⁸ We have already shown that UF₆ oxidizes the sulfur head of the thiol, causing the chain to rearrange. While the perfluoroalkane chain is bulkier than the hydrocarbon chains, the sulfur heads are spaced further apart to accommodate. While this surface is more tightly packed, all SAM surfaces contain defects that make the sulfur groups accessible to UF₆. Even though the fluorine chains should be repulsive to UF₆, they still experience massive disordering like the hydrocarbon surface.

Just as with the hydrocarbon surface, a peak at 949 cm⁻¹, which was previously attributed as an impurity peak, grows in over time of the experiment. Figure 5.12 shows how this peak grows in over the course of the experiment. Unlike the C18 surface, where this peak grows in linearly, for the F8H2 surface, this peak reaches a maximum and then levels off. Also shown in Figure 5.12 is the integrated absorbance for the CF₂ modes. As the CF₂ modes decrease, the peak at 949 cm⁻¹ increases. This suggests that these two processes may be related. For the C18 surface, we hypothesized that this peak belonged to carbon chains that were first cleaved and then fluorinated. For the F8H2 surface, the chain is mostly fluorinated with a very small alkyl chain close to the sulfur head. Assuming the peak at 949 cm⁻¹ belongs to gas phase fluorocarbons, the enhanced appearance of this feature is expected. If the reaction of the hydrocarbon proceeds by the chain first being cleaved then the chain being fluorinated, only cleavage is required for the fluorinated surface to show similar signals as the chains are already fluorinated. This then shows that the first step, cleaving the chains, happens quickly, while the chain fluorination proceeds much slower.
Figure 5.12: Integrated absorbance of an impurity peak at 949 cm$^{-1}$ and the CF modes of the SAM of a F8H2 surface exposed to 1.00 torr UF$_6$ vs exposure (in L).

Figure 5.13 shows how the CF$_2$ modes of the SAM change over time. The figure shows that as the CF modes decrease, the new CF modes at 1252 and 1223 cm$^{-1}$ increase over time. The CF modes, like the CH modes in the C18 surface, decrease quickly upon the introduction of UF$_6$. However, unlike the C18 surface, we see new CF modes appear that are red shifted from the pristine SAM. Red shifted peaks for the F8H2 surface are known to have a higher tilt angle, making them more parallel to surface.$^{52}$ While these new CF modes grow in quickly, they
decrease in intensity before leveling out. As shown in Figure 5.12 and mentioned previously, we hypothesize, based on the data, that UF₆ cleaves some of the SAM chains. This decrease in the new CF modes is likely the surface rearranging to accommodate for the loss in some of the SAM chains.

**Figure 5.13:** Integrated absorbance the CF modes of the pristine SAM and the new CF modes that appear after exposure of a F8H2 surface exposed to 1.00 torr UF₆ vs exposure (in L).
Because we see the appearance of new CF modes, even though these new modes suggest that the surface has undergone disordering, the F8H2 surface appears to be more robust. This is reflected in Figure 5.14, which shows a F8H2 surface that has been exposed to 0.01 torr UF$_6$. In this figure, there is no change seen in the CF modes. While the C18 surface showed a slight disturbance of the carbon chains at this pressure, the F8H2 surface does not seem to be affected at all. The more tightly packed fluorocarbon chains are able to resist UF$_6$ oxidizing the sulfur heads at low pressures.
Another factor that could be making the chains rearrange more is the adsorption of UO$_2$F$_2$ and UF$_6$ to the surface. The multiple bands that appear between 4000 and 4250 cm$^{-1}$ once UF$_6$ is introduced to the system belong to gas phase HF. The immediate production of HF gas suggests that UF$_6$ is hydrolyzed in the chamber to produce HF and UO$_2$F$_2$. Based on the asymmetric shape and peak position, the peak growing in at ~987 cm$^{-1}$ it is likely UO$_2$F$_2$ is adsorbing to the surface.
Figure 5.15 shows the integrated absorbance of adsorbed UF$_6$ and UO$_2$F$_2$ on the surface over the course of the experiment. As expected, based on the C18 surface, UO$_2$F$_2$ adsorbs to the surface over time. However, the behavior of adsorbed UF$_6$ is different for the F8H2 surface as compared to the C18 surface. While the C18 surface showed a decrease in the integrated absorbance, which we attributed to either the chains rearranging and surface sites becoming less favorable or UF$_6$ reacting after it adsorbed, UF$_6$ adsorbs on the F8H2 and then doesn’t desorb. This indicates that either the bulkier fluorine chains trap UF$_6$ in the surface better than alkane chains or adsorbed UF$_6$ has nothing to react with on the F8H2 surface. Because we don’t see any adsorbed UF$_6$ on the F8H2 surface that was exposed to 0.01 torr, as seen in Figure 5.14, it is more likely that the bulkier chains make it harder for UF$_6$ to get trapped in the chains, but once UF$_6$ does get into the chains, it is trapped.
**Figure 5.15:** Integrated absorbance of adsorbed UF₆ and adsorbed UO₂F₂ that appear after exposure of a F8H2 surface exposed to 1.00 torr UF₆ vs exposure (in L).

5.3.3 Amine Surface

5.3.3.1 Tungsten Hexafluoride

5.3.3.1.1 RAIRS

The final surface that was analyzed was an amine terminated surface made from 1-hexadecanethiol hydrochloride adsorbed to a gold substrate. For brevity, this surface will be called NH2 from here on out since it is a carbon chain with an amine terminal functional group.
Due to the amine terminal groups, the chains likely form a hydrogen bonding network over the entire surface. As a result, this H-bonding network creates “holes” on the surface as some terminal groups are pulled closer together. Also, in comparison to the C18 and F8H2 surfaces, the predicted intermolecular binding energy between a methyl amine molecule and a UF₆ molecule is much higher at ~15 kcal/mol.⁴ We anticipate the binding between both a WF₆ and UF₆ molecule to the NH2 surface to be much more attractive than the other two surfaces previously analyzed.

To determine how the NH2 surface reacts to WF₆ gas, we exposed a pristine surface to ~0.25 torr of WF₆ gas, as seen in Figure 5.16. The spectrum at the top shows the surface prior to gas exposure. The peaks at 2916 and 2848 cm⁻¹ belong to the asymmetric and symmetric stretches of the CH₂ modes that make up the carbon backbone of the SAM. It should be noted that there are no modes associated with the NH stretch in the pristine SAM spectrum. This is due to the H-bonding network that forms on the surface of the SAM between neighboring terminal amine groups. This network effectively locks the N-H group in a position that is parallel to the surface and therefore cannot be detected by RAIRS.
Figure 5.16: Reflection-absorption infrared difference spectra of a NH2 surface exposed to 0.25 torr WF$_6$ gas. The spectrum shown at the top is the SAM prior to exposure. Each spectrum, starting from the bottom, increases by $\sim 5 \times 10^7$ L up the figure.

Figure 5.16 shows that upon gas exposure and throughout the experiment, the CH$_2$ modes decrease. For both the C18 and F8H2 surfaces, several torr of WF$_6$ gas were needed before even a slight change in the SAM was seen. However, the SAM of the NH2 is affected at a much lower pressure, as predicted by the IBE’s. This is likely due to the lone pair of electrons on the terminal amine group. UF$_6$, acting as a Lewis acid, has a stronger binding energy with amine group.
At the same time of the CH\textsubscript{2} modes decreasing, a broad peak at $\sim 3280$ cm\textsuperscript{-1} appears. Figure 5.17 shows the integrated absorbances of the CH\textsubscript{2} modes and the peak at $\sim 3280$ cm\textsuperscript{-1} vs exposure (in Langmuir). This figure shows that as the CH\textsubscript{2} modes decrease, the peak at $\sim 3280$ cm\textsuperscript{-1} increases. This band is in the region of the NH stretch. This peak likely grows in as the WF\textsubscript{6} gas causes the chains to reorder, breaking the H-bond network that is formed by the pristine surface. Therefore, the NH stretch, which is not previously seen in the spectrum taken before exposure, is now visible.
Figure 5.17: Integrated absorbance of the CH and NH modes of the SAM during exposure to 0.25 torr WF₆ gas.

5.3.3.1.2 XPS

To characterize the surface after exposure, XPS was done before and after gas exposure. Figure 15.18 shows the high-resolution XPS data for the C 1s, S 2p, F 1s, W 4f, O 1s, and N 1s regions of a NH2 surface that was exposed to 0.25 torr of WF₆ for ~6.5 hours. To monitor how the SAM is affected by the gas, we can look at the C1 s, N 1s, and S 2p regions.
Figure 5.18: High-resolution x-ray photoelectron spectroscopy spectra of the C 1s, S 2p, F 1s, W 4f, O 1s, and N 1s regions of a NH2 surface before and after exposure to ~ 0.25 torr WF$_6$. Corresponding RAIRS data shown in Figure 5.15.

The C 1s region pre-exposure is fit with a peak at 285.0 eV with a FWHM of 1.2 eV and a peak at 286.2 eV with a FWHM of 1.8 eV. These peaks are consistent with the C-C bond of the carbon backbone and the C-S bond of thiol bound to gold. Post-exposure, these peaks are at 285.1 eV and 286.5 eV.

Pre-exposure, the N 1s region has a peak at 401.6 eV, which corresponds to protonated amine, NH$_3^+$, and a peak at 400.0 eV, which corresponds to an amine group. After WF$_6$ exposure, the intensity of the protonated amine decreases, while the intensity of the unprotonated increases.

The S 2p region both pre- and post-exposure has a peak at 162.0 eV for bound thiol. Both pre- and post-exposure regions has a peak at 163.6 eV for unbound thiol. While the intensity of this peak is large, especially when compared to the unbound thiol for the C18 surface, a high ratio of unbound thiol has been reported for amine terminated surface.$^{39,59,60}$ The lone pair of electrons on the amine will donate electrons to the gold substrate and form an Au-N bond.$^{61}$ This bonding can cause some misalignment of the chains on the surface, which creates gaps on the surface. These gaps, along with the gaps made by the h-bond network on the surface, leave the exposed sulfur groups able to oxidize easily.

The S 2p region pre-exposure has a very intense peak at ~168 eV. The intensity of this peak highlights the ability of sulfur to oxidize due to these gaps. However, the intensity of this peak decreases after exposure to WF$_6$, along with the unbound thiol peak. This indicates the WF$_6$
is removing these oxidized chains from the surface. For the C18 surface, we showed that WF$_6$ oxidized some of the thiols on the surface after exposure. Therefore, we expected the intensity of the oxidized sulfur peak to increase after exposure for the NH2 surface, not decrease. This means that some of the oxidized sulfur heads that are present pre-exposure are displaced after the surface becomes disordered.

While the F 1s region in Figure 5.18 shows a peak at 686.9 eV, we know that the SAM is not being fluorinated. A C-F bond would have a peak at a much higher binding energy of ~292 eV, which is not seen in this figure.$^{62}$ Since there is no change in the pre-exposure peak and no new peak in this region, this indicates that the terminal group remains unchanged as well.

Instead of the surface being fluorinated, the fluorine peak belongs to WF$_6$. Post-exposure, the W 4f region has a peak with the j= 7/2 peak at 36.0 eV. The tungsten peak is tricky to assign because both WF$_6$ and WO$_3$ have a tungsten atom with a +6 oxidation state, leading them to have very similar peak positions. Both WF$_6$ and WO$_3$ have been reported to have a j = 7/2 peak position ~36.0 eV.$^{34,63}$ For the C18 surface that was exposed to WF$_6$ gas, we assigned the peak in the W 4f to the solely be WO$_3$ because there was no peak in the F 1s region. However, for the NH2 surface, this peak seems to belong to both WF$_6$ and WO$_3$. The O 1s region has a peak at 531.2 eV, which is consistent with WO$_3$.

It is likely that both WO$_3$ and WF$_6$ exist on the surface. Since WF$_6$ was predicted to have a higher attraction to the amine surface when compared to the hydrocarbon surface, it is possible that more WF$_6$ remains on the surface after evacuation of the chamber as compared to the other two surfaces.$^4$ Then, only a top layer of WF$_6$ gets hydrolyzed when exposed to atmosphere, and a layer, or multilayers of WF$_6$ remains under the top oxide layer.
5.3.3.2 Uranium Hexafluoride

In addition to exposing a NH2 surface to WF$_6$, we exposed a pristine NH2 surface to 1.15 torr of UF$_6$ gas, as shown in Figure 5.19. As previously mentioned, the spectrum at the top is the surface prior to exposure, using s-polarized light as the background. Starting from the bottom spectrum and moving up, each spectrum increases exposure by $\sim 5 \times 10^8$ L. The spectrum prior to exposure has peaks at 2917 and 2848 cm$^{-1}$, which are assigned to the asymmetric and symmetric CH$_2$ modes of the SAM chain. Once the surface is exposed to UF$_6$, these modes immediately decrease and continue to slightly decrease over time. As with the NH2 surface that was exposed to WF$_6$ gas, we seem a peak appear $\sim 3251$ cm$^{-1}$ that is likely the N-H stretch of the terminal amine group.
Figure 5.19: Reflection-absorption infrared difference spectra of a NH2 surface exposed to 0.25 torr UF6 gas. The spectrum shown at the top is the SAM prior to exposure. Each spectrum, starting from the bottom, increases by ~5 x 10^8 L up the figure.

Figure 5.20 shows the integrated absorbance for the CH modes and band at ~3251 cm⁻¹ over time of the experiment. Like with the NH2 exposed to WF6 gas, this band at ~3251 cm⁻¹ grows in at the same rate that the CH modes decrease. It should be noted that the N-H stretch in the WF6 experiment appears ~ 3280 cm⁻¹, while the peak in the UF6 experiment is red shifted ~29 cm⁻¹. This shift in peak position could be due to the N-H on the amine having a weak bond
to the hexafluoride molecule. This shift implies that the amine terminal group has a stronger bond to the WF$_6$ molecule than to the UF$_6$ molecule.

![Graph showing integrated absorbance of CH and NH modes](image)

**Figure 5.20:** Integrated absorbance of the CH and NH modes of the SAM during exposure to 1.00 torr UF$_6$ gas.

As with the other surfaces, we exposed the NH2 to a lower pressure of UF$_6$ to observe if any change happens. Figure 5.21 shows the RAIRS data for a pristine NH2 surface exposed to ~ 0.01 torr of UF$_6$ gas. Starting from the bottom spectrum and moving up, each spectrum increases
exposure by $\sim 1 \times 10^7$ L. Unlike the other two surfaces, which showed very little rearrangement of the surface due to UF$_6$ gas, at a lower pressure, the surface still shows an immediate decrease in both CH modes, followed by a band appearing $\sim 3251$ cm$^{-1}$. This suggests that, as the computational data has shown, that UF$_6$ binds much stronger to the amine surface and will react and at a much lower amount.

5.4 Summary

Based on the literature, we expected WF$_6$ to act as a mild oxidizer and UF$_6$ to act as a strong oxidizer and possibly a fluorinating agent. We have shown using in situ RAIRS that WF$_6$ gas does not react with either a model hydrocarbon or fluorocarbon surface at relatively low pressures. However, WF$_6$ does react with a model amine surface. Based on the RAIRS data, the surface reorders itself as WF$_6$ reacts with the surface. The XPS data offers more insight into the reaction and suggests that WF$_6$ reacts more with unbound thiol chains.

In contrast to the WF$_6$ reactions, UF$_6$ was shown to be much more reactive, as expected. Based on the RAIRS data, for the hydrocarbon and fluorocarbon surface, UF$_6$ oxidizes the sulfur head and cleaves the chain from the surface rapidly. The cleaved chains from the hydrocarbon surface then react with other gas phase UF$_6$ molecules and are fluorinated. So, while UF$_6$ does not fluorinate the SAM surface, it is able to fluorinate a free hydrocarbon chain. Like with WF$_6$ gas, the amine surface is much more reactive with UF$_6$ than the other surfaces. The UF$_6$ gas causes the amine surface to rearrange, which is reflected in the appearance of the previously locked in place N-H stretches.
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CHAPTER 6: Summary and Future Outlooks

In summary, the whole of this work was focused on different aspects of an on-site near-real-time enrichment alpha detector for uranium hexafluoride (UF$_6$) gas. In Chapter 1, we explored the existing literature on reactions between UF$_6$ and organic materials. The general consensus was that UF$_6$ can act as strong oxidizing agent, and can sometimes act as a fluorinating agent, usually at higher temperatures. However, while most of the products were determined after reactions, the reaction pathway could only be guessed at. We showed in Chapter 5 that in situ reflection absorption infrared spectroscopy (RAIRS) during hexafluoride gas exposure of a model organic surface is good technique to offer insight into the actual reaction pathways.

In Chapter 3, we explored the feasibility of using commercially available alpha detectors for alpha spectroscopy of a UF$_6$ sample to determine enrichment. Overall, the idea should be possible even with modifications to the detector to protect it from destruction of UF$_6$ gas. The only reason that this method of alpha spectroscopy may not produce ideal spectra is because any amount of moisture in the device will react with UF$_6$ to form an oxide that will coat the surface of the detector. This oxide formation has been shown in the IR spectra from the in situ RAIRS studies.

While the modelling in Chapter 3 shows that alpha spectroscopy should be feasible, when actually put into practice, as in Chapter 4, the extent of oxide formation is enough to block most of the signal from the gas phase. Oxide formation is also confirmed in the quartz crystal microbalance (QCM) data. It was shown that even with an inert surface, at least a monolayer of oxide forms.
While only three surfaces were monitored during hexafluoride exposure using RAIRS in Chapter 5, this method has proved possible to determine reaction pathways with a multitude of different functional groups. One of the reasons for using self-assembled monolayers (SAMs) as the functional group is that they are a more crystalline surface, but another is that the terminal group can be tuned to a variety of different functional groups. For instance, we explored a methyl, a fluorocarbon, and an amine terminal functional group, but future works could examine the interactions between alcohols, carboxylic acids, ethers, etc. The literature referred to in Chapter 1, has shown that UF$_6$ reacts with all these groups. By utilizing in situ RAIRS, future works could determine the reaction pathways between these reagents and determine product formation.

To be able to actualize these experiments, a radioactive hood would be necessary to house an ultra-high vacuum system, as described in Chapter 2. With the correct set-up, the only limit to monitoring these reactions would be the availability of the SAMs. While some SAMs are available commercially, other can be modified synthetically. However, as we have shown in Chapter 5, no matter the SAM, UF$_6$ is shown to attack the thiol bond. However, if SAMs were chosen that were bulkier, perhaps the bulkier groups could better protect the thiol bond.

The types of surfaces that can be exposed and monitored using this system does not have to be limited to just SAMs on gold or even SAMs at all. SAMs deposited on different metal surfaces provide different packing densities, which could protect the thiol bond from oxidation. Also, as shown in Chapter 3, the density of the deposited material greatly affects the resulting alpha spectrum. With gold being one of the densest metals, by using that as the passivation layer on the detector face, resolution decreases. A different less dense metal, like silver, would allow
SAMs to still chemisorb, but a layer at silver at the same thickness would affect an alpha spectrum less than a layer of gold would.

However, the coatings for passivating the alpha detector do not have to be limited to ones that can chemisorb SAMs. We explored in Chapter 4 an alpha detector that had been coated by aluminum fluoride (AlF₃). We have shown in all Chapter 3, 4, and 5, that any amount of water in the system will react with UF₆ to form uranyl fluoride (UO₂F₂), which will adsorb to whatever surface you are monitoring. Ideally, any coating should be repulsive to both UF₆ and UO₂F₂.