High Throughput Study of the Structure Sensitive Decomposition of Tartaric and Aspartic Acid on Surfaces Vicinal to Cu(111) and Cu(100)

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

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TITLE

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Submitted in partial fulfillment of the requirements for

the degree of

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in

Chemical Engineering

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Abstract

There are many reactions that are sensitive to the surface structure of a catalyst. In order to obtain a comprehensive understanding of structure sensitive surface chemistry we use Surface Structure Spread Single Crystals (S$^4$Cs) that expose a continuous distribution of crystal planes across their surfaces. Those crystal planes that lack mirror symmetry contain terraces, monatomic steps, and kinks and can be described as chiral with an R or an S orientation. When coupled with spatially resolved surface analysis techniques, S$^4$Cs can be used to study the effects of surface structure and chirality on surface chemistry across a continuous distribution of crystal planes.

A set of six Cu S$^4$Cs has been created that spans all possible crystal planes of Cu. The Cu(111) S$^4$C was used to study the structure sensitivity of L- and D-tartaric acid (TA) decomposition and the Cu(100) S$^4$C was used to study the structure sensitivity of L-4$^{13}$C and D-aspartic acid (AA) decomposition. Isothermal Temperature Programmed Reaction Spectroscopy (TPRS) was implemented in which the S$^4$Cs with monolayers of TA and AA were held at a temperature below the temperature of peak decomposition observed in a standard TPR experiment (heating at 1 K/s). At various times during isothermal heating, the surface was cooled to quench the reaction. Spatially resolved X-ray Photoelectron Spectroscopy (XPS) was performed to identify those regions on the surface in which the adsorbates had decomposed and those in which they were still intact. On the Cu(111) S$^4$C which exposes both (100) and (110) step edges, TA decomposition is most sensitive to the density of (100) steps. AA
decomposition on the Cu(100) S\(^4\)C was enantioselective: L-AA-4\(^{-13}\)C decomposed on S surfaces before R surfaces while D-AA decomposed on R surfaces before S surfaces.

The decomposition of CH\(_3\)CH\(_2\)OH, CD\(_3\)CD\(_2\)OD, and CF\(_3\)CH\(_2\)OH on Zn(1100) was studied using temperature programmed reaction spectroscopy (TPRS). The decomposition products of each reaction were determined and a reaction mechanism was proposed for CH\(_3\)CH\(_2\)OH decomposition based on the product ratios and peak temperature locations. The CH\(_3\)CH\(_2\)OH decomposition mechanism includes the formation of two intermediate species on the surface: CH\(_3\)CH\(_2\)- to form CH\(_2\)=CH\(_2\) and CH\(_3\)CH\(_2\)O- to form CH\(_3\)CH=O.
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CHAPTER 1

1 Introduction

1.1 Motivation

Surface structure and composition play significant roles in the activity and selectivity of catalysts. Obtaining a fundamental understanding of the effects of surface structure on chemical reactions at surfaces is crucial to the development of new catalytic materials. A typical catalyst is composed of metal nanoparticles with complex surface structures dispersed on a support. For example, an industrial methanol synthesis catalyst for converting CO\textsubscript{2} and H\textsubscript{2} into CH\textsubscript{3}OH is composed of Cu nanoparticles on a ZnO/Al\textsubscript{2}O\textsubscript{3} support (27, 28). Because of this complexity, most research on the effect of a catalyst’s surface structure on reactivity is aimed at finding the optimal particle size and maximizing the active surface area. Several authors have studied the effect of catalyst particle size on reactivity and have found that some reactions exhibit an increase in activity with decreasing particle size, while others exhibit a decrease in activity with decreasing particle size (9, 29-33). Recently, a review paper was published claiming that trends between particle size and catalytic activity are linked to the presence of different sites on the nanoparticle (9). Figure 1 illustrates the three classes of structure sensitive reactions proposed by van Santen \textit{et al.} Reactions that exhibited an increase in activity with decreasing particle size were attributed to the presence of corner atoms or low coordination number atoms on the nanoparticle surface. The opposite trend of increasing activity with increasing
particle size was attributed to the presence of step edge sites on the nanoparticle surface highlighted by red atoms. In general, any trend in particle size and catalytic activity was linked to structure sensitive surface chemistry. However, at the operating conditions of industrial catalysts, it is not possible to determine what the active site is. Only correlations of particle size with activity can be measured accurately unlike the effect of the surface structure of the catalyst on activity. To counter this, many authors use single crystal surfaces to understand the influence of surface structure on catalytic reactions. Using a metal single crystal allows elimination of any effects of surface heterogeneity and low Miller index surfaces are a common choice for study because they are the most energetically stable crystal planes over a wide range of temperatures. The most well-known demonstration of structure sensitivity is the work done by Gerhardt Ertl who studied N\textsubscript{2} dissociation, the rate limiting step in ammonia synthesis, on the three low Miller index crystal planes of Fe. He won the Nobel prize for showing that the rates of N\textsubscript{2} dissociation varied greatly between Fe(111), Fe(110), and Fe(100) (34, 35).
1.2 Stereographic Triangle

A crystalline material is defined as a material in which the atoms are situated in a periodic array over large atomic distances (36). Because of the repetitive pattern of crystalline materials, they are often described in terms of small repeat entities called unit cells which are used to represent the symmetry of the crystal structure. Most metals have either a face centered cubic (FCC), body centered cubic (BCC), or a hexagonal close packed (HCP) crystal structure. The crystal plane exposed by a crystalline material depends on the direction that the crystal is cut and the surface structure can change depending on the exposed

---

Figure 1: Classes of structure sensitive reactions by Dr. Rutger A. van Santen. In Class I reactions, the rate increases with increasing particle size and is sensitive to step edges (in red). For Class II reactions, the rate increases with decreasing particle size which is attributed to corner or low coordination number atoms (in blue) on the nanoparticle. Class III reactions are independent of particle size (9).
crystal plane. The orientation of a crystal plane is defined by 3 Miller indices, \((hkl)\). Each Miller index can be defined as the reciprocal of the point where the plane intersects each Cartesian axis in the unit cell. For example, \(h\) is equal to the reciprocal of where the plane intersects the x-axis. The value of \(k\) refers to the y-axis and \(l\) to the z-axis. A single crystal metal polished into a perfect sphere would contain all possible crystal planes on the surface. All possible crystal orientations on that sphere can be mapped out using the stereographic projection, defined as a graphical tool to represent the planes of a 3-D spherical crystal in 2-D (37). Due to the symmetry of the FCC lattice, all possible crystal planes can be represented by a small triangular section of the stereographic projection. This triangle is called the stereographic triangle and can be used as a map to represent all crystal planes for an FCC metal. A single point on the stereographic triangle represents a unique crystal orientation. The surface structure of a crystalline material changes with the crystal orientation and the stereographic triangle can be used to map out these changes. Figure 2 displays the stereographic triangle along with several locations of different crystal planes on the stereographic triangle. The corners of the stereographic triangle are the three low Miller index crystal planes: \((100)\), \((110)\), and \((111)\). The low Miller index planes are called terraces as they are atomically flat and are the most symmetric. Crystal planes located along the edge of the stereographic triangle contain surfaces with terraces of either a \((111)\), \((100)\), or \((110)\) orientation that are separated by monatomic step edges. The \((211)\) crystal plane in Figure 2 is a surface with \((111)\) oriented terraces and \((100)\) oriented step edges. Crystal planes located within the stereographic triangle
contain surfaces with terraces, monatomic step edges, and kinks in the step edge. The (643) surface contains (111) terraces, (100) step edges circled in red and (110) kinks in the step edge circled in green.

Depending on the location of the crystal plane on the stereographic triangle, the density and orientation of sites on the surface can change. Figure 3 shows several examples of the crystal planes located along the edge of the stereographic triangle. The orientation of the step edge is indicated by a triangle for (111) steps, a square for (100) steps, and a rectangle for (110) step edges. The (711) plane shows an example of the surface structure for crystal planes between (100) and (311) on the edge of the stereographic triangle. These planes contain (100) terraces and (111) oriented steps. As the distance from the (100) plane increases, the terrace width decreases and the number of step edges separating the terraces increases. This trend occurs until the (311) plane. This surface is a fully stepped surface and contains an even mixture of (100) and (111) step edges.

Crystal planes between (311) and (111) on the edge of the triangle contain crystal planes with (111) terraces and (100) step edges. As the distance from the (111) plane increases, the (111) terrace width decreases and the density of (100) step edges increases up to the (311) plane. On the edge of the stereographic triangle from (111) to the (110) plane, there are crystal planes with (110) step edges and the density of (110) step edges increases until the (110) plane. The (110) plane is considered a (110) terrace, but is also considered a fully stepped surface. Crystal planes between (100) and (210) contain crystal planes similar to the (510) plane shown with (100) terraces and (110) step edges. The (100) terrace width
decreases and the (110) step density increases moving away from the (100) plane until reaching the (210) surface. There is a transition at the (210) plane between (100) terraces and (110) terraces. This surface is considered fully kinked and/or a maximum in (110) step density. Surfaces between (210) and (110) have (110) terraces with (100) step edges like the (750) plane shown.

![Stereographic triangle with images of different crystal planes on the stereographic triangle.](image)

Figure 2: Stereographic triangle with images of different crystal planes on the stereographic triangle. The corners of the triangle are the low Miller index crystal planes: (100), (111), and (110). The edges of the triangle contain surfaces with terraces separated by monatomic step edges. Crystal planes in the triangle contain terraces, steps edges, and kinks in the step edge. Surfaces created using Surface Explorer.
Several of the crystal planes shown in Figure 3 have been used to gain insight into the effect of surface structure on different chemical reactions. However, if all of these single crystals were used to study a reaction, entire areas of the stereographic triangle would be left unstudied. In order to gain a fundamental understanding of the effect of surface structure on catalytic activity, a continuous distribution of different surface orientations need to be studied in the same experiment under the same conditions. Using curved single crystals provides an effective way to study multiple surface orientations in the same experiment. If the crystal orientation and the shape of the curved single crystal are known, then the surface structure of each point on the surface can be

Figure 3: Examples of crystal planes located along the edges of the stereographic triangle. The step orientations are highlighted in red as a square for (100) step edges, a rectangle for (110) step edges, and a triangle for (111) step edges. Surfaces created using Surface Explorer.
determined using the stereographic triangle based on the location of the low Miller index planes and the high symmetry directions of the crystal.

Our group has created a set of Cu curved single crystals called Surface Structure Spread Single Crystals or $S^4$Cs. The samples are created from single crystal disks of Cu that are polished into spherical sections. Each $S^4$C is centered at a specific crystal plane and spans a 2-D area of the stereographic triangle with a continuous distribution of crystal planes on the surface. A single point on one of these $S^4$Cs is a unique surface orientation. Our group has created a library of six Cu $S^4$C samples centered at different crystal planes on the stereographic triangle. Figure 4 shows the orientations of the six Cu $S^4$Cs and their location on the stereographic triangle. The angle listed next to each $S^4$C is the angle between the crystal plane normal at the center of the $S^4$C and the edge of each $S^4$C. The set of six Cu $S^4$Cs spans the entire stereographic triangle with significant overlap. This means that contained within the set of six samples are all possible crystal planes of Cu.

Although samples have been created to study every surface orientation of Cu, a spatially resolved technique must be used to study these samples that can perform a measurement at a discrete points. X-ray Photoelectron Spectroscopy or XPS is a surface analysis technique used to determine the elemental composition of a surface. It can be used to determine the presence of different metals or adsorbates on the surface, but only in ultra high vacuum or UHV conditions. In an XPS experiment, a beam of X-rays is exposed to a sample in UHV which causes the emission of photoelectrons from atoms in the near surface region of a
sample. The energy of these emitted photoelectrons is measured by a detector to generate a spectrum of photoelectron counts/sec versus binding energy. The binding energy of photoelectrons are element specific and can be used to determine the elemental composition of a surface. In a spatially resolved XPS experiment, the X-ray beam is focused on a point 50-400 μm in diameter on the surface meaning that photoelectrons are only generated from that point and therefore the elemental composition at that point can be determined. Our lab has the ability to perform spatially resolved XPS on a sample in UHV. The spatially resolved XPS is coupled with software that can rapidly collect spectra at different points on the surface from a programmed grid of points. Using spatially resolved XPS and the Cu S^4Cs, the adsorption, desorption, and reaction of molecules across the surface can be measured in quick rapid succession. With this technique available, the Cu S^4Cs can be used to perform high throughput experiments to determine the effect of the Cu surface structure on adsorption, desorption, and reaction phenomena in a UHV environment.
1.3 Chirality

The reactions studied in this research are the decomposition of chiral molecules. The word chirality is defined as a spatial geometric property possessed by an object that cannot be superposed on its mirror image (38). The most basic example of chirality comes from the human hand as the left and right hand are non-superimposable mirror images of each other. Chirality is an important property of bio-molecules. Many amino acids, proteins, and sugars are chiral and the majority of life is homochiral or exists as one chirality over the other.
Two molecules with the exact same atomic structure with different chiralities can have vastly different chemical properties such as melting point, vapor pressure, and binding energy to enzymes (40-43). Molecules that have the same atomic structure but different chiralities are called enantiomers and the branch of study of these molecules is called stereochemistry (38). Because chirality has such an important influence on bio-molecules, chirality also has an important role in the development of pharmaceuticals. Two pharmaceutical enantiomers can have drastically different effects on the human body. The most common example is the case of R and S Thalidomide, a drug used to treat nausea in pregnant women. While one enantiomer treated nausea, the other binded irreversibly to the protein cereblon, an important protein in limb formation, and caused birth defects (43). Understanding the differences between enantiomers and developing techniques for isolating one enantiomer over the other is critical to creating new pharmaceuticals.

The most common nomenclature system for chirality is called the Cahn-Ingold-Prelog (CIP) convention (4). In this system, the substituent groups bound to the chiral center are assigned a priority number that depends on the atomic number or atomic mass number of the atoms immediately bound to the chiral center. A higher priority is assigned to substituents with a higher atomic number or atomic mass. For a molecule with four substituents, each substituent is assigned a number from 1 to 4 in order of decreasing priority. Once assigned, the lowest priority molecule (usually 4) is oriented into the page or away from the viewer with molecules 1, 2 and 3 pointed toward the viewer. Figure 5 illustrates
an example of two enantiomers labeled with priority numbers 1-4 and oriented with molecule 4 pointed into the page. If the arrangement of the ligands is such that the direction of rotation from 1 to 2 to 3 is clockwise, then the chiral center is designated as the R-enantiomer (rectus in Latin meaning right). If the direction of rotation from 1 to 2 to 3 is counter clockwise, then the chiral center is designated as the S-enantiomer (sinistra in Latin for left) (4). If there are two chiral centers in a molecule, the naming changes slightly and the definition of chirality becomes more complicated. For example, a molecule with 2 S oriented chiral centers can be labeled the D-enantiomer while a molecule with 2 R chiral centers can be labeled as the L-enantiomer.

Figure 5: Example of an R and S enantiomer using the Cahn-Ingold-Prelog (CIP) convention. The direction of rotation from priority atom 1-2-3 dictates the chirality. If the direction is clockwise, it is an R enantiomer, if it is counter-clockwise, it is an S enantiomer (4).

Crystal planes can also be referred to as chiral and can have an R or and S orientation. Only crystal planes with terraces, monatomic steps, and kinked step edges can be chiral because only these crystal plane lack mirror symmetry. These crystal planes are present within the stereographic triangle and their chirality is
dictated by the orientation of the three microfacets. These three microfacets (terraces, steps, kinks) can have either a (111), (100), or (110) orientation and the direction of rotation from the highest density facet (111) through the (100) facet to the lowest density facet, (110), is used to define the chirality. The microfacet plane density can be thought of as the metric for determining priority in terms of the Cahn-Ingold-Prelog (CIP) convention where the higher the density of the plane, the higher the priority. Figure 6 shows a ball model of a Cu(643) R and S surface. This crystal plane has (111) terraces (gray), (100) oriented steps (green), and (110) oriented kinks (blue). If the direction of rotation from the (111) microfacet through (100) to the (110) microfacet is counter-clockwise, the crystal plane is S oriented. If the direction or rotation from (111)→(100)→(110) is clockwise, then the crystal plane is R oriented. At elevated temperatures, high Miller index crystal planes like Cu{643} can undergo thermal roughening that changes the surface structure from the ideal surface model. Sykes et al. used STM and Monte Carlo simulation to determine the effect of annealing on a Cu{643} surface. He found that although the surface reconstructed, the surface chirality was maintained and steps, kinks, and terrace sites were still present on the surface (10).
The interaction of chiral molecules with naturally chiral surfaces has been studied on single crystals of Cu by Gellman et al (1-3, 5, 22, 41, 44-46). One of the first studies was on R-3-methylcyclohexanone on a Cu(643) R and S surface (1, 2). Figure 7 shows a Temperature Programmed Desorption (TPD) spectra from a saturated exposure of R-3-methylcyclohexanone on the Cu(643) R and S surfaces. The first peak at 225 K was attributed to desorption of R-3-methylcyclohexanone from terraces, the second peak at 350 K to desorption from step edges, and the third peak at 385 K to desorption from kinks. The highest temperature peak shows a difference of 3.5 K, but the difference is not well resolved as the peak width is around 25 K. Reactions with narrow peak widths in
a TPD experiment would be better suited to visualize enantiospecific differences in chiral molecules on chiral surfaces of Cu. One reaction of this type is called a surface explosion reaction.

Figure 7: TPD spectra of R-3-methylcyclohexanone on Cu(643)R&S surfaces. The first peak at 225 K was attributed to desorption of R-3-methylcyclohexanone from terraces, the second peak at 350 K to desorption from step edges, and the third peak at 385 K to desorption from kinks (1, 2).

1.4 Surface Explosions

A surface explosion can be defined as a reaction that has an autocatalytic increase in the reaction rate with extent of reaction. A surface explosion follows an autocatalytic reaction mechanism similar to free radical and polymerization reactions. In these mechanisms, a radical intermediate reacts and produces two intermediates, $\bullet \rightarrow 2\bullet$ which produce two more intermediates and so on and so
forth. In polymerization, this is usually referred to as either the propagation step or the branching step. Without a quench for the intermediate species, the reaction rate will increase exponentially until there are no more reactants left. For surface explosions, the radical intermediate is the presence of empty sites on the surface. As the number of empty sites increases, the reaction rate increases until all reactants decompose. This surface explosion reaction was first reported for formic acid decomposition on Ni low Miller index single crystals by Madix et al (47, 48). Similar surface explosion reactions have also been seen for acetic acid decomposition on Ni, H₂O decomposition on Ni and Cu, and for tartaric acid decomposition on Cu(110) (14, 49-54). A characteristic of a surface explosion is a narrow peak width in a TPRS experiment of 1-5 K. Since tartaric acid is a chiral molecule that undergoes a surface explosion with a narrow peak width, it a useful reaction to study on chiral surfaces to determine the effect of surface chirality on the reaction. The general form of a surface explosion reaction mechanism is shown in Equation 1.1 where ● represents an empty site on the surface. After molecule A₂ adsorbs on the surface, it reacts with another empty site before decomposing and desorbing as product B into the gas phase. After decomposing, two empty sites become available for the reaction which propagates the reaction until only empty sites are left on the surface. The first form of the surface explosion rate law is shown in Equation 1.2. In this rate law, the reaction depends on both the coverage of the molecule and the coverage of empty sites where θ is the fractional coverage of the molecule and the coverage of empty sites is equal to (1-θ).
Surface explosions have been studied extensively by the Gellman group on single crystals of Cu for chiral molecules such as L- and D- Tartaric Acid (TA) and L- and D- Aspartic Acid (AA) (3, 5, 14, 22, 41, 44, 45). Figure 8 shows a temperature programmed reaction spectroscopy (TPRS) experiment of saturated exposures of L- and D-TA on Cu(17,5,1)R&S surfaces and Cu(531)R&S surfaces (3). The difference between TPD and TPRS is that in a TPRS experiment, the molecules on the surface react to form products instead of desorbing. In each experiment, the rate of CO$_2$ desorption was measured because it is the primary product of tartaric acid decomposition. As described previously, the peak width in each TPR spectrum is $< 3$ K. On the Cu(531)$^R$ surface, the peak for L-TA occurred at 489 K before D-TA at 493 K while on the Cu(531)$^S$ surface, the opposite trend was exhibited as the peak for D-TA occurred before L-TA. This result showed that the chirality of the surface effected the decomposition reaction. On the Cu(17,5,1)$^{R&S}$ the chirality of the surface was also shown to have an effect on the decomposition reaction but the opposite effect was observed as L-TA decomposed before D-TA on the S surface and D-TA decomposed before L-TA on the R surface. Although both surfaces showed that the reaction was enantioselective, the trend in enantioselectivity changed between each surface showing that much is still unknown about the effect of both surface chirality and

\[ A_2 \bullet + \bullet \rightarrow 2A \bullet \rightarrow 2B_g + 2 \bullet \]  

(1.1)

\[ \frac{d\theta}{dt} = -k_e \theta (1 - \theta) \]  

(1.2)
surface structure on the reaction. The Cu(17,5,1) surface contains (100) terraces and (111) steps while the Cu(531) surface contains (111) terraces and (100) steps. This reaction has only been studied for a few select chiral single crystals of Cu and more work is required to truly understand the effect of surface structure and chirality on the reaction.

The kinetics of D and L-TA decomposition were studied on a Cu(110) single crystal by Dr. Mhatre et al. using TPRS (14). By performing TPRS experiments varying the initial coverage, the heating rate at saturation coverage, and the isothermal hold temperature at saturation coverage, he was able to model a rate law for the reaction. He also found that for TA decomposition on Cu(110), the rate law shown in Equation 1.3 was the best fit to the data.

\[
\frac{d\theta}{dt} = k_t \theta + k_e \theta(1 - \theta)^2 \tag{1.3}
\]

This rate law consists of two separate steps: and initiation step, \(k_t \theta\), and an explosion step, \(k_e \theta(1 - \theta)^2\). In this rate law, the initiation step creates vacancies by desorption or decomposition of TA and the explosion step depends on both the coverage of tartaric acid and vacancies on the surface. The rate of the explosion step increases with increasing vacancy concentration autocatalytically until completion.
Thesis Objectives and Outline

The interaction of chiral molecules on chiral surfaces has been studied extensively on Cu single crystals by Gellman and coworkers, more specifically reactions of chiral molecules that undergo surface explosions. However, the use of single crystals studies only discrete points on the stereographic triangle leaving entire regions left unstudied. With the Cu $S^4C$ library and the spatially resolved XPS, high throughput experiments can be performed to study surface explosion reactions on hundreds of unique surface orientations in the same experiment.

1.5 Thesis Objectives and Outline

The interaction of chiral molecules on chiral surfaces has been studied extensively on Cu single crystals by Gellman and coworkers, more specifically reactions of chiral molecules that undergo surface explosions. However, the use of single crystals studies only discrete points on the stereographic triangle leaving entire regions left unstudied. With the Cu $S^4C$ library and the spatially resolved XPS, high throughput experiments can be performed to study surface explosion reactions on hundreds of unique surface orientations in the same experiment.
goal of this research is to use these Cu S₄Cs to study the decomposition of L- and D-TA and L- and D-AA and gain a comprehensive understanding of the effect of surface structure and surface chirality on these reactions. Using these Cu S₄Cs, correlations can be developed between the different sites on the surface and their activity as the density of sites at each point on the S₄C is known.

Chapter 2 is a review of the research done on curved single crystal surfaces or S₄Cs over the past 100 years. It is divided into two separate sections: Physical Phenomena and Chemical Phenomena. The Physical Phenomena section describes changes in the physical properties with surface structure studied on S₄Cs like electronic structure, work function, magnetization, and thermally induced surface reconstruction. The Chemical Phenomena section covers changes in chemical reactivity with surface structure.

Chapter 3 describes the experimental techniques used in this research, mainly X-ray Photoelectron Spectroscopy (XPS) and Temperature Programmed Reaction Spectroscopy (TPRS), and the procedures used for setting up each experiment. It also details the characterization techniques used to confirm that the Cu S₄Cs used in each experiment have the expected surface structure. Optical profilometry was used to determine the shape of the surface, Laue back diffraction was used to determine the crystal orientation and location of high symmetry directions, and scanning tunneling microscopy (STM) was used to obtain atomic scale images of the Cu(111) S₄C surface.
Chapter 4 describes the experiments performed for L- and D-tartaric acid (TA) decomposition on the Cu(111) S\(^4\)C. A quench TPRS experiment was developed with spatially resolved XPS to analyze the progression of the decomposition reaction on several points on the Cu(111) S\(^4\)C. For both L- and D-TA the reaction occurred faster on crystal planes with (100) step edges compared to (111) step edges. The data was used to calculate the change in coverage of tartaric acid versus time at each point measured. Several models were fit to the data and used to calculate rate constants at each point on the surface and a best fit model was determined. The initiation step was the rate limiting step in the overall reaction. Correlations were then developed between the rate constants and the density of different sites on the surface and the surface chirality.

Chapter 5 describes the experiments for L-aspartic acid-4-\(^{13}\)C and D-aspartic acid (AA) decomposition on Cu(100) S\(^4\)C and for L-AA on the Cu(111) S\(^4\)C. The same type of quench TPRS experiment with spatially resolved XPS was used to visualize the reaction progressing across the Cu(100) S\(^4\)C. The decomposition reaction was proven to be chiral as D-AA remained adsorbed longest on S surfaces and L-AA-4-\(^{13}\)C remained adsorbed longest on R surfaces. XPS results showed that an intermediate was present on each surface at different times and under the conditions used in the quench TPRS experiments, C\(_2\)H\(_3\)N remained on the surface after the reaction reached completion. The XPS data was converted into coverage vs. time for AA, the intermediate, and C\(_2\)H\(_3\)N on the surface and several models were fit to the data. A best fit model was determined.
and correlations were developed for changes in the site density and surface chirality with surface structure.

Chapter 6 describes a different project studying CH$_3$CH$_2$OH, CD$_3$CD$_2$OD, and CF$_3$CH$_2$OH decomposition on a ZnO(100) single crystal using TPRS. The products and product ratios were determined and used to develop a reaction mechanism for the decomposition reaction. The formation of two separate intermediate species was included in the mechanism: CH$_3$CH$_2$O- bonded to a surface O site to form CH$_3$CH=O and CH$_3$CH$_2$- bonded to a Zn site to form CH$_2$=CH$_2$. CD$_3$CD$_2$OD and CF$_3$CH$_2$OH decomposition were used to gain insight into the transition state of the intermediates on the surface during the decomposition reaction and look for any deuterium isotope effects and fluorine substituent effects on the reaction.
CHAPTER 2

2 Review of Experimental Studies of Curved Single Crystal Surfaces

2.1 Nomenclature for S^4C Review

Several researchers use high symmetry crystallographic directions to define points studied on each S^4C. Crystal planes located along high symmetry directions have unique structural properties that can change depending on the location from a low Miller index crystal plane. In many cases the high symmetry directions are defined differently, making direct comparisons between results difficult.

To make the research mentioned in this review directly comparable and easier to understand, a new nomenclature system is used in defining the high symmetry directions mentioned in each paper. This system condenses all studies on S^4Cs into a single stereographic triangle and instead of using the high symmetry directions, it uses locations relative to the low Miller index crystal planes to define the location of a crystal plane on each S^4C. Figure 9 shows the stereographic triangle with the nomenclature for the directions on the edges of the triangle drawn and Table 1 shows each high symmetry direction and what it is referred to throughout the rest of the paper.

This nomenclature collapses each low Miller index plane studied into their crystal plane family which is possible because planes in the same family have the same structural properties. E.g., the (100), (-100), (010), (0-10), (001), and (00-1) planes are all in the \{100\} family and have the same surface structure. Then, by
referencing each family as one of the three corners of the stereographic triangle, all studies can be analyzed using one stereographic triangle. This would not be possible in analyzing studies of surface chirality, but experiments on chiral crystal planes are not discussed in detail in this work.

Figure 9: Nomenclature for high symmetry directions mentioned throughout the entire S^4C review and the location on the stereographic triangle.
### Table 1: Names of high symmetry directions on the stereographic triangle

<table>
<thead>
<tr>
<th>Starting crystal plane</th>
<th>Perpendicular High Symmetry Direction:</th>
<th>Referred to in Paper as:</th>
</tr>
</thead>
<tbody>
<tr>
<td>{111}</td>
<td>[112], [211], or [121]</td>
<td>From {111} to {100}</td>
</tr>
<tr>
<td>{111}</td>
<td>[112], [211], or [121]</td>
<td>From {111} to {110}</td>
</tr>
<tr>
<td>{100}</td>
<td>[011], [011], [011], or [011]</td>
<td>From {100} to {111}</td>
</tr>
<tr>
<td>{100}</td>
<td>[010], [010], [001], or [011]</td>
<td>From {100} to {110}</td>
</tr>
<tr>
<td>{110}</td>
<td>[110] or [110]</td>
<td>From {110} to {100}</td>
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<tr>
<td>{110}</td>
<td>[001] or [001]</td>
<td>From {110} to {111}</td>
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### 2.2 Physical Phenomena

The physical properties of a surface depend on its crystal structure. Differences in the atomic structure of crystal planes can have an impact on their catalytic activity and underlying surface phenomena such as adsorption, reaction, and desorption. The structure dependent physical properties of surfaces reviewed in this section include: the work function, electronic structure, electroreflectance, surface energy, magnetic anisotropy, and surface reconstruction. $S^4$Cs have been used to study the dependence of several of these physical properties on surface orientation.

#### 2.2.1 Work Function and Electronic Structure

The work function is a commonly measured surface physical property that can influence surface chemistry. The work function is the energy required to remove an electron at the Fermi energy level in the bulk of a metal or semiconductor through the surface to the vacuum energy level at a point immediately above the surface (55). The Fermi energy is defined as the energy
level that has a 50% probability of being occupied by an electron (56). In a metal at 0 K, this corresponds to the highest occupied energy level of the valence band in the ground state (57). For a semiconductor, there is a gap (1-10 eV) between the valence band and conduction band and the Fermi energy is midway between the top of the valence band and bottom of the conduction band (56). The emission of an electron from a metal or semiconductor surface can be induced thermally or by exposure to photons with energies greater than the work function. The minimum energy of a photon required to induce this electron emission is equal to the work function. The work function has been measured for most pure metals and semiconductors in the periodic table. The atomic structure of the surface can have a large impact on the work function. Atomically rough crystal planes have lower work functions than atomically smooth crystal planes. Adsorbates and dopants can also influence the work function. On metal surfaces, the change in the work function induced by adsorption is dictated by the dipole moment created by the adsorbate-surface bond. If the adsorbate is electropositive (electronegative) with respect to the metal, the work function will be lower (higher) than that of the clean surface.

The earliest studies of structure dependent surface properties that are determined by the work function measured photoelectric effects, contact potential differences, and thermionic emission (58-64). Rose and Farnsworth used single crystals to measure the contact potential difference between the \{111\} and \{100\} faces of Cu and found that at 900 °C in vacuum the \{100\} plane has a lower work function than the \{111\} plane (60, 61). The first study using an S^4C to measure
the structure sensitivity of a property related to the work function was reported by Linder in 1927 (58). He measured the photoemission current from points around the perimeter of a cylindrical ZnS\textsuperscript{4}C with a [1\( \overline{2} \) 10] axis; the circumference of which traces a 1-D path along the perimeter of the stereographic triangle. Figure 10 shows a plot of the photoemission current versus the angle between the [0001] direction and the surface normal at each point on the circumference of the ZnS\textsuperscript{4}C. The plot clearly shows that the photoemission current varies periodically with position around the circumference of the cylindrical ZnS\textsuperscript{4}C. The photoemission current reached a maximum near the \{0001\} plane and a minimum near the \{1120\} plane. The maximum photoemission current near the \{0001\} plane implies that the work function has a minimum at this orientation.
In the 1930’s, several researchers studied the work function of W S\textsuperscript{4}Cs by thermionic emission at temperatures in the range 1200-2100 K (62, 63).

Thermionic emission of electrons is detected when the temperature of a surface is sufficiently high that a measurable fraction of the electrons have energies greater than the work function and escape into the vacuum. Johnson \emph{et al.} measured thermionic emission from W S\textsuperscript{4}C wires oriented along the [110] axis to study the
orientation dependence of the work function of W with and without adsorbed Cs and K (62). Both Cs and K adsorbed on W lowered the work function relative to that of the clean surface at all surface orientations exposed around the circumference of the W S^4C wire. The work function of W depends on the surface orientation and Cs and K coverage. Martin et al. also used thermionic emission to study the orientation dependence of the work function of W, but used a spherical S^4C (63). The current emitted from W at 2100 K was measured on a fluorescent screen. The work functions of the clean W crystal planes increased in the following order: \{100\} < \{111\} < \{211\} < \{110\}. Martin et al. also observed that the adsorption of Cs, K, and Ba lowered the work function of W but reversed its dependence on surface orientation.

Based on these studies, Smoluchowski published a theoretical explanation for the anisotropy of the work functions of metals (64). In this published theory, the work function of a surface was attributed to two effects: electron smoothing parallel to the surface and electron spreading perpendicular to the surface. Electron spreading is defined as the extension of electron density into the bulk of the metal creating a charged double layer and increasing the work function. Electron smoothing is the forming of negatively charged valleys between atoms and positively charged hills on top of atoms across a surface. This smoothing creates a new equilibrium electron density that minimizes the energy of the surface. The smoothing effect is attributed to change in the work function of metals with surface structure. Changes in the surface roughness and density of exposed surface atoms cause changes in the electron density of a surface.
Smoluchowski derived formulas for the potential difference between the surface and the bulk for the \{100\}, \{110\}, \{111\}, and \{211\} crystal planes of ideal simple cubic and body centered cubic systems. An increase in the potential difference of a surface corresponds to an increase in the work function. The potential difference, \(dV\), was calculated using Equation 2.1 where \(x\) is the distance perpendicular to the surface, \(e\) is the elementary charge of an electron, and \(\sigma\) is the charge density per volume. This potential difference was calculated based on \(\sigma(x)\) perpendicular to the surface shown in Equation 2.2 where \(a\) is the width of the charge double layer, \(n\) is the number of electrons in a unit cell, \(d\) is the lattice constant, and \(p\) and \(q\) values change depending on whether the charge density profile is linear, quadratic, or a truncated pyramid. For a linear profile, \(p=0\) and \(q=2\), for a truncated pyramid, \(p=q=4\), and for a quadratic profile, \(p=2q-4\) and \(q\) depends on the intercept for \(\sigma(x)=0\). The charge density is assumed to depend only on the direction perpendicular to the surface. Assuming that the charge double layer has a width \(a\), the potential difference can be calculated. The values for \(a\) were calculated using Equation 2.3, where \(h\), \(k\), and \(l\) are the Miller indices of the crystal plane.

\[
V = -\frac{2\pi e x^2}{3} \sigma(x) \tag{2.1}
\]

\[
\sigma(x) = \frac{ne}{2a^2} (px^2 - qa|x| + a^2) \tag{2.2}
\]

\[
a = \frac{2d_{hkl}}{\sqrt{h^2k^2 + k^2l^2 + l^2h^2}} \tag{2.3}
\]
Smoluchowski calculated the surface potential differences of the BCC crystal planes mentioned previously and found that their values have the order \( \{110\} > \{211\} > \{100\} > \{111\} \). This trend is the same trend in the work function observed experimentally (64).

In the 1970’s and 1980’s, several researchers continued to measure the surface structure dependence of the work function and other related electronic properties using \( S^4Cs \) and improved methods. One property related to the work function is the electroreflectance, defined as the change in the reflectivity of 300-1000 nm light due to changes in the surface electronic structure of the electrode (65). In a typical electroreflectance experiment, a beam of light is exposed to an electrode in an electrochemical cell of a 0.1 M solution of \( Na_2SO_4 \) with a potential applied to the electrode. The reflected light is measured at a 62° angle from the incident beam by a spectrophotometer. The intensity of the reflected light relative to the incident light is measured and is proportional to the electrical conductivity on the electrode surface (66). Kotz et al. irradiated the surface of a cylindrical Cu \( S^4C \) oriented along the [ \( \bar{1} \) 10] axis with polarized and un-polarized light and measured the change in conductivity with orientation of the crystal surface at constant light energies (1.8 eV, 2.18 eV, and 3.8 eV) and electrode potential (-300 mV SCE). The largest reflectance change for both polarized and un-polarized light came from atomically rough crystal planes, such as \( \{311\} \) and \( \{110\} \), and the change increased with step density as measurement positions moved away from the close packed \( \{111\} \) and \( \{100\} \) planes and towards the atomically rough crystal planes (65, 67). The variation of reflectance with surface orientation
showed a similar trend as the work function and was attributed by Kotz et al. to enhanced surface polarizability on atomically rough surface orientations. In another type of experiment, Armitage et al. and Gardiner et al. separately looked at the change in intensity of X-ray induced backscattered electrons with surface orientation (68, 69). Both researchers found that for cylindrical W and Cu S\textsuperscript{4}Cs oriented along the [\bar{1}10] axis, the backscattered electron signal varied with surface orientation with maxima occurring at the three low Miller index crystal planes. Gardiner also measured the dependence of the work function on surface orientation of the cylindrical W S\textsuperscript{4}C by measuring the change in voltage with surface orientation induced by an electron beam (14). Figure 11 shows a plot of work function versus surface orientation of the cylindrical W S\textsuperscript{4}C. Consistent with the reports of Martin and Johnson in the 1930’s, the work function maximum was observed on the close packed (for BCC) \{110\} planes, with maxima at \{100\} and \{211\} planes and minima at the \{111\} and \{511\} planes (8). Although there is some disagreement between Gardiner’s results and earlier reports, the spatial resolution of this technique is 70 µm which is more accurate than previous measurements of work function from thermionic emission (8).
Electronic properties such as electron affinity and valence band structure can also vary with surface orientation. Ranke used angle resolved photoemission spectroscopy (ARPES) and Ultraviolet Photoelectron Spectroscopy (UPS) to characterize the electronic structure of cylindrical $S^4C$ of semiconductor materials (20, 70-72). He measured the orientation dependence of the electron affinity of a cylindrical GaAs $S^4C$ oriented along the $[\bar{1}10]$ axis and the work function and valence band structure of a cylindrical Ge $S^4C$ oriented along the $[1\bar{1}0]$ axis and a spherical Si $S^4C$ centered at the $\{100\}$ plane. The electron affinity of a semiconductor can be used to calculate the work function through Equation 2.4 where $\phi$ is the work function, $\chi$ is the electron affinity, $E_c$ is the

![Figure 11](image)

Figure 11: The measured work function versus orientation for a $[\bar{1}10]$ cylindrical W $S^4C$, corrected for the differences in the form of the I-V curves as described in the text. The work function maximum was observed on the close packed (for BCC) $\{110\}$ planes, with maxima at $\{100\}$ and $\{211\}$ planes and minima at the $\{111\}$ and $\{511\}$ planes (8).
energy of the conduction band edge, and $E_v$ is the energy of the valence band edge.

$$\phi = \chi + E_c - E_v$$  \hspace{1cm} (2.4)

For GaAs, the work function decreased with increasing step density (73). The work function of Ge had the same variation with step density as GaAs, but the orientation dependence of Ge was weaker (0.1 eV) than that of GaAs (0.6 eV). According to Ranke, the weak dependence of the work function of Ge on surface orientation is due to reduced charge smoothing effects (20). Ranke found that the location of the valence band edge energy of Ge was orientation dependent. Figure 12 shows a plot of the orientation dependence of the valence band edge energy on a cylindrical Ge $S^4$C oriented along the [011] axis. The valence band edge energy of the {110} and {511} planes were the closest to the Fermi energy and those of the {111} and {100} planes were furthest from the Fermi energy. The variations in the valence band edge energy were attributed to valence band bending induced by steps, causing the valence band edge energy to shift towards the Fermi energy. Ranke also used ARPES to study the orientation dependence of the valence band edge energy of a spherical Si $S^4$C centered at the {100} plane and found that the presence of step edges also shifts the position of valence band edge energy of the surface closer to the Fermi energy. Although the orientation dependence of the work function of single component semiconductors is weaker than for metal surfaces, the valence band structure is still significantly influenced by the surface orientation (71). Ortega et al. performed similar experiments using ARPES to look at the change in valence band energy center with surface
orientation of cylindrical Cu and Ag S\textsuperscript{4}C sections spanning ±15° from the \{111\} plane along the edge of the stereographic triangle. Similar to Ge and Si, the valence band center moved closer to the Fermi energy as the step density increased (74).

![Figure 12: Orientation dependence of the valence band edge energy at the surface of Ge\{110\} cylindrical S\textsuperscript{4}C. The different dots correspond to different experiments. The valence band edge energy of the \{110\} and \{511\} planes were the closest to the Fermi energy and those of the \{111\} and \{100\} planes were furthest from the Fermi energy (20).](image)

Studies of the electronic properties using S\textsuperscript{4}Cs clearly show that the surface orientation greatly alters the work function and electronic structure of the surface. For FCC and BCC metals, the work function is lower on surfaces that have a higher density of step edges or are more atomically rough than close packed crystal planes. The presence of step edges shifts the valence band edge energy closer to the Fermi energy for semiconductors and shifts the valence band
center closer to the Fermi energy for BCC metals. Many researchers postulate that as the valence band moves closer to the Fermi energy, the bond strength of adsorbates to the surface increases. The trend of increasing binding energy of adsorbates with increasing proximity of the valence band to the Fermi energy has been studied by many authors using density functional theory (DFT) to calculate the energy of the d-band center of transition metals (75-80). The binding energy of adsorbed CO, O, and H to multiple metals and metal alloys has been calculated and for each adsorbate the binding energy increases as the d-band energy moves closer to the Fermi energy. Figure 13 shows the theoretical dissociative adsorption energy for H₂ versus d-band center calculated using DFT for several metals and metal alloys. The overall linear trend shows that the adsorption energy becomes more negative or dissociative adsorption becomes more energetically favorable as the d-band center of the metal moves closer to the Fermi energy (79).
Figure 13: Dissociative adsorption of H$_2$ versus d-band center for several metals and metal alloys calculated using DFT. The overall linear trend shows that the adsorption energy becomes more negative or dissociative adsorption becomes more energetically favorable as the d-band center of the metal moves closer to the Fermi energy (79).

2.2.2 Surface Reconstruction

Surface reconstruction is the transformation of a crystal surface with one crystallographic orientation into smaller domains of one or more other orientations (21). The thermodynamic driving force for reconstruction is a net reduction in the surface free energy accompanied by a net increase in surface area. Faceting can be induced by thermal or chemical treatments. The influence of surface orientation on reconstruction has been studied using S$^4$Cs by several researchers. Gwathmey was one of the first to study this phenomenon by annealing spherical Cu S$^4$Cs at 1248 K in air and using optical microscopy and X-
ray diffraction to determine the orientations of crystal facets on the surface (81). He found that vicinal surfaces to the {111} and {100} crystal planes faceted into {111} and {100} microfacets and the number step edges around these poles decreased. Using LEED, Menzel studied faceting of spherical Au and Cu S$^4$Cs prepared in vacuum from solidification of droplets of melted metal on a SiO$_2$ substrate (82-85). After solidification, Au and Cu S$^4$Cs exposed a wide variety of crystal planes with flat areas forming around low Miller index crystal planes such as {111}, {110}, and {100}. LEED patterns were also observed for high Miller index planes such as {221}, {211}, and {311} on Cu and {551} and {722} on Au.

Olshanetsky et al. used LEED to characterize the surface orientations of many flat single crystals of Ge and Si (11, 86-89). Si and Ge have a diamond crystal structure consisting of two interpenetrating FCC lattices. For both Si and Ge, the step height on planes vicinal to the low Miller index planes depended on the step direction. Figure 14a shows the LEED pattern from a Si surface oriented 8° from {111} toward the {110} plane and Figure 14b shows the LEED pattern from a Si surface oriented 7° from {100} towards the {110} plane (11). Both LEED patterns show spot splitting of the {100} and {111} reciprocal lattice caused by the presence of step edges. This spot splitting was used to determine the step height and the terrace widths on each crystal plane. The Si surface orientated 7° from {100} towards the {110} plane had steps one {100} plane spacing high, while the Si surface oriented 8° from {111} toward the {110} plane had steps two {100} plane spacings high. Olshanetsky also observed that {110} planes of Si and Ge and those vicinal to {110} were unstable and facetted; Ge
planes vicinal to \{110\} reconstructed into \{17\ 15\ 1\} and \{10\ 9\ 2\} facets while Si planes vicinal to \{110\} faceted into \{75\ 1\} facets. LEED patterns for select crystal planes were obtained along the edges of the stereographic triangle. For crystal planes along the edge of the stereographic triangle from \{100\} to \{111\}, only \{511\}, \{711\}, \{311\}, and \{533\} planes were stable and gave distinct LEED patterns. Ranke also used LEED to analyze the reconstruction of the Si\{100\} surface and planes vicinal to Si\{100\} \((25,\ 90-92)\). Spot splitting and spot intensities of LEED patterns were used to determine the step structures. Rather than using single crystals, Ranke used a spherical Si\{100\} \(S^4C\). In previous studies, researchers found that the surface of Si near the \{100\} at room temperature formed two different types of terraces, A type and B type. Figure 15a shows a ball model of the reconstructed Si\{100\} terrace and the top of Figure 15b shows the difference between an A-type and B-type terrace. The A-type terrace surface consists of rows of Si atom dimers perpendicular to the step edge while the B type terrace surface has rows of Si dimers oriented parallel to the step edge. In papers discussing Si surface reconstruction, A-type terraces are called \((2\times 1)\) terraces and B-type terraces are called \((1\times 2)\) terraces \((25,\ 26)\). Ranke found that surfaces \(< 2^\circ\) from \{100\} towards the \{110\} plane contain A and B-type terraces separated by monatomic steps (shown in top of Figure 15b). Surfaces oriented 6-11\(^\circ\) from \{100\} towards the \{110\} plane have B-type terraces separated by diatomic height steps (shown in bottom of Figure 15b). A transition region from single to double height steps exists at orientations 2-6\(^\circ\) from \{100\} \((93,\ 94)\). At >11\(^\circ\) from Si\{100\} in all directions, the surfaces reconstructed into \{511\} and
{711} facets. The observations of Olshanetsky and Ranke are similar; diatomic height steps at orientations >6° from Si{100} towards the {110} plane and stable {511} and {711} facets >11° from {100} were observed in each study. This is one of numerous examples of similar observations being obtained from studies using multiple single crystal surfaces and studies using S\textsuperscript{4}Cs.

Figure 14: LEED images of different crystal planes of Si. a) LEED image using 45 eV beam energy of Si crystal plane 8° from {111} plane towards the {110} plane. b) LEED image using 48 eV beam energy of crystal plane 7° vicinal to {100} plane towards the {110} plane (11). Spot splitting shows the presence of step edges on each surface.
STM is a better tool for studying surface reconstruction than LEED and is ideally suited for use with S\textsuperscript{4}Cs. Hanbucken et al. studied surface reconstruction of Si\{100\} and Si\{111\} vicinal surfaces using STM and S\textsuperscript{4}Cs prepared by making concave dimples in single crystals (90, 91). For surfaces vicinal to Si\{111\}, the surface morphology depends on the azimuthal angle and distance from the \{111\} plane. From the \{111\} towards the \{100\} plane, the surfaces reconstruct by step bunching to form alternating monatomic and tri-atomic step edges with minimal kinks in the step edge. From the \{111\} plane towards the \{110\} plane, step bunching occurs to form facets with a high kink density creating a disordered surface. As distance from the \{111\} plane increased to 9-10°, the surface formed \{432\} facets oriented along high symmetry directions. For surfaces vicinal to Si\{100\}, the type of surface reconstruction varied with distance from the \{100\}

![Figure 15: a) Example of (2x1) reconstruction of Si(001) surface. Surface Si atoms form a covalent bond with an adjacent surface atom and form dimers on the surface. b) Examples of “A-type” and “B-type” terraces formed on a Si(001) vicinal surface with step edges present. The “A-type” terrace or (2x1) reconstructed terrace forms dimers perpendicular to the step edge and the “B-type” terrace or (1x2) reconstructed terrace forms dimers parallel to the step edge. Bottom image is characteristic of crystal planes located 6-11° from Si\{001\} with B-type terraces and double height steps (25, 26).](image)
plane. For surfaces <1° from {100}, monatomic step edges were present separating {100} A-type and B-type terraces. For surfaces 1-6° from {100}, both monatomic and diatomic steps were observed. At 6-9° from {100}, diatomic step edges were present separated by B-type terraces. At angles >9° from {100}, {911} and {711} facets were observed (92). The results from the dimpled Si{100} surface show surface reconstructions similar to those observed by Ranke on the spherical Si{100} S4C.

Surface reconstruction is influenced by both temperature and adsorbates. Field Ion Microscopy, FIM, has been used by several researchers to study surface reconstruction caused by changes in temperature and adsorption. In an FIM experiment, a spherical tip of a crystalline material is placed in UHV at cryogenic temperatures (20-80 K) in the presence of a noble gas such as Ne or He. At these temperatures, noble gases physisorb to the surface. A positive voltage is applied to the tip causing the ionization and emission of the adsorbed gas onto a fluorescent screen. The emitted ionized gas produces an atomic scale image of the surface on the fluorescent screen. Moore laid the groundwork for using FIM as a tool for calculating surface energy. By determining the number and location of atoms present on a spherical surface with a coordination number \( \leq 6 \), he could model FIM images by adjusting the radius of curvature of the sphere, crystal structure, and the distance between the kink atoms and a spherical fit (95).

Using FIM, STM, and Monte Carlo simulations, Szczechowicz et al. characterized surface reconstruction on spherical W{111} S4C tips and the effect of adsorbates such as O2 and Pd on surface reconstruction (96, 97). The presence
of Pd and O$_2$ caused faceting of high surface energy planes vicinal to \{111\} into \{211\} and \{110\} microfacets. When the tip was annealed, pyramids formed with \{211\} sides. As the temperature increased, the size of the \{211\} pyramids increased. Bryl et. al performed similar experiments on spherical Ir\{100\} S\£C tips to analyze the effect of annealing at temperatures in the range 500-1100 K and O$_2$ adsorption on surface reconstruction of Ir (98). After several cycles of cleaning by Ne$^+$ ion sputtering at 100-120 K and field evaporation, the Ir tips contained the \{100\}, \{110\}, \{111\}, and vicinal crystal planes on the same surface. After annealing the surface at 850 K in vacuum, kink atoms were no longer visible, only terraces and step edges. As the annealing temperature increased to 1100 K, the surface reconstructed into microfacets of \{100\} and \{111\} planes separated by regions of step edges more than one atomic height. After exposure of the clean surface to 1-6 L of O$_2$ and annealing at the same temperatures, the surface faceting drastically changed. The annealing temperature at which surface faceting was observed decreased from 850 K to 650-700 K. The presence of O on the surface caused the formation of \{110\} and \{311\} facets along with \{100\} and \{111\} planes on the surface at annealing temperatures above 700 K.

Using LEED, Ranke studied the effect of As, Sb, and Bi on surface reconstruction using a Si\{100\} spherical S\£C (99). After deposition of ~1 ML of As and annealing to 1000 K, the average step height changed from one or two atomic layers to four atomic layers on all surfaces vicinal to Si\{100\}. The addition of Bi and Sb caused the formation of monatomic steps on all planes.
within 10° of the \{100\} surface. The different surface reconstructions were attributed to differences in the surface strain due to the lattice mismatches as the lattice constants of As, Bi, and Sb >> Si.

Ortega et al. used room temperature STM imaging to study the surface reconstruction of Cu\{111\}, Ag\{111\}, and Au\{111\} single crystals polished into cylindrical S\(^4\)Cs centered around the \{110\} axis \((74),(100)\). The surface of each cylinder spanned 15° from the \{111\} plane towards the \{100\} plane and towards the \{110\} plane along the edge of the stereographic triangle. From 0-4° from Au\{111\}, the step density increased with distance from \{111\}. The planes vicinal to Au\{111\} and oriented 4-14° away from the \{111\} plane faceted into \{111\} terraces with widths of either 31 Å or 13 Å separated by monatomic step edges. Surfaces between the \{111\} plane and the \{110\} plane contained \{110\} steps while surfaces between \{111\} and the \{100\} plane contained \{100\} steps. The step orientation did not have an effect on the distribution of terrace widths \((100)\).

Cu and Ag did not facet at room temperature after polishing and contained surfaces with increasing step density and decreasing \{111\} terrace width as the distance from the \{111\} plane increased. The average terrace widths were consistent with the ideal surface structure.

At elevated temperatures, high Miller index crystal planes of Cu can undergo thermal roughening that changes the surface structure from the ideal surface model. Sykes et al. used STM and Monte Carlo simulation to determine the effect of annealing on a Cu\{643\} surface \((10)\). Cu\{643\} is a surface orientation with step edges, kinks, and terraces present and can be referred to as
chiral with an R or an S orientation. After annealing a Cu\{643\} single crystal to 1000 K, it was cooled down to 78 K and STM images were obtained. The number of kinks on the surface was smaller than for the ideal surface as thermal roughening caused kinks to coalesce and form longer step edges. Monte Carlo simulation was used to predict the effect of thermal roughening on the Cu\{643\} surface. The top of Figure 16 shows a ball model of the ideal Cu\{643\} surface (a) and the thermally reconstructed Cu\{643\} surface (b) and the bottom of Figure 16 shows the STM images of Cu\{643\} after annealing to 1000 K. The behavior of the simulated surface matches the STM images showing an increase in the step edge width and a decrease in the number of kinks. Although thermal roughening decreased the number of kinks on the surface, the surface chirality was maintained and steps, kinks, and terrace sites were still present on the surface.

De Alwis et al. created a set of six spherical Cu S^4Cs exposing surface orientations vicinal to the \{111\}, \{110\}, \{100\}, \{861\}, \{432\} and \{821\} planes (12). Collectively, these six S^4Cs expose a set of surfaces that spans the entire stereographic triangle. The room temperature surface structure of the Cu\{111\}\(\pm 11^\circ\) S^4C was analyzed using STM. The spherical shape of these S^4Cs was mapped using optical profilometry and the crystal structure was confirmed using Laue back diffraction. Figure 17 shows STM images of several different crystal planes on the Cu(111)\(\pm 11^\circ\) S^4C. From \{111\} towards the \{100\} plane and from \{111\} towards the \{110\} plane on the surface, the step density increases with distance from the \{111\} plane. Steps with kinks are present in STM images of surfaces oriented at angles away from high symmetry directions. Consistent
with the observations of Ortega (74, 100), the Cu surfaces did not facet into low Miller index crystal planes. The local structure of the crystal surfaces on the Cu(111)±11° S⁴C are representative of the ideal crystal structures and the general trend in step density on the S⁴C matches that predicted from the ideal surface model (42).

Figure 16: Top - Schematic of ideal and thermally roughened Cu\{643\} surface from Monte Carlo Simulation. Bottom STM images of Cu\{643\} surface after annealing to 1000K. Images taken at 78 K. The surface undergoes thermal roughening decreasing the number of kinks on the surface but the chirality of the surface is still maintained (10).
Figure 17: STM images of the Cu\{111\}±11°S\(^4\)C. a) Image of the \{111\} plane on the S\(^4\)C. b) 1×1 nm\(^2\) image of the \{111\} pole revealing the hexagonal close packed array of Cu atoms. c) and d) STM images taken at two points along the direction from \{111\} towards the \{100\} plane at 1 mm and 2 mm from the \{111\} pole. These reveal the increasing density of monatomic steps on the surface as the distance from the (111) pole increases. e) and f) STM images at points that are 1 mm from the \{111\} pole but angles that are ±30° from the high symmetry direction. These reveal monatomic steps that are rotated in different directions with respect to the high symmetry direction (12).
2.2.3 Magnetic Anisotropy

Magnetic properties can also vary with surface orientation. The magnetic anisotropy is defined as the directional dependence of a material’s magnetic properties (37). A magnetically anisotropic material will align its magnetic moment along a specific crystallographic direction. On a surface containing step edges, the magnetic moment can align perpendicular or parallel to the direction of the step edge. The change in magnetic anisotropy with surface structure was studied by Qiu et al. using cylindrical S^4Cs containing {100} and vicinal planes to determine the effect of step edges on magnetic anisotropy after deposition of ferromagnetic materials on anti-ferromagnetic substrates. To study magnetic anisotropy, hysteresis loops measuring changes in surface magnetization with an applied magnetic field were performed using a Surface Magneto Optical Kerr Effect (SMOKE) microscope. This microscope measures the change in polarized light reflected from a magnetized surface. The light polarization changes with the intensity of the magnetic field and this change is converted into a light intensity to create a plot of intensity versus applied magnetic field. To measure a magnetic hysteresis loop, a magnetic field along a fixed direction is applied to a surface and increased in strength until the surface becomes magnetized along the field direction. Then the magnetic field direction is reversed and the field strength increased. Once a ferromagnetic material is magnetized in one direction, it remains magnetized along that direction until subjected to a field of higher strength aligned in the opposite direction. The cycle of applying alternating
magnetic fields to a surface and measuring the changes in surface magnetization using a SMOKE microscope is a hysteresis loop (example shown in Figure 18a.)

Qiu et al. characterized several systems using cylindrical S\textsuperscript{4}C sections containing the \{100\} plane and vicinal surfaces including Fe on Ag\{100\} (23, 101), Fe on W\{100\} (24, 102), Fe on Cr\{100\} (103-105), Co on Cu\{100\} (23, 24, 106-110), Fe on Pd \{100\} (23, 24, 102, 111), and Ni on Cu\{100\} (23, 112-114).

Each substrate contained two surface regions; one region contained the flat \{100\} plane while the other region was curved to expose surfaces vicinal to the \{100\} plane but oriented toward the \{110\} plane from 0° to 10°. A layer of ferromagnetic material (Fe, Co, or Ni) between 1-50 ML was deposited on each substrate and magnetic hysteresis loops were generated by applying a magnetic field both parallel and perpendicular to the step edges at various temperatures below the Curie temperature, the temperature where a metal loses its magnetism (37). Figure 18a shows an example of a typical hysteresis loop generated when applying a magnetic field perpendicular and parallel to the step edges of Fe deposited on an Ag substrate 6° from the \{100\} plane (23). The degree of magnetic anisotropy is determined by the magnitude of magnetic field splitting, \(H_s\), and the direction of the easy axis, or direction of the magnetization vector, relative to the direction of the applied magnetic field. If \(H_s\) occurs when the magnetic field is applied parallel (perpendicular) to the step edge, then the easy axis is perpendicular (parallel) to the step edge. In Figure 18a, the \(H_s\) is observed when the magnetic field is applied perpendicular to the step edge, therefore the easy axis is parallel to the step edge.
Figure 18b shows a hysteresis loop of a magnetic field applied perpendicular to the step edge for Fe deposited on Ag\{100\} at various vicinal angles from the \{100\} plane, $\alpha$. As displayed in Figure 18b, the value of $H_s$ increased with increasing $\alpha$ (23). Depending on the system studied, this trend was either linear ($H_s \sim \alpha$) or quadratic ($H_s \sim \alpha^2$) where $\alpha$ is the angle of the surface normal away from the \{100\} plane. Figure 19a and b show plots of $H_s$ versus vicinal angle, $\alpha$, for two of the systems studied. For Fe deposited on a cylindrical W\{100\} S\textsuperscript{4}C, $H_s$ increases quadratically with vicinal angle while for Co on a cylindrical Cu\{100\} S\textsuperscript{4}C, the trend is linear. In both cases, the increase in $H_s$ with $\alpha$ was attributed to an increase in the step edge density with vicinal angle. The overall experimental results indicated that the linear trend was seen for FCC ferromagnetic films on FCC substrates while the quadratic trend was seen for BCC ferromagnetic films on BCC substrates.
Figure 19: Plots of $H_s$ versus vicinal angle, $\alpha$, from the $\{100\}$ plane for a) Fe on W and b) Co on Cu. For BCC metals deposited on a BCC substrate, the trend is a quadratic increase with $\alpha$ while for an FCC metal on an FCC substrate, the trend is a linear increase with $\alpha$. The step density also increases with increasing vicinal angle (24).
A model called the Neel pair bonding model was applied to the experimental data to explain the results. In this model, the magnetic anisotropy is dependent on the nearest neighbor bonds in a crystal and a uniaxial anisotropy is created when the lattice symmetry is broken at the step edge. The energy of this magnetic anisotropy is derived from the spin-orbit interaction energy of a crystal. For a simple cubic system, \( E = K(u_x^2u_y^2 + u_y^2u_z^2 + u_z^2u_x^2) \) where \( u_i \) is the unit vector of magnetization of direction \( i \) and \( K \) is the anisotropy constant based on the band structure of the metal. This equation is different for different crystal structures due to the changes in the orientation of nearest neighbor atoms and orientation of the step edge. For a BCC crystal structure with \{110\} steps, the anisotropy energy for small angles away from \{100\} becomes

\[
E = -K(cau_y u_z - \alpha^2 u_y^2 + \alpha^2 u_z^2)
\]

where \( \alpha \) is the angle away from the \{100\} plane. For an FCC crystal structure with \{110\} steps, the anisotropy energy for small angles away from \{100\} becomes

\[
E = -K(2cu_y^2 + 3\alpha u_z^2 + 2\sqrt{2}\alpha u_z u_y)
\]

For the in-plane step induced anisotropy \( u_z = 0 \) and the equations simplify to

\[
E = K\alpha^2u_y^2
\]

for the BCC case and

\[
E = -2Kcu_y^2
\]

for the FCC case. This gives a theoretical explanation for why BCC metals would have a linear trend of magnetic anisotropy with \( \alpha \) and FCC metals would have a quadratic trend with \( \alpha \).

Magnetic anisotropy depends not only on the step density, but also on the thickness of ferromagnetic material. Qiu et al. found that for films of Fe deposited on Pd, the presence of steps increased the Curie temperature of Fe on the order of
10-100 K depending on the film thickness (111). The film thickness where the direction of the magnetic anisotropy changes is called the spin reorientation transition (SRT). Qiu et al. was able to create a phase diagram for Fe on Cr{100} depicting changes in the in the direction of the magnetic anisotropy (easy axis) with step density and film thickness to determine the boundaries of the SRT (105). The effect of step orientation on magnetic anisotropy was also studied by Qiu et al. by measuring changes in the easy axis direction and magnetic coercivity (the resistance of a magnetic material to becoming demagnetized). Two separate cylindrical S^4Cs were used for these experiments; one exposed {111} steps, while the other exposed {100} steps. For NiO deposited on a cylindrical Ag{001} S^4C, the magnetic anisotropy on the surface is uniaxial: on {100} steps is parallel to the step edges while for {111} steps, the magnetic anisotropy is perpendicular to the step edge (115). This means that the step orientation as well as the film thickness can dictate the direction of magnetization. For FeMn films deposited on a cylindrical Cu{100} S^4C, the magnetic coercivity increased with step density for {100} steps but decreased with step density for {111} steps (110).

Cheng et al. extended Qiu’s work by measuring the magnetic anisotropy of Fe deposited on a cylindrical Pt {111} S^4C and vicinal planes. Pt is unique because an induced ferromagnetism is formed in Pt when in contact with ferromagnetic materials. In these experiments, Fe was coated on a cylindrical Pt{111}±15° S^4C spanning a 1-D path on the edge of the stereographic triangle. The presence of steps in the Pt substrate increased the Curie temperature of Fe on the order of 100 K/ML. Also, the magnetic anisotropy increased with vicinal
angle by $\alpha^4$ which is two powers higher than other substrates studied. This effect was attributed to anisotropy induced by step edges and the added magnetic polarization of Pt at the step edges (116, 117). The work by Cheng and Qiu showed that many magnetic properties can change with surface orientation.

### 2.2.4 Surface Energy

The variation of surface energy with surface orientation has been studied for over one hundred years. Wulff in 1901 was one of the first researchers to study surface energy anisotropy theoretically. The well-known graph that relates surface energy to crystal orientation is called a polar Wulff plot. Figure 20 shows an example of a polar Wulff plot where the dark line represents the surface free energy, $\gamma$. This graph is constructed based on the principle that for each crystal plane in the plot of surface energy versus crystal structure, $\gamma_1/h_1 = \gamma_2/h_2 = \ldots = \gamma_n/h_n$, where $h$ is the distance from the origin to the location of the crystal plane. As displayed in Figure 20 for lines OB$_1$, OB$_2$, and OA, $\gamma_A > \gamma_{B1}$, $\gamma_{B2}$ (13). A typical plot has cusps in surface energy located at the minimum energy crystal planes. Herring in 1953 further developed Wulff’s theory by showing that the crystal planes present on a sample are determined by the curvature of the crystal and that high surface energy crystal planes will facet into two or more low energy crystal planes depending on the crystal shape, temperature, and adsorbates on the surface (118). The broken bond model for determining the change in surface energy with surface orientation was the next development in the theory of surface energy anisotropy. This model calculates the energy of any surface orientation based on the atomic bonds broken to create the surface. Equations 2.5 and 2.6 show the
typical construction for calculating the surface energy using a summation of the energy of each bond broken to create a surface. For both equations, \( \gamma \) is the surface energy, and \( \vec{u}_j \) is the interatomic vector of the broken bond. In Equation 2.5, the surface energy is calculated by determining \( n(u_j) \), the number of bonds broken to create a surface with the original vector \( u_j \), calculating the energy of breaking that bond \( E_i \), and summing over all of the different types of bonds broken. In Equation 2.6, \( \Phi_i \) is the interaction potential energy of bond \( j \) between two atoms, \( \vec{h} \) is the vector of the normal of each crystal plane, and \( \Omega \) is the volume of the crystal per atom. Equation 2.6 can be derived from the general form of Equation 2.5 by assuming that the energy of breaking a bond, \( E_j = -\frac{1}{2} \Phi(u_j) \) which is derived assuming that the interaction potential between two atoms an infinite distance apart is zero (16, 119).

\[
\gamma(\vec{h}) = \sum_i E_i n(\vec{u}_i) \quad (2.5)
\]

\[
\gamma(\vec{h}) = \frac{1}{2|\vec{h}| \Omega} \sum_i \Phi_i (\vec{h} \cdot \sum_j \vec{u}_j) \quad (2.6)
\]
Differences between broken bond models come from changes in the equation used to calculate the interaction potential energy, $\Phi_i$. Three of these potential equations most commonly used are the Morse potential, Mie potential, and pairwise bonding model. Equation 2.7 is the interatomic potential equation for the Morse potential model. This potential is a function of $r$, the distance between two atoms in cm and parameters $\Phi_o$, the minimum potential, $r_o$, the bond length at minimum potential, and $a$, the dimensionless Morse constant that is element dependent. The Morse constant can be written in terms of the force.

Figure 20: Polar Wulff plot of surface free energy versus orientation of a crystal. Planes $B_1$ and $B_2$ correspond to cusps located at minima in surface free energy. Plane A will facet into planes $B_1$ and $B_2$ at high enough temperatures or if present on a sample with a small enough radius of curvature (13).
constant of a bond by performing a Taylor series expansion of Equation 2.7 around $r = r_0$ out to the second derivative. Assuming for a harmonic oscillator

$$\Phi''(r_e) = k_e,$$

the Morse constant can be represented by

$$a = \sqrt{\frac{k_e}{2\phi_o}}$$

where $k_e$ is the force constant of the bond at the minimum energy potential well. Equation 2.8 shows the Mie model for calculating the interaction potential energy. This energy is also a function of $r$, and includes $\Phi_o$ and $r_o$. The Mie model has adjustable parameters $m$ and $n$, where $m$ is related to the repulsive interaction between two atoms and $n$ is related to the attractive interaction. This functional form can be used to calculate the Lennard-Jones potential by setting $m = 12$ and $n = 6$ (16).

$$\phi(r) = \phi_o \left\{ \left[ 1 - \exp \left( a \left( 1 - \frac{r}{r_o} \right) \right) \right]^2 - 1 \right\}$$  \hspace{1cm} (2.7)

$$\phi(r) = \frac{\phi_o \left\{ n \left( \frac{r}{r_o} \right)^m - m \left( \frac{r}{r_o} \right)^n \right\}}{(m-n)}$$  \hspace{1cm} (2.8)

The pairwise bonding model uses a slightly different approach. This model assumes that the interaction potential of second and third nearest neighbors should be calculated and is some fraction of the nearest neighbor interaction energy such that $\Phi_i = \rho_i \Phi_i$. It also calculates the surface energy of each orientation, $\gamma_{hkl}$, by counting the number of bonds broken based on the orientation of the bond broken with respect to high Miller index directions of either <100>, <110>, <111>, or <211>. Equations 2.9-2.11 describe the pairwise bonding model calculations. In Equation 2.9, $\Phi$ and $\theta$ are the angles to locate $(hkl)$, $a$ is the lattice constant, $\Omega$ is the atomic volume, $\Phi_i$ is the interaction potential of
nearest neighbor atoms, and constants A, B, and C are calculated using Equation 2.10. The values of \((U_1, V_1, W_1)\) in Equation 2.10 are the location of the broken bond, \((U_2, V_2, W_2)\) describe the location of the nearest neighbor atom, and \((U_3, V_3, W_3)\) describe the location of the 2\(^{nd}\) nearest neighbor atom. The term \(|u_i|/a\) is the length of the \(i\)th bond and \(\rho_i\) is a fitted parameter for the nearest neighbor \((\rho_2)\) and second nearest neighbor \((\rho_3)\). In Equation 2.11, \(\Phi_u\) and \(\theta_u\) are the angles used to define the crystal orientation of the broken bond over \(p_i\), the total number of broken bonds with the orientation \(\Phi_u\) and \(\theta_u\).

\[
\gamma_{hkl} = \frac{\Phi_u a}{2\Omega} \left[ A \sin \phi \cos \theta + B \sin \phi \sin \theta + C \cos \phi \right] \tag{2.9}
\]

\[
A = U_1 \frac{|\vec{u}_1|}{a} + U_2 \frac{|\vec{u}_2|}{a} \rho_2 + U_3 \frac{|\vec{u}_3|}{a} \rho_3
\]

\[
B = V_1 \frac{|\vec{v}_1|}{a} + V_2 \frac{|\vec{v}_2|}{a} \rho_2 + V_3 \frac{|\vec{v}_3|}{a} \rho_3 \tag{2.10}
\]

\[
C = W_1 \frac{|\vec{w}_1|}{a} + W_2 \frac{|\vec{w}_2|}{a} \rho_2 + W_3 \frac{|\vec{w}_3|}{a} \rho_3
\]

\[
U_i = \sum_{1}^{p_i} \sin \phi_u \cos \theta_u
\]

\[
V_i = \sum_{1}^{p_i} \sin \phi_u \sin \theta_u \tag{2.11}
\]

\[
W_i = \sum_{1}^{p_i} \cos \phi_u
\]

In the 1960’s, Nicholas calculated the surface energy of all crystal planes of the stereographic triangle for FCC and BCC metals. To perform this calculation, the total number of every type of bond broken to create each surface was determined using a surface size of 300-500 atoms, then the interaction
potential of each bond was calculated using either the Mie or Morse potential models. The total surface energy per area was determined for each crystal plane and contour plots were made of the ratio of surface energy to the minimum energy plane over the entire stereographic triangle. Figure 21a and b show contour plots of the relative surface energy over the entire stereographic triangle for Ag (FCC) and W (BCC) using the Morse potential model. The minimum energy plane was \{110\} for W and \{111\} for Ag. Figure 21c and d show contour plots of surface energy calculated for BCC and FCC metals using m = 6 and n = 10. This model shows the same general trend as the Morse potential. In each FCC stereographic triangle, the maximum surface energy contours were found in the middle of the stereographic triangle near the \{531\} plane, a high Miller index surface with step edges and kinks. In each BCC triangle, there were two maxima in surface energy present around the \{10,5,4\} and the \{765\} planes (16). When compared to the experimental data on surface energy available at the time (120), the best fits came from the Morse potential model of metals where the Morse constant \(a \approx 4\) and from the Mie potential model of \(m = 6\) and \(n = 10\) (16).

The surface energy of different crystal planes can be determined experimentally using Field Ion Microscopy (FIM). Grenga used FIM to study the surface energy and faceting behavior of W, Ir, and Fe at high temperatures and in the presence of H\(_2\). From FIM images, the size of surface facets were determined experimentally and compared to surface energy anisotropy calculations based on several broken-bond models. For BCC metals Fe and W, the Mie potential best predicted the experimental results with \(n = 5\) and \(m = 8\) for W and \(n = 6\) and \(m = \)
12 for Fe. For Ir, an FCC metal, the pair wise bonding model with $\rho_2 = 0.4$ and $\rho_3 = 0.2$ had the best fit to experimental data. For all models, the trends in experimental data agree with theoretical calculations showing that the largest facets are those with the lowest surface energy (121-123).

Figure 21: a) Contour plot of surface energy of Ag over the entire stereographic triangle with respect to $\{111\}$ plane calculated using the Morse potential with $a = 4.265$. b) Contour plot of surface energy of W over the entire stereographic triangle with respect to $\{110\}$ plane calculated using Morse potential with $a = 4.279$ c) Contour plot of surface energy of FCC metal using Mie potential model with $m = 6$ and $n = 10$. D) Contour plot of surface energy of BCC metal using Mie potential model with $m = 6$ and $n = 10$ (16).
Menzel and Jeschkowski performed surface energy calculations on spherical droplets of FCC metals prepared in vacuum from solidification of droplets of melted metal on a SiO$_2$ substrate. By measuring the diameter of facets of the low index faces on each of the droplets (created due to the surface energy anisotropy at the melting point), the relative surface energies compared to the \{111\} plane were calculated. For Cu, the surface energy of the \{111\} plane, $\gamma_{\{111\}}$ was greater than $\gamma_{\{100\}}$ while for Au, Ag, Ni, and Pb, $\gamma_{\{100\}} > \gamma_{\{111\}}$. All of these experimental trends match the predictions of the relative surface energies calculated by Nicholas (124-127).

Changes in surface energy with surface orientation have also been calculated using density functional theory (DFT). Vitos et al. used DFT to calculate the surface energy of the \{111\}, \{110\}, and \{100\} planes of most metals in the periodic table. Both the local density approximation (LDA) and generalized gradient approximation (GGA) were used separately for calculating the ground state energies of each metal. For all FCC metals calculated, the surface energy of \{111\} < \{100\} < \{110\} while for BCC metals the surface energy of \{110\} < \{100\} < \{111\} (128). LDA values were found to better agree with experimental data than GGA values. Yu et al. calculated the surface energy of 35 different crystal planes on the edge of the stereographic triangle of Pb to determine trends of surface energy with step density, step orientation, and predictions made by the broken bond models. Maxima in surface energy occurred at the \{210\} plane and \{311\} planes (maxima in step density) and the \{110\} plane (a fully stepped surface). Minima occurred at the \{100\} and \{111\} planes (129).
Figure 22 shows a plot of the surface energy vs. surface orientation for the ideal broken bond model compared to DFT calculations. The broken bond model predicts the same trends as DFT, showing that the broken bond models used in the 60’s and 70’s are still an effective predictor of general trends in surface energy with surface orientation. The only differences between these two models are that DFT accounts for surface relaxation and charge smoothing which causes an overall lowering in the predicted surface energy values.

Figure 22: Comparison of calculated $\gamma(\theta)$ versus $\theta$ functions in the [001] and [110] zones for the ideal broken surface bond model and the full DFT results for relaxed Pb surfaces. The two data sets are matched at the (111) orientation. The same general trends are observed for both DFT and broken bond models (129).
2.2.5 Physical Phenomena Discussion

Table 2 shows all of the metals and traits studied for the different physical phenomena mentioned as well as a brief synopsis of the trends found. Work function studies show that the work function of a metal is highly anisotropic. In both experimental and theoretical studies of the work function, it is generally observed that more atomically rough crystal planes or those with a higher step density have a lower work function which agrees with the theory proposed by Smulochowski. This trend occurs for almost all FCC and BCC metals. More complex crystal structures such as diamond cubic and zinc blende in semiconductors display weaker work function anisotropy, but analysis of shifts in the valence band edge show that there is still anisotropy in the surface electronic structure of semiconductors. Reports of surface energy measurements and calculations show a similar trend as work function in that crystal planes with a higher surface energy have a lower work function. The largest discrepancies in surface energy studies are the values for {111} and {100} planes of an FCC metal. Since the {100} and {111} plane are close in energy, whether {111} or {100} plane has a higher surface energy seems to depend on the metal. The surface energy and work function of these planes are so similar, that differences in the number of electrons and inter-atomic spacing may have an impact in determining these values.

Analysis of surface reconstruction on $\text{S}^4\text{Cs}$ and single crystals showed that the faceting behavior changes with surface orientation and metal. $\text{Cu S}^4\text{Cs}$ are especially stable against faceting; in multiple studies, $\text{Cu}$ did not facet and high
Miller index crystal planes maintained a surface structure close to its ideal shape predicted by theory (10, 12, 74). The only conditions that cause faceting of Cu are heating near its melting point close to atmospheric pressure. The faceting behavior of Ag was similar to Cu but more evidence is needed on Ag to confirm its resistance to faceting (74). Other metals studied such as W, Au, Si, Ge, and GaAs are not as stable as Ag or Cu and facet into low Miller index crystal planes at temperatures above 300K depending on the overall pressure and partial pressures of adsorbates. Au, Si, and Ge surfaces reconstruct after standard polishing treatments.

Both LEED and STM have been used to analyze the structure of various S^4Cs and single crystals. STM appears to be a better technique for studying changes in surface structure with orientation on S^4Cs as STM can better visualize subtle changes between crystal surfaces and step distributions and is more accurate in calculating step densities than performing intensity and spot splitting analysis using LEED. STM also has an added advantage of increased spatial resolution as the size of an STM tip is much smaller than the electron beam diameter used in LEED. For single crystals, both techniques are useful but it is more important to have the smallest spatial resolution possible for S^4Cs since a single spot on an S^4C can contain hundreds of different crystal planes if the spot size is too large.

Qiu et al. found that many magnetic properties of ferromagnetic metals depend on step density. Among these properties are magnetic anisotropy, coercivity, SRT, and Curie temperature. For FCC ferromagnetic films deposited
on FCC metals, there is a linear increase in magnetic anisotropy with step density while for BCC ferromagnetic films deposited on BCC metals, there is a quadratic increase of magnetic anisotropy with step density. This can be attributed theoretically using the Neel pair bonding model that takes into account lattice symmetry (24). For ferromagnetic films with a different crystal structure than the substrate, the explanation is not well understood. Qualitatively, the magnetic anisotropy is likely due to a combination of the breaking of lattice symmetry at the step edge and the lattice mismatch between the film and the substrate. Qiu et al. postulated that for ferromagnetic films with a different crystal structure than the substrate, the metal with the stronger spin orbit coupling will determine whether there is a quadratic and linear relationship between $H_s$ and $\alpha$. If the FCC metal is stronger, the magnetic anisotropy should have a linear dependence but if the BCC metal is stronger, then the magnetic anisotropy will have a quadratic dependence. The exception to this rule is the study of Fe on curved Pt which has an $\alpha^4$ dependence, but this is due to the magnetic polarization of Pt that doesn’t occur on the other substrates studied.

In general, these studies looked at changes in physical properties of crystal surfaces with step density and step orientation. The presence of steps on a single crystal surface causes a decrease in the work function, an increase in the surface energy, and an increase in the magnetic anisotropy. The step orientation does not have as great an effect on these physical properties as the step density. The reconstruction of metal surfaces changes with each metal and with the temperature and pressure conditions studied. Cu and Ag appear to be the most
stable as $S^4$Cs of these metals have a structure that best resembles the ideal structure from cleavage of a crystal.
Table 2: Physical Phenomena Studied on Curved Single Crystal Surfaces

<table>
<thead>
<tr>
<th>Metal</th>
<th>Crystal Structure</th>
<th>Trait Studied</th>
<th>Technique Used</th>
<th>Trends</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co on Cu</td>
<td>FCC on FCC</td>
<td>Magnetic Anisotropy</td>
<td>Magneto Optical Kerr Effect</td>
<td>magnetic anisotropy increased linearly step density. Step type changes orientation of easy axis</td>
<td>Qiu (106-109)</td>
</tr>
<tr>
<td>Fe on Pt</td>
<td>BCC on FCC</td>
<td>Magnetic Anisotropy</td>
<td>Magneto Optical Kerr Effect</td>
<td>magnetic anisotropy increased with step density by α²</td>
<td>Cheng (116, 117)</td>
</tr>
<tr>
<td>Fe on Ag</td>
<td>BCC on FCC</td>
<td>Magnetic Anisotropy</td>
<td>Magneto Optical Kerr Effect</td>
<td>magnetic anisotropy increased quadratically step density</td>
<td>Qiu (23, 101)</td>
</tr>
<tr>
<td>Fe on Cr</td>
<td>BCC on FCC</td>
<td>Magnetic Anisotropy</td>
<td>Magneto Optical Kerr Effect</td>
<td>magnetic anisotropy increased linearly step density</td>
<td>Qiu (103-105)</td>
</tr>
<tr>
<td>Fe on W</td>
<td>BCC on BCC</td>
<td>Magnetic Anisotropy</td>
<td>Magneto Optical Kerr Effect</td>
<td>magnetic anisotropy increased quadratically step density</td>
<td>Qiu (24, 102)</td>
</tr>
<tr>
<td>Fe on Pd</td>
<td>BCC on FCC</td>
<td>Magnetic Anisotropy</td>
<td>Magneto Optical Kerr Effect</td>
<td>magnetic anisotropy increased linearly step density</td>
<td>Qiu (24, 102, 111)</td>
</tr>
<tr>
<td>FeMn on Co/ Cu</td>
<td>BCC on FCC</td>
<td>Magnetic Anisotropy</td>
<td>Magneto Optical Kerr Effect</td>
<td>FeMn films eliminate magnetic anisotropy</td>
<td>Qiu (110)</td>
</tr>
<tr>
<td>Ni on Cu</td>
<td>FCC on FCC</td>
<td>Magnetic Anisotropy</td>
<td>Magneto Optical Kerr Effect</td>
<td>Spin reorientation transition increases quadratically with step density</td>
<td>Qiu (112-114)</td>
</tr>
<tr>
<td>NiO on Ag</td>
<td>FCC</td>
<td>Magnetic Anisotropy</td>
<td>Magneto Optical Kerr Effect</td>
<td>magnetic anisotropy increases with step density and direction depends on step orientation</td>
<td>Qiu (115)</td>
</tr>
<tr>
<td>All FCC and BCC</td>
<td>BCC and FCC</td>
<td>Surface Energy Anisotropy</td>
<td>Theoretical</td>
<td>Surface Energy of all fcc and bcc metals based on Mie and Morse potentials calculated</td>
<td>Nicholas (16)</td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>Surface Energy Anisotropy</td>
<td>Microscopy</td>
<td>Surface Energy of {111}&gt;{100}</td>
<td>Jeschkowski /Menzel (124-127)</td>
</tr>
<tr>
<td>Fe</td>
<td>BCC</td>
<td>Surface Energy Anisotropy</td>
<td>Field Ion Microscopy</td>
<td>Surface Energy of {111} &gt; {211} &gt; {100} &gt; {110}</td>
<td>Kumar/Grenga(122)</td>
</tr>
<tr>
<td>W</td>
<td>BCC</td>
<td>Surface Energy Anisotropy</td>
<td>Field Ion Microscopy</td>
<td>Surface Energy of {210}&gt;{311}&gt;{110}&gt;{100}&gt;{111}</td>
<td>Kumar Grenga (123)</td>
</tr>
<tr>
<td>Ag, Ni, Pb, Au</td>
<td>FCC</td>
<td>Surface Energy Anisotropy</td>
<td>Microscopy</td>
<td>Surface Energy of ( {100} &gt; {111} )</td>
<td>Jeschkowski/Menzel (125)</td>
</tr>
<tr>
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</tr>
<tr>
<td>Ag</td>
<td>FCC</td>
<td>Surface Reconstruction</td>
<td>STM</td>
<td>No faceting occurs on vicinal planes of Ag{111} and valence band moves closer to Fermi edge as step density increases</td>
<td>Ortega (74)</td>
</tr>
<tr>
<td>Au</td>
<td>FCC</td>
<td>Surface Reconstruction</td>
<td>LEED</td>
<td>Large flats for {111}, {110}, and {100} formed along with smaller {551} and {722}</td>
<td>Ggrosser, Menzel (83-85)</td>
</tr>
<tr>
<td>Au</td>
<td>FCC</td>
<td>Surface Reconstruction</td>
<td>STM</td>
<td>Vicinal planes of Au{111} towards {100} and {110} facet into systems of 13 A and 31 A wide terraces</td>
<td>Ortega (74)</td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>Surface Reconstruction</td>
<td>STM</td>
<td>Spherically curved Cu single crystal does not facet but maintains ideal structure</td>
<td>De Alwis (12)</td>
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<tr>
<td>Cu</td>
<td>FCC</td>
<td>Surface Reconstruction</td>
<td>Optical Microscopy</td>
<td>Heating &gt; 900 C enlarges facets of {100} and {111} planes</td>
<td>Gwathmey (81)</td>
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<tr>
<td>Cu</td>
<td>FCC</td>
<td>Surface Reconstruction</td>
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<td>Large flats for {111}, {110}, and {100} formed with smaller {221}, {211}, and {311} planes</td>
<td>Melle, Menzel (82, 83, 85)</td>
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<tr>
<td>Cu</td>
<td>FCC</td>
<td>Surface Reconstruction</td>
<td>STM</td>
<td>No faceting occurs on vicinal planes of Cu{111} and valence band moves closer to Fermi edge as step density increases</td>
<td>Ortega (74)</td>
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<tr>
<td>Cu</td>
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<td>Surface Reconstruction</td>
<td>STM</td>
<td>Cu{643} undergoes thermal roughening when annealed to 1000 K but maintains surface chirality</td>
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<tr>
<td>GaAs</td>
<td>Zinc blende</td>
<td>Surface Reconstruction</td>
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<td>One layer steps form around GaAs{111}, double layer steps form around GaAs{110}</td>
<td>Ranke (130)</td>
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<td>Ge</td>
<td>Diamond Cubic</td>
<td>Surface Reconstruction</td>
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<td>Crystal planes near {110} facet into {17 15 1} and {10 9 2} orientations.</td>
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<td>Material</td>
<td>Crystal Structure</td>
<td>Surface Reconstruction</td>
<td>Technique</td>
<td>Surface Facets</td>
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<td>O on Ir</td>
<td>FCC</td>
<td>Surface Reconstruction</td>
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<td>At &gt;850 K, surface facets into {111} and {100} planes. With O adsorbed it facets into {110}, {113}, {100}, and {111} planes.</td>
<td>Bryl (98)</td>
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<tr>
<td>Si</td>
<td>Diamond Cubic</td>
<td>Surface Reconstruction</td>
<td>LEED</td>
<td>Crystal planes near {110} facet into {751} orientations.</td>
<td>Olshanetsky, Tong (11, 86, 88, 132, 133)</td>
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<td>Si {111}</td>
<td>Diamond Cubic</td>
<td>Surface Reconstruction</td>
<td>STM</td>
<td>{432} facets with single and triple layer steps form from {111} to {100} and step bunching with lots of kinks occurs from {111} to {110}</td>
<td>Hanbucken (90, 91)</td>
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<tr>
<td>Si {100}</td>
<td>Diamond Cubic</td>
<td>Surface Reconstruction</td>
<td>STM</td>
<td>Single layer steps occur (&gt;2^\circ), double layer steps (6-9^\circ), {911}, {711}, and {511} form (&gt;9^\circ)</td>
<td>Hanbucken (92)</td>
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<td>Work function</td>
<td>Contact Potential</td>
<td>{111} is electropositive compared to {100} : {100} lower work function than {111}</td>
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<td>Cu</td>
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<td>GaAs</td>
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<td>Work Function/Electron Affinity</td>
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<td>Ge</td>
<td>Diamond Cubic</td>
<td>Work Function</td>
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<td>Valence band edge has maxima at {110} and {511} &gt; {111}, {100}</td>
<td>Ranke (20, 72)</td>
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<tr>
<td>Si</td>
<td>Diamond Cubic</td>
<td>Work Function</td>
<td>Photoemission</td>
<td>Valence band edge has maxima at {110} and {511} &gt; {111}, {100}</td>
<td>Ranke (70, 71, 93, 94)</td>
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<tr>
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<td>Work Function</td>
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<td>Work function {100} (&lt; {111} (&lt; {211} (&lt; {110} )</td>
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<td>W</td>
<td>BCC</td>
<td>Work Function</td>
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<td>Work function of {111}, {511} (&lt; {211} (&lt; {100} (&lt; {110} )</td>
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<td>Work Function</td>
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2.3 Chemical Phenomena

One of the main uses of $S^4Cs$ is studying the effect of crystal structure on adsorption and reaction of different molecules. $S^4Cs$ have been used to understand a number of different chemical phenomena including crystal growth, adsorption, desorption, oxidation, etching, and removal of surface species. Using this data, many qualitative trends of surface structure with chemical reactivity have been discovered.

2.3.1 Crystal Growth

One of the earliest chemical properties studied for orientation dependence was the growth of crystals. Stranski was one of the first researchers to write about the theory of crystal growth and postulated that for a crystal grown above 0 K, the surface will have some roughness due to thermal fluctuations on the surface (134, 135). Frenkel in 1945 later showed that the roughness of these surfaces will exist in the form of step edges and kinks (136). Burton in 1951 theorized that the growth of a crystal occurs only through the advancement of monomolecular steps and the growth will take place through the advancement of these steps to form new molecular layers. The rate of this advancement of steps is dependent on the steps structure but not its orientation and steps are created due to the formation of screw dislocations from imperfections in the crystal. Kinks will also form along these step edges and are energetically favorable under the conditions for crystal growth from the vapor. The energy for the formation of kinks will be much less than the evaporation energy of the metal under super-saturation conditions used.
during crystal growth. After crystal growth, low index crystal planes will remain flat at equilibrium at most temperatures except near the melting point of a crystalline material (137).

Gwathmey performed experiments on the growth of crystals and developed several experimental methods for growing single crystal rods and spheres (138). The four techniques used by Gwathmey for growing single crystals were growth from molten metal, growth from solid state by inducing strain in a polycrystalline material at high temperatures, deposition from the vapor, and electrochemical deposition from solution. The polishing techniques for preparing single crystals and spheres for study were based on combinations of mechanical polishing with pastes and cloths of varying grit size and chemical polishing with acid solutions. A separate polishing technique was developed by Gwathmey for each metal and crystal plane and its efficacy was confirmed using X-ray diffraction and optical microscopy techniques. For Cu, the \{111\} planes were polished using AgNO₃ dissolved in HNO₃ while \{100\} planes of Cu were polished using CuCl₂ dissolved in HCl (138).

After growing these single crystal spheres and preparing them, Gwathmey et al. performed several experiments on the orientation dependence of metal deposition and the effect of deposited metal on surface reactivity. For electrochemical deposition of Cu on spherical Cu S⁴Cs, the size of the \{111\} > \{210\}, \{110\} > \{100\} and metal deposits on the \{111\} plane were monocrystalline while deposits on the \{100\} plane were polycrystalline. Ag electrodeposited on Cu had a similar trend in the area of deposits formed as the
{111} > {110} > {100} regions on the Ag sphere. For electrochemical
deposition, the largest crystal facets formed have lowest rate of deposition while
in electrochemical etching, the largest crystal facets remaining are the ones that
etch at the fastest rate (139). The effect of deposited metal on the surface
reconstruction was also studied by Gwathmey et al. In an environment of H$_2$ and
O$_2$ to form H$_2$O on spherical Cu S$^4$Cs, the addition of Ag had no effect, but the
addition of Zn to the Cu surface caused enhanced reactivity on the {100} and
{111} planes (140).

Leidheiser and Gwathmey analyzed the rates of Co and Ni deposition with
surface orientation on spherical Cu and Ni S$^4$Cs. For Ni electrodeposition on Ni
and Cu, deposits on {100} faces remained monocrystalline and deposited at a
faster rate than {111} faces, which formed polycrystalline deposits with a
preferred {100} orientation. This experiment showed that {100} was the preferred
orientation for Ni deposited on Cu and Ni. Leidheiser also studied the rate of Co
deposition versus orientation from a salt solution on Cu spherical S$^4$Cs. The
following trend was observed for the rate of Co deposition with crystal plane on
Cu: \{210\}, \{310\} > \{211\}, \{311\} > \{100\} > \{110\} > \{111\}. This overall trend
showed that high Miller index crystal planes containing step edges had a higher
rate of Co deposition than the low Miller index crystal planes (141, 142).

Cochrane looked at the orientation of metal films deposited on Cu{110}
and Cu {111} single crystals. For Ni and Cu electrodeposited on Cu{110}, the
metal film preferentially formed a {110} structure at low thicknesses but became
polycrystalline as the film thickness increased. For Zn and Cd deposited on
Cu{110}, the films were polycrystalline at all thicknesses. Ag and Cr deposited on C{111} and Cu{110} orients itself with the underlying single crystal structure until a critical thickness where it becomes polycrystalline. The critical find by Cochrane was that for each metal there is a critical thickness where the deposited film transitions from being oriented to becoming polycrystalline and this value depends on the differences between the lattice constant and the crystal structure of the deposited film and the underlying single crystal (143).

For metal deposition on S\textsuperscript{4}Cs, the surface orientation with the highest deposition rate changes with each metal. In general, a metal depositing on the surface will form the same crystal structure as the substrate. However, at a critical thickness, the deposited metal transitions from a single crystal structure to a polycrystalline structure. This transition appears to be impacted by the differences between the lattice constant of the depositing film and the lattice constant of the substrate. Similar lattice constants will remain mono-crystalline at higher thicknesses than for metals with different lattice constants.

2.3.2 Adsorption – Diatomic

2.3.2.1 Background – Single Crystal Studies

The orientation dependence of the adsorption of diatomic molecules has been studied extensively using single crystal surfaces. Delchar and Ehrlich studied the effect of the surface structure on the chemisorption of N\textsubscript{2} on W. The changes in work function with N\textsubscript{2} adsorption were measured at 300 K in vacuum using W\{110\}, \{111\}, and \{100\}. The W\{110\} plane did not chemisorb N\textsubscript{2} but
W{100} and W{111} were active toward N$_2$ chemisorption (144). Rhodin studied the chemisorption of N$_2$ on the low Miller index planes of Cu. He calculated the isothermal heats of adsorption of N$_2$ at temperatures between 70 and 90 K on Cu{110}, Cu{111}, and Cu{100} single crystals and how they varied with coverage and crystal plane. The heats of adsorption for 1 ML of N$_2$ exhibited the following trend: Cu{110} > Cu{100} > Cu{111}. This trend was attributed to the density of atoms on the surface; more open and atomically rough surfaces bind N$_2$ better than close packed surfaces (145, 146). Gerhardt Ertl won a Nobel Prize in 2007 for his work on N$_2$ dissociation, the rate limiting step in NH$_3$ synthesis, on single crystals of Fe. Using AES, the rates of dissociation of N$_2$ were calculated on the low Miller index crystal planes of Fe{111}, Fe{110}, and Fe{100} in UHV. Ertl et al. found that the rate of N$_2$ dissociation on Fe was 20 times higher on Fe{111} than Fe{100} and Fe{100} had an N$_2$ dissociation rate 4 times higher than Fe{110}. By analyzing TPD spectra from adsorbed N$_2$, the activation energy of associative desorption of N$_2$ was calculated. This activation energy of desorption of N$_2$ with crystal plane exhibited the following trend: Fe(110) >> Fe(100) > Fe(111) showing that the reaction was most energetically favorable on the Fe{111} plane (147, 148). This work was furthered by Somorjai et al. when he studied the rate of NH$_3$ synthesis on Fe{111}, Fe{110}, and Fe{100} under high temperatures and high pressures. The relative rates of NH$_3$ formation were 418:25:1 for Fe{111}, Fe{100}, and Fe{110} and matched the same trend seen for N$_2$ dissociation providing evidence that N$_2$ dissociation is the rate limiting step in NH$_3$ formation (149, 150). Both of these researchers showed that more
atomically open crystal planes or those with more low coordination atoms on the surface are more active toward \( \text{N}_2 \) dissociation.

Rye studied the structure sensitivity of \( \text{H}_2 \) adsorption on single crystal planes of W by calculating the sticking probability using TPD spectra. The sticking probability for \( \text{H}_2 \) varied greatly with crystal structure. The \{111\} plane had a sticking probability of ~1, the \{211\} and \{100\} planes were similar with a sticking probability of 0.55 while \{110\} had the lowest sticking probability of 0.2. The sticking probability increased with decreasing atomic density on the surface; more open and atomically rough crystal planes had a higher sticking probability of \( \text{H}_2 \) on W (151).

Ross et al. used electrochemical methods to study the orientation dependence of \( \text{H}_2 \) adsorption on single crystal Pt electrodes. Using an electrochemical cell and performing cyclic voltammetry sweeps of \( \text{H}_2 \) bubbled in a 0.1 M \( \text{HClO}_4 \) solution, the binding energy of \( \text{H}_2 \) on Pt\{111\}, Pt\{211\}, and Pt\{100\} was calculated. The binding energy for \( \text{H}_2 \) was 9.2 kcal/eq on Pt\{211\}, 6.44 kcal/eq on \{100\}, and 3.0 kcal/eq on \{111\}. Ross postulated that \( \text{H}_2 \) adsorbs preferentially at \{100\} oriented step edges because \( \text{H}_2 \) had the highest binding energy on stepped Pt\{211\} (152). Yamamoto et al. used the same cyclic voltammetry technique to study \( \text{H}_2 \) adsorption on Pt\{100\}, Pt\{111\}, and Pt\{110\} except performed experiments in an \( \text{H}_2\text{SO}_4 \) solution as opposed to \( \text{HClO}_4 \). Ross found similar results; \( \text{H}_2 \) had a higher binding energy on Pt\{110\} and Pt\{100\} than Pt\{111\} (153). Yeager et al. also performed the same experiment as Yamamoto and Ross with similar experimental conditions and found that \( \text{H}_2 \) had a
higher binding energy on Pt{100} than Pt{111} (154). The trends observed in each of these studies were consistent.

Peden *et al.* studied the conversion of NO and CO to N₂ and CO₂ over Rh{110} and Rh{111} single crystals. The dissociation of NO and conversion to N₂ was used as the metric for activity and experiments were run at pressures between 1 and 100 Torr of NO and CO gas mixtures at 525-675 K. Rh{110} was between 1.3 and 6.3 times more active toward NO dissociation than Rh{111} and had a lower activation energy than Rh{111} (27.2 kcal/mol vs. 34.8 kcal/mol). Rh{110} also exhibited a higher selectivity for producing N₂ over N₂O than Rh{111} in the overall reaction making Rh{110} an overall better catalyst for the NO-CO reaction than Rh(111) (155).

Erley *et al.* studied CO dissociation on Ni{111} and Ni{511} single crystals using TPD coupled with LEED and AES to look at the state of CO on the surface. CO was exposed to each surface at 1 x 10⁻⁸ Torr and 300 K. The TPD spectra for Ni{111} contained only 1 peak at 473 K from molecular desorption of adsorbed CO, but the Ni{511} surface had an additional peak at 800 K which was attributed to associative adsorption of CO from step edges on the surface. Using AES, Erley found that after molecular desorption of CO at 473 K, the amount of surface C was 6% of the saturated surface which came from dissociated CO at step edges occurring between 400 and 480 K. The presence of a weakened CO bond at step sites was also found on Ni{511} using EELS providing further evidence of the enhanced CO dissociation activity on step edges (156, 157).
Fu and Somorjai analyzed differences in adsorption behavior of CO, CO$_2$ and D$_2$ on Cu$\{311\}$ and Cu$\{110\}$ single crystals using LEED, TPD, and AES. They found that CO$_2$, CO and D$_2$ chemisorb on Cu$\{311\}$ but only physisorb on Cu$\{110\}$ in UHV. After exposure to CO at 150 K on Cu$\{110\}$, there was only one peak in the TPD spectra at ~200 K while for Cu$\{311\}$ there were peaks at both 200 K and 400 K showing the presence of a CO species with a higher binding energy on the Cu$\{311\}$ plane. D$_2$ adsorbed on the Cu$\{311\}$ surface at 150 K, but did not adsorb on Cu$\{110\}$ at exposures $< 1 \times 10^{-7}$ Torr. Also, both the forward and reverse reaction for CO$_2$ dissociation to CO and adsorbed O occurred on the Cu$\{311\}$ surface and not the Cu$\{110\}$. These experiments showed that step edges are more active towards the chemisorption and dissociation of diatomic molecules and CO$_2$ dissociation than the $\{110\}$ plane (158).

The work presented here is only a small sample of the research on the orientation dependence of diatomic molecule adsorption and dissociation on single crystals, but several qualitative trends are apparent. More atomically open crystal planes like FCC$\{110\}$ and BCC$\{111\}$ are the most active toward chemisorption and dissociation of diatomic molecules. The effect of step edges has been studied less extensively on single crystals, but there is evidence that the presence of step edges enhances the surface reactivity for adsorption and dissociation. Diatomic molecules such as CO, H$_2$, N$_2$, O$_2$, and NO have been extensively researched on single crystal surfaces but have also been studied on
The information on O₂ adsorption and oxidation is so extensive that it will be included in a separate section later in this review.

**2.3.2.2 Diatomic Adsorption S₄Cs Studies**

Some of the first studies on adsorption of diatomic molecules on S₄Cs were performed by Leidheiser and Gwathmey (159, 160). In each experiment, CO was exposed to spherical S₄Cs of Ni, Fe, and Co between 450 and 600°C and the thickness of C deposited was measured using X-ray diffraction. On the spherical Ni, Fe, and Co S₄Cs, high Miller index crystal planes inside the stereographic triangle where \( h \neq k \neq l \) were the most active towards CO dissociation. For the FCC metals Ni and Co, the trend for increasing dissociation activity was as follows: \( \{hkL\} > \{hLL\} > \{111\} > \{110\} > \{100\} \). For Fe, a BCC metal, the trend for increasing dissociation activity was as follows: \( \{hkL\} > \{hLL\} > \{hhL\} > \{hL0\} > \{111\}, \{110\} > \{100\} \). Crystal planes containing kinks were the most active for CO dissociation followed by crystal planes with step edges while low Miller index crystal planes were the least active.

Murayama *et al.* used FIM methods to study the adsorption and dissociation of CO on spherical Ni S₄Cs by measuring changes in the work function on the surface (161). Murayama found that CO preferentially adsorbed on stepped crystal planes of \( \{310\} \) and \( \{hL0\} \) of Ni at 295 K and this adsorption increased the work function of the surface. After heating the Ni surface to 470 K, CO molecularly desorbed from low Miller index crystal planes (111), (110), and (100) but dissociated on high Miller index planes like \( \{310\} \), \( \{510\} \), and vicinal
planes. This work showed that step edges play an important role in the
dissociation of CO.

Singh and Grenga used spherical $S^4$Cs of Ru to study adsorption of CO at
823 K at atmospheric pressure (162). Differences in reflection high energy
electron diffraction spectra or RHEED were examined and optical micrographs
were used to determine active sites for CO dissociation and the structure of the
surface after the reaction. They found that CO dissociated and produced a layer
of graphite and not carbide or oxide on the Ru surface. Similar to the results of
Leidheiser for CO on spherical Ni $S^4$Cs, the active sites for dissociation were step
dges surrounding low Miller index planes.

Caracciolo et al. used cylindrical Ni $S^4$Cs and AES to study the structure
sensitivity of CO dissociation. Figure 23 shows a rough image of the cylindrical
Ni $S^4$C used in the CO dissociation experiments. The Ni $S^4$C contains the {111},
{100}, and {110} planes and all vicinal crystal planes spanning a 1-D path around
the stereographic triangle from {100} – {111} – {110}. Figure 23 also shows the
amount of C deposited on the $S^4$C surface versus orientation after exposure to CO
at 0.6 Torr for 3 minutes and 10 minutes at 600 K. The amount of C is plotted as
a ratio of C/Ni using the peak areas from AES. There were maxima in C
deposition at the {311} and {110} planes and minima at the {111} and {100}
planes. The amount of C deposited from CO dissociation increased with
increasing distance from the low Miller index planes of {100} and {111} showing
that the rate of C deposition increased with increasing step density. Caracciolo et
al. also postulated that the phase of C formed on the surface could play a role in
the type of hydrocarbon formed in Fischer-Tropsch synthesis on Ni catalysts. Theoretically, carbidic C produces smaller chain hydrocarbons like CH₂ and C₂H₄ while graphitic C produces longer chain hydrocarbons (18, 163).

Figure 23: Ratio of C to Ni signal from AES of cylindrical Ni S⁴C section after exposure to 0.6 Torr CO at 600 K for 3 minutes and 10 minutes. There are maxima at the {311} and {110} planes and minima at the {100} and {111} planes (18).

Adsorption of NO at 60, 130, and 300 K on a cylindrical Ge S⁴C with a [110] axis was studied in UHV by Ranke using AES and Photoelectron spectroscopy. AES was used to determine the atomic ratios of N, O, and Ge on the surface while Photoemission spectroscopy was used to determine the state of N and O adsorbed on the surface. The adsorption and dissociation of NO at all
temperatures was strongly orientation dependent. At 60 K and 130 K, molecular NO adsorbed on the surface with maxima on the \{100\} and \{331\} planes and minima at \{111\} and \{110\} planes. At 300 K, NO dissociated on all crystal planes with maxima in adsorbed O and N at \{911\}, \{211\}, and \{221\} planes with minima at \{100\}, \{110\}, and \{111\} planes. Overall, the dissociation of NO was strongly enhanced by step edges (164).

The most recent work on studying the effect of surface orientation on diatomic molecule adsorption is the use of a cylindrical Ni S\textsubscript{4}C with a [110] axis by Hahn \textit{et al.} to study the effect of surface structure on D\textsubscript{2} adsorption and desorption (7). A molecular beam was used to determine trends in the sticking coefficient with surface orientation at three different kinetic energies. Hahn \textit{et al.} found that crystal planes with higher densities of \{100\} steps and smaller terrace widths had a significantly higher sticking coefficient for low kinetic energy D\textsubscript{2} while the opposite trend occurred for high kinetic energy D\textsubscript{2}; the sticking coefficient was highest for Ni\{111\}. Spatially resolved temperature programmed desorption (SR-TPD) experiments were also performed using a narrow molecular beam to expose D\textsubscript{2} to a 2° section of the cylinder surface. Figure 24 shows the TPD spectra of associative desorption of D\textsubscript{2} at 2° increments away from \{111\}. The high temperature D\textsubscript{2} desorption peak shifted from 361 K toward 380 K as the distance from the \{111\} plane increased. The peak desorption temperature of D\textsubscript{2} increased with increasing step density showing that step edges have a higher binding energy for D\textsubscript{2}. 
The most common conclusion for research on the adsorption and
dissociation of diatomic molecules on $S^4$Cs is that more atomically rough crystal
planes and those containing step edges are more active. This trend is consistent in
UHV experiments, high pressure and high temperature gas phase reactions, and
electrochemical experiments. Similar trends were found on both single crystal
samples and $S^4$Cs, showing that there is a consistency in the results.

Figure 24: TPD spectra from associative desorption of $D_2$ from a cylindrical Ni
$S^4$C with a [110] axis at various distances from the {111} plane. The desorption
peak for $D_2$ increases with increasing step density of Ni. (7).

2.3.3 Adsorption – Hydrocarbons

Many researchers studied interactions of hydrocarbons with $S^4$Cs
including adsorption, decomposition, hydrogenation, and oxidation. The first
documented work of hydrocarbon adsorption of an $S^4$C to our knowledge was the
work by Cunningham and Gwathmey in 1957. Cunningham and Gwathmey
studied the effect of surface orientation on \( \text{C}_2\text{H}_4 \) hydrogenation and decomposition on Ni single crystals and a spherical Ni S\(^4\)C. For single crystals of Ni, the rate of \( \text{C}_2\text{H}_6 \) formation from stoichiometric mixtures of \( \text{H}_2 \) and \( \text{C}_2\text{H}_4 \) between 323 and 473 K varied with crystal plane. The \{321\} surface had the highest rate of formation followed by \{111\} > \{110\} > \{100\} at all temperatures studied. \( \text{C}_2\text{H}_4 \) decomposition to surface C was studied on the spherical Ni S\(^4\)Cs using an optical microscope to observe the C deposition patterns. Figure 25 shows the C deposition on a Ni sphere after exposure to \( \text{C}_2\text{H}_4 \) at 723 K for 15 minutes with the stereographic triangle inset. The image shows that C deposits did not form on the \{111\} or \{100\} planes of Ni, but deposits were the largest on the \{110\} and vicinal planes between the \{110\} and \{100\} (6).

![Figure 25: C deposition by C\(_2\)H\(_4\) on a spherical Ni S\(^4\)C observed using an optical microscope with stereographic triangle inset. C deposits did not form on the \{111\} or \{100\} planes of Ni, but deposits were the largest on the \{110\} and vicinal planes between the \{110\} and \{100\} (6).](image-url)
Whalley et al. used spherical Ni S\textsuperscript{4}C tips to study the adsorption of H\textsubscript{2}, C\textsubscript{2}H\textsubscript{2}, C\textsubscript{2}H\textsubscript{6}, and C\textsubscript{2}H\textsubscript{4} using Field Emission Microscopy (FEM). In an FEM experiment, a high voltage is applied to a spherical tip in UHV near a fluorescent screen to produce an image. The bright spots are formed by emission of electrons from the sample and can be directly correlated with the work function. Crystal planes with a higher work function will emit fewer electrons and appear as dark spots. The changes in work function can be correlated to the adsorption of different species on the surface. Whalley et al. determined that the trend in C\textsubscript{2}H\textsubscript{4} adsorption activity at 295 K were as follows: \{211\} > \{111\} > \{100\}. After heating the Ni S\textsuperscript{4}C to 623-673 K, the \{111\} and \{100\} planes desorbed C\textsubscript{2}H\textsubscript{4} while the \{211\} planes formed graphite or carbonaceous C layers due to the decomposition of C\textsubscript{2}H\textsubscript{4}. The trends in surface orientation with C\textsubscript{2}H\textsubscript{2} adsorption were similar to C\textsubscript{2}H\textsubscript{4} adsorption. At 295 K, C\textsubscript{2}H\textsubscript{2} preferentially adsorbed on \{211\} surfaces, but also adsorbed on \{210\} and \{320\} planes of Ni (165, 166).

Vang et al. used DFT combined with STM to study the dissociation of C\textsubscript{2}H\textsubscript{4} on stepped Ni crystal planes. In STM images of C\textsubscript{2}H\textsubscript{4} on a Ni\{111\} single crystal, C\textsubscript{2}H\textsubscript{4} only adsorbed and dissociated at room temperature on step edges present due to imperfections in the \{111\} plane. Islands did not form and C\textsubscript{2}H\textsubscript{4} did not adsorb on the \{111\} terraces. Exposure of Ni\{111\} to C\textsubscript{2}H\textsubscript{4} at 500 K showed growth of carbidic C islands from step edges. Using DFT, adsorption energies for C\textsubscript{2}H\textsubscript{4} on different surface sites were calculated. The energy for adsorption of C\textsubscript{2}H\textsubscript{4} on a step edge of Ni\{211\} is -0.76 eV while on the Ni\{111\} plane it’s -0.16 eV. These DFT calculations match the results seen in STM as
C\textsubscript{2}H\textsubscript{4} preferentially adsorbed at step edges. The reaction pathway for C\textsubscript{2}H\textsubscript{4} decomposition was calculated on different surfaces using DFT and the Ni\{211\} plane had a lower activation energy for each elementary step. They concluded that step edges are more active for C\textsubscript{2}H\textsubscript{4} adsorption and essential for C-C bond breaking (167).

Caracciolo \textit{et al.} also studied the decomposition of C\textsubscript{2}H\textsubscript{4} on Ni, but used a cylindrical Ni S\textsuperscript{4}C containing all crystal planes on the edge of the stereographic triangle from \{100\}-\{111\}-\{110\} (described previously) (163). Caracciolo \textit{et al.} exposed 0.1 Torr C\textsubscript{2}H\textsubscript{4} to the Ni S\textsuperscript{4}C at 550 K then heated the sample to 800 K and used AES at to look at the changes in amount of C deposited with surface orientation. They found that the deposition of C was anisotropic with maxima at the \{15,1,1\} and \{511\} planes and minima at the \{100\} and \{311\} planes. Upon heating the surface to 800 K, the anisotropy of C coverage on the surface increased with larger maxima forming on the \{111\}, \{110\}, and \{15,1,1\} with minima on the \{100\} and \{311\} planes. The results correlated well with the C\textsubscript{2}H\textsubscript{4} decomposition experiments performed by Cunningham on the \{100\} plane and \{100\} vicinals of the spherical Ni S\textsuperscript{4}C. Caracciolo \textit{et al.} discussed that some results were different than Cunningham’s around the \{111\} plane on Ni; in Cunningham’s experiment there was a minimum in C coverage around the \{111\} plane after exposure to C\textsubscript{2}H\textsubscript{4}. The reason for this discrepancy was attributed to the lower C\textsubscript{2}H\textsubscript{4} exposure and temperature conditions used by Caracciolo and that Cunningham in 1957 did not have techniques to look at impurities on the surface or defects in the crystal structure.
Davis and Somorjai studied the effect of step edges and kink sites on the adsorption of H$_2$ and hydrogenation and dehydrogenation of cyclohexene (C$_6$H$_{10}$) and cyclohexane (C$_6$H$_{12}$). TPD and uptake experiments were performed on Pt(12,9,8), Pt(10,8,7), Pt(654), and Pt(321). Each of these crystal planes contain \{111\} terraces with step edges and different densities of kinks. These experiments were compared to results on Pt(557), a crystal plane with only \{111\} terraces and step edges, and Pt(111). TPDs of H$_2$ adsorbed at 305 K were performed on each crystal plane. Three distinct peaks were present in the TPD spectra of adsorbed H$_2$ for Pt(12,9,8) at 353 K, 413 K, and 493 K while only the two lower temperature peaks were visible on the stepped Pt(557) surface and only the lowest temperature peak was observed on Pt(111). This experiment showed that the adsorption of H$_2$ was different on terraces, step edges, and kink sites and that H$_2$ desorption had the highest activation energy on kink sites followed by step edges (168).

For cyclohexene dehydrogenation at 423 K, the overall turnover number and poisoning time followed this trend: Pt(654) > Pt(557) > Pt(111). This result showed that the Pt(654), a surface with steps kinks and terraces, was a better catalyst than Pt(557), a surface with only steps and terraces, and Pt(111) was the least active and most easily poisoned. Cyclohexene hydrogenation also showed a similar trend in activity after adsorption of 1 ML O on each surface. For cyclohexane dehydrogenation activity at 423 K, (321) > (654) > (10,8,7) > (12,9,8) > (557) > (111). The surface with the highest kink density, (321), had the highest activity. This trend in surface orientation showed a positive correlation
between the density of kink sites and cyclohexane dehydrogenation activity. The surface orientations with kink sites present were more active than surfaces with step edges. They concluded that the presence of kink sites enhanced the overall activity for \( \text{H}_2 \) chemisorption and dehydrogenation of hydrocarbons and that the presence on chemisorbed \( \text{H}_2 \) at kink sites increases the stability of catalysts (168).

For hydrocarbon adsorption and decomposition, crystal planes that are more atomically rough like \{110\} or those with step edges are more active than \{100\} and \{111\}. For reactions involving hydrogenation and dehydrogenation of hydrocarbons, it appears that crystal planes with kink atoms (such as \{321\} and \{654\}) were the most active followed by crystal planes with step edges(\{755\} and \{h11\}) and lowest activity occurred on the low Miller index crystal planes. These trends were exhibited both in UHV conditions and under ambient pressure conditions.

2.3.4 Adsorption - \( \text{H}_2\text{O} \) and \( \text{H}_2\text{S} \)

The adsorption of \( \text{H}_2\text{O} \) and \( \text{H}_2\text{S} \) on \( \text{S}^4\text{Cs} \) was primarily studied by Ranke on different surface orientations of semiconductor materials. The adsorption of \( \text{H}_2\text{S} \) was first studied by Ranke on a cylindrical Ge \( \text{S}^4\text{C} \) using UPS and AES. After exposure to 2 L \( \text{H}_2\text{S} \) at 300 K, there was a maximum in coverage at the \{100\} plane and a minimum at the \{111\} plane showing a preferential adsorption on the \{100\} plane. There were also local maxima observed on the \{211\} and \{221\} planes and a local minima at the \{311\} plane. UPS was used to determine bonding state of the species adsorbed on the \{100\} and \{111\} planes of Ge. At
300 K, H$_2$S dissociated and formed adsorbed H and SH species on \{100\} while H$_2$S was molecularly adsorbed on the \{111\} plane. The enhanced adsorption of H$_2$S around the \{100\} plane was attributed to step edges and \{100\} terraces (169, 170). Ranke found similar results on a spherical lens S$^4$Cs of Si centered at the \{100\} plane as \{100\} terraces caused dissociation H$_2$S into H and SH species (17). H$_2$S adsorption was also studied on cylindrical GaAs S$^4$Cs, another common semiconductor material (169, 171-173). Although GaAs and Ge are isoelectronic, both had a very different orientation dependence for H$_2$S adsorption. For a 10 L exposure of H$_2$S at 150 K, the \{110\} plane and surface orientations between \{111\} and \{311\} had local maxima in coverage while the \{111\} and \{100\} planes had a local minima (169). As terminated surfaces had a higher sticking probability and higher coverage of sulfur than Ga terminated surfaces. Ranke concluded that \{110\} facets, step edges, and As terminated crystal planes preferentially adsorbed H$_2$S on GaAs (169, 173). After sputtering the GaAs cylinder surface, the adsorption of H$_2$S was enhanced showing that defects in surface structure become active sites for H$_2$S adsorption (171).

Ranke also studied H$_2$O adsorption on Si single crystals, cylindrical S$^4$Cs, and spherical lens S$^4$Cs. UPS was used to look at the binding state of H$_2$O on Si surfaces. H$_2$O on \{100\} planes formed a chemisorbed state even at temperatures as low as 100 K. This state of H$_2$O, called H$_2$O$^{(100)}$, preferentially adsorbs on \{100\} facets caused a rearrangement of surface atoms. At temperatures above 150 K, H$_2$O dissociates into H and OH on crystal planes containing \{100\} terraces (174, 175). Figure 26 shows a drawing of the spherical lens S$^4$C of Si.
centered at {100} used by Ranke in H$_2$O adsorption experiments. This S$^4$C contains eight repeated sections of the stereographic triangle on the surface and spans 15° from the {100} plane to the edge. On this Si{100} spherical lens S$^4$C, the presence of step edges caused a decrease in the adsorption and dissociation rate of H$_2$O and the saturation coverage of O decreased with increasing step density (17). The results on the spherical lens S$^4$C were confirmed using single crystal samples of Si as similar results were obtained (176, 177).

![Figure 26: Drawing of spherical lens S$^4$C of Si centered at the {100} plane. This spherical S$^4$C contains eight equivalent sections of the stereographic triangle, one of the sections is labeled with several crystal planes along the edge of one of the triangles (17).](image)

H$_2$O adsorption was studied by Ranke on Ge cylindrical S$^4$Cs with a [1$ar{1}$0] axis (170, 178). Ranke found that the behavior of H$_2$O on Ge is much different than H$_2$S adsorption on Ge. Although H$_2$O preferentially adsorbed and dissociated on {100} planes of Ge like H$_2$S, the sticking probability of H$_2$O across the
cylindrical Ge $^{4}$C is over 1000 times lower than H$_{2}$S. While H$_{2}$S preferentially adsorbed on crystal planes between the {111} and {311}, H$_{2}$O had no significant change in adsorption activity between these surface orientations. While H$_{2}$O has a maximum in H$_{2}$O coverage at {111}, the H$_{2}$S coverage has a minimum at {111}. UPS was implemented by Ranke to explain these differences. At 300 K, UPS measurements confirmed that H$_{2}$S adsorbs molecularly on Ge{111} while H$_{2}$O dissociates on Ge{111}. UPS also confirmed that the species formed on {100} after H$_{2}$O and H$_{2}$S adsorption are radicals of OH and SH. The most reactive crystal planes dissociate H$_{2}$S and H$_{2}$O while the least reactive crystal planes molecularly adsorb these species. Ge{100} dissociates H$_{2}$O into H and OH species completely from 140-300 K while on Ge{111} only a fraction of the H$_{2}$O molecules dissociate. At 450 K, H$_{2}$O dissociates fully into O and 2H while on Ge{100} the OH species remains stable. More work is required for a better understanding of adsorption of H$_{2}$O and H$_{2}$S on semiconductor materials.

There has been significant work on H$_{2}$O adsorption on semiconductor S$^{4}$Cs, but little research has been done on H$_{2}$O adsorption on S$^{4}$Cs of FCC metals to our knowledge. However, several researchers have used single crystal surfaces to understand the mechanism for H$_{2}$O adsorption and its dependence on surface orientation. Harrington et al. studied the associative and dissociative adsorption of D$_{2}$O on Ni{110} (179). D$_{2}$ desorption mass analysis was used to determine the activity of D$_{2}$O decomposition on the Ni{110} surface. Ni{110} was exposed to 5 x 10$^{-8}$ Torr of D$_{2}$O and the change in desorption of D$_{2}$ with time was measured. Between 500 and 800 K, D$_{2}$O dissociated into D$_{2}$ which desorbs into the gas
phase and O which remains on the surface. A maximum in D$_2$O dissociation activity occurred at 600 K on Ni\{110\}. After an induction period of 2 L exposure of D$_2$O with no measurable D$_2$ desorption, D$_2$ formation increased rapidly with a peak at 3 L exposure then decreased to zero gradually with exposure time. The D$_2$ desorption behavior was explained via an autocatalytic reaction mechanism. In the proposed mechanism, the presence of adsorbed oxygen accelerates the rate of D$_2$O dissociation autocatalytically until the surface adsorbed O accumulates on the surface and blocks sites from further D$_2$O adsorption. The proposed steps for this reaction included reversible adsorption of a weak chemisorbed D$_2$O molecule that once adsorbed, diffuses rapidly to either a defect site or an oxygen island edge where it decomposes into O adsorbed and D$_2$ gas (179).

Kasza et al. studied the adsorption of H$_2$O using TPD and desorption mass analysis of D$_2$O on Ni\{110\} and Ni\{760\} to study the effect of step edges on the reaction. The Ni\{760\} surface contains \{110\} terraces separated by \{100\} steps. The TPD spectra of a 0.75 ML of D$_2$O at 130 K on stepped Ni\{760\} had four desorption peaks corresponding to different adsorbed species: 160 K for multilayer, 212 K for chemisorbed layer, 250 K for H-bonded chemisorbed species, and 340 K for dissociated DO and O recombinative desorption. Desorption mass analysis showed that D$_2$O dissociated on Ni\{760\} into D$_2$ and O at temperatures as low as 398 K while D$_2$O didn’t dissociate on Ni\{110\} until > 500 K showing that the Ni\{760\} was much more active for D$_2$O autocatalytic decomposition than Ni\{110\} (52).
Bennendorf et al. also studied autocatalytic decomposition of H\textsubscript{2}O using Ni\{111\}, Ni\{665\}, and Ni\{221\} to look at the effect to step edges on the reaction kinetics. Using TPD of adsorbed H\textsubscript{2}O, they found that all three crystal planes contained a desorption peak at T=175-180 K, but Ni\{665\} and Ni\{221\} had higher temperature desorption peaks at 225 K, 260 K, and 325 K. The peak at 175-180 K was attributed to molecular desorption of H\textsubscript{2}O from \{111\} terraces, the peak at 225 K was attributed to molecular desorption of H\textsubscript{2}O from step edges, and the peaks at 260 K and 325 K were from associative recombination of dissociatively adsorbed H\textsubscript{2}O. Measurements of the work function of the surface after H\textsubscript{2}O adsorption was used to calculate the dipole moment of H\textsubscript{2}O on each surface. The dipole moment of H\textsubscript{2}O was higher on Ni\{665\} and Ni\{221\} compared to Ni\{111\} due to the presence of step edges (180).

Limited research has been performed to understand the effect of surface structure on H\textsubscript{2}O and H\textsubscript{2}S adsorption. For Ge and Si, the \{100\} plane is the most active surface orientation for the chemisorption and dissociation of H\textsubscript{2}S and H\textsubscript{2}O. Vicinal planes to Ge and Si\{100\} with step edges present are also active. For GaAs, the \{110\} plane and crystal planes with step edges present had the highest activity for H\textsubscript{2}S adsorption and dissociation. The adsorption of H\textsubscript{2}O on metals has not been studied on S\textsuperscript{4}Cs like semiconductors, but from the limited data it appears that H\textsubscript{2}O decomposition is autocatalytic on Ni and the reaction is enhanced by the presence of step edges.
2.3.5 Adsorption - Nitrogen Species

Several researchers studied the adsorption of non-diatomic N species such as NO$_2$, N$_2$O, and NH$_3$. Arlow et al. performed N$_2$O adsorption experiments on a cylindrical Cu S$^4$Cs centered at the [\(\bar{1}10\)] axis. At room temperature, N$_2$O dissociated into N$_2$, which desorbed into the gas phase, and O which remained adsorbed on the surface. AES was used to determine the change in O coverage with surface orientation. Maxima in the coverage of O was observed on the \{110\} and \{311\} crystal planes at every exposure of N$_2$O while minima in O coverage occurred on the \{100\} and \{111\} planes. The \{110\} plane was the most active for N$_2$O dissociation at low exposures \(< 60\) L. Arlow et al. concluded that the adsorption of N$_2$O is structure sensitive and more atomically rough crystal planes and those with step edges are the most active for N$_2$O dissociation. Step edges and atomically rough crystal planes were proposed to have an enhanced sticking probability of N$_2$O (181, 182).

NO$_2$ adsorption at 300 K on a cylindrical Ge S$^4$C was studied by Ranke using AES. The dissociation of NO$_2$ to O and NO occurred on all crystal planes (183). NO desorbed from the surface upon formation and O remained on the surface after dissociation. A minimum in O coverage was observed on the \{111\} planes of Ge. NH$_3$ adsorption was also studied by Ranke on the same cylindrical Ge S$^4$C at temperatures \(\leq 200\) K using UPS and XPS (184). The orientation dependence for molecular adsorption of NH$_3$ was much stronger than NO$_2$. At 200 K, NH$_3$ preferentially adsorbed on Ge\{100\} planes and vicinal surfaces to Ge\{100\} with minima in adsorption at Ge\{111\} planes. UPS confirmed that NH$_3$
chemisorbed on Ge\{100\} planes due to observed charge transfer to the surface and not on Ge\{111\} planes. The structure sensitivity of NH₃ adsorption was also studied on Ni single crystals theoretically using DFT. Vang et al. found that the rate determining step for NH₃ decomposition on Ni was the associative desorption of N to N₂ and that Ni\{110\} is much more active for NH₃ decomposition than Ni\{111\} and stepped Ni\{211\} (185).

2.3.6 Oxygen

2.3.6.1 Bulk Oxidation

The most widely studied adsorbate on S⁴Cs is O₂. The two phenomena studied for O₂ on S⁴Cs is O₂ adsorption and bulk oxidation. O₂ adsorption occurs at low partial pressures of O₂ and remains on the surface. Bulk oxidation occurs at high partial pressures of O₂ and causes an oxide to form on the surface that can grow and diffuse into the bulk of a material. One of the first reported oxidation studies was done by Elam who studied the oxidation of Cu at temperatures > 1173 K in air (186). X-ray diffraction was used to study the oxidation pattern on a polycrystalline Cu sample and Elam found that oxide striations occurred preferentially along \{110\} and \{100\} planes of Cu and not on \{111\} planes. The oxide formed was Cu₂O and maintained the same crystal structure as the underlying plane before assuming a \{110\} orientation. Some of the earliest work on understanding the structure sensitivity of bulk oxidation was done by Mehl and McCandless in the early 1930’s studying the oxidation of several single crystal planes of Fe, a BCC metal. At temperatures < 473 K in air, the rates of oxidation exhibited the following trend: Fe\{100\} > Fe\{111\} > Fe\{110\}. The oxidation of
single crystals of Cu was also studied by Mehl and McCandless and the rate of oxidation of the three low Miller index planes of Cu was found to vary with temperature and partial pressure of O₂ (187, 188).

Gwathmey was the first reported author to study oxidation on an S₄C. Gwathmey used spherical Cu S₄Cs to study the oxidation of Cu under various temperatures and partial pressures of O₂ (189-191). X-ray diffraction was used to determine the structure of the oxide formed and interference microscope pictures were taken to examine the thickness of the oxide layer formed on each crystal plane on the surface. Gwathmey found that in air at temperatures from 473-1273 K, the {100} planes of Cu oxidized faster than the {111} planes. After an exposure of air for one minute to the Cu S₄C at 473 K, planes along {hk0} lines and {100} planes contained the highest oxide thickness, much thicker than the {110} and {111} planes. Between 30 minutes and an hour, {hk0} and {100} planes still had the thickest oxide followed by the {110} and {311} planes while {111} planes remained oxide free (191). Gwathmey’s hypothesis was that densely packed crystal planes are less active for oxidation in air than atomically rough crystal planes. Excluding the {100} plane, this trend was observed in his results. The oxidation of spherical Cu S₄Cs in air was also studied by Gwathmey at temperatures between 343 and 453 K (192). In this study, the oxide thickness was measured with time using an interference microscope only on the {100}, {111}, {110}, and {311} planes on the Cu sphere. At all temperatures in this range, the trend for film thickness and rate of oxidation was {100} > {111} > {110} > {311}. This is different than the trend exhibited from 473-1273 K, but
Gwathmey admits that although each surface was carefully prepared, techniques were not available to measure impurities on each surface that could affect the activity. Either way, these experiments showed that oxidation of Cu is a structure sensitive reaction and the structure sensitivity of oxidation can change with temperature.

Gwathmey also looked at the oxidation activity of spherical Cu S^4Cs by using stoichiometric mixtures of H_2 and O_2 gas (189, 193, 194). The effect of surface orientation on H_2O formation and oxidation of Cu was analyzed along with the change oxidation activity with partial pressure of O_2. For 4:1 and 3:1 ratios of H_2 to O_2 between 673 K and 803 K, the \{100\} face of Cu was the most active followed by \{110\} with the \{111\} plane having the lowest oxidation activity. Experiments using a range of 0.5-20% O_2 partial pressures were also performed at 673 K and the change in oxidation activity of Cu\{100\} and Cu\{111\} was observed. The results showed that Cu\{111\} was more active between 0.5 and 2.5% O_2 while for all experiments above 2.5% O_2, Cu\{100\} was more active than Cu\{111\}. These experiments showed that the structure sensitivity of oxidation depends on the partial pressure of reactants as well as the temperature.

Gwathmey also studied the changes in the oxide crystal structure with oxide thickness on spherical Cu S^4Cs. The Cu_2O oxide consistently formed first in each experiment and was crystalline followed by CuO which is polycrystalline and disordered. The oxide thickness of the transition from Cu_2O to CuO varied with surface orientation at all temperatures studied. For example, at 450 °C the oxide formed on the \{100\} plane remained crystalline up to 500 nm thick while
the oxide on the \{111\} plane became polycrystalline after a thickness of 250 nm. The orientation of the Cu$_2$O oxide surface varied depending on the Cu crystal plane before exposure. While the \{100\} and \{111\} planes formed a Cu$_2$O\{111\}, the \{110\} and \{311\} plane formed a Cu$_2$O\{110\} (195).

Menzel et al. also studied the oxidation of spherical Cu S$^4$Cs prepared in vacuum from solidification of droplets of melted metal on a SiO$_2$ substrate (15, 196-198). The type of oxide formed on the spherical droplets varied with surface orientation of Cu. Using LEED, Menzel created a map of six different oxide regions and their location on the edge of the stereographic triangle. Figure 27 shows the domain map of the different oxide structures observed as well as the superstructure in Wood’s notation of the different regions. The \{100\} and \{111\} planes with the highest atomic density and no step edges had distinct behavior compared to planes with step edges. For example, the \{100\} plane formed c(2x2) oxide structure while oxides on crystal planes between \{110\} and \{111\} planes all have the same c(6x2) pattern. An important find worth noting is that the change between oxide regions between the \{100\} and \{110\} plane occur at the \{210\} plane, the maximum in step density on that edge of the stereographic triangle. The \{111\} plane did not form an oxide structure showing that the conditions studied were not able to oxidize the \{111\} surface (15, 196-198).
The main find from studies of the bulk oxidation of Cu S\textsuperscript{4}Cs is that the reaction is highly structure sensitive and the type of structure sensitivity depends on both the temperature and the partial pressure of O\textsubscript{2}. Overall, the \{100\} plane of Cu was more reactive for bulk oxidation than \{111\} plane. For both Fe and Cu, the \{100\} plane was the most active toward bulk oxidation over the more atomically rough \{110\} for Cu and \{111\} for Fe. This is very different than the trend exhibited for the adsorption of other species where more atomically rough crystal planes are consistently more active.

Figure 27: Domains of oxide structures determined by LEED on a spherical Cu crystal. Region 1 forms a c(6x2) oxide structure, Region 2 forms a p(1x1) oxide, Region 3 at the \{100\} plane forms a distinct c(2x2) overlayer, Region 4 forms c(1x1), Region 5 at the \{111\} plane doesn’t form an oxide under the experimental conditions, and Region 6 forms (311) and (322) planes but no oxygen overlayer structure (15).
2.3.6.2 Oxygen Adsorption

Several researchers studied the adsorption of O\textsubscript{2} in UHV. Woodruff \textit{et al.} used a cylindrical Cu S\textsuperscript{4}C with a [\(\bar{1}10\)] axis to analyze the adsorption of O\textsubscript{2} in UHV using AES. Figure 28 (left) shows a drawing of the cylindrical Cu S\textsuperscript{4}C used by Woodruff. The [\(\bar{1}10\)] axis was chosen for the cylindrical Cu S\textsuperscript{4}C studied because it includes the three low Miller index crystal planes, \{100\}, \{110\}, and \{111\} planes on the same surface at 4 different locations 90° apart. The surface of the cylinder includes crystal planes along the edge of the stereographic triangle from \{100\} – \{111\} – \{110\} and only varies in 1-D radially around the axis of the cylinder, and not along the axis of the cylinder. Figure 28 shows the coverage of O\textsubscript{2} versus orientation on the cylindrical Cu S\textsuperscript{4}C after exposure to 2 L and 5 L O\textsubscript{2} at room temperature in a UHV chamber. He found that atomically rough surfaces like \{311\} and \{110\} had a higher sticking probability of O\textsubscript{2} than atomically smooth surfaces like \{111\} and \{100\} (199, 200).

Woodruff \textit{et al.} performed similar experiments on O\textsubscript{2} adsorption on Ni using a cylindrical Ni S\textsuperscript{4}C with a [\(\bar{1}10\)] axis (201). Unlike Cu, the initial adsorption activity of O\textsubscript{2} was isotropic, but the bulk oxidation activity of Ni was highly anisotropic. According to Woodruff, the Ni\{111\} surface oxidized fastest and the Ni\{100\} surface oxidized the slowest. The explanation of this trend was attributed to the number of oxide nuclei on each surface orientation. The \{111\} surface has a higher number of nuclei during oxidation and the oxide layer on
{111} has a larger distance from the Ni substrate layer than {100}. Step edges on Ni had the opposite effect than on Cu by disrupting further adsorption of O₂ past θ = 0.25.

Gardiner used a similar technique as Woodruff to study O₂ adsorption of a cylindrical W S₄C with the same [110] axis (8). The sticking probability of O₂ was similar on all crystal planes of W except an absolute minimum at the {110} planes of the cylinder, the closest packed crystal plane for a BCC metal.

Ranke also studied changes in O₂ adsorption activity with surface orientation using a cylindrical GaAs S₄C with a [110] axis and AES (202-205). Surfaces of GaAs have the added complexity of being As or Ga terminated e.g. the (111) plane is Ga terminated while the (111) plane is As terminated. Using AES, Ranke found that the sticking probability of O₂ on low Miller index planes exhibited the following trend: {100} > {111} > {110} and step edges enhanced the sticking probability of O₂ on the surface (204, 205). Ga terminated crystal planes were more active than As terminated planes. UPS spectra were used to determine the state on O₂ binding on the surface. O adsorbed at step edges had a higher binding energy than O adsorbed at terraces (203). Ranke also studied the orientation dependence of O₂ adsorption of a cylindrical Si S₄C with a [110] axis using AES (206, 207). The O₂ adsorption activity of Si was orientation dependent, but had a weaker dependence than GaAs. For 2 L, 3.5 L and 10 L exposures of O₂ at 300 K, there were clearly defined minima in O coverage at the {110} and {311} planes with maxima at the {100} and {111} planes. After a
monolayer of O$_2$ had been adsorbed, the bulk oxidation of the surface became isotropic.

O$_2$ adsorption was also studied by Ranke on a cylindrical Ge S$^4$C at 300 K and 650 K (208). Like GaAs, there is enhanced O$_2$ adsorption at 300 K on stepped surfaces between the {111} and {110} planes showing that O$_2$ adsorption is enhanced by step edges. There is also a maxima at the {100} plane and a minima at the {111} and {110} plane similar to the trends seen for H$_2$O adsorption. At 650 K, the O$_2$ adsorption behavior changes slightly. Step enhanced adsorption still occurs on vicinal surfaces to Ge{110} and Ge{311}, but there is a maximum in adsorption on Ge{111}. The changes in behavior from 300 K to 650 K at the {111} plane were attributed to diffusion of O$_2$ into the lattice which can occur at 650 K and cause surface reconstruction. The UPS spectra of Ge after O$_2$ adsorption also showed that the shift in the oxidation states of Ge varied with crystal structure where {100} had the greatest shift away from the Fermi energy for all states at all temperatures.

Lawton et al. used spherically curved Cu S$^4$Cs to study the O$_2$ adsorption activity of Cu. Spherically curved S$^4$Cs have an advantage over cylindrical S$^4$Cs because they span a 2-D area of the stereographic triangle which includes crystal planes with both step edges and kinks within the stereographic triangle (12). The bottom left of

Figure 29 shows an image of the Cu S$^4$C along with the location of different high symmetry directions on the S$^4$C surface. The surface studied was
centered at the (111) plane of Cu and spanned 11° from the center in all directions and called Cu(111) ± 11° S^4C. The top left of

Figure 29 shows the area spanned on the stereographic triangle by the Cu(111) ± 11° S^4C and the locations of the high symmetry directions on the triangle. Spatially resolved XPS was implemented to look at changes in the coverage of O with exposure and could focus on a region of the S^4C as small as 200 μm in diameter, which spans less than 0.1° on the stereographic triangle taking into account the radius of curvature. The XPS was coupled with STM measurements to look at the atomic structure of the oxide and determine if the step edge orientation had an effect on the O_2 adsorption activity and oxide structure. The right plot on

Figure 29 shows the coverage of O along high symmetry directions of the Cu(111) ± 11° S^4C after exposure to 30 L O_2 at 300 K. The coverage was determined using spatially resolved XPS from {111} towards the {100} plane and from {111} towards the {110} plane. As the high symmetry direction changes, so does the orientation of the step edge. On the Cu(111) ± 11° S^4C, crystal planes located from {111} towards the {100} plane (green direction) have {100} oriented step edges while crystal planes from {111} towards the {110} plane (red direction) have {110} oriented step edges. After 30 L exposure, the coverage of O increased with increasing distance away from the (111) plane in all directions. Since the step density also increases with distance from the (111) plane, the results showed that the O_2 adsorption activity increased with increasing step density. Figure 30 shows STM images of the Cu(111)±11° S^4C after exposure to
30 L O$_2$ at 300 K. The green line shows the direction from \{111\} towards the \{100\} plane and the red line shows the direction from \{111\} towards the \{110\} plane. In each image the oxide, Cu$_2$O, formed preferentially at the step edges represented by the dark patches. The STM image on the green line shows that the (100) step edges remain straight while the STM image on the red line shows the (110) step edges forming a sawtooth pattern once O is adsorbed with the edges forming parallel to \{100\} planes. These images show that after O$_2$ adsorption, (100) step edges remained straight and maintain their crystal structure while (111) step edges reconstruct to form (100) step edge facets. From both spatially resolved XPS and STM, the results show that the O$_2$ adsorption activity increases with step density and although (100) is the preferred orientation of the oxide formed at step edges, the oxidation activity does not change with step orientation (209).

The adsorption of O$_2$ on Pt was studied using multiple single crystal surfaces and not S$^4$Cs. Ross used Pt electrodes of Pt\{111\}, Pt\{100\}, and Pt\{311\} to study the orientation dependence of the O$_2$ reduction reaction on Pt in a 3-electrode setup in an acidic environment (210). Although the overall activity of each Pt surface was similar, the cyclic voltammetry measurements showed that O$_2$ adsorbed on the Pt\{311\} surface had a higher binding energy than on Pt\{100\} and Pt\{111\} showing that step edges bind O$_2$ more strongly than terraces on Pt.

For O$_2$ adsorption studies, the most widely studied metal was Cu. Over a span of 80 years and using a multitude of different experimental techniques, the results are similar. Crystal planes with a higher density of step edges are more
active for O$_2$ adsorption on Cu than atomically flat crystal planes. Of the three low Miller index crystal planes of Cu, the activity for O$_2$ adsorption has the following trend: \{110\} > \{100\} > \{111\}. Other surfaces that exhibited a similar trend to Cu are Si, Ge, GaAs, and Fe. This trend is different than for bulk oxidation where the \{100\} plane is more active for bulk oxidation than \{110\}. This shows that although the activity for oxygen adsorption is higher on \{110\}, the oxide grows faster on the \{100\} plane. More work is required to fully understand the nature of the structure sensitivity of the oxidation of Pt, Ni and W. The change in structure sensitivity with temperature and partial pressure needs to be studied further in order to gain a true understanding of the effect of surface structure on oxygen adsorption activity.

Figure 28: Left: Drawing of Cu cylindrical S$^4$C used in experiments by Woodruff et al. Right - Coverage of O from AES signal after exposure to 2 L and 5 L O$_2$ at 300 K. There are maxima in the spectra at the \{311\} and \{110\} planes and minima at the \{111\} and \{100\} planes (199).
Figure 29: Bottom left) Image of the Cu(111)±10° S⁴C along with high symmetry directions. Top left: Area spanned by Cu(111)±10° S⁴C on the stereographic triangle and corresponding high symmetry directions. Right: Spatially resolved XPS spectra of Cu(111)±10° S⁴C after exposure to 30 L O₂ at 300 K. The percent O was calculated based on the peak areas from Cu and O spectra. The coverage of O increased with increasing step density (209).

Figure 30: STM images of several crystal planes on Cu(111) ± 10 S⁴C after exposure to 30 L O₂ at room temperature. Images shown are 100 x 100 nm. Inset triangles show the edges of {100} planes on the surface. Adsorption of O₂ caused faceting of (110) step edges while (100) step edges remained straight (209).
2.3.7 Etching

Another chemical phenomena studied on $S^4Cs$ is etching. The rate of etching by both liquids and gases has been shown by many researchers to depend on surface orientation. In general, the low Miller index planes remained on surfaces after etching compared to surfaces with step edges and kinks. The difference between the etching rates on the three low Miller index crystal planes changed depending on the etching conditions.

Gwathmey analyzed the changes in electrochemical etching with surface orientation on spherical Cu $S^4Cs$. When a Cu $S^4C$ was immersed in a CuSO$_4$ and H$_2$SO$_4$ mixture, it became an octahedron showing that the {111} planes of Cu etched faster than the {100} planes. Gwathmey used the same experiment to show that for the rate of ortho-phosphoric acid etching on Cu, {110} > {111} > {100} (211).

Lacmann et al. developed a theory of etching anisotropy by studying the crystal faces present on Cu spheres after etching. This theory was tested using several experiments on spherical Cu $S^4Cs$. According to the theory, the crystal planes present on a single crystal sphere after etching, called dissolution forms, consist of microscopic terraces of equilibrium faces. Dissolution forms of etched spherical crystals depend on the crystal planes present before etching at equilibrium (or equilibrium forms), velocity of etching at step edges, and radius of curvature of spherical crystals. Faces that dissolve the fastest are those present in the highest amount after etching/dissolving while the opposite is true for crystal
growth (212). This theory was also implemented to determine the relationship between step spacing and the velocity of dissolution. Equation 2.12 shows the dissolution velocity, \( v_s \), as a function of step spacing, \( \lambda \), the concentration gradient between the surface and saturated solution, \( \Delta C \), and \( K' \), a coefficient representing the ratio of the velocity of the detachment of step edge atoms from the crystal and the velocity of the diffusion of detached atoms from the surface to the bulk solution (213).

\[
v_s = a\Delta C \frac{(\lambda^2 + 1)^{1/2}}{K' + (\lambda^2 + 1)^{1/2}}
\] (2.12)

To test this theory, two separate experiments were performed. First, spherical Cu S\(^4\)Cs were immersed in solutions of HNO\(_3\) at concentrations from 3.7 to 21 mol % held at 298 K, 323 K, 358 K, and boiling temperatures to test the effect of temperature and dissolution velocities on etching. The three crystal planes present after etching in each condition were \{311\}, \{111\}, and \{100\} planes along with macroscopic etch pits. The velocities of dissolution were then calculated based on the width of the etched faces and the distance of each plane to the center of the crystal. The velocities of dissolution increased with increasing concentration of HNO\(_3\) and increasing temperature (214). The theory matched the predicted crystal plane present at each micro facet on the crystal sphere. The dissolving form present on each crystal plane was dependent on the value of \( K' \). If the velocity of detachment of step atoms is high at values of \( K' > 10 \), then the crystal will retain its spherical shape, but if the velocity of volume diffusion is high at values of \( K' \leq 10 \), the crystal will form a flat region of one crystal.
orientation. In another experiment, electrochemical etching was performed on the spherical Cu S\(^4\)Cs in an H\(_2\)SO\(_4\) and CuSO\(_4\) solution with varying anodic overpotentials to observe differences in the dissolution forms. Using an overpotential of \(> 100\) mV caused isotropic etching of the Cu spheres while using an overpotential of 20 and 60 mV caused the formation of micro facets of \{111\} planes on the surface with \{100\} steps. This showed that the overpotential directly controlled the velocity of the detachment of steps and thus controlled the etching properties of Cu spheres (215).

Schmidt et al. performed extensive studies of the etching of Pt microspheres under various atmospheres at high temperatures to analyze the faceting behavior using Scanning Electron Microscopy (SEM) (19, 21, 216, 217). SEM was used to image the spheres after etching and laser reflectance measured the area of different facets on the sphere. The size of each microfacet was estimated from the reflectance measurement and their location on the sphere was used to determine the orientation of each flat. Plots of facets formed over the entire stereographic triangle were constructed using these techniques. Schmidt found that at high temperatures in NH\(_3\), CO, and C\(_3\)H\(_8\) atmospheres at temperatures \(> 900\) K the types of facets formed varied not only with the type of gas but also with the partial pressure of gas exposed to each Pt sphere. Figure 31 shows SEM images of two Pt microspheres, one after exposure to NH\(_3\) at 1250 K (top), the other one after exposure to CO at 1150 K (bottom) along with a stereographic triangle for each reaction showing the different facets formed based on their crystallographic location. For NH\(_3\) etching, the Pt\{111\}, \{100\}, \{110\},
and $\{421\}$ planes remained on the surface of the sphere. For CO etching, Pt$\{111\}$, $\{100\}$, $\{110\}$, and $\{310\}$ planes were the most stable and remained on the surface. Areas around the Pt$\{100\}$ and $\{111\}$ planes increased on vicinal surfaces while planes located within the stereographic triangle and vicinal to Pt$\{110\}$ formed $\{421\}$ facets in NH$_3$ environments and $\{310\}$ facets in CO environments. This result shows that the reacting gas has a clear effect on the faceting behavior and surface energy of different crystal planes. Not only did the gas present affect the faceting behavior, but the partial pressure of a reactant also changed the surface orientations present on the Pt microspheres. In a 10% NH$_3$ atmosphere, the Pt$\{210\}$ plane was not present on the stereographic triangle while in 20% NH$_3$ atmosphere, the Pt$\{210\}$ plane formed in several regions near the location of the $\{210\}$ plane on the surface. In every case studied, the low Miller index planes of $\{111\}$ and/or $\{100\}$ were present most likely due to their low surface energy (19). A correlation between the diameter of the sphere and the stability of certain crystal planes was also determined experimentally by Schmidt et al. At a critical radii, if a crystal plane becomes meta-stable or unstable and will form facets of a low surface energy crystal plane (21). Schmidt also studied electrochemical etching of these Pt microspheres using cyanide and aqua regia. In these systems, the change in etching rate with surface orientation was determined and rate of etching followed this trend in each case: $\{210\} > \{110\} > \{100\} > \{111\}$ which happens to be the same trend as the surface energy (217).
In each study of etching, the low Miller index crystal planes of {111}, {100}, and {110} remained on S\textsuperscript{4}C surfaces after each experiment. This trend was seen for high temperature etching by gases in vacuum, etching by acids in solution, and by electrochemical etching. Whether the {111}, {100}, or the {110} plane was more stable changed with the etching conditions and the metal. The {111} and {100} planes have the lowest surface energy and it makes sense that the lowest energy crystal planes are the most prevalent after etching.

Figure 31: Right - SEM micrographs of Pt spheres after etching in 20% NH\textsubscript{3} in air at 1250 K and 50% CO environments in air at 1150 K. Left - Stereographic triangles showing crystal planes present over all regions after etching. After exposure to 20% NH\textsubscript{3} at 1250 K, the Pt microsphere contained facets of {111}, {100}, {421}, and {110}. After exposure to 50% CO at 1150 K, the Pt microsphere contained facets of {111}, {100}, {310}, and {110} (19).
2.3.8 Removal of Surface Species

The removal of adsorbed species by gas phase reactants using $S^4Cs$ has also been studied, but not as extensively as adsorption phenomena. Several researchers studied the change in removal rate of several adsorbed species with surface orientation. After forming an isotropic layer of an adsorbate on an $S^4C$, the removal of the adsorbate was analyzed by measuring the changes in amount remaining on the surface with orientation using UHV techniques such as XPS and AES.

Caracciolo et al. studied the removal of C by O$_2$ after C$_2$H$_4$ decomposition from a Ni cylindrical $S^4C$ containing a 1-D path on the stereographic triangle from \{100\}-\{111\}-\{100\} (mentioned previously) (163). O$_2$ was exposed to the surface at 1 x $10^{-7}$ Torr at 800 K in UHV to remove the adsorbed C and AES was used to monitor the change in C signal with time. Surface orientations with step edges had a faster removal rate of surface C than the low Miller index planes of \{111\} and \{100\}. The removal rate of C on stepped crystal planes and the \{110\} plane was autocatalytic while the removal rate was first order on the \{111\} and \{100\} crystal planes of Ni. This showed that C adsorbed on atomically rough crystal planes such as \{110\} and stepped crystal planes are more active toward oxidation than on \{111\} and \{100\} planes. Caracciolo et al. also studied the removal of C by H$_2$ after CO decomposition. In this experiment, the Ni cylindrical $S^4C$ was exposed to 0.6 Torr CO at 600 K for 10 min to form a uniform layer of C. The cylindrical Ni $S^4C$ was then exposed to 2 Torr of H$_2$ at 600 K and the removal of C was measured after 10 minutes using AES (18).
coverage of C was the lowest on crystal planes between \{331\} and \{110\} and between \{211\} and \{111\} while the coverage of C was the highest on crystal planes between \{311\} and \{100\}. Ni\{111\} and Ni\{100\} had the lowest initial coverage of C and the lowest rate of C removal from the surface. The orientation dependence of surface C was attributed to the presence of step edges with terraces enhancing H$_2$ adsorption to form hydrocarbons to remove adsorbed C. Caracciolo also claimed that the phase of the deposited carbon played a role in the rate of C removal. The phase of C was estimated from shifts in the C peak location in AES. As the surface roughness and step density increased, the amount of graphitic C increased and was more easily removed from the surface than carbidic C. Another interesting phenomena is that the step orientation had a significant effect on the rate of C removal by H$_2$. The \{110\} step edges, present on crystal planes between \{111\} and \{110\}, had a very high removal rate of C. For \{100\} step edges, present on crystal planes between \{111\} and \{100\}, a transition in activity occurs at the \{311\} plane, the maximum in \{100\} step density. There is a sharp decrease in the amount of C removed for surface orientations between \{311\} and \{100\} which contain crystal planes with \{100\} terraces and \{111\} steps. An interesting future study would be to determine whether the step orientation or terrace orientation had an effect on the phase of C formed and its removal rate by H$_2$ and O$_2$.

Arlow et al. performed a similar experiment as Caracciolo et al. using a Cu cylindrical \textsuperscript{84}C with a [1\overline{1}0] axis to study the removal of adsorbed O$_2$ using CO and H$_2$ (181). Before each experiment, 5000 L of O$_2$ was exposed to the Cu
cylinder enough for isotropic adsorption of O to form a uniform layer on each crystal plane on the surface. The rate of O removal was monitored with exposure to CO and exposure to H₂ (in separate experiments). Figure 32 shows the coverage of O versus orientation on the cylindrical Cu S⁴C after various exposures of CO at 610 K. Surface orientations with a high coverage of O remaining on the surface are the least active. For O removal by CO, the highest activity was seen on crystal planes between {311} and {100} and between {311} and {111}. Minima in activity were seen on the {311}, {110}, and {100} planes. These results showed that the rate of O removal by CO is higher on surfaces where both step edges and terraces are present. This is in contrast to the results for O₂ adsorption discussed previously where the maximum activity occurred on the {311} and {110} planes which have maxima in the density of step edges. Both O₂ adsorption and CO oxidation reactions were considered highly structure sensitive, but the trend for CO oxidation was much different than for O₂ adsorption studied previously (182). Figure 33 shows a plot of the experimental data with a model of the rate of removal of O by CO on different surface orientations. The removal of adsorbed O by CO followed a Langmuir-Hinshelwood type mechanism as the removal rate of O was slow at the beginning of CO exposure, reached a maximum, then decreased to zero. Proposed CO adsorption sites were exposed metal atoms on the surface and these sites were needed for CO to react with adsorbed O to produce CO₂. Arlow further postulated that CO preferentially adsorbed to the top of step edges while O₂ adsorbed to the bottom of step edges.
Hopster *et al.* performed a similar experiment as Arlow *et al.* to study oxidation of CO to CO$_2$ by surface O on Pt single crystals and the effect of partial pressure on reactivity (218). Hopster used a Pt{111} and Pt{14, 1, 1} to look at the effect of step edges on the sticking probability of O$_2$ and the reaction probability of CO$_2$ formation. The sticking probability of O$_2$ and coverage of O was higher on the stepped Pt{14, 1, 1} than on Pt{111} at all partial pressures of O$_2$/CO studied. However, the reaction probability for CO$_2$ formation on both surfaces depended heavily on the partial pressure ratio of O$_2$ to CO or $P_{O_2}/P_{CO}$. For $P_{O_2}/P_{CO} < 2$, the stepped Pt(14, 1, 1) surface had a higher reaction probability while for $P_{O_2}/P_{CO} > 2$, Pt(111) had a higher reaction probability. This trend was attributed to the blocking of active sites by O$_2$ adsorbed at step sites. At lower O$_2$ partial pressures, there are more empty sites available for CO adsorption.

In this section, C removal and O removal by gas species was studied on Cu, Ni, and Pt single crystals and S$^4$Cs. For these reactions, the common trend exhibited is that crystal planes with both terraces and step edges present were the most active. This is counter to what was seen for diatomic adsorption and O$_2$ adsorption as the {311} and {110} planes were the most active but for C and O removal these planes were inactive. The hypothesis is that for C and O removal, terrace sites are needed for the adsorption of gaseous species to react with the adsorbed species at the step edges. On {311} and {110} planes, the surface is saturated with adsorbed C or O and there are fewer empty sites for the gaseous species (H$_2$, CO, O$_2$) to adsorb and react.
Figure 32: Coverage of O versus orientation on a cylindrical Cu $S^4$C after exposures to CO at 610 K (219). For O removal by CO, the highest activity was seen on crystal planes between Cu{311} and Cu{100} and between Cu{311} and Cu{111}. Minima in activity were seen on Cu{311}, Cu{110}, and Cu{100}. These results showed that the rate of O removal by CO is higher on crystal planes where both step edges and terraces are present.
Figure 33: Plotted rate of removal of adsorbed O by CO from a cylindrical CuS4C with a [1\overline{1}0] axis at several surface orientations. The rates were calculated from plots of the change of O coverage with exposure of CO measured using AES. Planes between Cu\{311\} and \{100\} and between Cu\{111\} and Cu\{311\} were the most active for O removal from the surface (181).
2.4 Discussion of Chemical Phenomena

There have been numerous papers published on changes in chemical phenomena with surface orientation. The quantity monitored in most studies is the coverage of adsorbates and how it changes with time or exposure, but other researchers use sticking coefficient, adsorption energy, and binding energy when the calculation is possible. The most common experiments on both single crystals and S^4Cs were the determination of the activity on the three low Miller index crystal planes: \{100\}, \{110\}, and \{111\}. From a qualitative perspective, the adsorption or dissociation activity of diatomic molecules is the highest on the \{110\} plane, followed by the \{100\} plane, with the closest packed \{111\} plane having the lowest activity. This trend was consistently observed in UHV studies on both single crystal and S^4Cs and most researchers concluded that more atomically rough crystal planes were the most active. This overall trend is not absolute and can change with partial pressures of reactants and temperature. When high Miller index crystal planes were used in experiments, or planes containing step edges and kinks, the activity for diatomic molecule adsorption or dissociation was typically higher than the low Miller index crystal planes. In some cases, the \{110\} plane had a similar activity to crystal planes with step edges, but this is expected at the \{110\} plane is considered to be a fully stepped surface (the surface atoms have a coordination number of 7).

Hydrocarbon species and N containing species followed a similar qualitative trend as diatomic molecules. Crystal planes with step edges were more active toward adsorption of \text{NO}_2, \text{NH}_3, \text{N}_2\text{O}, \text{and hydrocarbon dissociation and}
decomposition to forming a surface C species. This trend was consistent for studies in both UHV and at ambient pressures. For hydrocarbon dehydrogenation and hydrogenation, surfaces with a larger density of low coordination atoms, whether they are step edges, kink sites, or defects, had a higher reaction rate than atomically flat low Miller index crystal planes. Whether step edges or kinks have a higher activity toward these reactions is not clearly defined.

Adsorption of H$_2$S and H$_2$O was mostly studied on semiconductors. For Ge and Si, the {100} plane and crystal planes with step edges had enhanced chemisorption activity at low temperatures, and enhanced dissociation activity at temperatures above 300 K. Adsorption of these species has not been studied on S$^4$Cs of FCC, BCC, or HCP metal crystals to the best of our knowledge. More work is needed to obtain a better understanding of the effect of surface structure on H$_2$O and H$_2$S adsorption.

For the studies of oxidation and O$_2$ adsorption on S$^4$Cs, Cu was the most commonly studied metal. In almost every study mentioned, the {111} plane of Cu was the least active toward oxidation and O$_2$ adsorption except at very low partial pressures of O$_2$ at pressures > 1 Torr. In the early studies by Gwathmey, the {100} plane of Cu was the most active toward oxidation at ambient and high pressures of air and O$_2$. In UHV studies, the {110} plane and surfaces with step edges had the highest activity toward O$_2$ adsorption. From the study by Lawton et al., the Cu$_2$O preferentially formed along {100} step edges and {111} step edges reconstructed to form the preferred {100} step edge as the amount of O adsorbed increased. However, the rate of O$_2$ adsorption was the same on both step
orientations. It appears that the preferential orientation for the oxide to grow is the \{100\} plane of Cu which would explain why at higher pressures of air and O\textsubscript{2}, Cu\{100\} has the highest rate of oxide formation. For BCC metals studied (W and Fe), the lowest rate of oxidation occurred on the \{110\} plane, the closest packed plane of the BCC metal. It appears that for both FCC and BCC metals, the closest packed plane had the lowest rate of oxidation and O\textsubscript{2} adsorption. For the O\textsubscript{2} adsorption studies on semiconductor materials by Ranke, \{100\} planes and planes with step edges had the highest rate of oxidation. In general, it appears that the \{100\} plane has the highest rate of oxidation and crystal planes with step edges have the highest rate of initial O\textsubscript{2} adsorption and dissociation.

Surfaces remaining on S\textsuperscript{4}Cs after etching were either the \{111\}, \{100\}, or \{110\} planes. The rates of etching between the three low Miller index planes depended on the concentration of etching solution, the type of etching solution, the temperature, and the initial orientation of the single crystal or S\textsuperscript{4}C. There was no clear evidence in each of the papers mentioned whether there was an absolute answer to which crystal plane was the most resistant to etching.

For the removal for surface C and O, crystal planes containing both step edges and terraces had the highest rate of reaction. The consensus among the researchers mentioned was that the initial deposition of C and O occurred preferentially at step edges. Without empty metal sites available at terraces, additional gas species cannot adsorb and react with the surface C and O at step edges. This lead researchers to the idea that this type of reaction follows a Langmuir-Hinshelwood mechanism as opposed to an Eley-Rideal mechanism.
where the gaseous species does not adsorb to the surface before reacting. This is why crystal planes between \{311\} and \{111\} or \{311\} and \{100\} were the most active for these types of reactions while crystal planes like \{110\}, a fully stepped surface, and \{311\} with the highest step density, only had moderate activity.

For the adsorption studies, the overall trend is that crystal planes containing step edges were more active in each reaction. This gives evidence to the idea that on real catalysts, the active sites for reaction are low-coordination number atoms (7 or less). Whether step edges (coordination number of 7) or kink sites (coordination number of 6) are more active is still not well understood. The majority of studies on S\(^4\)Cs focus on the effect of changing step density. Cylindrical S\(^4\)Cs contain only the low Miller index crystal planes and crystal planes with step edges so studying effects of kink atom density is not possible. Although cylindrical S\(^4\)Cs contained different step orientations on the surface, very few conclusions were drawn on the effect of step orientation on activity. On spherical S\(^4\)Cs, the study of the effect of kink atoms on chemical phenomena is possible, but this was not a focus of any S\(^4\)C study so far. To gain a comprehensive fundamental understanding of the effect of crystal structure on chemical reactivity, crystal planes within the stereographic triangle containing kink atoms must be studied. Real catalysts contain atoms with coordination numbers less than 7 so obtaining an understanding on the effect of kink atoms on chemical reactivity is the next obvious step in breaching the structure gap of understanding the activity of under coordinated atoms on real catalysts.
2.5 Experimental Methods Comparison

Table 3 contains a list of all the experimental techniques mentioned in this review for both the physical and chemical phenomena studied. The list is organized in order of decreasing spatial resolution and includes the measured quantity of each technique. For measuring atomic scale surface structure, STM provides an excellent ability to image changes in different sites such as step edges and kinks with temperature and the adsorption of gas species. SEM, FIM, and FEM have a similar maximum spatial resolution with an added benefit being able to obtain larger images than STM from secondary electrons. While FEM and FIM can be used directly to determine the surface orientation, SEM needs to be used in conjunction with another technique like electron back scatter diffraction to determine surface orientation. Or, like in the case of Schmidt et al., assumptions in the crystal surface orientation can be made based on the point location relative to the low Miller index planes on the S^4C. These four techniques mentioned have the highest spatial resolution.

Spatially resolved XPS and UPS can both be used to determine if adsorbates are present on a spot < 100 μm on a surface. Spatially resolved XPS is also useful in determining the surface composition of multiple metals while for spatially resolved UPS it is more difficult to interpret the spectra. These techniques are limited by the size of the incident beam of X-rays or UV rays which are controlled by a crystal used for focusing. The SMOKE microscope also has a low spatial resolution of 20 μm due to the use of a slit to decrease the size of the incident beam of light. For spatially resolved TPD, the molecular
beam was used for increasing the spatial resolution to 400 μm spot size while for a normal TPD the resolution depends on the size of the sample. In general, the spatially resolved techniques are controlled by the size of the incident beam on each surface and not by the detector. What limits the techniques from developing higher spatial resolutions is the decrease in signal from a smaller spot size measured by the detector. As the spatial resolution decreases, the number of surface orientations contained within a single measurement increases.

Developing an XPS, TPD, or SMOKE technique with spatial resolution < 1μm would allow for a better determination of the effects of changing surface orientations on $S^4Cs$, but would require both the development of decreasing the beam size and increasing signal measured by the detector.
### Table 3: Spatial resolution of experimental techniques mentioned by order of decreasing spatial resolution

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<th>Method</th>
<th>Acronym</th>
<th>Quantity Measured</th>
<th>Spatial Resolution (in μm)</th>
<th>Source</th>
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<td>Photoemitted Valence electrons with Binding energy &lt; 100 eV</td>
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<td>Ultraviolet Photoelectron Spectroscopy</td>
<td>UPS</td>
<td>Photoemitted Valence electrons with Binding energy &lt; 100 eV</td>
<td>2000</td>
<td>Ranke (20)</td>
</tr>
<tr>
<td>X-ray Photoelectron Spectroscopy</td>
<td>XPS</td>
<td>Photoelectrons</td>
<td>4000</td>
<td>Ranke (204, 205)</td>
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<tr>
<td>Temperature Programmed Desorption</td>
<td>TPD</td>
<td>Ionized Gases</td>
<td>size of sample</td>
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<tr>
<td>Cyclic Voltammetry</td>
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<td>Current changes with voltage</td>
<td>size of sample</td>
<td></td>
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2.6 Theoretical Considerations

Most papers published on the subject of structure sensitivity form qualitative conclusions. In both computational and experimental catalysis papers, little work has been done on developing a quantitative model to explain the changes in reactivity with crystal structure seen experimentally or a model that takes into account multiple surface sites. Most conclusions make generalized statements that more “atomically open” or “atomically rough” crystal planes have enhanced adsorption activity or a higher sticking probability. To our knowledge, only a few authors made an attempt to model the effect of surface structure on chemical phenomena.

Burton made several additions to the work done by Wulff to determine the surface energy as a function of orientation during crystal growth and metal deposition. Burton showed that the equilibrium shape of a crystal is related to the free energy/unit length by a constant. The total edge free energy, $F_o$, of the critical nucleus, (or critical size of a certain orientation) can be calculated according to Equation 2.13 where $n_o$ is the number of atoms in the crystal plane, k is Boltzmann’s constant, T is temperature, and $\alpha$ is the saturation ratio of actual metal concentration in the vapor to the equilibrium value. Based on the formulation of the critical nucleus surface energy $F_o$ in Equation 2.13, the constant relating the surface energy, $f (\theta)$, to the orientation in the Wulff plot, $r(\theta)$, should be related to $\alpha$, shown in Equation 2.14 (137).
\[ F_o = 2n_o kT \ln \alpha \]  
\[ kT \ln \alpha = \frac{f(\phi)}{r(\phi)} \]  \hspace{1cm} (2.13) \hspace{1cm} (2.14)

Arlow et al. applied a model to the experimental AES data of the removal of adsorbed O by CO and H\textsubscript{2} on a cylindrical Cu S\textsuperscript{4}C. The step feeding model proposed by Arlow et al. calculated the overall sticking coefficient on each crystal plane using a weighted average of the two low Miller index planes present on each surface orientation. Equation 2.15 shows the calculation for the sticking coefficient of a vicinal crystal plane \( v \), \( s_v \), as a function of fractional coverage, \( \theta \) (181). In this equation, \( \varphi \) is the angle between the low Miller index planes A and B and \( \alpha \) is the angle between the vicinal plane and crystal plane A. Then using Equation 2.16 for fractional coverage, where \( E \) is the exposure in Torr*sec and \( K \) is the equilibrium constant of adsorption, the change in coverage with time can be calculated using Equation 2.17 where \( P \) is pressure (181). These equations were applied to the AES data for both the adsorption of O and the removal of O by CO. Figure 33 shows the fitting of the step feeding model to the experimental data as \( d\theta/dt \) versus the coverage of O remaining on the surface for several crystal planes on the cylindrical Cu S\textsuperscript{4}C. The model for O removal matched the experimental trends as the highest rate was seen at an intermediate coverage of O on each crystal plane and the crystal plane between \{311\} and \{100\} reached the highest relative rate. The steady state reaction conditions could also be determined using this model by finding the value of \( d\theta/dt \) where the CO removal and O adsorption rates are equal. The overall reaction is highly structure sensitive and that the structure sensitivity is dependent on the partial pressures of the reactants.
\[ K = s_v(\theta) = s_A(\theta)[(\phi - \alpha) / \phi] + s_B(\theta)[\alpha / \phi] \]  

(2.15)

\[ \theta = \frac{0.5KE}{KE + 1} \]  

(2.16)

\[ \frac{d\theta}{dt} = P(0.5K - 2K\theta + 2K\theta^2) \]  

(2.17)

Schmidt et al. wrote a review paper documenting the effect of different etching environments on the surface of catalysts (21). Although a model was not applied to their experimental work on the etching of Pt microspheres, they did outline several factors that contribute to the faceting of crystal surfaces. Etching was classified as two distinct processes: thermal etching, which occurs at high temperatures in the presence of un-reactive gases, and catalytic etching, which occurs at lower temperatures in the presence of reactive gases. Catalytic etching is a faster process than thermal etching. The behavior of both thermal and catalytic etching was found to depend strongly on the atmosphere and the partial pressure of gases near the surface. In general, the ability of an S^4C to facet increases with increasing partial pressures of O_2 and S_2 at high temperatures and pressures, but is less likely to facet in reducing environments, at higher H_2 partial pressures, in vacuum, or at lower temperatures.

The first analysis performed by Schmidt et al. to understand etching behavior was based on thermodynamics. The fundamental equations to describe etching were derived using a simplified system. Assume that a crystal is being cleaved along a specific plane to create a new surface at a constant temperature and constant volume. The Hemholtz free energy of the system is only a function of the work done to create the surface and chemical potential of different
components in the system shown in Equation 2.18. Based on this definition of Hemholtz free energy, $F$, and defining the work done on the system as the work needed to create an incremental amount of new surface ($dW = \gamma dA$), a formula was derived by Schmidt et al. for the change in surface energy using Equation 2.19. Two important thermodynamic parameters are then defined, the surface excess entropy in Equation 2.21, $s^s$, and the surface excess in Equation 2.20, $\Gamma_i$.

Then based on the ideal gas law, the chemical potential can be written as $\mu_i = \mu_{i0} + kT(lnP_i)$ and the surface excess can be written in terms of the partial pressure of component $i$ shown in Equation 2.22, the Gibbs adsorption isotherm, which shows the effect of pressure on the surface energy of a system. These equations show that the change in surface energy has a component or pressure dependent term, $-\Gamma_i d\mu_i$, and a temperature dependent term, $-s^s dT$ that can both affect the surface energy of a crystal. In general, for a given metal and gas interaction, there is a critical pressure and a critical temperature necessary for the crystal surface to have a large enough surface energy for faceting to occur.

$$dF = \gamma dA + \sum_i \mu_i \Gamma_i dN_i \quad (2.18)$$
$$d\gamma = -s^s dT - \sum_i \Gamma_i d\mu_i \quad (2.19)$$
$$\left( \frac{\partial \gamma}{\partial \mu_i} \right)_{T, \nu_i} = -\Gamma_i \quad (2.20)$$
The calculation for the effect of pressure and temperature on surface free energy and faceting behavior was reported by Schmidt et al. based on the equations above, but derived by Gjostein et al. Based on the $\gamma$-plot theorized by Herring, Gjostein used a thermodynamic model for adsorption from the gas phase on the surface energy of low Miller index crystal planes (cusps in the $\gamma$-plot) based on the presence of steps and kinks as defect sites in the low Miller index crystal plane (220, 221). The thermodynamic model was based on the following six different reactions occurring at equilibrium shown in Equation 2.23. The first three reactions show the adsorption of gas molecule, $G$, on the surface with low Miller index terraces, $S$, step site defects, $L$, and kink site defects, $D$. The final three reactions are the diffusion of adsorbed molecules among the three surface sites. The change in the Gibbs free energy for adsorption of a gas molecule on each site of the system can be calculated from Equation 2.24, where $\mu_{ig}$, is the chemical potential of a gas molecule adsorbed at site I, $\mu_{i}$ is the chemical potential of the free surface site I, and $\mu_{g}$ of the gas molecule in the gas phase. The equation used to calculate the surface energy of a crystal plane vicinal to a low Miller index plane is given by Equation 2.25 where $\alpha$ is the angle between the vicinal plane and the low Miller index plane, $M$ is the number of step sites/cm, $S$ is the step height in cm, $\gamma_{o}$ is the surface energy of the low Miller index plane in
E/cm², γ₁ is the surface energy of a step site/cm, and γ₂ is the interaction energy between step sites (221).

\[
\begin{align*}
G + S & \leftrightarrow G_S \\
G + L & \leftrightarrow G_L \\
G + D & \leftrightarrow G_D \\
G_S & \leftrightarrow G_L \\
G_S & \leftrightarrow G_D \\
G_L & \leftrightarrow G_D
\end{align*}
\] (2.23)

\[
\delta G = \mu_{g_i} \frac{\delta n_{g_i}}{N} - \mu_i \frac{\delta n_i}{N} - \mu_g \frac{\delta n_g}{N} 
\] (2.24)

\[
\gamma = \gamma_o + \gamma_I \frac{S}{2} \alpha^2 + \frac{\gamma_I}{S^2 M} \alpha^2 
\] (2.25)

Using these equations along with the Gibbs adsorption isotherm shown in Equation 2.22, an equation was derived for the slope of the γ-plot at the cusps around low Miller index planes and how this value changed with reduced partial pressure. This equation was arrived assuming one of two possible reactions can occur on two separate sites. For one site, the reactant is assumed to preferentially bind to defect sites and can either dissociate (Bₜ) or not dissociate (B) upon adsorption. For the other site, the reactant is assumed to preferentially bind to non-defect surface sites (terraces) and can either dissociate (Aₜ) or not dissociate (A). Equations 2.26-2.29 represent each of the four possible reactions. The reduced pressure is given by \(x\) or \(x_d\), the relative non dissociative adsorption energy on steps is given by \(K\), the relative dissociative adsorption energy on steps is given by \(K_d\). The quantity \(A_{oo}\) shown in Equation 2.30 represents the ratio of
surface energy between a step and a terrace on a clean surface, $B_{oo}$ shown in Equation 2.31 and represents the ratio of the step-step interaction energy and terrace surface energy on a clean surface. $A_o$ and $B_o$ in Equation 2.32 and 2.33 represent the surface energy ratio of the saturated step sites with the clean low Miller index surface. The other parameters are as follows: $M$ is the number of steps/cm on a line perpendicular to the step edge, $\gamma_{lo}$ is the surface free energy of the interaction between two steps on a clean surface, $\gamma_{lo}$ is the surface free energy of a step site on a clean surface, $\gamma_{oo}$ is the surface energy of the low Miller index plane clean (or with no gas adsorbed), $S$ is the step height ($S=1$), and $N_{ls}$ is the saturation concentration of surface atoms at step sites.

$$A = A_{oo} - A_o \ln(1 + Kx) \quad (2.26)$$

$$A_d = A_{oo} - 2A_o \ln(1 + K_d x_d^{1/2}) \quad (2.27)$$

$$B = B_{oo} + B_o \ln \left[ \frac{1 + x}{(1 + Kx)^2} \right] \quad (2.28)$$

$$B_d = B_{oo} + 2B_o \ln \left[ \frac{1 + x_d^{1/2}}{(1 + K_d x_d^{1/2})^2} \right] \quad (2.29)$$

$$A_{oo} = \frac{\gamma_{lo}}{S \gamma_{oo}} \quad (2.30)$$

$$B_{oo} = 1 + \frac{2\gamma_{lo}}{S^2 M \gamma_{oo}} \quad (2.31)$$

$$A_o = \frac{kTN_{ls}}{S \gamma_{oo}} \quad (2.32)$$

$$B_o = 1 + \frac{2kTN_{ls}}{S^2 M \gamma_{oo}} \quad (2.33)$$
Figure 34 shows the change in the slope of the cusp in the $\gamma$-plot, represented by a function of $B, B_d, A, \text{ or } A_d$, as a function of reduced pressure of reactant for several binding energies, $K$ or $K_d$. For gas that binds to step sites ($B$ or $B_d$) and values of $K$ or $K_d \geq 0.1$, the slope of $\gamma$ will decrease with increasing pressure meaning there is a net increase in the surface energy. For step sites and values of $K$ or $K_d \leq 0.1$, the slope of $\gamma$ increases and reaches a maximum indicating that for low binding energies of an adsorbate, adsorption decreases the surface energy. For gas that binds to terrace sites ($A$ or $A_d$), the slope of the cusp will decrease with increasing pressure at all values of $K$ or $K_d$, showing an increase in the surface energy with increasing adsorption. Figure 34 shows these trends for all cases.
Gjostein also developed a similar analysis for the conditions required for faceting of a crystal surface. He combined the quadratic dependence of $\gamma$ versus $\alpha$ in Equation 2.34 with the equations for parameters A and B to derive an equation to describe the conditions necessary for faceting of crystal planes (221). Equation 2.35 shows the equation derived by Gjostein to describe the criteria for faceting.

Figure 34: The effect of reduced pressure on the slope of the surface energy at the cusps located near low Miller index surfaces. $K$ and $K_d$ are measures of the non-dissociative and dissociative adsorption energies at step sites and $x$ and $x_d$ are reduced pressure values. For gas that binds to step sites ($B$ or $B_d$) and values of $K$ or $K_d \geq 0.1$, the slope of $\gamma$ will decrease with increasing pressure. For step sites and values of $K$ or $K_d \leq 0.1$, the slope of $\gamma$ increases and reaches a maximum. For gas that binds to terrace sites ($A$ or $A_d$), the slope of the cusp will decrease with increasing pressure at all values of $K$ or $K_d$ (21).
From this equation, there are three separate faceting regimes based on the value of B for crystal planes located near a cusp in the Herring plot of γ versus α. For small values of α, if \( B < \frac{\gamma_o}{\gamma_{oo}} \), no faceting will occur for all values of α. If \( B > \frac{\gamma_o}{\gamma_{oo}} \), then there are two different faceting behaviors predicted. The roots of the quadratic equation shown in Equation 2.36 for calculating the value for \( \alpha_c \) where faceting occurs can be real or imaginary based on the value of B. If the condition for faceting is met (\( B > \frac{\gamma_o}{\gamma_{oo}} \)), then the transition from a real to an imaginary root occurs under the condition listed in Equation 2.36. If \( \frac{\gamma_o}{\gamma_{oo}} < B < B_c \) then faceting will occur for all crystal planes \( 0 < \alpha < \alpha_c \). However, if \( B > B_c \), then all crystal planes facet regardless of the value of α.

\[
\frac{\gamma_o}{\gamma_{oo}} + A\alpha - \frac{B}{2} \alpha^2 \leq B \quad (2.34)
\]

\[
\frac{\gamma_o}{\gamma_{oo}} - B + A\alpha_c - \frac{B}{2} \alpha_c^2 = 0; \quad B >> \frac{\gamma_o}{\gamma_{oo}} \quad (2.35)
\]

\[
B_c = \frac{\gamma_o}{2\gamma_{oo}} \left\{ 1 + \left[ 1 + 2 \left( \frac{\gamma_o}{\gamma_{oo}} \right)^2 A^2 \right]^{1/2} \right\} \quad (2.36)
\]

Because \( B \) is a function of the reduced pressure of a reacting gas (shown in Equation 2.28 and 2.17), a plot was created of the value of \( B \) versus reduced pressure for cases where \( B \) is always less than \( B_c \) and for the case where some values of \( B \) are greater than \( B_c \). In Figure 35a, a crystal plane with orientations \( 0 < \alpha < \alpha_c \) will only facet in the pressure range between \( P_f \) and \( P_{f}' \). However, for Figure 35b, crystal planes with orientations \( 0 < \alpha < \alpha_c \) will facet between \( P_f \) and \( P_c \) and \( P_{c}' \) and \( P_{f}' \). Between \( P_c \) and \( P_{c}' \), faceting will occur for all crystal planes.
regardless of the value for \( \alpha \). Based on the thermodynamic analysis, both Schmidt and Gjostein postulated that for a given metal and gas interaction, there is a critical pressure necessary for faceting to occur.

![Faceting behavior plot](image)

**Figure 35:** Faceting behavior plotted as parameter \( B, B_d \) versus pressure for a) \( B_m < B_c \) and b) \( B_m > B_c \) where \( B_m \) is the maximum value for \( B(P) \) and \( B_c \) is the critical value for faceting. For plot a) when \( \gamma_{\alpha}/\gamma_{\alpha0} < B_m < B_c \), faceting will occur from \( P_f \) to \( P_f' \) for the angular region \( 0 < \alpha < \alpha_c \). For plot b) when \( B_m > B_c \) faceting will occur for all \( \alpha \) and will occur between \( 0 < \alpha < \alpha_c \) from \( P_f \) to \( P_c \) and from \( P_c' \) to \( P_f' \) (21).

Apart from thermodynamic models, Schmidt also discussed the influence of mass transfer limitations and kinetic limitations on the faceting of crystal surfaces (21). Schmidt used a 2-D model consisting of an active region for etching and an inactive region. On the active region, a reversible reaction occurs where the metal is removed and evaporates from the surface. On the inactive region, no reaction occurs, but the metal from the active region is assumed to be deposited on the inactive region to resolve the mass balance of metal atoms. Also, at steady state, the total production rate of the surface reaction was assumed to equal to the evaporation rate of the metal plus the rate of deposition of the metal. Equation
2.37-2.39 show the rate of surface reaction, $r_t$, the rate of metal evaporation, $r_e$, and the rate of metal deposition, $r_d$. Each variable used to model the system was made dimensionless to generalize to system for any size catalyst. The dimensionless product concentration of metal atoms $u = C/C_{es}$ where $C_{es}$ is the equilibrium concentration of metal atoms on the surface before reaction, the dimensionless x axis is $\xi = x/\delta$ bound from 0 to $L/\delta$, and dimensionless y axis is $\eta = y/\delta$ bound from 0 to 1. Using these equations, he was able to solve the steady state diffusion equation of the system and create contour profiles of the movement of surface atoms from a mass transfer controlled and reaction controlled case. The mass transfer controlled case assumes that the reaction reaches equilibrium quickly while the reaction controlled case assumes a finite reaction rate on the surface, Figure 36 shows the contour profiles of a dimensionless area for the reaction limited case and the diffusion limited case. Each line on the plot represent a line of constant $u$ and shows that for the diffusion limited case, the product diffuses further from the maximum concentration $C_{es}$ at (0,0) than for the reaction limited case.

$$\tilde{r}_t = -\frac{DC_{e}^r}{L} \int_0^{1/\delta} \left( \frac{\partial u}{\partial \eta} \right)_{\eta=0} d\xi$$  \hspace{1cm} (2.37)

$$\tilde{r}_e = -\frac{DC_{e}^r}{L} \int_0^{L/\delta} \left( \frac{\partial u}{\partial \eta} \right)_{\eta=1} d\xi$$ \hspace{1cm} (2.38)

$$\tilde{r}_d = -\frac{DC_{e}^r}{L} \int_{1/\delta}^{L/\delta} \left( \frac{\partial u}{\partial \eta} \right)_{\eta=0} d\xi$$ \hspace{1cm} (2.39)
Analysis has been performed to model the effect of surface structure on crystal growth, etching of crystal planes induced by both temperature and pressure, and on understanding CO oxidation activity. One of the only attempts to model surface reactivity based on surface structure was the work done by Arlow et al. This model is insufficient to obtain an understanding of the effect of step edges or kinks on reactivity as it focuses on the differences in reactivity of microfacets of the low Miller index planes rather than obtaining trends on the effect of step sites. The work done by Gjostein is a good theoretical model that describes the different possible systems of etching behavior based on the type of adsorption and changes in the partial pressure of reactants. Application of this model to experimental data would be difficult as it requires calculations of many parameters such as $\gamma_{\text{ls}}, \gamma_{\text{lo}}$, and $N_{\text{ls}}$. With reasonable estimates for these parameters, this model could be applied to many different etching processes.
2.7 Future Considerations

From all of the work presented in this review, it is clear that the effect of surface structure on chemical reactivity is still not well understood. General trends have been discovered in select cases, but overall these trends are only valid for certain temperatures, pressures, and reactants. The use of S$^4$Cs is a way to help bridge the structure gap as S$^4$Cs have a controlled number of low coordination sites such as step edges and kinks that are representative of low coordination atoms on real catalysts. However, there is still a large gap in knowledge that needs to be filled.

One way for this to occur is with the development of spatially resolved techniques. Spatially resolved XPS and UPS systems are widely in use today.
along with STM, a technique that has resolution down to the atomic level. Unfortunately these systems have to be used in vacuum and can’t be used under the conditions of real catalysts at higher temperatures and pressures. Near-ambient XPS systems are currently being developed as well but not for spatially resolved systems. Near ambient XPS systems use differential pumping to increase the signal and the signal increases with decreasing operating pressure. With spatially resolved XPS there is an increase in signal with increasing spot size. Because of this, the development of a spatially resolved near ambient XPS system would have trouble producing enough signal at high pressures and small spot sizes. A technique that would be useful is a spatially resolved TPD system that could record the signal of desorbing species at hundreds of discrete points on a single sample. This would allow for the use of $S^4$Cs to determine the binding energy of adsorbates and produce data to map out the effect of step density and kink density on binding energy.

Another easier development would be to use the techniques already available to perform new experiments. The effect of kink atoms of reactivity has not been studied on $S^4$Cs and spatially resolved techniques applied to this would be the next step in understanding the chemistry occurring on under-coordinated atoms of real catalysts. Also studying two different $S^4$Cs of the same crystallographic orientation but different metals in the same experiments would help gain insight into the effect of surface structure and composition simultaneously on a given reaction. If these new experiments are performed successfully, then new models can be created to take account for multiple reaction
sites on the surface and form some quantitative measurements of rate constants for step edges, kink sites, and terraces.

There are several researchers that are working on creating nanocrystals that preferentially expose one of the three low Miller index planes in the form of nanoprisms, cubes, octahedrons, etc. In most cases, these shape controlled nanoparticles are created by using a chemical agent such as a salt, organic ligand, or even gas molecules such as CO, to preferentially bind to one crystal facet and control the growth of the nanocrystal (222-224). This type of research has been applied primarily to Pt, but has also been attempted on Ag, Au, Pd, and Rh (223). In general, each technique can form nanoparticles that preferentially expose either \{111\} or \{100\} facets and in a select few cases can expose \{110\} and \{411\} facets. Pt nanocubes exposing \{100\} facets have shown greater activity than traditional Pt catalysts in oxygen reduction reactions and methanol oxidation and overgrown cubes exposing \{411\} planes were 2.3 – 5.6 times more active than traditional Pt catalysts for ethanol and formic acid oxidation (225, 226). This research shows that in many cases, using shape controlled nanoparticles to expose a specific surface orientation can increase the rate of activity over traditional polycrystalline catalysts. If these techniques could be applied to expose high Miller index crystal planes containing step edges and kinks, there could be an even further enhancement in catalytic activity.
2.8 Conclusions

$S^4Cs$ have been used to study a wide variety of physical and chemical phenomena both in vacuum and under ambient and high pressure conditions. The physical phenomena section showed that atomically rough surfaces and those with step edges have a lower work function and higher surface energy than low Miller index crystal planes. The presence of step edges causes an increase in the magnetic anisotropy and shifting of the valence band edge toward the Fermi energy. Surface reconstruction is effected by both the temperature and partial pressure of reactants and can cause the faceting of high surface energy crystal planes into low surface energy crystal planes. The chemical phenomena studied on $S^4Cs$ showed that the presence of step edges enhances the activity of surface reactions. For FCC metals, the presence of step edges enhanced the adsorption, dissociation, and decomposition activity for reactions both in vacuum and at high temperatures and pressures. For semiconductor surfaces, enhanced activity for chemical reactions occurred on reconstructed $\{100\}$ terraces. The oxidation activity changes depending on whether it’s the adsorption of $O_2$ or bulk oxidation. The adsorption activity of $O_2$ follows a similar trend as diatomic molecules; step edges and $\{110\}$ terraces have the highest activity. For bulk oxidation, $\{100\}$ planes are the most readily oxidized after the initial adsorption of $O_2$. Etching reactions were the most diverse in activity as the crystal planes present after etching depended on many factor. In general, the low Miller index planes of $\{100\}$ and $\{111\}$ were the most stable and resistant to etching. The removal of surface species, a reaction containing a preadsorbed species and a gas phase
species, was the most active on crystal planes containing both step edges and terraces such as \{511\} and \{15,1,1\}. All of these simple reactions studied are structure sensitive and S^4Cs have been used successfully to understand the nature of this structure sensitivity and should continue to be applied to studying surface phenomena and bridging the structure gap in understanding catalytic reactions.

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<td>Diatomic adsorption</td>
<td>Cyclic voltammetry</td>
<td>Binding Energy of H&lt;sub&gt;2&lt;/sub&gt; on Pt(110) and Pt(100) &gt; Pt(111) (153)</td>
<td></td>
</tr>
<tr>
<td>Rh</td>
<td>FCC</td>
<td>Diatomic adsorption</td>
<td>Desorption mass analysis</td>
<td>Activation energy for NO dissociation on Rh(110) &gt; Rh(111) (155)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Diatomic adsorption</td>
<td>TPD, AES</td>
<td>CO dissociation activity on Ni(511) &gt; Ni(111) due to steps (156, 157)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>Diatomic adsorption</td>
<td>TPD, AES</td>
<td>CO, CO&lt;sub&gt;2&lt;/sub&gt;, and D&lt;sub&gt;2&lt;/sub&gt; chemisorb and dissociate on Cu(311) not Cu(110) (158)</td>
<td></td>
</tr>
<tr>
<td>Ni, Co</td>
<td>FCC</td>
<td>Diatomic adsorption</td>
<td>X-ray Diffraction</td>
<td>Dissociation rate of CO on Ni and Co 450-600°C: (hkl) &gt; (h11) &gt; (111) &gt; (110) &gt; (100) (159)</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>BCC</td>
<td>Diatomic adsorption</td>
<td>X-ray Diffraction</td>
<td>Dissociation rate of CO on Fe: (hkl) &gt; (h11) &gt; (hhl) &gt; (hl0) &gt; (111), (110) &gt; (100) (160)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Diatomic Adsorption</td>
<td>FIM</td>
<td>CO preferentially adsorbs and dissociates on {h10} planes over low Miller index planes (161)</td>
<td></td>
</tr>
<tr>
<td>Ru</td>
<td>HCP</td>
<td>Diatomic adsorption</td>
<td>RHEED</td>
<td>CO dissociates at steps around low Miller index planes (162)</td>
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</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Diatomic adsorption</td>
<td>AES</td>
<td>C deposited from CO dissociation increased with increasing step density (18, 163)</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>Diamond cubic</td>
<td>Diatomic adsorption</td>
<td>AES, UPS</td>
<td>NO dissociation and chemisorptions is highest on (100) steps (164)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Diatomic adsorption</td>
<td>SR-TPD</td>
<td>D&lt;sub&gt;2&lt;/sub&gt; binding energy increases with distance from (111) (7)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Hydrocarbon Adsorption</td>
<td>Desorption mass analysis</td>
<td>Ethane formation rate from 50-200°C on (321) &gt; (111) &gt; (110) &gt; (100) (6)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Hydrocarbon Adsorption</td>
<td>X-ray Diffraction</td>
<td>For ethylene decomposition at 450°C, (110) &gt; (100), (111) (6)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Hydrocarbon Adsorption</td>
<td>FEM</td>
<td>Ethylene adsorption and decomposition occurs on {211} over {100} and {111} (165)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Hydrocarbon Adsorption</td>
<td>FEM</td>
<td>Acetylene adsorption and decomposition occurs preferentially on {211} and {210} planes (166)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Hydrocarbon Adsorption</td>
<td>AES</td>
<td>Ethylene decomposition maxima at (111), (110), and (511), minima at (100) and (311) (163)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Hydrocarbon Adsorption</td>
<td>DFT, STM</td>
<td>(211) plane has lower energy barrier for ethylene decomposition than (111) (167)</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>FCC</td>
<td>Hydrocarbon Adsorption</td>
<td>Desorption</td>
<td>For cyclohexene and</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Shape</td>
<td>Adsortion Type</td>
<td>Analysis Method</td>
<td>Adsorption and Chemisorption Details</td>
<td></td>
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<tr>
<td>Ge</td>
<td>Diamond cubic</td>
<td>H₂O and H₂S adsorption</td>
<td>AES and UPS</td>
<td>Preferential adsorption of H₂S occurs on {100} terraces and step edges (169, 170)</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>Zinc Blende</td>
<td>H₂O and H₂S adsorption</td>
<td>AES and UPS</td>
<td>{110} facets, step edges, and As terminated crystal planes preferentially adsorbed H₂S (169, 171)</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>Diamond cubic</td>
<td>H₂O and H₂S adsorption</td>
<td>AES and UPS</td>
<td>{100} causes dissociation of H₂S over {111} (17)</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>Diamond cubic</td>
<td>H₂O and H₂S adsorption</td>
<td>AES and UPS</td>
<td>Saturation coverage and dissociation of H₂O decreases with distance from {100} (17)</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>Diamond cubic</td>
<td>H₂O and H₂S adsorption</td>
<td>AES</td>
<td>H₂S preferentially adsorbs on step edges on planes between {211} and {311} (170, 178, 212)</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>Diamond cubic</td>
<td>H₂O and H₂S adsorption</td>
<td>UPS</td>
<td>{100} dissociates H₂O and H₂S into H, OH, and SH radicals (170, 178, 212)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>H₂O and H₂S adsorption</td>
<td>Desorption mass analysis</td>
<td>D₂O decomposes on Ni(110) autocatalytically into adsorbed O and D₂ (179)</td>
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</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>H₂O and H₂S adsorption</td>
<td>Desorption mass analysis</td>
<td>Ni(760) more active than Ni(110) for autocatalytic decomposition of H₂O (52)</td>
<td></td>
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<tr>
<td>Ni</td>
<td>FCC</td>
<td>H₂O and H₂S adsorption</td>
<td>TPD, work function</td>
<td>Ni(665) and Ni(221) have a higher binding energy for H₂O than Ni(111) due to the presence of step edges (180)</td>
<td></td>
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<tr>
<td>Cu</td>
<td>FCC</td>
<td>Nitrogen Species</td>
<td>AES</td>
<td>N₂O dissociation has maxima on {311} and {110} and minima on {100} and {111} (182)</td>
<td></td>
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<tr>
<td>Ge</td>
<td>Diamond cubic</td>
<td>Nitrogen Species</td>
<td>AES</td>
<td>NO₂ dissociation has a minimum in activity at {111} (183)</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>Diamond cubic</td>
<td>Nitrogen species</td>
<td>AES</td>
<td>NH₃ preferentially adsorbs on {100} terraces over {111} (184)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>FCC</td>
<td>Nitrogen species</td>
<td>DFT</td>
<td>Ni{110} more active for NH₃ dissociation to N than Ni{111} and Ni{211} (185)</td>
<td></td>
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<tr>
<td>Cu</td>
<td>FCC</td>
<td>Oxidation</td>
<td>X-ray Diffraction</td>
<td>Oxide forms along {110} and {100} striations over {111} (186)</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>BCC</td>
<td>Oxidation</td>
<td>X-ray Diffraction</td>
<td>Rate of oxidation in air at 200°C: Fe(100) &gt; Fe(111) &gt; Fe(110) (187)</td>
<td></td>
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<tr>
<td>Cu</td>
<td>FCC</td>
<td>Oxidation</td>
<td>X-ray Diffraction</td>
<td>Rate of oxidation of low Miller index planes varied with temperature and pO₂ (188)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>Oxidation</td>
<td>X-ray Diffraction</td>
<td>In air from 200 - 1000°C, {100} plane oxidized faster (189-191)</td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>Structure</td>
<td>Process</td>
<td>Technique</td>
<td>Details</td>
<td></td>
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<tr>
<td>Cu</td>
<td>FCC</td>
<td>Oxidation</td>
<td>X-ray Diffraction</td>
<td>{hk0} and {100} oxidize faster than {110} and {311} while (111) remains oxygen free after 1 hour exposure to air at 200 °C (191)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>Oxidation</td>
<td>Interference Microscopy</td>
<td>trend for film thickness and rate of oxidation in air from 70-180°C was (100) &gt; (111) &gt; (110) &gt; (311) (192)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>Oxidation</td>
<td>X-ray Diffraction</td>
<td>Oxidation rate for 0.5-2.5% O₂: {111} &gt; {100}, oxidation rate for &gt;2.5% O₂: {100} &gt; {111} (189, 193, 194)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>Oxidation</td>
<td>X-ray Diffraction</td>
<td>Oxidation rate for 0.5-2.5% O₂: {111} &gt; {100}, oxidation rate for &gt;2.5% O₂: {100} &gt; {111} (63, 67, 68)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>Oxidation</td>
<td>LEED</td>
<td>Mapped 6 distinct oxide structures based on location at edge of stereographic triangle (15, 196-198)</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>FCC</td>
<td>Oxidation</td>
<td>AES</td>
<td>{311} and {110} have maxima in sticking probability of O₂, {100} and {111} have minima (199, 200)</td>
<td></td>
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<tr>
<td>Ni</td>
<td>FCC</td>
<td>Oxidation</td>
<td>AES</td>
<td>{111} oxidized faster than {100}, initial O₂ adsorption is isotropic on Ni (201)</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>BCC</td>
<td>Oxidation</td>
<td>AES</td>
<td>Initial oxidation activity has a minimum at {110} plane (69)</td>
<td></td>
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<tr>
<td>GaAs</td>
<td>Zinc Blende</td>
<td>Oxidation</td>
<td>AES</td>
<td>Sticking probability of oxygen: {100} &gt; {110} &gt; {111} (202, 204, 205)</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>Zinc Blende</td>
<td>Oxidation</td>
<td>AES</td>
<td>Step edges and Ga terminated crystal planes have enhanced oxygen adsorption activity (202, 204, 205)</td>
<td></td>
</tr>
<tr>
<td>GaAs</td>
<td>Zinc Blende</td>
<td>Oxidation</td>
<td>UPS</td>
<td>O has a higher binding energy at step edges (203)</td>
<td></td>
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<tr>
<td>Si</td>
<td>Diamond Cubic</td>
<td>Oxidation</td>
<td>AES</td>
<td>Oxygen coverage after exposure at room temperature: maxima at {100} and {111}, minima and {110} and {311} (206, 207)</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>Diamond Cubic</td>
<td>Oxidation</td>
<td>AES</td>
<td>Maxima in oxygen adsorption steps between {100} and {110} and on {100} at 300 K (208)</td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>Diamond Cubic</td>
<td>Oxidation</td>
<td>AES</td>
<td>Maxima in oxygen adsorption steps near {110} and {311} and on {111} at 650 K (208)</td>
<td></td>
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<tr>
<td>Cu</td>
<td>FCC</td>
<td>Oxidation</td>
<td>STM, spatially resolved XPS</td>
<td>Initial adsorption of oxygen is enhanced by step edges. Oxidation occurs preferentially at {100} step (209)</td>
<td></td>
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<tr>
<td>At. No.</td>
<td>Symmetry</td>
<td>Process</td>
<td>Technique</td>
<td>Description</td>
<td></td>
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<tr>
<td>58</td>
<td>FCC</td>
<td>Oxidation</td>
<td>Cyclic voltammetry</td>
<td>Oxygen has a higher binding energy on {311} than {100} and {111} showing enhanced binding energy at steps (210)</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>FCC</td>
<td>Oxidation</td>
<td>Cyclic voltammetry</td>
<td>Oxidation activity decreases with increasing kink atom density (168)</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>FCC</td>
<td>Etching</td>
<td>Chemical</td>
<td>{111} planes of Cu etched faster than the {100} planes in H₂SO₄ (211)</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>FCC</td>
<td>Etching</td>
<td>Chemical</td>
<td>Rate of etching by orthophosphoric acid {110} &gt; {111} &gt; {100} (211)</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>FCC</td>
<td>Etching</td>
<td>Chemical</td>
<td>After HNO₃ etching, {311}, {111}, and {100} planes remained (214)</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>FCC</td>
<td>Etching</td>
<td>Electro-chemical</td>
<td>At overpotentials &lt; 100 mV, {111} microfacets form after etching by H₂SO₄ (215)</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>FCC</td>
<td>Etching</td>
<td>SEM, Electro-chemical</td>
<td>Rate of etching by cyanide and aqua regia: (210) &gt; (110) &gt; (100) &gt; (111) (217)</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>FCC</td>
<td>Etching</td>
<td>SEM, Electro-chemical</td>
<td>After etching by CO, NH₃, C₃H₈ at &gt; 900 K, {111}, {110}, and {100} microfacets remained on surface (19, 216)</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>FCC</td>
<td>Removal Surface Species</td>
<td>AES</td>
<td>Rate of carbon removal by oxygen faster on {110} and stepped crystal planes than {100} and {111} (163)</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>FCC</td>
<td>Removal Surface species</td>
<td>AES</td>
<td>Carbon removal rate by H₂ greatest on crystal planes between {331} and {110} and between {211} and {111}; {100} and {111} planes had minima in removal rate (18)</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>FCC</td>
<td>Removal Surface species</td>
<td>AES</td>
<td>Graphitic carbon forms on atomically rough crystal planes and is easier to remove from surface (18)</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>FCC</td>
<td>Removal Surface species</td>
<td>AES</td>
<td>Rate of CO oxidation faster on Pt(14,1,1) than (111) only at low partial pressures of oxygen (218)</td>
<td></td>
</tr>
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</table>
CHAPTER 3

3 Experimental Methods

3.1 UHV Systems

Three separate UHV chambers were used to run experiments on the Cu $\text{S}^4\text{Cs}$, Cu single crystals, and the ZnO(1$\bar{1}$00) single crystal. The top of Figure 37 shows a drawing of the location of each component in UHV chamber 2 along with a zoomed in picture of one of the Cu $\text{S}^4\text{Cs}$ mounted to the vertical manipulator arm. In the bottom of Figure 37 are pictures of UHV chamber 1 and UHV chamber 2. The components on UHV chamber 1 and UHV chamber two are similar enough that the drawing is a fair representation of both chambers. UHV chamber 1 was used to sputter and anneal Cu $\text{S}^4\text{Cs}$ to produce a LEED pattern and to perform all experiments on the ZnO(1$\bar{1}$00). This chamber was equipped with an Omicron NSE 10 ion gun for sputter cleaning of the sample, a Dycor quadrupole mass spectrometer for identification and quantification of desorption products; a Specs x-ray source and an Omicron EA125 hemispherical analyzer for performing X-ray Photoelectron Spectroscopy (XPS); a leak valve for background dosing; and a PHI Low Energy Electron Diffraction (LEED) system. Each sample was mounted to a manipulator arm suspended vertically in the chamber. This arm is attached to a bellows and a rotary stage and is capable of moving in x, y, and z directions and rotating with respect to the z-axis. UHV chamber 2 was also used for sputtering and annealing of the Cu $\text{S}^4\text{Cs}$ to produce a LEED pattern.
This chamber was equipped with a Dycor mass spectrometer, a PHI 04-161 ion gun, OSI vacuum LEED optics, and a manipulator arm with the same capabilities as the arm in UHV chamber 1.

UHV chamber 3 was used to perform all experiments using spatially resolved XPS. The UHV chamber 3 consists of two sections separated by a gate valve. Figure 38 contains a picture of the two sections of UHV chamber 3. The first section where samples are loaded is called the prep chamber (top image of Figure 38) and the second section is called the analysis chamber (upper image of Figure 38). The prep chamber is equipped with a Hiden quadrupole mass spectrometer (circled in orange), a RBD Tech 04-165 ion gun (circled in blue), an ion gauge, an evaporative doser for either aspartic acid or tartaric acid evaporation (circled in green), a translator arm for transferring samples between the prep chamber and analysis chamber (circled in red), and two stages capable of heating the sample and controlling the temperature of each sample (one of them circled in white). The quadrupole mass spectrometer was attached to a manipulator arm to lower the mass spec within 10 mm of the sample. A stainless steel cone was attached to the end of the mass spectrometer to increase the signal during TPRS experiments. The analysis chamber (bottom image) also called the Thetaprobe was equipped with an ion gun, UV source, x-ray source, hemispherical energy analyzer, two cameras, and a flood gun all from Thermo Fisher Scientific. A stage capable of heating the sample, controlling the temperature, and translating each sample was present in the middle of the analysis chamber.
Figure 37: (Top) Drawing of the components on UHV chamber 1 and images of a Cu S\textsuperscript{4}C mounted to the vertical manipulator arm. (Bottom) Image of UHV chamber 1 (left) and UHV chamber 2 (right).
Figure 38: (Top) Prep chamber in UHV chamber 3. The prep chamber is equipped with a Hiden quadrupole mass spectrometer (circled in orange), a RBD Tech 04-165 ion gun (circled in blue), an ion gauge, an evaporative doser for either aspartic acid or tartaric acid evaporation (circled in green), a translator arm (circled in red), and two stages capable of heating the sample and controlling the temperature of each sample (one of them circled in white). (Bottom) analysis chamber for performing spatially resolved XPS.
3.2 Sample Mounting

In UHV chambers 1 and 2, each sample was attached to two Ta wires at the end of a manipulator arm mounted vertically in the UHV chamber. The crystal mount was in thermal contact with a liquid N$_2$ reservoir and the sample was heated resistively through the Ta wires by direct current to access temperatures in the range 100 – 1000 K. The temperature was measured using a K-type thermocouple spotwelded to each sample and was controlled using a computer.

The Cu S$^4$Cs were directly spotwelded to the Ta wires along the edges of the S$^4$C and the thermocouple was spotwelded to a Ni foil which was spotwelded to the edge of the Cu S$^4$C. The thermocouple needed to be spotwelded together before being attached to the Ni foil or the current used to heat the sample would affect the temperature reading. The ZnO(1100) single crystal was not capable of being spotwelded to the Ta wires directly. Instead, the ZnO(1100) was attached to a Ta plate using a Ag based paste called Pyroduct-597-A by Aremco. After using the paste to attach the sample to the Ta plate and spotwelding the Ta wires to the plate, the assembly was heated to 800 K for two hours to cure the paste. Curing the paste under these conditions allows for high thermal and electrical conductivity. The thermocouple was spotwelded to the back of the Ta plate and used to control the temperature.

In UHV Chamber 3, each S$^4$C was attached to a sample holder in one of three ways shown in Figure 39. This sample holder contains a ceramic heater to
heat the sample and two clips with thermocouple wires attached to read the
temperature of the sample. Several techniques were attempted to mount each S\textsuperscript{4}C
on this holder. In the first setup (left), the sample was attached directly to the
ceramic heater using Pyroduct 597-A, a thermally and electrically conducting Ag
based paste and an N-type thermocouple was spotwelded to a Ni foil which was
spotwelded to the side of the S\textsuperscript{4}C. This setup was unsuccessful as after several
cycles of annealing the S\textsuperscript{4}C > 800 K, the sample detached from the ceramic heater
leading to poor thermal contact and poor temperature control. In the second setup
(center), a Cu wire bundle was mixed with the Pyroduct 597-A paste, and the Cu
S\textsuperscript{4}C was pressed down at two edges onto the Cu/Ag paste bundle using Ni clips
wrapped with Cu foil. This setup had excellent thermal contact and temperature,
but the experimental results obtained using this setup were inconsistent leading to
the conclusion that the force of the clips and the contact of the Cu foil caused
damage to the surface. The final setup (right) was used in each of the
experimental results shown. Each S\textsuperscript{4}C was attached to the sample holder by doing
the following: attaching a 0.25 mm thick Cu plate (99.9999\% pure from
Goodfellow) to the ceramic heater using Pyroduct 597-A, a thermally and
electrically conducting Ag based paste, and two Ni clips to apply pressure to the
Cu plate. Each S\textsuperscript{4}C was then attached to the Cu plate using the Pyroduct 597-A
paste. An N-type thermocouple was spotwelded to a piece of Ni foil (0.025 mm
thick) that was spotwelded to each S\textsuperscript{4}C to measure the temperature. This
mounting setup created good thermal contact between the ceramic heater and each
S\textsuperscript{4}C and prevented the separation of each S\textsuperscript{4}C during annealing and movement.
between the prep chamber and the analysis chamber. This setup allowed for the best thermal conductivity while also preventing the Cu S\textsuperscript{4}C from shifting or becoming detached while the sample was moved between chambers or stages and preventing damage to the surface.

![Sample Mounting Setups](image)

Figure 39: Images of three sample mounting setups of Cu S\textsuperscript{4}C in UHV Chamber 3 on the sample heater. This sample holder contains a ceramic heater to heat the sample and two clips with thermocouple wires attached to read the temperature of the sample. The setup on the right had the best thermal contact and was used in all experiments.

3.3 Experimental Techniques

3.3.1 Temperature Programmed Reaction Spectroscopy (TPRS)

Thermally induced desorption and reaction of adsorbed species is a common method used in surface science to study reaction kinetics. These types of experiments are referred to as either Temperature Programmed Desorption (TPD) or Temperature Programmed Reaction Spectroscopy (TPRS). Both of these experiments consist of four steps and each step is illustrated in Figure 40:

1) Sputtering an annealing the surface until it is free from contamination
2) Adsorption of a reactant exposed from a leak valve or doser with the sample held at a low temperature (T=T\textsubscript{o}).
3) Moving the sample in front of a mass spectrometer and heating it at a constant rate, $\beta$ in K/sec, starting at $T_0$.

4) Using the mass spectrometer to record the desorption of molecules from the surface as the temperature increases.

In a TPD or TPRS experiment, molecules are exposed to a sample surface at a temperature where adsorption is favorable. As the temperature increases, the probability of the adsorbed molecules either desorbing or reacting increases. At a certain temperature, the molecules with either desorb from the surface or react to form different products that can also desorb from the surface. The mass spectrometer is used to measure the species desorbing and determine the temperature location of peaks for each desorbing species. The mass spectrometer measures specific masses as $m/q$ ratios since molecules are ionized as they enter the mass spectrometer. The signal measured by the mass spectrometer is proportional to the partial pressure of material desorbing from the surface and proportional to the desorption rate.

The rate of desorption can be defined as the change in the fractional coverage of an adsorbate with time shown in Equation 3.1. For reactions occurring on a surface, the rate of desorption is usually written as a function of the fractional coverage of surface species, $\theta_i$, and a rate constant, $k$. The rate constant shown in Equation 3.2 is a function of temperature, the desorption energy, $\Delta E_{des}$, in kJ/mol, a pre-exponential factor, $\nu$, usually assumed as $\sim 10^{13}$ sec$^{-1}$, and the universal gas constant, $R$, in $8.3145$ J/mol*K. The reaction order on the coverage is usually $n=0, 1, \text{ or } 2$. 
The rate constant and the coverage of adsorbate both change with temperature while the sample is heated in a TPD experiment. Figure 41 illustrates an example of how these values change with temperature and the corresponding desorption spectra from the mass spectrometer listed as the rate of desorption in red. At low temperatures, the coverage of adsorbate is high, but the rate constant is very low. As the temperature increases, the rate constant and the rate of desorption increases. However, the coverage decreases as molecules desorb and at a certain temperature the rate of desorption reaches a maximum and then drops to zero once the coverage of adsorbed species on the surface reaches zero.

In a TPD experiment, the location of the temperature peak and the heating rate can be used to determine the desorption energy barrier, $\Delta E_{des}$. For molecules that desorb from the surface, the desorption energy, $\Delta E_{des}$, is lower than the energy barrier to react. In a TPRS experiment, molecules will undergo a surface reaction and form products that can be measured using the mass spectrometer. Molecules that react have a lower activation energy, $\Delta E_a$, than the desorption energy barrier, $\Delta E_{des}$, and TPRS can be used to determine the different products formed in a surface reaction and to measure $\Delta E_a$. The reactions studied in this research form products and are all classified as TPRS experiments.

\[ r_{des} = -\frac{d\theta}{dt} = -\frac{dT}{dt} \frac{d\theta}{dT} = -\beta \frac{d\theta}{dT} \qquad \Rightarrow \quad r_{des} = k \theta_i^n \quad (3.1) \]

\[ k(T) = vexp \left( -\frac{\Delta E_{des}}{RT} \right) \quad (3.2) \]
Figure 41: Example of a TPD spectra with changes in coverage (blue dotted line), desorption rate (red line), and the rate constant (green dotted) with temperature. At low temperatures, the coverage of adsorbate is high, but the rate constant is very low. As the temperature increases, the rate constant and the rate of desorption increases (3).
3.3.2 X-ray Photoelectron Spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) is a technique used to determine the elemental composition of a surface. In an XPS experiment, X-rays of a specific energy (either 1486.6 eV Al-Kα from an Al source or 1253.6 eV Mg-Kα from a Mg source) are exposed to a sample in UHV. When an atom absorbs a photon with an energy in excess of the binding energy of a core electron, a phototelectron is emitted into vacuum with a specific kinetic energy \( KE \). The emitted photoelectrons are detected by an analyzer, usually a hemispherical energy analyzer, with an aperture positioned close to the sample surface shown in Figure 42. The emitted photoelectrons enter this aperture and are focused using a series of electrostatic lenses into a small entrance slit to the hemispherical energy analyzer. The analyzer then scans emitted photoelectrons at a specific \( KE \) by adjusting the voltages of the inner and outer hemisphere to allow only electrons at a specified \( KE \) to reach the detector. The electron binding energy \( BE \) is calculated using the following energy balance:

\[
BE = h\nu - KE - \phi \quad (3.3)
\]

where \( h\nu \) is the energy of the incident X-rays and \( \phi \) is the work function or the energy needed to move an electron from the Fermi level of the sample into vacuum. The electrons measured by the analyzer produce a spectra of electron counts/sec vs. \( BE \). The electron \( BE \) is element specific and therefore surface composition can be determined from the peak areas of a spectrum of photoelectron counts/sec versus \( BE \). Although x-rays can penetrate into the bulk of the sample, only photoelectrons from atoms in the near surface region have a
high enough $KE$ to escape into vacuum making XPS a surface sensitive technique. XPS can also be used to determine the oxidation state of an element. The binding energy of core level electrons can shift 1–3 eV due to changes in the valence band structure from chemical bonding. These shifts can be used to determine what elements are bonded to each other for the near surface region of a sample.
Figure 42: Rough drawing of hemispherical energy analyzer used in XPS experiments. The emitted photoelectrons enter this aperture and are focused using a series of electrostatic lenses into a small entrance slit to the hemispherical energy analyzer. The analyzer then scans emitted photoelectrons at a specific KE by adjusting the voltages of the inner and outer hemisphere to allow only electrons at a specified KE to reach the detector. Image from www.uksaf.org
3.3.3 Scanning Tunneling Microscopy (STM)

STM is a UHV technique used to obtain atomic scale images of a surface. A scanning tunneling microscope uses a tip of a metal (usually W) filed down to one atom at the apex. When a high voltage is applied to this tip and it is held a few Angstroms from a surface, a small current on the order of 1 nA is registered. This current comes from a quantum mechanical phenomenon called tunneling where low energy electrons can be transferred from the tip to the sample to the surface even through a high potential energy barrier. As the tip moves across a surface, the tunneling current changes with the surface topography and this change can be used to generate an image of the surface with a spatial resolution on the order of < 0.1 Angstroms in z and 1 Angstroms in x and y.

3.3.4 Low Energy Electron Diffraction (LEED)

LEED was used in this research to check that the surface of each S\textsuperscript{4}C was clean and crystalline after polishing and sputtering and annealing in UHV. In a LEED experiment, an electron beam (between 20 and 500 eV) is exposed to a crystalline sample. The electron beam causes both elastic and inelastic scattering of electron waves from the atoms on the sample surface. A series of screens held at high voltages is used to isolate the elastically scattered electrons from the surface to contact a phosphor screen. Electron diffraction occurs if there is constructive interference of the scattered waves. This happens if the waves scattering off of the atoms differ by multiples of the wavelength, also known as
Bragg’s law shown in Equation 3.4 where $h$ is an integer value, $a$ is the distance between atoms, $\varnothing_h$ is the angle of the scattered electron and $\varnothing_o$ is the energy of the incident electron. If the surface is crystalline, diffraction occurs and spots will form on the phosphor screen. An image is generated of the reciprocal lattice of the crystalline material and can be used to identify the crystal orientation of a surface.

$$a(\sin \varnothing_h - \sin \varnothing_o) = h \lambda \quad (3.4)$$

### 3.4 Sample Preparation

Each Cu S$^4$C was created by polishing a single crystal into a spherical section. Single crystals of Cu(110), Cu(100), Cu(111), Cu(861), Cu(432), and Cu(821) of 99.999% purity were purchased from Monocrystals company. A spherically shaped epoxy mold with sandpaper and various polishing cloths attached and a rotating wheel were used to perform the polishing of the crystal. The radius of curvature of the epoxy mold changed depending on the desired radius of curvature of the sample. Sandpaper from 220 – 1200 grit was used to form a spherical shape from the flat crystal and polishing pastes from 6 μm diamond down to 0.05 μm alumina were used to decrease the surface roughness until the surface had a mirror finish with no scratches or imperfections present. The details of this polishing procedure are listed elsewhere (12).

After polishing, a ZYGO NewView 7000 Optical Surface Profiler was used to determine whether each sample had a spherical shape after polishing and to confirm that there were no imperfections on each S$^4$C. Optical Profilometry
uses an optical green laser (550 nm wavelength) to determine the height of a sample (0.5 μm resolution) versus a reference height as a function of \(x\) and \(y\) position (4.4 μm resolution). For the Cu S\(^4\)Cs, the profilometer stitches together 1x1 mm\(^2\) areas of each sample to generate a surface profile. This surface profile was then fit to a sphere to determine the radius of curvature and to find the radius from the center of each S\(^4\)C where the spherical fit no longer applies. In general, both the height of the S\(^4\)C and the local orientation of each point on the surface was used in fitting. The height profile of the sample can show that a sphere fits the data, but doesn’t show if there are local deviations in the surface profile. The local surface orientations were calculated by fitting a plane to each point on the surface. To do this, the local curvature was calculated at each point by fitting a plane to all points within a 50 μm radius for the raw data. The angle, \(\alpha\), between the center of the S\(^4\)C and the normal of the plane at each point was calculated for the raw data. A spherical fit was applied to the raw data using Equation 3.5 where \(z_m\) is the height form the model, \(R\) is the radius of curvature of the sphere, and \(x_o\) and \(y_o\) are the coordinates of the sample center. The values of \(R\), \(x_o\), and \(y_o\) were adjustable parameters for the spherical fit and the sum of squared errors between the height of the raw data and the spherical fit were used to determine the value for \(R\), \(x_o\), and \(y_o\). Once these values were determined, the angle of the plane normal for the spherical fit, \(\alpha_m\), could be calculated at each point using Equation 3.6 where \(r\) is the radius from the center of the S\(^4\)C.

\[
z_m = \sqrt{R^2 - (x - x_o)^2 - (y - y_o)^2} \tag{3.5}
\]
After optical profilometry, Laue back diffraction was used to determine whether the bulk crystal structure of each S\textsuperscript{4}C was maintained and to determine the location of the high symmetry directions on the S\textsuperscript{4}C surface. An optical laser was used in conjunction with Laue back diffraction to determine the location of the crystal plane of the original single crystal on the surface ideally located near the center of each S\textsuperscript{4}C. Figure 43 shows a picture of a Cu S\textsuperscript{4}C setup for exposure to X-rays (top) and exposure to the optical laser (bottom). Each S\textsuperscript{4}C was mounted to a goniometer capable of rotating the sample about the x and y axis and the goniometer was attached to a stage capable of translating the sample orthogonal to the direction of the X-ray. The goniometer stage assembly was fixed to an aluminum holder that can mount on an optical rail. The sample was positioned 3 cm in front of the X-ray source and exposed to X-rays at 20 kV and 25 mA for 15-20 minutes. The sample will diffract X-rays in specific directions based on the orientation of the bulk lattice vectors in the S\textsuperscript{4}C according to Bragg’s law. These directions appear as white spots on a film that is mounted directly in front of the X-ray source. The location of the spots on the film relative to the X-ray source and to each other spot can be used to find the location of the original orientation of the single crystal. Greninger developed a graphical method that uses a chart and a known distance between the sample and the X-ray beam (in this case the distance was always 3.0 cm) to convert the x and y coordinate on the film into angle coordinates $\delta$ and $\gamma$ (228). The angle coordinates in relation to other spots on the film can be used to determine the angle between each spot. Once the

$$\alpha_m = \left| \tan^{-1} \frac{-r}{\sqrt{R^2 - r^2}} \right|$$

(3.6)
angles between each spot are known, trial and error and Equation 3.7 can be used to determine the orientation of each diffraction spot, where A and B are the normals of the crystal planes for the two spots on the film and $\theta$ is the angle between the two spots.

\[
\cos^{-1}\frac{A \cdot B}{\|A\|\|B\|} = \theta
\]  

(3.7)

Figure 43: Picture of Laue back diffraction setup and optical laser setup. Each $S^4C$ was attached to a goniometer capable of rotating the sample about the $x$ and $y$ axis and the goniometer was attached to a stage capable of translating the sample orthogonal to the direction of the X-ray.

Figure 44 shows an illustration of the steps used to determine the location of the (111) plane on the Cu(111) $S^4C$. Once the location of the (111) plane is determined from the diffraction photograph, the sample is rotated so that the (111) plane is perpendicular to the incident X-ray beam. Once the (111) plane in the bulk is perpendicular to the X-ray beam, the goniometer stage assembly is mounted on a separate optical rail in front of an optical laser mounted in the same position as the X-ray beam. The sample is then translated in $x$ and $y$ until the laser reflects off of the surface directly back into the incident beam. The point on the
surface where this occurs is the location of the (111) plane on the surface. With the location of the (111) plane on the surface known and crystal orientation of the diffracted spots on the film known, the location of the high symmetry directions on the $S^4C$ (or the edges of the stereographic triangle) are known. This procedure was applied to the three low Miller index Cu $S^4Cs$ and scratches on the side of the crystal were used to indicate the high symmetry directions.

![Diagram](image)

Figure 44: Procedure for Laue back diffraction experiment used to determine the location of the (111) plane on the surface. In the first step, the sample is rotated so that the (111) plane is perpendicular to the incident X-ray beam. In the second step, the goniometer stage assembly is mounted on a separate optical rail in front of an optical laser mounted in the same position as the x-ray beam. The sample is then translated in x and y until the laser reflects off of the surface directly back into the incident beam. The point on the surface where this occurs is the location of the (111) plane on the surface (12).

### 3.5 $S^4C$ Preparation Results: Cu(100) and Cu(111) $S^4Cs$

Although the procedures described above were applied to a set of 6 Cu $S^4Cs$, only the Cu(100) and Cu(111) $S^4C$ were used in this research and will be mentioned here. Figure 45 shows the results from modeling the optical profilometry data for the Cu(100) $S^4C$ and the Cu(111) $S^4C$. The plots on the left
show the height of the sample in μm versus radius from the center for the raw data (black) and a spherical fit. For both the Cu(100) and Cu(111) S⁴C, the sphere fits the data well until > 4 mm from the center where each surface becomes over curved at the edges. The right of Figure 45 shows a contour plot of the angle deviation between a spherical fit and the raw data across each S⁴C. For the Cu(111) S⁴C, the angle deviation is less than 1° within 4.5 mm of the center where the deviation is >1° only at the edges of the S⁴C. For the Cu(100) S⁴C, the angle deviation is less than 1° only within 4.3 mm of the center. Since each S⁴C is over curved at the edges, only points ≤ 4 mm from the center of each S⁴C will be measured in experiments.
After determining that each \( S^4C \) had the desired spherical shape from optical profilometry, each sample was mounted on a glass slide and added to the goniometer setup shown in Figure 43 for Laue back diffraction. The left of Figure 46 shows a picture of the Laue Back Diffraction results from the Cu(111) \( S^4C \) after aligning the (111) plane of the \( S^4C \) with the center of the film. The bright spot at the center of the film is from the X-ray beam and the four black spots are located on the photo holder to orient the film with an \( x \) and \( y \) axis. The orientation of each spot was determined using Equation 3.7 and using the “\( x \)” as the (111) point on the film. As expected, the diffraction pattern for the Cu(111)

\[
\begin{align*}
\text{Cu(111) } S^4C \\
\text{Cu(100) } S^4C
\end{align*}
\]
S\textsuperscript{4}C showed three fold symmetry and six high symmetry directions on the surface. There were seven diffraction spots on the film and their orientation is shown on the film in white. The high symmetry directions were determined from the orientation of the diffraction spots (indicated in white) and are shown in red and green and labeled with respect to the nearest low Miller index plane. The three {211} planes are located along the high symmetry direction between the {111} plane and the {100} plane and the {331} plane is located along the high symmetry direction between the {111} and the {110} plane. The Laue back diffraction pattern is different than the “Stereographic Projection” shown in the right of Figure 46. The Laue diffraction image is projected into the page while the stereographic projection is out of the page. The right of Figure 46 shows the stereographic projection centered at the {111} plane and demonstrates the high symmetry direction locations as they would appear on the Cu(111) S\textsuperscript{4}C sitting on top of the page. The same procedure for the Cu(111) S\textsuperscript{4}C was applied to the Cu(100) S\textsuperscript{4}C. Figure 47 shows the results of Laue back diffraction on the Cu(100) S\textsuperscript{4}C. The Cu(100) S\textsuperscript{4}C has four fold symmetry and eight high symmetry directions on the surface. There were eight spots corresponding to one of two lattice vectors shown in white as either {210} or {311}. The four {210} planes are located along the high symmetry direction between {100} and {110} shown in orange and the four {311} planes are located along the high symmetry direction between {100} and {111} shown in green. From these spots, the location of the high symmetry directions and the orientation of the high symmetry directions are known.
Figure 46: Laue back diffraction results of Cu(111) S\textsuperscript{4}C after centering. The three \{211\} planes are located along the high symmetry direction between the \{111\} plane and the \{100\} plane and the \{331\} plane is located along the high symmetry direction between the \{111\} and the \{110\} plane. The location of the high symmetry directions in relation to the surface of the S\textsuperscript{4}C is shown in the stereographic projection.
The general trends in the surface structure of crystal planes across the stereographic triangle has been mentioned previously. Crystal planes located along the edge of the stereographic triangle contain surfaces with terraces separated by monatomic step edges and crystal planes located in the stereographic triangle contain surfaces with terraces, step edges, and kinks in the step edge. Not only does the density of these sites change with location on the stereographic triangle, but the orientation of the site can change. On the low Miller index Cu $\text{S}_4\text{C}$, the change in both the density of sites and the orientation of sites is known.

3.6 Ideal Surface Trends in $\text{S}_4\text{Cs}$

The general trends in the surface structure of crystal planes across the stereographic triangle has been mentioned previously. Crystal planes located along the edge of the stereographic triangle contain surfaces with terraces separated by monatomic step edges and crystal planes located in the stereographic triangle contain surfaces with terraces, step edges, and kinks in the step edge. Not only does the density of these sites change with location on the stereographic triangle, but the orientation of the site can change. On the low Miller index Cu $\text{S}_4\text{Cs}$, the change in both the density of sites and the orientation of sites is known.

Figure 47: Laue back diffraction results after centering for Cu(100) $\text{S}_4\text{C}$. There were eight spots corresponding to one of two lattice vectors shown in white as either \{210\} or \{311\}. The four \{210\} planes are located along the high symmetry direction between \{100\} and \{110\} shown in orange and the four \{311\} planes are located along the high symmetry direction between \{100\} and \{111\} shown in green. The location of the high symmetry directions in relation to the surface of the $\text{S}_4\text{C}$ is shown in the stereographic projection.
The ideal surface structure can be determined for any point on the S$^4$C from its relative location from the high symmetry direction and from the low Miller index plane. Figure 48 shows a drawing of the Cu(100) S$^4$C and the Cu(111) S$^4$C with the high symmetry directions and step orientations labeled. For the Cu(111) S$^4$C, as the distance from the (111) plane increases, the step density increases. The Cu(111) S$^4$C has two different step orientations present on the surface: (100) step edges and (110) step edges. Along the high symmetry directions in green on the surface are crystal planes with (100) oriented step edges and along the red directions are crystal planes with (110) step edges. The orientation of the step edge is labeled by the orientation of the plane perpendicular to the step edge. The orientation of the terrace of all crystal planes on the Cu(111) S$^4$C is (111). The Cu(100) S$^4$C also has two different step orientations present: (111) step edges and (110) step edges. Along the high symmetry directions in black on the surface are crystal planes with (111) oriented step edges and along the orange directions are crystal planes with (110) step edges. The orientation of the terrace on all surfaces on the Cu(100) S$^4$C is (100). The kink density increases moving azimuthally away from the high symmetry directions. A maximum in kink density occurs halfway between each high symmetry direction for both the Cu(111) and Cu(100) S$^4$C. Each S$^4$C contains sections of alternating chiralities. There are four alternating S and R regions on the Cu(100) S$^4$C and three alternating S and R regions on the Cu(111) S$^4$C. Regions of the same chirality on the S$^4$C contain identical surface structures.
Figure 48. Drawing of step orientations on Cu(111) S$^{4}$C (top) and Cu(100) S$^{4}$C (bottom). The Cu(111) S$^{4}$C has (100) step edges and (110) step edges. Along the high symmetry directions in green on the surface are crystal planes with (100) oriented step edges and along the red directions are crystal planes with (110) step edges. For the Cu(100) S$^{4}$C, Along the high symmetry directions in black on the surface are crystal planes with (111) oriented step edges and along the orange directions are crystal planes with (110) step edges.
3.7 STM Results Cu(111) S₄C

To confirm the results of the optical profilometry and Laue back diffraction, the Cu(111) S₄C was sent to Professor Charlie Sykes to perform STM measurements. The advantage of STM is that it can be used to obtain atomic scale images of different points on the S₄C and determine whether or not the real structure of the surface matches the ideal surface. First STM was used to locate the (111) plane on the S₄C. Figure 49a shows an STM image of a region near the (111) plane. The 100 x 100 nm image shows no discernible change in the surface structure indicating a wide terrace. A 1 x 1 nm image taken at the same spot shows a hexagonal pattern characteristic of the close packed (111) plane. Figure 49c was taken along the [11̅2] high symmetry direction in red (towards the (110) plane) and shows the presence of step edges on the surface and Figure 49d along the same direction further from the (111) plane has a higher density of step edges. These images show that the step density increases as the distance from the (111) plane increases. Also these images show straight step edges with no kinks as predicted by the ideal surface. Figure 49d and Figure 49e are taken at roughly an equal distance from the (111) plane but along opposite high symmetry directions. The structure of these two surfaces looks nearly identical showing that the step density is similar at equivalent distance away from the (111) plane. Figure 49f and g were taken 30° away from the [1̅1̅2] high symmetry direction in green (towards the (100) plane) where a maximum in kink density is present on the surface. Both of these images show the presence of step edges and kinks in the step edge. Although the density of kinks is decreased due to step bunching
explained in Chapter 1, the overall chirality of these two surfaces is maintained. From these STM images, it is clear that the trends predicted by the idea surface model are still present on the S$^4$C. Now that the surface structure at each point on the surface is known, surface reactions can be performed to develop correlations between the surface structure and activity.

Figure 49: STM images of the Cu(111) S$^4$C. Each image unless otherwise specified is 100 x 100 nm a) Image of the (111) pole of the S4C revealing an atomically flat surface. b) 1x1 nm$^2$ image of the (111) pole revealing the hexagonal close packed array of Cu atoms. c) and d) STM images taken at two points along the [112] direction. The density of steps on the surface increases as the distance from the (111) pole increases. e) STM image 2 mm along [112] direction. f) and g) STM images at points that are 1 mm from the (111) pole but angles that are ±30° from the [112] direction (12).
CHAPTER 4

4 L- and D-tartaric acid decomposition on a Cu(111) S^4C

4.1 Introduction

Tartaric acid, TA [HOOC-CH(OH)-CH(OH)-COOH] is a molecule with two chiral centers that exists as one of three possible forms: achiral meso-TA (2R,3S), chiral L-TA (2R,3R), and chiral D-TA (2S,3S). The molecular structures of L- and D-TA are shown in Figure 50. TA contains carboxyl groups at C atoms 1 and 4 and alcohol groups on C atoms 2 and 3. During heating, adsorbed TA undergoes explosive decomposition on both achiral and chiral crystal planes of Cu (5, 14, 22, 229). Crystal planes with step edges, terraces, and kinks and located inside the stereographic triangle are considered chiral and can have R or S orientation depending on the direction of rotation between the (111), (100), and (110) microfacets. Chiral molecules can exhibit enantiospecific behavior on chiral crystal planes (1-3, 5, 22, 44-46). For example, in a TPRS experiment on a chiral surface of given handedness, one enantiomer of TA will decompose at a lower temperature than the other. Figure 51 shows an example of this for a TPRS experiment of D-TA on Cu(643)^R&S crystal planes (5). On the Cu(643)^S surface, the peak for D-TA decomposition occurs at 486 K which is 10 K lower than that of L-TA on the Cu(643)^R at 496 K.
L- and D-TA have also been studied previously on Cu(651)\textsuperscript{R&S} surfaces (14, 22). A new type of isothermal TPRS experiment was developed to study this reaction. In a normal TPRS experiment, the sample is heated at a constant rate until the adsorbed molecule reacts yielding a peak decomposition maximum rate at a
temperature, $T_p$. In an isothermal TPRS experiment, the sample is heated to and held at a constant temperature $T_{iso} < T_p$. For TA, decomposition occurs on the surface at a delayed time. As $T_{iso}$ is decreased, the time delay increases and the peak width increases. For chiral molecules such as L- and D-TA, this can be used to increase the separation between the decomposition peaks of each enantiomer on the surface and provide further evidence if the reaction is enantioselective.

Figure 52 is an isothermal TPRS experiment for D- and L-TA decomposition on a Cu(651)$^S$ surface (14, 22). As the isothermal hold temperature decreases for both enantiomers, the peak time increases, the peak height decreases, and the peak width increases. The area under the peak remains constant since isothermal TPRS experiments are all performed at a constant saturated coverage of TA. For D-TA on Cu(651)$^S$, the peak time delay is higher than for L-TA at value of $T_{iso}$. The difference between enantiomers is greatest at the lowest value of $T_{iso} = 450$ K. The peak for L-TA occurs at 400 seconds while the peak for D-TA occurs at 500 seconds. This 100 second difference in the decomposition times of L- and D-TA on the chiral Cu(651)$^S$ surface clearly shows that the reaction is enantioselective.
Figure 52: Isothermal TPRS experiment of saturated exposures of L- and D-TA on a Cu(651)\textsuperscript{s} surface. At 450 K, L-TA decomposes 100 seconds before D-TA. Experimental data obtained by Dr. Holsclaw (14, 22).
TA decomposition has been studied extensively on an achiral Cu(110) single crystal (14). Previous work has shown that TA binds to (110) at low coverages as a bitartrate species through two carboxyl groups or a monotartrate species at high coverages through one carboxyl group on the surface. For a saturated monolayer at 405 K $\theta_{TA}=1$, TA is present as the monotartrate species. Mhatre et al. used TPRS, LEED, and STM to develop a rate law for TA explosive decomposition and determine the state of the surface at various times during the isothermal reaction. TPRS monitoring multiple desorption signals was used to determine that the major products of TA explosive decomposition were CO$_2$, H$_2$O, and H$_2$ with minor products including several small hydrocarbons. Using TPRS experiments at variable coverage, heating rate, and $T_{iso}$, Mhatre et al. fit several kinetic models to the data. The rate law that best fit the collective results of the TPRS experiments was $-\frac{d\theta_{TA}}{dt} = k_i\theta_{TA} + k_e\theta_{TA}(1 - \theta_{TA})^2$ where $\theta_{TA}$ is the fractional coverage of TA on the surface, $(1 - \theta_{TA})$ is the fractional coverage of empty sites on the surface, $k_i$ is the initiation rate constant, and $k_e$ is the explosion rate constant. The proposed rate law consists of two steps, an initiation step and an explosion step. In the initiation step, TA is consumed, presumably by molecular desorption or decomposition, leaving empty sites. Once the number of empty sites reaches a critical coverage, explosive decomposition occurs increasing exponentially in rate as the number of empty sites increases until all TA has decomposed.

Mhatre et al. were also able to determine whether the initiation step is reversible or irreversible (14). An isothermal TPRS experiment was performed
with D-TA on Cu(651)\textsuperscript{S} using $T_{iso} = 440$ K and resulting in a decomposition peak after 360 s. This experiment was then repeated, except that after every 100 seconds of annealing the sample was cooled to 300 K to quench the reaction, before then heating back to 440 K. If the peak time for the quenching experiment is the same as the isothermal TPRS without quenches, then the initiation process is irreversible. Figure 53 displays both the isothermal TPRS experiment and the isothermal TPRS experiment with quenching. The decomposition reaction peak occurs after holding at $T_{iso} = 360$ s independent of whether or not the reaction is quenched showing that the TA decomposition initiation step is irreversible. This has also been observed on Cu(110) using LEED and STM where the coverage of TA decreases from $\theta_{TA}=1$ to $\theta_{TA}=0.9$ when the surface is held at 450 K.

In this research, we will determine the structure sensitivity of L- and D-TA decomposition on planes vicinal to Cu(111). We will show that TA decomposition is most sensitive to the density of (100) step edges. We will also determine that the rate law developed for TA decomposition on Cu(110) also applies to crystal planes vicinal to Cu(111) by using XPS and TPRS to calculate the coverage vs. time at multiple points on the Cu(111) S\textsuperscript{4}C and fitting several different models to the data. The initiation step is the rate limiting step in TA decomposition. Correlations between the site density and TA explosive decomposition activity were developed for step density, step orientation, and kink density.
The Cu(111) S\(^4\)C was cleaned in UHV chamber 2 until a LEED pattern was obtained across the entire S\(^4\)C surface. For one cleaning cycle, the S\(^4\)C was held at 700 K and sputtered with 1 kV Ar\(^+\) ions at 8 μA for 30-40 minutes then annealed for 5 minutes at 850 K. Over 20 cycles of sputtering and annealing were performed until a LEED pattern was obtained. Figure 54 shows LEED patterns of two locations on the Cu(111) S\(^4\)C surface with a beam energy of 150 eV and a

4.2 Experimental

Figure 53: Isothermal TPRS experiments of saturated exposures of D-TA on the Cu(651)\(^S\) surface. Top spectrum is isothermal TPRS at 450 K while bottom spectrum is isothermal TPRS at 450 K with quenches every 100 seconds. In spite of the quench cycles, the reaction still occurs after 360 s at 450 K showing that initiation of the TA decomposition is irreversible. Experiments performed by Dr. Holsclaw (14).
screen voltage of 4.85 kV. The left image was taken at the center of the Cu(111) S$_4$C and the right image was taken at the right edge of the crystal. In both images, the LEED pattern is hexagonal which is characteristic of the (111) plane. The right image shows the hexagonal pattern with broader spots and spot splitting circled in white. This is an expected result; as the distance from the (111) plane increases, the density of step edges increases and step edges cause spot splitting and broadening in LEED (94, 130, 230, 231).

After the LEED pattern was obtained, the Cu(111) S$_4$C was removed from UHV chamber 2 and placed in the UHV chamber 3 prep chamber after mounting the S$_4$C to the sample heater using the procedure explained in Chapter 3. The prep chamber was pumped down and baked out for 24 hours at 370 K while keeping the TA doser at < 340 K using a cooling fan to prevent dosing. After the prep chamber was pumped down and baked out, the Cu(111) S$_4$C was heated to 370 K for 2 hours then from 300 K to 800 K in steps of 100 K for 30 minutes each. This procedure was implemented to cure the Aremco Pyroduct 597-A silver paste and to degas the sample heater. The other components of the prep chamber were degassed after the sample heating procedure was finished. The Cu(111) S$_4$C was then moved into the analysis chamber and the high symmetry directions were located on the S$_4$C. Scratches made in the side of the crystal corresponding to the high symmetry directions were located using the optical microscope in the analysis chamber. A pair of scratches represented a high symmetry direction towards a {110} plane and a single scratch represented a high symmetry direction toward a {100} plane. Four of the high symmetry directions were marked around
the edge of the crystal. The directions toward the \{100\} and \{110\} are located
directly opposite each other or 180° from each other. Line scans in the
Thetaprobe software were created from each \{100\} to each \{110\} direction across
the surface. The intersection of these line scans were used to locate the \{111\}
crystal plane on the surface.

Figure 54: LEED pattern of Cu(111) S\textsuperscript{4}C in UHV chamber 2 at 90 K. Screen
voltage of 4.85 kV and beam energy of 150 eV used to obtain both patterns.

Figure 55 displays images of the TA doser with key components circled.
The doser is composed of two Cu heating wire feedthrough (red), a K-type
thermocouple feedthrough (blue), a Cu cold sink (white), a rotating Al mask
(green), and an Al body on a mounting flange. Ta wire was attached to the Cu
heating wire feedthrough using a barrel connector and wrapped around the Al
body and encased in alumina paste. Passing a current from 1-8 A through the Ta
wires was used to heat the doser to \(\leq 450\) K. A K-type thermocouple was
attached to the side of the Al body using a screw. The temperature of the doser
was controlled using a computer. Two vials containing L- or D-TA could be
attached to the Al body upside down. The TA vials were prepared by adding 0.1
g of L- or D-TA (99% pure from Sigma Aldrich) to each vial and dissolving it in distilled H₂O. The vials were then covered and left until the TA formed crystals at the bottom of each vial. This process allowed the TA vials to be mounted upside down in the doser. Only one enantiomer was present on the doser at any point in time. For D-TA experiments, only D-TA was present in the doser. The same was true for L-TA. When L-TA vials were removed and D-TA vials added, the doser and mask were rinsed with acetone, isopropyl alcohol, and dipped in boiling water to prevent any cross contamination between L- and D-TA. A doser temperature of 363 K was sufficient to deposit a multilayer of L- and D-TA onto the Cu(111) S⁴C while keeping the pressure in the prep chamber constant.

![Figure 55: Photographs of TA doser used in prep chamber. The doser is composed of two Cu heating wire feedthrough (red), a K-type thermocouple feedthrough (blue), a Cu cold sink (white), a rotating Al mask (green), and an Al body on a mounting flange. Two vials of TA (L- or D-) are mounted upside down in an Al body.](image)

The Cu(111) S⁴C was cleaned by sputtering and annealing in the prep chamber. The S⁴C was held at 650 K and sputtered with 2 kV Ar⁺ ions with a sputtering current of 10 μA for 40 minutes and then annealed for 10 minutes at 800 K. This cleaning cycle was repeated until an XPS spectrum of 100% Cu with
no contamination was obtained. Spectra for Cu, O, C, and Ag were obtained at multiple points across the inner 3.5 mm of the Cu(111) S^4C before TPRS experiments were performed. Ag was measured to confirm that Ag from the paste did not migrate to the surface.

Each quench TPRS experiment took 4-6 hours to perform not including the time for spatially resolved XPS. First the Cu(111) S^4C was sputtered and annealed for 2 cycles of cleaning described above in the prep chamber. Then the sample was cooled to ≤ 400 K and moved from the prep chamber into the analysis chamber. XPS scans of Cu, O, and C were obtained at five points on the Cu S^4C surface in the analysis chamber: The first point was at the (111) plane, and the other four points were located ±4 mm from the (111) plane along two orthogonal directions. If the surface composition each of the five points was >99 % Cu, the experiment was continued, otherwise more cleaning cycles were performed in the prep chamber. After XPS, the clean Cu(111) S^4C was moved into the prep chamber and placed on a stage underneath one of the vials of the TA doser. L- or D-TA was exposed to the S^4C for 45 minutes while the S^4C was held at a temperature <330 K to allow deposition of a multilayer film. A 45 minute exposure was sufficient to form a multilayer of L- or D-TA on the surface. After forming a multilayer on the surface, the S^4C was moved from the prep chamber into the analysis chamber and spatially resolved XPS was performed at the same five points as on the clean surface. Once the presence of the TA multilayer was confirmed on each point using XPS, the sample was moved into the prep chamber, heated to 405 K, and held there for >10 minutes to remove the
multilayer and leave a monolayer of TA on the surface. The top of Figure 56 shows XPS spectra of C 1s and O 1s for a multilayer and monolayer of L-TA. The C 1s and O 1s peaks consist of contributions from COO$^-$ and COH groups on the surface. After heating the sample to 405 K, the C and O signals decreased leaving 15±1 at% C and 22±1 at% O on the surface at each of the 5 points. The C:O ratio in TA is 2:3 so the ratio of 15:22 at% is expected. XPS of the monolayer was not performed in every experiment to limit any damage by the X-rays of the adsorbed TA. XPS of the multilayer was performed in every experiment to confirm that the doser was functioning properly. The bottom of Figure 56 shows XPS spectra of C 1s and O 1s at the Cu(111) plane after an isothermal TPRS experiment. After the reaction, there are still small amounts of C and O remaining on the surface. For D-TA there is an average of 3±1 at% O and 4±1 at% C after the isothermal TPRS. For L-TA there is an average of 2±1 at% O and 3±1 at% C left. This means that ~10% of the O and ~20% of the C in the monolayer of TA remain on the surface after complete decomposition. This was observed for both normal and isothermal TPRS experiments.

After heating the sample to 405 K and forming a monolayer of L- or D-TA, quench TPRS experiments were performed. Figure 57 shows an example of an isothermal TPRS experiment and a quench TPRS experiment for L-TA on the Cu(111) $^4$C. Plotted in blue is the temperature versus time and plotted in black is the mass spectrometer signal at $m/q$=44 versus time. The Cu(111) $^4$C is heated at 1 K/s and then held at 450 K, well below the temperature of the peak observed at ~490 K in a normal TPRS. The top of Figure 57 shows an example of
an isothermal TPRS at 450 K; the temperature is held constant at 450 K and TA decomposes into CO\textsubscript{2} and other products over 800 seconds until it has decomposed on the entire S\textsuperscript{4}C surface. In a quench TPRS experiment shown in the bottom of Figure 57, the sample is heated to 450 K and then held at 450 K, but before the reaction has reached completion across the entire S\textsuperscript{4}C surface, the heater is turned off and the sample cools quenching the reaction on the surface. After the sample is quenched, it is moved from the prep chamber to the analysis chamber and spatially resolved XPS is performed to identify the points at which TA has decomposed on the surface. The quench TPRS experiments were performed after various different extents of reaction to gain a visual representation of the reaction occurring across the entire S\textsuperscript{4}C surface with time. For L-TA (D-TA), spatially resolved XPS was performed at 121 (225) points within a radius of 3.2 mm from the (111) plane on the S\textsuperscript{4}C. This distance from (111) was used so that all measured points were within the spherical region of the S\textsuperscript{4}C. XP spectra were obtained for Cu 2p\textsubscript{3/2}, O 1s, and C 1s electrons at each point on the surface after the quench TPRS. An X-ray spot size of 400 μm in diameter was used for both L- and D-TA. The XPS spectra across the entire surface took between 4 and 7 hours to obtain depending on the number of points measured on the surface. Because of this, each quench TPRS was performed by starting with a clean surface and after the XPS scan was completed, the Cu(111) S\textsuperscript{4}C surface was sputtered and annealed to prepare the surface for the next quench TPRS experiment.
Figure 56: (Top) XPS of C 1s and O 1s of monolayer and multilayer L-TA on Cu(111) plane on Cu(111) $S^4C$. Monolayer of TA is 15±1 at % C and 22±1 at % O. (Bottom) XPS of Cu(111) plane after isothermal TPRS experiment. ~3 at % O and 3 at % C remain on the surface after the reaction.
Figure 57: Isothermal TPRS (top) vs. Quench TPRS (bottom) for L-TA on Cu(111) S⁴C. The signal at \( m/q = 44 \) corresponding to CO₂ desorption vs. time is shown in black and temperature vs. time is shown in blue. In the quench TPRS experiment, the sample is heated to 450 K and then held at 450 K, but before the reaction has reached completion across the entire S⁴C surface, the heater is turned off and the sample cools quenching the reaction on the surface.
4.3 Results

Before the quench TPRS experiments could be performed, standard TPRS of saturated exposures of both L and D-TA were performed to determine the peak temperature for CO$_2$ desorption. The first TPRS experiment performed for each enantiomer was a normal TPRS at a heating rate of 1 K/s. The saturated exposure conditions were determined using XPS to confirm the presence of a monolayer on the surface after forming a multilayer and heating the surface to 405 K for > 10 minutes. Figure 58 shows TPRS experiments for saturation exposures of L- and D-TA on the Cu(111) S$^4$C. The signal from $m/q = 44$ corresponding to CO$_2$ desorption was measured in the mass spectrometer using a heating rate of 1 K/s. Each peak has a FWHM of ~10 K and a peak location between 490 and 495 K. Multiple saturated TPRS experiments were performed and the peak location ranged between 490 and 495 K for both enantiomers. The peak widths and temperatures for CO$_2$ desorption from L- and D-TA decomposition are similar. This is an expected result because the Cu(111) S$^4$C contains crystal planes of both R and S chirality and the overall TPRS spectra contains contributions from multiple crystal planes of each chirality. Because the S$^4$C exposes a distribution of crystal planes, the peak widths for both L and D-TA are significantly broader (FWHM ~ 10 K) than for TA decomposition peaks seen previously on Cu(110), Cu(17,5,1)$^{R&S}$, and Cu(643)$^{R&S}$ (FWHM ~2 K) (3, 5, 14).

After determining the peak temperature for a normal TPRS, isothermal TPRS experiments were performed at several isothermal reaction temperatures. The purpose of performing the isothermal TPRS experiments at different
temperatures is to determine an ideal isothermal reaction temperature for the quench TPRS experiments. If the isothermal reaction temperature is too high and the peak width is too narrow, quenching the reaction will be difficult and fewer quench times will be possible. If the isothermal reaction temperature is too low, a peak will not be visible in the mass spectrometer because the reaction rate is too low and the peak signal is too small to be recorded. Figure 59 displays the isothermal TPRS experiments measuring CO$_2$ desorption from the decomposition of saturated exposures of L-TA on Cu(111) S$^4$C. In these isothermal TPRS experiments, the Cu(111) S$^4$C is heated at 1 K/s and held below the peak temperature of ~490 K observed in a standard TPRS experiment. As described in the experimental section, the decomposition reaction still occurs and as the isothermal reaction temperature decreases, the time delay for the reaction onset increases. The peak width for the decomposition reaction also broadens as the isothermal reaction temperature decreases. For L-TA, an isothermal reaction temperature of 450 K resulted in a CO$_2$ desorption peak signal high enough to be recorded by the mass spectrometer and a peak width of >600 seconds which allows multiple quench times during the reaction. For both L- and D-TA, an isothermal hold temperature of 450 K was used for all quench TPRS experiments.
Figure 58: TPRS of saturated L- and D-TA monolayers on Cu(111) S\textsuperscript{4}C. A heating rate of 1 K/s used from 350 - 600 K. The signal at \( m/q = 44 \) corresponding to CO\textsubscript{2} desorption was measured.

Figure 59: Isothermal TPRS for saturated monolayers of L-TA on Cu(111) S\textsuperscript{4}C. In each experiment, the Cu(111) S\textsuperscript{4}C was heated at 1 K/s and held at the temperature indicated until a reaction occurred. The signal at \( m/q = 44 \) was used to measure CO\textsubscript{2} desorption.
Figure 60 shows the quench TPR spectra for L- and D-TA on the Cu(111) S\(^4\)C. Seven quench experiments were performed for D-TA decomposition and six quench experiments were performed for L-TA. These include the 100% experiment, which is an isothermal TPRS experiment where TA has decomposed at all points on the S\(^4\)C, and a 0% experiment. In the 0% experiment, the S\(^4\)C was heated to 450 K, then immediately cooled down to < 400 K before the reaction could occur at any point on the surface. The extent of reaction, \(X\), reported as the fraction of TA that had decomposed following quenching at a given time, was calculated from both the XPS data and the TPRS data. The extent of reaction was calculated from the TPRS data as the area of the quenched TPR spectrum divided by the area of the TPRS that reached 100% decomposition. The fraction reacted was also calculated from the XPS data using the peak areas of the O 1s signal peak and C 1s at all points measured on the surface. After each quench time, \(t\), O 1s and C 1s XP spectra were obtained at discrete points, \(i = 1 \ldots N\), distributed around the (111) point. The areas under the O 1s and C 1s XP peaks, \(I_i^O(t)\) and \(I_i^C(t)\) respectively, were determined at each point across the Cu(111) S\(^4\)C surface. The extents of reaction, \(X^O(t)\) and \(X^C(t)\), based on the O 1s and C 1s XP peak areas, were then determined for each quench time using equations 4.1 and 4.2, respectively. The extent of reaction, \(X(t)\), reported throughout the rest of this work is the average of \(X^O(t)\), \(X^C(t)\) and the extent of reaction determined from the area under the TPRS curves. All of the values used to calculate the extents of reaction are listed in Table 5 for D-TA and Table 6 for L-TA.
\[
X^O(t) = \left(1 - \frac{\sum_{i=1}^{N} I^O_i(t)}{\sum_{i=1}^{N} [I^O_i(0) - I^O_i(\infty)]}\right) \times 100
\]

\[
X^C(t) = \left(1 - \frac{\sum_{i=1}^{N} I^C_i(t)}{\sum_{i=1}^{N} [I^C_i(0) - I^C_i(\infty)]}\right) \times 100
\]

Figure 60: Quench TPRS of L and D-TA on Cu(111) S\(^4\)C. The extent of reaction displayed on each figure is calculated from the XPS O 1s and C 1s XPS peak areas and the TPRS peak areas. The signal measured for each quench TPRS is \(m/q = 44\) from CO\(_2\) desorption. The isothermal reaction temperature in each experiment is 450 K.

Table 5: Extents of reaction determined by O peak area ratio, C peak area ratio, and TPRS peak area ratio for D-TA. The extents of reaction, \(X^O(t)\) and \(X^C(t)\), based on the O 1s and C 1s XP peak areas, were determined for each quench time using equations 5.1 and 5.2 for \(N = 225\) points.

<table>
<thead>
<tr>
<th>Percent Reacted</th>
<th>(X^O(t))</th>
<th>(X^C(t))</th>
<th>TPRS Percent</th>
<th>Time at 450 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.16</td>
<td>0.05</td>
<td>0.10</td>
<td>175</td>
</tr>
<tr>
<td>31</td>
<td>0.32</td>
<td>0.33</td>
<td>0.30</td>
<td>285</td>
</tr>
<tr>
<td>63</td>
<td>0.64</td>
<td>0.69</td>
<td>0.55</td>
<td>380</td>
</tr>
<tr>
<td>74</td>
<td>0.71</td>
<td>0.80</td>
<td>0.70</td>
<td>450</td>
</tr>
<tr>
<td>94</td>
<td>0.93</td>
<td>0.97</td>
<td>0.90</td>
<td>518</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>623</td>
</tr>
</tbody>
</table>
Table 6: Extents of reaction determined by O peak area ratio, C peak area ratio, and TPRS peak area ratio for D-TA. The extents of reaction, \(X^O(t)\) and \(X^C(t)\), based on the O 1s and C 1s XP peak areas, were determined for each quench time using equations 4.1 and 4.2 for \(N = 121\) points.

<table>
<thead>
<tr>
<th>Percent Reacted</th>
<th>(X^O(t))</th>
<th>(X^C(t))</th>
<th>TPRS Percent</th>
<th>Time at 450 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>46</td>
<td>0.48</td>
<td>0.46</td>
<td>0.44</td>
<td>386</td>
</tr>
<tr>
<td>60</td>
<td>0.59</td>
<td>0.60</td>
<td>0.62</td>
<td>460</td>
</tr>
<tr>
<td>74</td>
<td>0.73</td>
<td>0.74</td>
<td>0.73</td>
<td>547</td>
</tr>
<tr>
<td>85</td>
<td>0.79</td>
<td>0.85</td>
<td>0.91</td>
<td>638</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>780</td>
</tr>
</tbody>
</table>

Figure 61 shows an example of an O concentration map obtained from spatially resolved XPS on the Cu(111) S\(^4\)C after adsorption of a saturated monolayer of D-TA, but before heating to induce isothermal decomposition, so \(t = 0\) and \(X = 0\). The 225 points at which measurements were made are indicated as black dots and the X-ray spot diameter of 400 \(\mu m\) is shown as a blue circle. XP spectra for Cu2p\(_{3/2}\), O 1s, and C 1s were obtained at the 225 points indicated and lying on seven concentric rings centered on the (111) planes and with a maximum radius of 3.2 mm. The X-ray spot size is large enough that there is some overlap between the measured points. The O concentration in at\% was calculated from the peak area ratios of the O 1s, C 1s, and Cu 2p\(_{3/2}\) XP spectra using the Wagner sensitivity factors (232). At \(X = 0\) there is a uniform concentration of D-TA across the surface with an average of 22±1 at\% O. The color scale of the concentration map indicates the at\% O at each point. The red color indicates a point on the surface where TA has not begun to decompose while green indicates a point at which the TA has decomposed completely.
The white and black lines across the O concentration map in Figure 61 indicate the edges of the stereographic triangle superimposed on the surface. Along the white lines are crystal planes which expose (111) terraces separated by straight (110) step edges while along the black lines are crystal planes which expose (111) terraces separated by straight (100) step edges. As the distance from the (111) plane increases, the step density increases. Maxima in the density of kink sites along the step edges occur midway between (100) and (110) step edge directions. These regions are chiral and there are three R regions and three S regions on the Cu(111) $S^4C$ indicated in yellow.

Figure 61: O concentration map for a saturated monolayer of D-TA on the Cu(111) $S^4C$. The X-ray spot size is 400 μm and is shown as a blue circle. O 1s XP spectra were obtained at the 225 points indicated and lying on seven concentric rings centered on the (111) planes and with a maximum radius of 3.2 mm. The edges of the stereographic triangle are shown as lines and the orientation of the step edges exposed along each line is indicated.
Figure 62 displays a progression line of the extent of the decomposition reaction for both L- and D-TA on the Cu(111) S\textsuperscript{4}C. Each circle is an O concentration map measured at 121 points across the S\textsuperscript{4}C within 3.3 mm of the (111) surface for L-TA and 225 points within 3.2 mm of the (111) surface for D-TA. The progression line spans $X = 0 \rightarrow 100$ and the value of $X$ for each concentration map is indicated in red for L-TA and blue for D-TA. For both L- and D-TA, there is 22±1 at% on the surface at $X = 100$ and 2-3 at% O remaining on the surface at $X = 100$ displayed in the timeline. To convert the O 1s XPS maps into maps of TA coverage, $\theta_{TA}$, the local coverages for all points and $X = 0$ were assumed to be $\theta_{TA} = 1$ and the local coverages at $X = 100$ were set to $\theta_{TA} = 0$. The variation in the fractional compositions of C and O across the surface was ±1 at% at $X = 0$ and 100. For the extents of reaction between $X = 0$ and 100, the local TA coverages, $\theta_{TA}(\vec{r}_i, X)$, were calculated using

$$\theta_{TA}(\vec{r}_i, X) = \frac{I_O(\vec{r}_i, X) - I_O(\vec{r}_i, 100)}{I_O(\vec{r}_i, 0) - I_O(\vec{r}_i, 100)}$$  \hspace{1cm} (4.3)$$

where $\vec{r}_i$ is the position of point $i$ on the S\textsuperscript{4}C surface and $I_O$ is the O 1s photoemission intensity measured from the area under the O 1s XPS peak. An analogous expression could be written for the C 1s photoemission intensity and used to estimate $\theta_{TA}(\vec{r}_i, X)$. Equation 4.3 accounts for the presence of O and C remaining on the surface after reaction, $X = 100$. This procedure was used to calculate $\theta_{TA}(\vec{r}_i, X)$ from both $I_O$ and $I_C$. The higher concentration of O and its greater sensitivity in XPS (232) make $I_O$ a better metric than $I_C$ for determination of $\theta_{TA}$. 

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Both L- and D-TA have similar reaction patterns in the sense that the regions of highest decomposition activity are identical for both adsorbates. The first thing to note is that the O concentration maps reveal the three-fold symmetry of the region vicinal to the (111) plane. Note also, that there is a region of the Cu(111) S₄C surface at about 2.5 mm from the (111) pole along the direction towards one o’clock that is defective. Visual inspection of the Cu(111) S₄C indicated some damage to the surface at this point and the concentration maps indicate that this region exhibits anomalously low TA decomposition activity. Across the rest of the surface, the highest activity for TA decomposition lies along the directions exposing the straight (100) step edges and the lowest activity appears along the directions exposing the straight (110) step edges. This result is the most notable when comparing the concentration maps at $X = 74$. The expected result is that L- and D-TA decomposition kinetics are sensitive to the surface chirality. In that case, the concentration maps would not be symmetric with respect to the mirror symmetry directions. Seen previously on Cu(643)⁰⁷ surfaces, L-TA would remain longer on S crystal planes while D-TA would remain longer on R crystal planes. Instead, the decomposition reaction of both enantiomers is sensitive to the step orientation. Both L- and D-TA react on (100) step edges (black line) first followed by (110) step edges (white line) and finally the (111) plane at the center.
The O, C, and Cu at % on the S\textsuperscript{4}C surface were also calculated at each point on the surface and at each overall extent of reaction. The O concentration is a better metric for the local extent of reaction than the C concentration because of its higher signal strength in XPS. However, the C 1s signal confirms that the species initially on the surface is actually TA and also reproduces the reactivity pattern observed using the O concentration map. Figure 63 compares O and C concentration maps of D-TA in at % on a single extent of reaction progression line. The O concentration ranges from 0-21 at % while C concentration ranges from 0-15 at %. This comparison plot clearly shows that the trends in the disappearance of O and C from the surface versus X reproduce one another.
As noted earlier, at some point during these experiments, a scratch formed on the top right region of the $\text{S}^4\text{C}$ surface. This scratch results in significant O and C remaining on the surface at high value of $X$ and clearly breaks the apparent threefold symmetry observed for the tartaric acid decomposition kinetics across the Cu(111) $\text{S}^4\text{C}$. If this point was not a scratch, it would be repeated every 120° on the edge of the $\text{S}^4\text{C}$. Data points affected by the scratch were removed when performing further data analysis to calculate rate constants.

Figure 63: C and O concentration maps in at % for D-TA Cu(111) $\text{S}^4\text{C}$ at various values of $X$. The O concentration ranges from 0-21 at % while C concentration ranges from 0-15 at %. C and O maps follow the same pattern of behavior while maintaining a 3:2 ratio of O:C on the portions of the surfaces where D-TA has not reacted.
4.4 Discussion

4.4.1 Rate Law Modeling

In order to calculate rate constants for TA decomposition at each of the points studied on the Cu(111) S^4C surface, the XPS data and TPRS data must be used to determine the TA coverage, $\theta_{TA}$, versus time. For D-TA on Cu(111) S^4C, XPS maps versus time were obtained at 225 different points. For L-TA, there are 121 such data sets. Once the XPS maps were converted to $\theta_{TA}(\vec{r}, X)$ using Equation 4.3, the reaction time was determined for each value of $X$. The time used in calculating the rate constants was the time the sample was held at $T = 450$ K and is listed in Table 5 and Table 6 for each data point. The maps of $\theta_{TA}(\vec{r}, t)$ can be fit to rate laws for the explosive decomposition of TA, in order to determine maps of the relevant rate constants at 450 K across the S^4C surface.

One of the first rate laws to be proposed for explosive decomposition of adsorbates on surfaces is

$$r = -\frac{d\theta_{TA}}{dt} = k_e \theta_{TA}(1 - \theta_{TA}). \quad (4.4)$$

In this rate law, as applied to TA, the decomposition rate depends on the fractional coverage of TA, $\theta_{TA}$, the fractional coverage of empty sites, $(1 - \theta_{TA})$, and one rate constant, $k_e$ (51, 233). Integration of this rate law yields the relationship between time, $t$, and $\theta_{TA}$.

$$t = \frac{\ln(1 - \theta_{TA}) - \ln(\theta_{TA})}{k_e} + t_0 \quad (4.5)$$
The issue with this rate law is that for an initial coverage of $\theta_{TA} = 1$, the boundary condition for the integral at $t = 0$, the equation is undefined and can only be solved if the initial condition is changed to $\theta_{TA} < 1$. Physically the interpretation of this situation is that the surface explosion reaction requires the presence of some vacancies and in their absence the reaction never starts, independent of the temperature. Initial work on the explosion reactions suggested that there must be some concentration, $f$, of initiation sites, the nature of which was not determined. To adjust this model to be solvable at $\theta_{TA} = 1$ those researchers added the parameter, $f$, to the rate law representing a coverage of initiation sites on the surface shown in Equation 4.6 (48, 234).

$$ r = -\frac{d\theta_{TA}}{dt} = k_e \theta_{TA}(1 - \theta_{TA} + f) \quad (4.6) $$

Prior work has examined the explosive decomposition of TA on low Miller index Cu surfaces and on chiral high Miller index planes with high densities of kinks sites (3, 5, 14, 22). The fact that TA decomposition occurs by an explosive mechanism on both suggest that defects such as kink sites are not the nuclei for initiation of the explosion process. Instead, it has been hypothesized that a better description of the explosion initiation process is via an independent initiation step. Rate laws parameterized by two rate constants have been shown to predict accurate trends for TA decomposition on a Cu(110) single crystal shown in Equation 4.7.

$$ R_{mn} = -\frac{d\theta_{TA}}{dt} = k_i \theta_{TA}^m + k_e \theta_{TA}(1 - \theta_{TA})^n \quad (4.7) $$
These rate laws are parameterized by an initiation rate constant, $k_i$, and an explosion rate constant, $k_e$. This rate law describes a mechanism in which there are two steps to explosive decomposition. In the first step, TA desorbs from the surface (or decomposes) creating an empty site or vacancy on the surface.

Whatever its nature, Mhatre et al. have observed that this initiation step is irreversible (14). In the presence of vacancies, TA can undergo explosive decomposition which creates additional vacancies on the surface.

In the course of this work we will consider six kinetics models for TA decomposition on the Cu(111) S$^4$C, each differing in the reaction order of the initiation step and the order of the explosion reaction in vacancy concentration, $R_{mn}$ ($m = 0, 1; n = 1, 2, 3$). Because the data set for D-TA includes more points on the surface (225) than that for L-TA (121) and also includes measured at seven values of $X$ over the six values measured for L-TA, only the data set for D-TA was used to identify the kinetic model that best fits the data. The rate laws for models $R_{01}$, $R_{11}$ and $R_{12}$ have analytical solutions for time $t$ as a function of $\theta_{TA}$, $k_i$, and $k_e$, but the other three rate laws do not. To be consistent in comparing the ability of these rate laws to fit the data, numerical integration was used to predict $\theta_{TA}(t; k_i, k_e)$ at each point on the surface. The ode45 solver in Matlab was used to numerically integrate each rate law and calculate the difference between the coverage predicted by the different models and the experimental coverage at each point on the S$^4$C surface. The lsqnonlin function was used to fit the predictions of each model to the experimental data for $\theta_{TA}(t; \tilde{r})$. The input to the lsqnonlin function is a vector of calculated errors and which is used to adjust the values of
$k_i$ and $k_e$ minimize the sum of squared errors between the predictions of each model and the experimental data. The error vector input to \textit{lsqnonlin} was the difference between the experimental determined value of $\theta_{TA}(t; \tilde{\eta})$ and the coverage predicted by the model using \textit{ode45}. Values of $k_i(\tilde{\eta}_j)$ and $k_e(\tilde{\eta}_j)$ were calculated for each of the 225 points on the $S^4C$ surface for all six of the rate laws. To check whether the numerical solver and the analytical solution were consistent, values of $k_i(\tilde{\eta}_j)$ and $k_e(\tilde{\eta}_j)$ calculated by the numerical solver were plugged into the analytical solution for all 225 points for the $R_{12}$ model. The coverage vs. time of all 225 points predicted by the model for the numerical and analytical solutions were identical. After the $k_i(\tilde{\eta}_j)$ and $k_e(\tilde{\eta}_j)$ values were determined for all 225 points for each model, parity plots of $\theta_{TA}^{exp}(t; \tilde{\eta}_j)$ versus $\theta_{TA}^{mdl}(t; \tilde{\eta}_j)$ were created.

The left of Figure 64 shows the parity plots comparing $\theta_{TA}^{exp}$ with $\theta_{TA}^{mdl}$ at all points on the Cu(111) $S^4C$ surface and at all extents of reaction for the rate laws $R_{01}$, $R_{02}$ and $R_{03}$ for which the initiation step is zero order in $\theta_{TA}$. Of these three models for the rate law, the one with the best fit to the experimental value of $\theta_{TA}^{exp}$ is $R_{01}$. However, none of the rate law with $m = 0$ fits the data as well as those with $m = 1$. The right of Figure 64 shows the parity plots for the three rate laws $R_{11}$, $R_{12}$ and $R_{13}$ for which the initiation step is first order in $\theta_{TA}$. The fits to the $R_{1n}$ rate laws are clearly superior to those for the $R_{0n}$ rate laws and the best fits are achieved for the $R_{12}$ and $R_{13}$ rate laws. The sum of squared errors calculated for each model over all across the Cu(111) $S^4C$ and for all extents of
reaction studied is displayed in each parity plot in Figure 64. For the zero order initiation step models in Figure 64, \( m=0 \), as the exponent, \( n \), on the vacancy coverage in the explosion term of the rate laws increases, the total sum of squared errors also increases for the zero-order rate laws. For the first-order initiation step models in Figure 64, \( m=1 \), there is a clear decrease in the sum of squared errors between the \( R_{11} \) and \( R_{12} \) models. However, the sum of squared errors for the \( R_{12} \) and \( R_{13} \) models are similar. The analysis of the sum of squared errors and the parity plots show that the \( R_{12} \) and \( R_{13} \) models are the best fits for the D-TA data.
The sum of squared errors totaled across the Cu(111) S$^4$C surface can be used to determine which model is the best fit to all of the data but does not give

\[ R_{m,n} = k_i \theta^m + k_e (1-\theta)^n \]

Figure 64: Parity plots of all models. Each plot shows the $\theta_{TA}^{exp}$ from the experimental data plotted against each model $R_{m,n}$ along with a line where $\theta_{TA}^{exp} = \theta_{TA}^m$. The analysis of the sum of squared errors and the parity plots show that the $R_{12}$ and $R_{13}$ models are the best fits for the D-TA data.

The sum of squared errors totaled across the Cu(111) S$^4$C surface can be used to determine which model is the best fit to all of the data but does not give
clear insight into whether $\theta_{TA}^{exp}(t; \tilde{r}_j)$ is fit better by the model at some points on the Cu(111) S\textsuperscript{4}C than others. A map of the sum of squared errors at each point across the Cu(111) S\textsuperscript{4}C surface can be used to determine whether there are trends in the fit of each model with surface structure. Figure 65 displays maps of the sum of squared errors in the coverage across the Cu(111) S\textsuperscript{4}C for each of the models. This figure shows whether there are surface orientations at which a given model does not fit the data well. The scale of each of the maps is 0 to 0.2. The maximum possible sum of squared errors at a given point is 7 because the maximum error is 1 at each extent of reaction measured. This means the maximum of the scale is 3% of the maximum possible value. The rate laws with zero-order initiation steps, $m = 0$, all have large errors at points with a high density of step edges near the edge of the Cu(111) S\textsuperscript{4}C and at points vicinal to the (111) plane at the center. The $R_{01}$ model also has large errors on the crystal planes with (110) step edges and no kinks. As the order in vacancy concentration, $n$, of the explosion step increases for $m = 0$ models, the fitting improves along the (110) step edges but does not improve at points with a high step edge density. The overall sum of squared errors from the parity plots and from the maps across the S\textsuperscript{4}C surface is significantly lower for the first-order initiation models, $R_{1n}$ than for the $R_{0n}$ models. $R_{12}$ and $R_{13}$ fit the data better than any of the other models. Figure 66 shows a comparison of the six rate laws for one point on the Cu S\textsuperscript{4}C surface. The point circled in blue has a high density of straight (100) step edges and exhibits relatively high reactivity compared to other points on the S\textsuperscript{4}C. The colors of the lines in Figure 66 correspond to the rate laws in the highlighted
boxes. The experimental data is shown as gold triangles. The first-order initiation models, $R_{1n}$, fit the data very well. For these rate laws, the reaction proceeds so quickly that $k_e \rightarrow 0$ and each of the first order rate laws approach

$$-\frac{d\theta}{dt} = k_i \theta.$$ This is the same behavior as a first order decay reaction. For the zero order initiation models at the same point, as $k_e \rightarrow 0$, the rate laws approach

$$-\frac{d\theta}{dt} = k_i.$$ The solution of this equation is a linear decrease in the coverage with time based on the value of $k_i$ and does not fit the data well for points where TA decomposes quickly. The point on the surface in Figure 66 is an example of the coverage vs. time behavior that is fit poorly by the $m=0$ models at the edges of the S$_4$C.

The superiority of the fit of either $R_{12}$ or $R_{13}$ the data set cannot be determined. Additional experiments would be necessary to differentiate these models: either a new set of experiments at a lower isothermal hold temperature or more measurements between $X = 0$ and 30. However, the $R_{12}$ rate law was found to be the best fit to the kinetics of TA decomposition on the Cu(110) single crystal based on a comprehensive set of variable coverage, variable heating rate and isothermal TPRS experiments (14). For this reason and based on the sum of squared errors analysis, the values of $k_i$ and $k_e$ from the $R_{12}$ model have been used to discuss the structure sensitivity of TA decomposition on the Cu(111) S$_4$C.
Figure 65: Sum of squared error maps for all models. $R_{01}$ model does not fit the data well along (110) step edges and the $R_{02}$ and $R_{03}$ models break down at high step densities on the edges of the Cu(111) S$^4$C. The $R_{11}$ model also does not fit the data well along (110) step edges. The $R_{12}$ and $R_{13}$ models are the best fit to the data.
Figure 66: Coverage vs. time for experimental data and the six rate laws for point indicated in blue on the map of at % O for \( X = 63 \). This point has a high density of (100) step edges. The color of each line corresponds to the color of the box around each rate law shown. The \( R_{0n} \) models are a poor fit to the data at this point on the \( S^4C \) because the data follows a first order exponential decay.

### 4.4.2 Best fit trends of \( k_i \) and \( k_e \)

Using the \( R_{12} \) model, values of \( k_i \) and \( k_e \) were calculated at 225 points on the Cu(111) \( S^4C \) surface for D-TA and at 121 points on the \( S^4C \) surface for L-TA. Rate constant values were calculated for the raw data with the points in the damaged region removed. Plots of \( \theta_{TA} \) versus \( t \) for D-TA on four select points on the Cu(111) \( S^4C \) are shown in Figure 67 and the locations of the points are displayed on the \( \theta_{TA} \) map at \( X = 74 \). A good metric for the progression of the reaction is the time needed to reach \( \theta_{TA} = 0.33 \) or \( t_{1/3} \) which will be used to compare the reaction progression on the four surfaces. Each of the four points shown has a significantly different surface structure. Point 1 has a high density of
straight, close-packed (100) step edges separated by (111) terraces. The value for $k_l$ is a maximum value of all 225 points on the surface at $1.2 \times 10^{-2}$ s$^{-1}$ and the value for $k_e = 1.6 \times 10^{-7}$ s$^{-1}$ is a minimum. The $\theta_{TA}(t)$ data for Point 1 is similar to an exponential decay which is expected for $k_l \gg k_e$ and at Point 1 $t_{1/3} = 92$ s. Point 2 has the same step density as Point 1, however, the step edges are kinked and have the highest possible density of kinks along a step edge. This surface is chiral and contains S-kinks formed by (100) and (110) microfacets that are one atomic spacing in. The value of $k_l$ at Point 2 is $1.2 \times 10^{-3}$ s$^{-1}$, roughly one tenth that of Point 1, but $k_e = 2.5 \times 10^{-2}$ s$^{-1}$, five orders of magnitude higher than the value of $k_e$ at Point 1. Regardless of this increase in $k_e$, the value of $t_{1/3} = 305$ s, three times that of Point 1. Point 3 contains the same density of step edges as Points 1 and 2 but these are straight, close-packed (110) steps separating (111) terraces. The value of $k_l = 3.4 \times 10^{-4}$ s$^{-1}$, over twenty times lower than that at Point 1 and even though $k_e$ increases to $k_e = 3.1 \times 10^{-2}$ s$^{-1}$, $t_{1/3} = 526$ s is much longer than at either Points 1 or 2. Point 4 is the location of the (111) plane on the $S^4C$ surface and contains no steps. The value of $k_l = 8.3 \times 10^{-5}$ s$^{-1}$ is a minimum at Point 4 relative to the rest of the $S^4C$ while the value of $k_e = 9.7 \times 10^{-2}$ sec$^{-1}$ is a maximum and the value of $t_{1/3} = 581$ s is a maximum at Point 4. At each of the four points on the $S^4C$, the $R_{12}$ model appears fit to the experimental data well.
Figure 67: (top) Location of four coverage vs. time plots on contour plot of the $X = 74$ experiment of D-TA on Cu(111) $S^4$C. (bottom) Coverage vs. time of experimental data and best fit model for four points on Cu(111) $S^4$C. The value of $k_i$ is a maximum at Point 1 and a minimum at Point 4. The units of each rate constant is second$^{-1}$ or s$^{-1}$. 
The $\theta_{TA}(t; \tilde{r}_i)$ curves calculated for all 225 points using the $R_{12}$ model are displayed as a waterfall plot in Figure 68. The curves are ordered along the $z$-axis by increasing values of $t_{1/3}$. At low values of $t_{1/3}$, the $\theta_{TA}(t; \tilde{r}_i)$ looks like exponential decay. As $t_{1/3}$ increases, the initiation period becomes more obvious. As $t_{1/3}$ reaches a maximum value at 581 seconds, the shape of the $\theta_{TA}(t; \tilde{r}_i)$ curves has a time delay of 200-300 seconds before the coverage decreases rapidly to zero. Figure 68 also includes a plot of the value of $k_l$ versus $t_{1/3}$ for the $R_{12}$ model for all 225 points. As the value of $t_{1/3}$ decreases, so does the value of $k_l$. The waterfall plot and the change in the value of $k_l$ with $t_{1/3}$ and of the $R_{12}$ model clearly show that the rate limiting step in the reaction is the initiation step, $k_l\theta_{TA}$.

Figure 68: Waterfall plot of $\theta_{TA}(t; \tilde{r}_i)$ predicted by the $R_{12}$ model for D-TA at all 225 points. The $z$-axis is ordered by increasing $t_{1/3}$ into the page. The plot of the right shown the trend of $k_l$ vs. the $t_{1/3}$. As $k_l$ increases, the value of $t_{1/3}$ decreases.
On the Cu(111) plane, L- and D-TA should exhibit the same $\theta_{TA}(t)$ because Cu(111) is an achiral surface. Figure 69 shows a plot of $\theta_{TA}(t)$ for L- and D-TA on Cu(111) and the fit of the $R_{12}$ model with the values for $k_l$ and $k_e$ shown for each enantiomer. The value for $t_{1/3}$ of L-TA on Cu(111) point is 710 s and for D-TA is 581 s which is a difference of ~20%. Although the $\theta_{TA}(t)$ plot differ slightly, the values for $k_l$ and $k_e$ are similar.

Maps of $k_l(\vec{r})$ on the Cu(111) S$^{44}$C for L- and D-TA are displayed in Figure 70 and the maps of $k_l(\vec{r})$ are shown in Figure 71. Both L- and D-TA show a similar trend in $k_l$ and $k_e$. For D-TA (L-TA) the values of $k_l$ range from a maximum of $1.2 \times 10^{-2}$ s$^{-1}$ ($1.1 \times 10^{-2}$ s$^{-1}$) on surfaces with a high density of (100) step edges to a minimum at of $8.3 \times 10^{-5}$ s$^{-1}$ ($6.4 \times 10^{-5}$ s$^{-1}$) on the (111) plane. The values of $k_e$ for D-TA (L-TA) range from $1 \times 10^{-7}$ s$^{-1}$ on surfaces with a high density of (100) step edges to $9.7 \times 10^{-2}$ s$^{-1}$ ($7.9 \times 10^{-2}$ s$^{-1}$) on the (111) orientation. For both L and D-TA, as the density of (100) step edges increase along the black lines, the value of $k_l$ increases dramatically. The value of $k_e$ approaches zero on crystal planes with (100) step edges and remains relatively constant except for surfaces with (110) step edges and near the (111) plane at the center. The explosion rate constant $k_e$ seems to effect the rate at which the coverage decreases with time once the explosion reaction occurs. The value of $k_l$ is more sensitive to the density of (100) step edges than (110) step edges.
Figure 69: $\theta_{TA}(t)$ from experimental data and the predictions of the $R_{12}$ model for L- and D-TA on the (111) plane of the Cu(111) $S^4C$. The values for $k_i$ and $k_e$ are shown in blue for D-TA and green for L-TA.
Figure 70: Maps of $k_l(\overrightarrow{r})$ for L- and D-TA on the Cu(111) S^4C. The data points from the scratch were removed and the values of $k_l$ in the outer two rings of data points were averaged every 120°. As the density of (100) step edges increases, the value of $k_l$ increases. The minimum value of $k_l$ occurs on the (111) plane.

Figure 71: Maps of $k_e(\overrightarrow{r})$ for L- and D-TA on Cu(111) S^4C. The data points from the scratch were removed and the values of $k_e$ in the outer two rings of data points were averaged every 120°. The value of $k_e$ is higher on (110) step edges than on (100) step edges and reaches a maximum on the (111) plane.
There is a clear increase in the activity of TA explosive decomposition and increasing values of $k_i$ with increasing (100) step edge density, the rate limiting step in the overall decomposition reaction. These $k_i$ values can also be used as the basis for quantitative correlations between activity and the density of different sites across the Cu(111) S$^4$C. The data for D-TA was used in this quantitative analysis since there were more experimental data points available and the trends between D-TA and L-TA are similar. For an ideal surface, the equations for calculating the linear densities of step edges have been calculated by Dr. Holsclaw in his PhD thesis for surfaces vicinal to (111) as the inverse of the terrace width, $\frac{1}{w} = \frac{\sqrt{3} \sin \theta}{a}$, where $a$ is the lattice constant of Cu (0.361 nm) and $\theta$ is the angle between the surface $(hkl)$ and the (111) plane. The linear step density (# of steps/µm) has been used to determine the trends in TA explosive decomposition activity. The right of Figure 72 displays the different points used to correlate $k_i$ with step density. These points are plotted on a map of $k_i(\vec{r})$ on the Cu(111) S$^4$C calculated from the raw data with the data in the damaged region removed. The black points are surfaces with only straight, close packed (100) step edges and the blue points are surfaces with only straight, close-packed (110) step edges. As the distance from the center increases, the step density increase is independent of the step orientation. The $k_i$ data used is from the $R_{12}$ model from the $\theta_{TA}(t; \vec{r})$ raw data with the damaged points removed from the analysis. The left panel of Figure 72 is a plot of $k_i$ versus the linear step density along the directions exposing surfaces with just (100) and (110) steps. As the density of (100) step edges increases, $k_i$ increases more rapidly than for (110) step edges. A
line was fit to each of the data sets and the equation of the best fit line is displayed on each plot. For both (100) and (110) step edges, there is a positive correlation between the density of step edges and $k_l$. The slope of the best fit line for (100) step edges is $1.76 \times 10^{-5} \frac{\mu m}{step\cdot sec}$ which is over ten times higher than for (110) step edges.

![Graph](image)

Figure 72: (left) Trend of $k_l$ with linear (100) and (110) # of steps/μm on points for D-TA on Cu(111) S4C with no kinks. The value of $k_l$ increases more rapidly with (100) step edge density than (111) step edge density. (right) measured points in plot of $k_l$ vs. # of steps/μm on contour plot of $k_l$ with the scratch points removed.

The value of $k_e$ has the opposite trend with step density compared to $k_l$.

The left panel of Figure 73 is a plot of $k_e$ versus the linear step density along the same directions and at the same points used for determining the trends with $k_e$.

The values for $k_e$ on surfaces with (110) step edges are consistently higher than on (100) step edges but the change with step density is similar along both
directions. The slope of the best fit line for (100) step edges is \(-6.5 \times 10^{-5} \frac{\mu m}{step/sec}\) which is very close to the value of \(-7.0 \times 10^{-5} \frac{\mu m}{step/sec}\) for (110) step edges. There is a clear decrease in \(k_e\) with increasing step density for both (100) and (110) step edge directions.

Figure 73. (left) Trend of \(k_e\) with linear (100) and (110) # of steps/\(\mu m\) on points for D-TA on Cu(111) S4C with no kinks. The change in \(k_e\) with step density is similar for both (100) and (110) step edge density. (right) measured points in plot of \(k_e\) vs. # of steps/\(\mu m\) on a map of \(k_e\).

In addition to step density, the density of kink sites can also influence surface reaction kinetics. To determine the effect of kink sites on the reaction, the dependence of \(k_i\) on azimuthal angle was determined at a constant distance from the (111) plane. The maximum in the kink density at a fixed radius occurs at a 30° angle from the directions containing the surfaces with (100) and (110) step edges lines, bisecting the angle defined by the edges of the stereographic triangle. The kink density also increases as the distance away from the (111) plane.
increases. The outer circle of points was used to determine the dependence of \( k_l \) on the kink density because the outer ring contained the most data points. The right of Figure 74 shows a map of \( k_l \) and \( k_e \) for D-TA. The measured points around the circle do not line up exactly with the high symmetry directions except at two points on the Cu(100) S\(^4\)C. One of those points is indicated on the maps of \( k_l \) and \( k_e \) to the right of Figure 74 and set as the 0° point. This point was the angle of reference and used to calculate the angle of each point from a (100) step edge. Moving from the (100) step edge line azimuthally towards the red line at constant radius, the linear density of (110) kinks along the step edge increases until reaching the red line at 30°. The ideal surface at the 30° has the maximum possible kinks formed by (100) and (110) microfacets that are one atomic spacing in width. Moving azimuthally from the red line to the (110) step edge line, the density of (100) kinks decreases to zero at the (110) step edge line. The bottom plot of Figure 74 plots of the values of \( k_e \) versus angle from the (100) step edge. The trend in \( k_e \) is the opposite that of \( k_l \) between 30° and 60° where the value of \( k_e \) increases moving towards the direction of (110) step edges. From 0° and 30°, the value of \( k_e \) remains relatively constant at minimum values approaching \( 1 \times 10^{-7} \) s\(^{-1} \). The value of \( k_l \) has been indicated previously as the rate limiting step as it scales directly with \( t_{1/3} \). The trend of \( k_l \) with angle from (100) step edge shows an increase with (100) kinks with \( k_l \) until the surface at 30° where \( k_l \) reaches a plateau and remains constant as the density of (110) kinks decreases to zero at 0°. This clearly indicates that (100) kinks are more active for D-TA decomposition than (110) kinks.
Figure 74: \( k_{\parallel} \) vs rotation angle from (100) step edge for D-TA on Cu(111) \( S^4C \). The pattern in kink density with rotation is repeated every 60° so every point on the plot of \( k_{\parallel} \) vs. angle from the (100) step edge is an average of equivalent points every 60°. The arrows above the plot indicate the direction of each site increasing. The value of \( k_{\parallel} \) increases with (100) kink density but remains constant with \( k_e \).
4.5 Conclusions

The explosive decomposition of L- and D-TA was studied on a Cu(111) S$^4$C. This S$^4$C exposed a continuous distribution of different crystal planes having known densities of the different types of sites at each point on the surface. Quench TPRS experiments in conjunction with spatially resolved XPS were used to visualize the progression of the decomposition reaction with time at 225 points on the surface for D-TA and 121 points for L-TA. Overall, the reaction was more sensitive to the step orientation than the surface chirality for both L- and D-TA. Surfaces with (100) step edges were the most active followed by those with (110) step edges and finally the (111) plane was the least active surface. Several rate law models were tested using the experimental data and the best fit to the data was found to be $R_{12} = k_i \theta_{TA} + k_e \theta_{TA} (1 - \theta_{TA})^2$. Values of $k_i$ and $k_e$ were calculated for the best fit model and $k_i \theta_{TA}$ was determined to be the rate limiting step in explosive decomposition of TA.
CHAPTER 5

5  D- and L-Aspartic Acid Decomposition on Cu(100) and Cu(111) S^4C

5.1  Introduction

Aspartic Acid, AA [HOOC-CH(NH₂)-CH₂-COOH] is an α-amino acid with one chiral center at the α-C atom. It is a chiral molecule chemically similar to tartaric acid, TA, making it a good candidate to study its reactivity on Cu and whether the reaction is enantioselective. The structure of AA is a four C backbone and two carboxylic acid groups like TA. Figure 75 depicts the two enantiomers of AA with the C atoms labeled. The C1 atom is on the carboxyl group closest to the amine group while the C4 atom is on the carboxyl group furthest from the amine group. Unlike TA, there is only one chiral center on AA on the C2 atom and AA contains an amine group that is not present on TA.

![Figure 75: Drawings of D- and L-AA with C atoms labeled. Two carboxyl groups are on the C1 and C4 atoms. The C1 atom is the one closest to the chiral center, C2 with the amine group (3).](image)

The adsorption and decomposition of L- and D-AA have been previously studied on a Cu(110) single crystal (3). Mhatre et al. used TPRS measuring the
rate of CO$_2$ desorption to determine the decomposition behavior of AA at varying coverages, heating rates, and isothermal hold temperatures. Figure 76 displays the TPR spectra of varying coverage of AA on the Cu(110) single crystal. The trends in AA decomposition at varying coverage are similar to the trends exhibited by TA. As the initial coverage of AA on the surface increased, the peak width decreased and the peak desorption temperature increased. The TPRS peak temperature reached a maximum for a saturated initial coverage of AA with a narrow peak FWHM of ~3 K. In the isothermal TPRS experiments, the decomposition of AA occurred with the peak time increasing as the isothermal hold temperature decreased. These are all characteristics of a surface explosion mechanism seen for TA showing that AA on Cu also undergoes a surface explosion (3, 14, 22). A major difference between the behavior of TA and AA decomposition on Cu(110) single crystal is the presence of a high temperature shoulder in the TPRS spectra observed for AA decomposition but not for TA decomposition. To determine the source of the shoulder, TPRS was used to determine the decomposition products apart from CO$_2$. Mhatre et al. found that the major products of AA decomposition were CO$_2$, H$_2$, and C$_2$H$_3$N (3).
An advantage of studying AA decomposition compared to TA is that isotopomers of AA are commercially available. Several varieties of isotopically labeled L-AA are available and can be used to determine specific atoms in AA that end up in different products during a reaction. L-AA-1\(^{13}\)C was used previously to determine which C atoms in AA were present in the CO\(_2\) and C\(_2\)H\(_3\)N products (3). Figure 77 shows a TPRS of a saturated exposure of L-AA-1\(^{13}\)C for several different \(m/q\) ratios referring to different products. The spectra shows that \(m/q = 44\) for CO\(_2\) has a desorption peak at 535 K while \(m/q = 45\) for \(^{13}\)CO\(_2\) has a desorption peak at 539 K at the same temperature as \(m/q = 41\) for C\(_2\)H\(_3\)N. This experiment showed that the carboxyl group of the C4 atom decomposes before the carboxyl group on the C1 atom. From this data, a two step reaction was proposed for AA decomposition shown in Figure 77 which involves the formation of an
intermediate species on the surface during the reaction. This intermediate species accounted for the shoulder observed previously at temperatures above the sharp desorption feature which is not present in TA decomposition. Several rate laws were applied to the TPRS data and it was found that the best fit rate law was

\[ r_{Asp} = -\frac{d\theta_{Asp}}{dt} = k_i \theta_{Asp} + k_e \theta_{Asp} (1 - \theta_{Asp})^2, \]

the same type of rate law as the best fit to TA decomposition on Cu(110) single crystal.

AA adsorption and decomposition was also studied on chiral Cu single crystals (44, 45). Yun et al. studied the competitive adsorption of L- and D-AA on Cu(3,1,17)R&S surfaces. Using L-AA-1\(^{13}\)C with D-AA, the amount of each molecule could be separately determined when mixtures of these enantiomers were exposed to the same surface. Different ratios 1\(^{13}\)C L- and D-AA were exposed to the Cu surface and TPRS was used to determine the ratio of the coverages of each enantiomer. The adsorption energies were calculated by applying a competitive adsorption isotherm model to the coverage data and using

\[ K = \exp \left( \frac{-\Delta G}{RT} \right) \]

for calculate \( \Delta G_{ads} \) for each enantiomer. The ratio of the equilibrium constants of each enantiomer were then used to calculate \( \Delta \Delta G \), the enantiospecific difference in the adsorption energies, which was \( \Delta \Delta G = 3.15 \pm 0.29 \text{ kJ/mol} \) for D/L on Cu(3,1,17)\(^R\) and L/D on Cu(3,1,17)\(^S\). This difference showed that the adsorption of D-AA was preferred on Cu(3,1,17)\(^S\) and L-AA adsorption was preferred on Cu(3,1,17)\(^R\).

This work will determine whether or not AA decomposition is enantioselective of Cu surfaces vicinal to Cu(100) and Cu(111). We will use the same techniques of isothermal quench TPRS and spatially resolved XPS used for
TA decomposition to observe AA decomposition occurring across the Cu(100) and Cu(111) S^4C. On the Cu(111) S^4C, we will show that the surface chirality effects the decomposition of L-AA which remains adsorbed longer to R regions of the S^4C located 20° from the high symmetry directions with (100) step edges. On the Cu(100) S^4C, we will provide clear evidence that the reaction is enantioselective on crystal planes at the edge of the S^4C and that on these crystal planes, D-AA remains adsorbed longer on S crystal planes and L-AA-4-^{13}C remains adsorbed longer on R crystal planes. We will also show that the intermediate proposed by Mhatre et al. is present on many crystal planes on the Cu(100) S^4C and Cu(111) S^4C during the reaction for extended periods of time. The results will also show that C_2H_3N remains on the surface after the isothermal TPRS experiments of AA on the Cu(100) S^4C but not on the Cu(111) S^4C. From this, a rate law and reaction mechanism is proposed accounting for the intermediate and acetonitrile formation on the surface for the Cu(100) S^4C.
The first experiments performed were with L-AA on the Cu(111) $S^4$C. The sample mounting was not changed from the experiments on L- and D-TA. The Cu(111) $S^4$C was left in the analysis chamber while vacuum was broken in the prep chamber and the TA doser was replaced with the AA doser. The same sputtering and annealing conditions on the Cu(111) $S^4$C used during the TA experiments were used for the AA experiments in UHV chamber 3: the $S^4$C was

Figure 77: TPRS spectra of a saturated exposure of L-AA-1-$^{13}$C on Cu(110) single crystal at multiple $m/q$ ratios. This TPRS experiment showed that the first carboxyl group of AA to decompose is on the C4 atom. Included is the two step proposed reaction based on the TPRS data (3).

5.2 Methods

The first experiments performed were with L-AA on the Cu(111) $S^4$C.
held at 650 K and sputtered with 2 kV Ar$^+$ ions with a sputtering current of 10 $\mu$A for 40 minutes and annealed for 10 minutes at 800 K.

The Cu(100) S$^4$C was cleaned in UHV chamber 2 by sputtering and annealing cycles until a LEED pattern was obtained across the entire S$^4$C surface. For one cleaning cycle, the S$^4$C was held at 700 K and sputtered with 2 kV Ar$^+$ ions at a background pressure of $1 \times 10^{-6}$ Torr with sputtering current of 6 $\mu$A for 40 minutes and annealed at 850 K for 10 minutes. Over 30 cycles of sputtering and annealing were performed until a LEED pattern was obtained. Figure 78 shows an example of the LEED pattern from the Cu(100) S$^4$C with a beam energy of 130 eV and screen voltage of 4 kV. This pattern was present across the entire surface with some limited spot spreading and splitting at the edges of the S$^4$C.

UHV chamber 1 is equipped with XPS which was used to check the cleanliness of the Cu(100) S$^4$C. XPS showed that the surface was 100% Cu after sputtering and annealing. After obtaining the LEED pattern and clean XPS spectrum, the Cu(100) S$^4$C was removed from UHV chamber 1 and mounted to the UHV chamber 3 sample holder using the procedure outlined in Chapter 3 and loaded into the prep chamber. Before pumping down, the TA doser was removed from the prep chamber and replaced with the AA doser. The prep chamber was then pumped down and baked out at 370 K for 24 hours. After bakeout, the S$^4$C was heated to 370 K for 2 hours then from 300 to 800 K in steps of 100 K for 30 min each to cure the Aremco Pyroduct 597-A silver paste and to degas the sample heater. All other components were then degassed including the AA doser up to 360 K.
Figure 79 shows two images of the AA doser mounted in the prep chamber. Like the TA doser, Ta wires are attached to the Cu feedthrough using barrel connectors circled in blue. The bare Ta wire is wrapped around a large glass vial incased in alumina paste and is used to heat the doser. The bare Cu wire wrapped around the bottom of the large glass vial circles in red is used to hold the large glass vial in place. Unlike the TA doser, the heating wires are pasted around a large glass vial instead of an Al body. Passing a high current through the Ta wires from 1-5 A was capable of heating the doser to < 500 K. The temperature is measured by a K-type thermocouple that is attached to the side of the larger glass vial using alumina paste and the temperature of the doser is controlled by a computer. The right image shows how the AA is mounted in the doser. There is a smaller glass vial circled in green inside the large glass vial that contains either L-AA-4-\textsuperscript{13}C or D-AA (99%, Sigma Aldrich). This small glass vial is attached to the larger glass vial using alumina paste on the inside of the large
glass vial and a piece of silica with additional alumina paste to hold it upright. When switching AA enantiomers, the smaller vial inside the larger one was removed and replaced with a brand new vial. Before adding the new vial of AA, the large outer glass vial was rinsed with isopropyl alcohol, acetone, and boiling water to prevent contamination.

![Image of AA doser](image_url)

Figure 79: Images of the AA doser used in the prep chamber. Ta wires are attached to a Cu feedthrough using barrel connectors (circled in blue). The bare Ta wires are wrapped around a large glass vial and encased in alumina for heating the doser. A Cu wire is used to hold the large glass vial in place (circled in red). A smaller vial inside the larger one contains one enantiomer of AA circled in green.

The Cu(100) S$^4$C was cleaned by sputtering and annealing in the prep chamber. During sputtering, the sample was held at 700 K and sputtered with 2 kV Ar$^+$ ions with a sputtering current of 10 μA for 40 minutes and annealed in the analysis chamber for > 10 minutes between 750 and 800 K. Annealing in the prep chamber caused some additional O contamination on the surface so the analysis chamber was used to anneal the S$^4$C. These cycles were repeated until an XP
spectra of ≤1 % O and <1% C was observed at the (100) plane and 4 other points located ±4 mm from the (100) plane along two orthogonal directions. Like the Cu(111) S$^4$C, Ag was also measured across the surface to make sure none of the Ag paste ended up on the S$^4$C.

After the surface was cleaned, the location of the Cu(100) plane was determined using the scratches in the side of the crystal and the optical microscope in the analysis chamber. On the side of the Cu(100) S$^4$C, four sets of scratches were made representing the locations of the high symmetry directions on the surface. Three scratches were used to represent the high symmetry direction towards the \{111\} plane. The middle scratch of the three indicated the actual direction. Two scratches were used to represent the high symmetry direction toward the \{110\} plane. Line scans in the Thetaprobe were used to locate the \{100\} plane on the crystal by setting the ends of the line scans at the high symmetry direction scratches and locating where they intersected on the surface. These locations were saved and used in each future experiment so that each XPS scan was centered at the \{100\} plane.

The quench TPRS experimental procedure for L-AA-4-$^{13}$C and D-AA on the Cu(100) S$^4$C and for L-AA on the Cu(111) S$^4$C were the same as for L- and D-TA on the Cu(111) S$^4$C and are summarized below:

1) Sputter and Anneal Cu S$^4$C for two cycles.

2) Perform XPS of five points on the Cu S$^4$C surface to determine if it is clean

3) Expose Cu S$^4$C to multilayer of AA with sample at <330 K
4) Perform XPS of 5 points of multilayer of AA on Cu S\(^4\)C to check doser

5) Heat Cu S\(^4\)C to 405 K for > 10 minutes

6) Perform quench TPRS experiment

7) Perform spatially resolved XPS on 225 points on Cu S\(^4\)C

The only difference between the TA and AA decomposition experiments the dosing conditions for the AA doser. To determine the dosing conditions to produce a multilayer of AA, the Cu(100) S\(^4\)C was placed on the stage underneath the doser with the doser held at several temperatures from 360 K – 450 K for 30 minutes. After dosing, the sample was moved into the analysis chamber for XPS. Scans of N 1s, C 1s, O 1s, and Cu 2p\(_{3/2}\) were performed to determine whether a multilayer was formed on the surface. The temperature found to produce a multilayer of AA was 438 K, significantly higher dosing temperature than for TA (360 K). The difference in the dosing temperature is most likely due to the different mounting setups for the vials. In the AA doser, a large glass vial contains the aspartic acid vial as opposed to an Al body. The glass vial does not conduct heat as well as the stainless steel meaning that although the outer glass vial is measuring 438 K, the actual temperature of the inner vial of AA is much less.

For L-AA-4\(^{13}\)C and D-AA, spatially resolved XPS was performed 225 points within 3.4 mm from the (100) plane on the S\(^4\)C. For L-AA on the Cu(111) S\(^4\)C, spatially resolved XPS was performed on 225 points within 3.2 mm of the (111) plane. These distances were used to maximize the number of points measured while still remaining in the spherically fit region of each S\(^4\)C. XP
spectra were obtained for Cu 2p$_{3/2}$, O 1s, N 1s, and C 1s electrons were obtained at each point on the surface after the quench TPRS. The same X-ray spot size of 400 μm diameter was used in these experiments.

5.3 Results

5.3.1 TPRS of L-AA-4-$^{13}$C and D-AA on Cu(100) S$^4$C

Before the quench TPRS experiments were performed, standard TPRS of saturated exposures of both L-AA-4-$^{13}$C and D-AA were performed to determine the peak temperature for CO$_2$ desorption. Figure 80 shows a TPRS of a saturated exposure of L-AA-4-$^{13}$C and D-AA on the Cu(100) S$^4$C using a heating rate of 1 K/s. The $m/q$ ratios measured were $m/q = 45$ for $^{13}$CO$_2$ (only for L-AA-4-$^{13}$C) $m/q = 44$ for CO$_2$ desorption and $m/q = 41$ for C$_2$H$_3$N desorption. The signal of $m/q = 41$ is multiplied by a factor of five on the D-AA plot to compare better with the signal from $m/q = 44$. For D-AA, The signal from $m/q = 44$ has sharp peak at 501 K with a tailing shoulder between 510 and 520 K. The signal from $m/q = 41$ has a peak at 503 K with a clearly defined shoulder at ~512 K. The peak at 503 K most likely corresponds to the decomposition of one of the COO groups in D-AA while the tailing shoulder extending to > 520 K representing the decomposition of the second COO group of D-AA. Similar to the results seen on the Cu(110) single crystal, the peak for C$_2$H$_3$N desorbing from the surface occurs after the peak for COO. However, the desorption of C$_2$H$_3$N in this case has two peaks, one 2 K above CO$_2$ desorption and a tailing shoulder 12 K above CO$_2$ desorption which was not observed on Cu(110) single crystal.
The difference between AA decomposition on Cu(110) single crystal and the Cu(100) S⁴C can be clearly observed using the L-AA-4-¹³C. Isotopically labeled AA is used to help distinguish the decomposition of the COO groups on AA. If one of the COO groups contains ¹³C, the signal from m/q = 45 can be used to monitor desorption of ¹³CO₂ separately from m/q = 44 for CO₂. On Cu(110) single crystal, the TPRS experiments of L-AA-1-¹³C showed that the COO group furthest from the amine group (C4, m/q = 44) decomposed before the other (C1 m/q = 45) (3). On Cu(100) S⁴C, L-AA-4-¹³C was used with the ¹³C present on the COO group on C4 furthest from the amine group. This means that the peak for m/q = 45 should occur before m/q = 44 in a TPRS experiment. The right plot of Figure 80 shows a saturated TPRS of L-AA-4-¹³C on the Cu(100) S⁴C. There is a peak in m/q = 45 at 500 K with no shoulder present. For m/q = 44, there is a peak at 502 K with a broad shoulder extending out to 520 K. The shape of the
spectrum for $m/q = 41$ follows a similar trend as $m/q = 44$ with a high temperature shoulder extending out to 520 K. As expected, the peak for $m/q = 45$ occurs before $m/q = 44$ since the $^{13}$C atom is on C4, the COO group furthest from the amine group on C2. The desorption of the second COO group for L-AA-4-$^{13}$C on Cu(100) S$^{4}$C is significantly different than for L-AA-1-$^{13}$C on the Cu(110) single crystal. The high temperature shoulder in the desorption of CO$_2$ on Cu(100) S$^{4}$C doesn’t exist in the desorption of CO$_2$ on Cu(110) single crystal. Figure 81 shows a comparison of D and L-AA-4-$^{13}$C decomposition on the Cu(100) S$^{4}$C. The plots in red are from L-AA-4-$^{13}$C and the plot in blue is from D-AA. The desorption spectrum of $m/q = 41$ are the same for both enantiomers which is expected since the C atoms on the C$_2$H$_3$N are not isotopically labeled. For D-AA, the base of the peak extends from 490 K to 520 K which is the same temperature spanned by the combination of $m/q = 44$ and $m/q = 45$ from L-AA-4-$^{13}$C. The TPRS of $m/q = 44$ for both L-AA-4-$^{13}$C and D-AA have a tailing shoulder above the initial peak at ~500 K.

The different results for the TPRS of L-AA-4-$^{13}$C on the Cu(110) single crystal and the Cu(100) S$^{4}$C are not unexpected. The Cu(110) single crystal contains one surface orientation of (110) terraces while the Cu(100) S$^{4}$C contains surfaces with (100) terraces as well as (111) steps, (110) steps, and kinks in the step edge. To confirm that the difference between the Cu(110) single crystal and the Cu(100) S$^{4}$C is not due to the different terrace structure, TPRS experiments were performed with L-AA-4-$^{13}$C on a Cu(100) single crystal in UHV chamber 2. Figure 82 shows a comparison of TPRS of a saturated exposure of L-AA-4-$^{13}$C
between the Cu(100) S^4C and the Cu(100) single crystal. The signal has been adjusted for the Cu(100) single crystal so that the peak heights are equivalent for a better comparison. For m/q = 45, there is a peak for $^{13}$CO$_2$ desorption at 504 K for the single crystal compared to 500 K for the Cu(100) S^4C. For m/q = 44 and 41, the desorption behavior between the Cu(100) S^4C and Cu(100) single crystal are very different. The signals from m/q = 44 for CO$_2$ and m/q = 41 for C$_2$H$_3$N on the Cu(100) single crystal does not have a shoulder present after the initial peak maximum. Both of these surfaces have (100) terraces, but on the Cu(100) S^4C there are also step edges and kinks present on the surface. This shows that the presence of step edges and kinks on the Cu(100) S^4C alters the desorption behavior of the second CO$_2$ group and C$_2$H$_3$N in the decomposition reaction of AA on the Cu(100) S^4C.

Figure 81. Comparison of TPRS experiments of saturated exposures of D-AA and L-AA-4-$^{13}$C on Cu(100) S^4C. 1 K/s heating rate was used for both enantiomers. The peaks for m/q=41 are the same for both enantiomers because the C atoms in C$_2$H$_3$N for both species are unlabelled. Both L-AA-4-$^{13}$C and D-AA TPR spectra have a tailing shoulder after the initial peak at ~ 500 K.
Several isothermal TPRS experiments were performed for saturated exposures of D-AA on the Cu(100) S^4C to determine the optimal temperature for performing quench TPRS experiments. These experiments are shown in Figure 83 using m/q = 44 to measure CO\textsubscript{2} desorption from the decomposition reaction. The trends seen before for L- and D-TA decomposition are also present for D-AA; as the isothermal hold temperature decreases, the time delay of the peak increases and the peak width decreases. For future quench TPRS experiments of both L-AA-4-\textsuperscript{13}C and D-AA on Cu(100) S^4C, 460 K was chosen. The peak width

Figure 82: Comparison of TPRS of L-AA-4-\textsuperscript{13}C on Cu(100) S^4C and Cu(100) single crystal. The peak locations are similar for L-AA-4-\textsuperscript{13}C on Cu(100) S^4C and the Cu(100) single crystal but there is no shoulder present in the TPR spectra of the Cu(100) single crystal.
is 200 seconds enough to perform several quench experiments with a large enough peak height to be recorded by the mass spectrometer.

Figure 84 shows an isothermal TPRS experiment at 460 K for D-AA (left) and L-AA-4\textsuperscript{13}C (right). For L-AA-4\textsuperscript{13}C, the peak for \( m/q = 45 \) begins roughly 50 seconds before the peak for \( m/q = 44 \) showing that even in an isothermal TPRS experiment, the \textsuperscript{13}CO\textsubscript{2} group furthest from the amine on L-AA-4\textsuperscript{13}C reacts first. Both peaks end at the same time at \(~200\) seconds after the desorption begins. The spectra for \( m/q = 44 \) and \( m/q = 45 \) are not the same peak area for L-AA-4\textsuperscript{13}C because the baseline signal for \( m/q = 44 \) is an order of magnitude higher than \( m/q = 45 \) due to contributions of CO\textsubscript{2} from the background. For both L-AA-4\textsuperscript{13}C and D-AA, there is not a significant peak present for \( m/q = 41 \) meaning that either

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\textbf{Figure 83:} Isothermal TPRS experiments at various temperatures for D-AA on Cu(100) S\textsuperscript{4}C. As seen with TA decomposition, the time delay increases at the isothermal hold temperature decreases. An isothermal hold temperature of 460 K was selected for the quench TPRS experiments.
C$_2$H$_3$N remains on the surface after an isothermal TPRS experiment or that the signal from desorption is too small to register on the mass spectrometer. XPS will be used after the quench TPRS experiments to confirm which of these is correct.

Figure 84: Isothermal TPRS 460 K for L-AA-4-$^{13}$C (right) and D-AA (left) decomposition on Cu(100) S$^4$C. The peak for m/q = 45 occurs 30 seconds before m/q = 44 while there is no peak for m/q = 41.

The quench TPRS experiments for L-AA-4-$^{13}$C and D-AA on Cu(100) S$^4$C are displayed in Figure 85. The first experiment performed for both L-AA-4-$^{13}$C and D-AA was the 0% quench TPRS where the S$^4$C was heated to 460 K, then cooled down to < 400 K before AA can decompose at any point on the surface. For D-AA t = 20 seconds at 460 K and for 4-$^{13}$C L-AA t = 30 seconds for the 0% experiments. The TPRS spectra for these experiments are not shown here as both experiments do not have a peak. Eight quench experiments were completed for D-AA and seven were completed for L-AA-4-$^{13}$C including the 0 % and 100 % experiment. The 100% experiment is an isothermal TPRS experiment where AA has decomposed at all points on the S$^4$C. In this case, the extent of reaction, listed through the rest of this section as $X(t)$, is displayed as percent of AA that has decomposed for each quench TPRS experiment. The $X(t)$ for each quench TPRS was calculated as the average of the TPRS peak area ratio.
(peak area of the quench divided by the peak area of the $X = 100$ experiment) and $X^0(t)$ based on the O 1s XPS peak areas calculated using Equation 4.1 shown previously in Chapter 4. These values are listed in Table 7 for D-AA both and L-AA-4-$^{13}$C. The C at% was not used for an extent of reaction calculation due to the presence of excess C remaining on the surface in the $X = 100$ experiment that will be explained further in the XPS section.

![Figure 85: Quench TPRS of D-AA (left) and L-AA-4-$^{13}$C on Cu(100) $S^{4}$C. The x-axis is in time at isothermal hold temperature 460 K. The extents of reaction listed as percent reacted are calculated from the TPRS peak area ratios and the O peak areas from XPS.](image)

### Table 7: Extent of reaction calculations for D-AA and L-AA-4-$^{13}$C. Each value of $X(t)$ is calculated from the TPRS peak area ratio and the value of $X^0(t)$.

<table>
<thead>
<tr>
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5.3.2 TPRS of L-AA on Cu(111) S\textsuperscript{4}C

The left of Figure 86 shows a saturated TPRS experiment of L- and D-AA on the Cu(111) S\textsuperscript{4}C. The baseline peak width for both L- and D-AA is ~ 40 K. L-AA has a peak at 505 K while D-AA has a peak at 507 K. Both L- and D-AA have the same general shape as the saturated TPRS of D-AA on the Cu(100) S\textsuperscript{4}C with a small shoulder at a temperature above the initial peak extending out to > 520 K. The FWHM for both peaks is about 10 K which is five times wider than the TPRS peaks observed for saturated exposures of AA on previous single crystal experiments (3, 44, 45). This is an expected result because the Cu(111) S\textsuperscript{4}C contains crystal planes of both R and S chirality and the overall TPRS spectra contains contributions from multiple crystal planes of each chirality. The right of Figure 86 displays two isothermal TPRS experiments for L-AA on the Cu(111) S\textsuperscript{4}C. The baseline peak width for the isothermal TPRS at 480 K is only 100 seconds while for 470 K the baseline peak width is > 350 seconds. This peak width is large enough to perform multiple quenches and therefore 470 K was used as the isothermal hold temperature for the quench TPRS experiments for L-AA on the Cu(111) S\textsuperscript{4}C. Figure 87 shows the quench TPRS experiments for L-AA on the Cu(111) S\textsuperscript{4}C. Only five total experiments were performed for L-AA including the $X = 0$ and $X = 100$ experiments described previously. The percentages displayed in the plot were calculated using the same equations as for 4-$^{13}$C L- and D-AA on the Cu(100) S\textsuperscript{4}C.

Quench TPRS experiments were not performed for D-AA on the Cu(111) S\textsuperscript{4}C due to significant damage to the surface which occurred between the end on
the L-AA experiments and the beginning of the D-AA experiments. This is the reason the only work reported for D-AA on the Cu(111) S$^4$C is the saturated TPRS experiment performed. The Cu(111) S$^4$C had to be removed and repolished to remove the damaged regions of the surface. After repolishing, it must be characterized using profilometry and Laue back diffraction and cleaned in another UHV chamber until a LEED pattern is obtained before D-AA experiments can be performed.

Figure 86: Left: Saturated TPRS of D- and L-AA on Cu(111) S$^4$C. Peak locations for both enantiomers are between 505 and 507 K and the peak FWHM are ~ 10 K. Right: Isothermal TPRS of L-AA on Cu(111) S$^4$C. The width of the 470 K isothermal TPRS is > 350 seconds making it a good temperature to use for quench TPRS experiments.
Before performing any quench TPRS experiment, the conditions for forming a monolayer of AA were determined. AA can exist in several forms on a Cu surface and XPS can be used to determine the state of AA on the surface after by analyzing shifts in the peaks of C 1s, O 1s, and N 1s spectra. Mhatre et al looked at the state of L-AA on a Cu(110) single crystal in both a multilayer and monolayer (3). Using XPS, he found that multilayer L-AA was present on the surface as a zwitterionic form [HOOC-CH₂-CH(NH₃)⁺(COO⁻)] in the multilayer and as a bi-aspartate species [-OOC-CH₂-CH(NH₂)-(COO⁻)] in the monolayer.

A similar analysis was performed for multilayer and monolayer adsorption of D-AA on the Cu(100) S⁴C. In each experiment as described previously, the Cu(100) S⁴C was exposed to each enantiomer of AA for one hour with the sample

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**Figure 87:** Quench TPRS experiments for saturated exposures of L-AA on Cu(111) S⁴C. An isothermal hold temperature of 470 K was used for each experiment. The percentages displayed in the plot were calculated using the same equations as for 4-¹³C L- and D-AA on the Cu(100) S⁴C for extent of reaction, X.

### 5.3.3 XPS of L-AA-4-¹³C and D-AA on Cu(100) S⁴C

Before performing any quench TPRS experiment, the conditions for forming a monolayer of AA were determined. AA can exist in several forms on a Cu surface and XPS can be used to determine the state of AA on the surface after by analyzing shifts in the peaks of C 1s, O 1s, and N 1s spectra. Mhatre et al looked at the state of L-AA on a Cu(110) single crystal in both a multilayer and monolayer (3). Using XPS, he found that multilayer L-AA was present on the surface as a zwitterionic form [HOOC-CH₂-CH(NH₃)⁺(COO⁻)] in the multilayer and as a bi-aspartate species [-OOC-CH₂-CH(NH₂)-(COO⁻)] in the monolayer.

A similar analysis was performed for multilayer and monolayer adsorption of D-AA on the Cu(100) S⁴C. In each experiment as described previously, the Cu(100) S⁴C was exposed to each enantiomer of AA for one hour with the sample
held <330 K to produce a multilayer of AA on the surface. Figure 88 shows XP spectra of O 1s, N 1s, and C 1s for a multilayer of D-AA on the Cu(100) plane of the Cu(100) S^4C. A * is used to indicate the atom in each of the chemical groups that is measured by each spectrum. Gaussian peak fitting was used to determine the presence of different chemical groups on the S^4C surface. For O 1s, there are two peaks at binding energies of 531.4 eV for CO*O* and 532.7 eV for CO*O*H. For N 1s, there are also two peaks at binding energies of 401.5 eV for N*H_3^+ and 399.1 eV for NH_2. To be consistent with the analysis of Mhatre et al., four peaks were fit to the C 1s XP spectrum which contains a broad peak with two distinct features between 283 and 291 eV. This spectrum can be fit by four binding energy peaks: 285.3 eV for C*H_2, 286.6 eV for HC*NH_2, 287.8 eV for C*OO, and 288.9 eV for C*OOH. The peaks for C*H_2 and HC*NH_2 are not well resolved. These XP spectra indicate that the species on the surface is zwitterionic AA [HOOC-CH_2-CH(NH_3)^+(COO-)] (3). The peak areas in these XP spectra were used to determine the at% of each element on the surface by integrating the peak areas and using the Wagner library sensitivity factors (232). This analysis of the multilayer was performed on the Cu(100) point on the surface and the other four points were located ±4 mm from the (100) plane along two orthogonal directions. For each point, the average at% was 32% O, 32% C, and 8% N on the surface.

To create a monolayer of D-AA on the surface, the Cu(100) S^4C was heated to 405 K for > 10 minutes. Figure 89 shows XP spectra of O 1s, N 1s, and C 1s for a monolayer of D-AA on the Cu(100) plane of the Cu(100) S^4C. The O
1s spectrum now only contains one peak at a binding energy of 531.4 eV for CO*O* and the N 1s spectrum also only contains one peak at 399.1 eV for NH$_2$. The peaks for CO*O*H and N*H$_3^+$ have disappeared. The C 1s spectrum now contains three peaks: 285.3 eV for C*H$_2$, 286.6 eV for HC*NH$_2$, and 287.8 eV for C*OO. Although the two peaks for C*H$_2$ and HC*NH$_2$ are not well resolved, the peak for C*OOH at 288.9 eV clearly disappears as indicated by the black line in the C 1s spectrum. This change in the XP spectra gives evidence that the AA species on the surface is now the bi-aspartate species [(‘OOC)-CH$_2$-CH(NH$_2$)-(COO‘)] in the monolayer. The at % analysis was also performed on the monolayer on the same five points as the multilayer. Each of the five points now contains 16 at % O, 16 at % C, and 4 at % N which is the correct ratio of C:O:N in AA.
Figure 88: XP spectra for O 1s, N 1s, and C 1s for a multilayer of D-AA on the Cu(100) plane of the Cu(100) S\textsuperscript{4}C. There are two peaks in the O 1s XP spectra at binding energies of 531.4 eV for CO*O* and 532.7 eV for CO*O*H and two peaks in the N 1s XP spectra at binding energies of 401.5 eV for N*H\textsubscript{3} and 399.1 eV for NH\textsubscript{2}. For C 1s there are two broad peaks fit to four binding energy peaks: 285.3 eV for C*H\textsubscript{2}, 286.6 eV for HC*NH\textsubscript{2}, 287.8 eV for C*OO, and 288.9 eV for C*OOH.
Once the conditions for producing a monolayer and the temperature for performing the isothermal TPRS were determined, quench TPRS experiments were performed. A map of the at % of O after adsorption of a saturated monolayer of D-AA is displayed in Figure 90 before heating to induce isothermal decomposition, so \( t = 0 \) and \( X = 0 \). The 225 points measured are indicated by black dots and the same spot size of 400 \( \mu \)m used for TA experiments was also used for all AA experiments. The O at % was calculated from the peak area ratios.

Figure 89: XP spectra of a monolayer of D-AA on the Cu(100) plane of Cu(100) \( \mathbb{S}^4 \)C. The monolayer only contains one peak in N 1s at 399.1 eV for N*H\(_2\) and one peak in O 1s at 531.4 eV for CO*O*. The peak at 288.9 eV in the C 1s spectra for C*OOH has completely disappeared. These are all characteristic of the bi-aspartate species on the surface.
of the O 1s, C 1s, and Cu 2p\textsubscript{3/2} XP spectra using the Wagner sensitivity factors (232). The at\% of O across the entire surface for the X = 0 experiment is uniform at around 14±1 at\% O. This map shows that the amount of D-AA across the surface is uniform showing that there is a monolayer present at each point measured.

The orange and black lines across the at \% O map indicate the locations of the edges of the stereographic triangle superimposed on the surface. The crystal planes located along these lines contain step edges and no kinks. As the distance from the (100) plane increases, the step density increases. Crystal planes along the black lines have (100) terraces with (111) step edges while crystal planes along the orange lines have (100) terraces with (110) step edges. This S\textsuperscript{4}C has four fold symmetry with four R chiral regions and four S chiral regions indicated in yellow.

Quench TPRS experiments were performed with both L-AA-4\textsuperscript{13}C and D-AA on the Cu(100) S\textsuperscript{4}C. The decomposition of D-and L-AA exhibited enantioselective behavior on the Cu(3,1,17)\textsuperscript{R&S}, a chiral crystal plane with located 9° from the Cu(100) plane, so our hypothesis is that this reaction will also show enantioselective behavior on the Cu(100) S\textsuperscript{4}C. The expected result is that a single enantiomer of AA will remain on S chiral regions longer than R chiral regions and the other enantiomer will remain longer on R chiral regions than S chiral regions.
Figure 90: XPS map of at % O for D-AA monolayer on the Cu(100) S₄C. The X-ray spot size is 400 μm. O 1s XP spectra were obtained at the 225 points indicated and lying on seven concentric rings centered on the (111) planes and with a maximum radius of 3.4 mm. The edges of the stereographic triangle are shown as lines and the orientation of the step edges exposed along each line is indicated.
Figure 91 displays a progression line of the extent of the decomposition reaction for both L-AA-4-13C and D-AA on the Cu(100) S^4C. Each circle is a map of the at % O measured at 225 points within 3.4 mm from the (100) surface for both L-AA-4-13C and D-AA plotted on a progression line by extent of reaction, $X$. The progression line spans $X = 0 \rightarrow 100$ and the value of $X$ for each map is indicated in red for L-AA-4-13C and blue for D-AA. For both L-AA-4-13C and D-AA, there is 3-4 at% O remaining on the surface at $X = 100$. For D-AA, the decomposition reaction occurs first on surfaces with (111) step edges as indicated by the $X = 12$ experiment. As the reaction progresses, D-AA remains on the (100) plane at the center of the S^4C and at the edges of the S^4C in S chiral regions of the surface. The (100) plane and these S areas are the last regions on the S^4C to react. For L-AA-4-13C, surfaces near the (100) plane at the center and at the edges of the S^4C in R chiral regions are the last points where L-AA-4-13C decomposes. The reaction pattern of both D- and L-AA-4-13C show the expected four-fold symmetry and show that the (100) plane is one of the last surfaces to react. Figure 92 shows a close up maps of at % O for D-AA and 4-13C L-AA. The $X = 38$ map for L-AA-4-13C and the map of $X = 50$ for D-AA best display the difference in the reaction pattern between the two enantiomers. For D-AA, the edges of the R regions of the surface have ~9 at% O while the edges of the S regions still have 14 at% O, close to the value for a monolayer of D-AA. The opposite trend is present for L-AA-4-13C; the edges of the R regions near the (110) step edge have 14 at% O while the edges of the S regions only have ~9 at % O. The difference in these reaction patterns clearly show that the
decomposition of 4-$^{13}$C L- and D-AA is enantioselective. At the edges of the 
Cu(100) S$^4$C, D-AA reacts on R surfaces and remains on S surfaces, while L-AA- 
4-$^{13}$C reacts on R surfaces and remains on S surfaces.

Figure 91: Maps of at % O for L-AA-4-$^{13}$C and D-AA on Cu(100) S$^4$C plotted 
vs. $X$ on a progression line. D-AA first decomposes on crystal planes along 
the directions exposing straight (100) step edges (black) then reacts on R 
regions of the S$^4$C, followed by R regions and the (100) plane. L-AA-4-$^{13}$C 
decomposes on S regions of the S$^4$C, followed by R regions, and finally the 
(100) plane.
Throughout the reaction progression timeline for both L-AA-4-\(^{13}\)C and D-AA decomposition, a significant portion of the (100) S\(^4\)C contains between 8-10 at% O. Between X = 30 and 60 for both enantiomers, this species is present on the majority of points on the surface. Eventually, the amount of O across the entire Cu(100) S\(^4\)C is between 3 and 4 at% O at X = 100 for both enantiomers. This provides evidence that there may be an intermediate species present on the surface during the reaction that is not AA. XPS was used previously by Mhatre et al to identify this intermediate species on a Cu(110) single crystal (3). Figure 93 shows a comparison of the C 1s XP spectra of a monolayer of L-AA (left) and a partially decomposed L-AA on the Cu(110) single crystal. The monolayer of L-AA contains two clear peaks in the C 1s spectrum: one peak that contains contributions from the C*H\(_2\) and C*HNH\(_2\) at 285 eV and one that corresponds to two C*OO groups on the surface. After partial decomposition, the peak at 285 eV
does not change, but the C*OO peak decreases in intensity. The C*OO peak does not completely disappear showing that there is still a C*OO group in the molecule. The structure of this intermediate was determined from the XP spectra as [OOC-CH(NH$_2$)-CH$_2$].

Figure 93: XP spectrum of C1s of L-AA on Cu(110) single crystal for a monolayer of L-AA (left) and after partial decomposition of L-AA (right) performed by Dr. Mhatre. After partial decomposition of L-AA, the peak at ~288 eV for C*OO decreases while the peak at ~285 eV doesn’t change. The partially decomposed species was identified as [OOC-CH(NH$_2$)-CH$_2$] (3).

Figure 94 shows a comparison of the C 1s XP spectra for two surfaces on the Cu(100) S$^4$C after the X = 50 experiment for D-AA along with their location on the Cu(100) S$^4$C from the map of at% O. The point in black and the point in red have the same surface structure but different chiralities: the point in black has an R chirality and the point in red has the S chirality. The color of the point corresponds to the color of the XP spectra. Each C 1s spectra was fit by two peaks; one peak for the two C species without O (C*H and C*HNH$_2$) and one peak for the C*OO group. The red point has 14 at% O and two clear peaks in the XP spectrum of C 1s showing that a monolayer of AA is present. The black point
has ~9 at% O and the peak area for C*OO is 50% less than for the red point. The peak for CH and CHNH$_2$ at ~285 eV shifts 0.5 eV to a slightly lower binding energy but the peak area remains the same. The C 1s spectra and the at% O both provide evidence that the intermediate species formed on the R surface is [OOC-CH(NH$_2$)-CH$_2$].

![C 1s XPS comparison of two surfaces in X=50 experiment of D-AA on the Cu(100) S$^4$C. The red point on the S surface contains D-AA while the black point on the R surface contains the intermediate species, [OOC-CH(NH$_2$)-CH$_2$].](image)

The XP spectra of C 1s for AA contains two well resolved peaks. In calculation of the at % of each element on the surface (Cu, C, O, and N) the at % of the two C peaks were calculated separately, one peak at ~285 eV for the C*H and C*HNH$_2$ species and one at ~288 eV for the C*OO species. Separating the two C peaks gives insight into the type of species on the surface since the O peak does not shift or contain two well resolved peaks in the XP spectra. The
maximum amount of each C peak in XPS was roughly 8 at % on the surface. Figure 95 shows a comparison of the C 288 eV at % and the O at % maps on progression timeline of extent of reaction, X, for D-AA on the Cu(100) S⁴C. The maps for C 288 eV do not look as well defined as the O maps because the range of at % is smaller for C (0-8 at %) and in general there is more signal from O 1s than C 1s. However, the general trend in the reaction across the Cu(100) S⁴C is similar for C 288 eV and O. For the X = 100, the average at % of O left on the surface is 4 and the average at % of C 288 eV is < 2. This provides further evidence that the species formed in the decomposition of AA on the S⁴C surface is CO₂ from the carboxyl groups.
The other observed product in AA decomposition is \( \text{C}_2\text{H}_3\text{N} \). In a standard TPRS experiment on the Cu(100) \( \text{S}^4\text{C} \), a peak for \( \text{C}_2\text{H}_3\text{N} \) was observed using \( m/q \) = 41 with a sharp peak at 503 K and a tailing shoulder extending out to 520 K. In the isothermal TPRS experiments, a peak for \( m/q \) = 41 was not observed providing evidence that \( \text{C}_2\text{H}_3\text{N} \) does not form or desorb from the surface at 460 K. Analyzing the C 285 eV peak and the N 1s peak in XPS can determine whether or not \( \text{C}_2\text{H}_3\text{N} \) is adsorbed on the surface. Figure 96 shows the maps of C 1s 288 eV, C 1s 285 eV, and N 1s for the \( X = 0 \) and \( X = 100 \) quench TPRS experiments. The at % of C scales from 0-8 while it scales from 0-4.5 for N. The C 288 eV map shows a clear decrease in at % between the \( X = 0 \) and \( X = 100 \) quench TPRS experiments while the C 285 eV map does not change. For N at %
there is an overall decrease in signal on the surface but in general there is still a
significant amount of N present after the $X = 100$ experiment. The average value
of the at% of C 288 eV across the surface is 6±1 at% for $X = 0$ and 1.5 ± 0.5 at %
for $X = 100$. For C 285 eV, the average value is 8±1 at % for $X= 0$ and 7±1 at %
for $X=100$ showing that this value does not change much. The average value of N
at% changes from 3.5±0.5 to 2.5±0.5. This provides evidence that the $C_2H_3N$
species remains on the surface after the isothermal TPRS experiment.

Figure 96: Maps of C 288 eV, C 285 eV, and N for $X=0$ and $X=100$ TPRS
experiments of D-AA on the Cu(100) S^4C. The average value of at% C 288
eV across the surface is 6 ± 1 for $X= 0$ and 1.5 ± 0.5 for $X = 100$. For C 285
eV, the average at % value is 8 ± 1 for $X= 0$ and 7 ± 1 for $X = 100$ showing
that this value does not change significantly. The average value of N at %
changes from 3.5 ± 0.5 to 2.5 ± 0.5. This shows that $C_2H_3N$ remains on the
surface.
To better visualize the change in C 1s and N 1s XPS spectra with time, Figure 97 shows the raw XPS spectra for N1s and C1s at the Cu(100) plane for four different quench TPRS experiments shown in purple. Also included across the spectra is a line to show if there is a shift in any of the peaks with extent of reaction, X. As the X increases, the peak at C 288 eV clearly decreases to ~ 0 while the peak for C 285 remains constant. The only change in the C 285 eV peak is a slight shift from 285.5 eV to 284.5 eV. The N signal does not change until the X=100 experiment where is decreases slightly and shifts form 399.3 eV to 398.5 eV. The presence of both of these peaks after the isothermal TPRS suggests that C2H3N remains on the surface after an isothermal TPRS at 460 K. The small but noticeable shift to a lower binding energy suggests that the species is no longer bound to O, which usually shifts the peak to a higher binding energy, which provides further evidence that the species is C2H3N. It is possible that not all of the C 285 eV signal is from C2H3N as the presence of O on the surface after the reaction suggests that some of the C could be C and O atoms on the surface. The binding energy of graphitic carbon is 284.5 eV which is too close to the C 285 eV peak for C*H and C*HNH2 to resolve.
The same experiments were performed for determining the conditions for producing a monolayer of L-AA on Cu(111) $S^4C$ as for L-AA-4-$^{13}$C and D-AA on the Cu(100) $S^4C$. L-AA was exposed to the Cu(111) $S^4C$ held at $< 330$ K for one

5.3.4 XPS of L-AA on Cu(111) $S^4C$

Figure 97: XP spectra of C1s and N1s on the Cu(100) plane at several extents of reaction. As the extent of reaction increases, the peak at C 288 eV clearly decreases to ~ 0 while the peak for C 285 remains constant. The N signal does not change until the $X=100$ experiment where is decreases slightly and shifts form 399.3 eV to 398.5 eV.
hour to produce a multilayer. Figure 98 displays XP spectra of O 1s, C 1s, and N 1s for a multilayer of L-AA on the Cu(111) S$^4$C in black. Just like observed with D-AA on the Cu(100) S$^4$C, there is a broad peak in the O 1s spectrum for the multilayer containing contributions from CO$^*$O$^*$ groups at 531.4 eV and CO$^*$O$^*$H groups at 532.7 eV in L-AA. There is also a large peak at 402 eV in the N1s spectra with contributions from NH$_3^+$ and NH$_2$ groups and two broad features in the C 1s spectra at 289 eV and 286 eV observed for the multilayer. The Cu(111) S$^4$C was heated to 405 K for > 10 minutes to form a monolayer on the surface. The red lines in Figure 98 show the XP spectra of O 1s, C 1s, and N 1s for the monolayer of L-AA on the Cu(111) S$^4$C. There is a clear decrease in all three spectra from the multilayer to the monolayer. There are still two peaks in the spectra for C 1s with a clear shift in the high binding energy peak from 289 eV peak to 288 eV. The O 1s spectra shifts to a smaller peak at 531.4 eV for the CO$^*$O$^*$ group and the N 1s spectra shifts from 402 eV for NH$_3^+$ in the multilayer to 399.5 eV for NH$_2$ in the monolayer. The change in the XP spectra from the multilayer to the monolayer clearly shows a change in the surface species from a zwitterionic AA species [HOOC-CH$_2$-CH(NH$_3$)$^+$((COO$^-$))] in the multilayer to a bi-aspartate species ['OOC-CH$_2$-CH(NH$_2$)-(COO$^-$)] in the monolayer and that heating the sample at 405 K for >10 min produces a monolayer on the S$^4$C surface.
After the conditions for producing a monolayer were determined, the quench TPRS experiments at 470 K were performed for L-AA on the Cu(111) S^4C. Figure 99 shows a progression line of the extent of reaction from $X = 0 - 100$ of the maps of at% O, C, and N for the quench TPRS experiments of L-AA on the Cu(111) S^4C. Each scan consists of 225 total points on the inner 3.2 mm from the (111) plane at the center. The edges of the stereographic triangle...
superimposed on the $S^4C$ surface are shown as white lines for the direction exposing (110) step edges and black lines for the direction exposing (100) step edges. The R regions of the surface are indicated in yellow and the S regions are indicated in burgundy. The maps span 0 to 14 at % for O, 0 to 16 at % for C, and 0 to 5 at % for N. The $X = 100$ experiment shows that there are two regions on the surface that still have a significant amount of O and C on the surface. The high O at % region on the top of the $S^4C$ comes from the scratch on the $S^4C$ surface that was observed previously in the TA experiments. The high O at % on the bottom of the $S^4C$ was observed after this experiment and showed that another scratch formed sometime after the TA experiments were completed but before the AA experiments began. The clearest indication of the reaction occurring on the $S^4C$ surface comes from the O at % maps. The $X = 30$ experiment shows that the decomposition reaction occurs first along directions exposing (110) step edges while surfaces along the (100) step edges remain un-reacted. The $X = 60$ experiment shows that the surface chirality influences the reaction. The reaction pattern shows three-fold symmetry along the (100) step edge directions in black. In the R regions of the surface close to the (100) step edges, there is a higher at % of O than in the S regions of the surface. Close to crystal planes with a high density of (110) step edges, the amount of O reaches a minimum value of 3-4 at %. The $X = 90$ experiment shows a similar pattern to $X = 60$: the R regions close to the (100) step edges have the highest at % of O from 6-7 at % apart from the scratches on the surface. The C and the N maps show similar patterns as the O
maps. There is not a map shown for $X = 100$ for N because there were not peaks present for N on the surface except at the scratch points on the S$^4$C.

For $X=60$, there appears to be three different regions on the surface that could indicate the presence of three different species on the surface. Figure 100 shows the O 1s XP spectra of three points on the Cu(111) S$^4$C after the $X=60$ experiment along with their location on the $X=60$ map of at% O. The crystal plane at Point 1 in red contains (100) step edges with R oriented kinks while the crystal plane at Point 2 in black contains the same surface structure with S.
oriented kinks. The crystal plane at Point 3 in blue is achiral and contains a high density of (110) step edges. As expected from the maps, the at % of O on Point 1 is the highest at 9 % followed by Point 2 at 6 % with Point 3 having the smallest amount of O at ~3%. The O peak does not shift as the amount of O decreases. The O peak does not give any new information on the type of species at each point, but the C 1s XP spectra can be used to determine the state of species on the S^4C surface. Figure 101 contains the C 1s spectra for the same three points measured on Figure 100. Point 1 in red on the R region contains two peaks for C*OO at 288 eV and C*H and C*HNH2 groups at ~285 eV showing that the species on the surface is AA. Point 2 in black on the S region also contains two peaks but the peak at 288 eV for C*OO is about 50% of the height while the peak at 285 eV remains unchanged. This indicates that the species on the surface is the intermediate species [-OOC-CH(NH2)-CH2]. The C 1s XP spectra at Point 3 does not contain a peak at 288 eV showing that the species does not contain any C*OO groups and is either atomic C or C2H3N on the surface.
Figure 100: (Left) Map of at % O for X = 60 quench experiment for L-AA on Cu(111) S^4C. (Right) XP spectra of select points on the Cu(111) S^4C indicated in green on the map. The XP spectra shows that Point 1 has 9 at% O, Point 2 has 6 at % O, and Point 3 has ~3 at % O.

Figure 101. (Left) Map of at % O for X=60 quench experiment for L-AA on Cu(111) S^4C. (Right) C 1s XP spectra of select locations of Cu(111) S^4C indicated in green. There are three different species on the Cu(111) S^4C after the quench. AA is present on Point 1, the intermediate [OOC-CHNH2-CH2] is on Point 2, and C2H3N is on Point 3.
For X=100, there were no visible peaks for N present although there are peaks present for O and C in the XP spectra. This provides evidence that for AA decomposition on the Cu(111) S^4C, C_2H_3N does not remain on the surface after the isothermal TPRS experiments. However, the signal for N 1s is very low for 2-3 at% on the surface so it is possible that the N 1s peak could have been present if a longer dwell time was used during the XPS scans at each point. To confirm whether or not this is the case, the C 1s XP spectra for the X=100 quench experiments were compared between D-AA on Cu(100) S^4C, where C_2H_3N is present in the surface after decomposition, and L-AA on the Cu(111) S^4C. Figure 102 compares the maps of C 285 eV and 288 eV for the X=100 isothermal TPRS experiments for D-AA on Cu(100) S^4C (right) and L-AA on the Cu(111) S^4C (left). For both D-AA on Cu(100) S^4C and L-AA on the Cu(111) S^4C, the map of C 288 eV looks the same with the average at% across the surface < 3 showing that the C*OO groups decompose on each surface. The maps of C 285 eV for each surface is much different. The average at% of C 285 eV on the Cu(100) S^4C is 7±1 while for Cu(111) S^4C the average is 4±1 at% (discluding the scratch points). The at% of O not shown is about equal to the amount of C 285 eV left on the Cu(111) S^4C while this is not the case for Cu(100) S^4C. Figure 103 shows a comparison of the raw XP spectra for C 1s, O 1s, and N 1s on the Cu(111) and Cu(100) planes on each S^4C for the X=100 isothermal TPRS experiment. The N 1s shows a small peak on the Cu(100) plane but there is no discernible peak on the Cu(111) plane. The O 1s spectra for the Cu(111) and Cu(100) plane both have a peak at ~531.5 eV with roughly 3-4 at% O on each surface. The C 1s
spectra for the Cu(100) plane is twice the peak area of the Cu(111) plane. Figure 102 and Figure 103 both provide evidence that C$_2$H$_3$N is not present on the Cu(111) $S^4C$ after the X=100 isothermal TPRS at 470 K.

Figure 102: Comparison of C 285 eV and 288 eV maps for X = 100 quench experiment for D-AA on Cu(100) $S^4C$ and L-AA on Cu(111) $S^4C$. The average at % of C 285 eV on the Cu(100) $S^4C$ is 7 ± 1 while for Cu(111) $S^4C$ the average is 4 ± 1 at % (not including the scratch points).
STM of AA on Cu(111)

STM has been used previously to study the phases of TA formed on a Cu(110) single crystal during an isothermal TPRS experiment (14, 229, 235-237). STM images showed that the phase of TA on the surface changed during the experiment and that Cu adatoms were observed on the surface within the peak temperature during a TPRS experiment. This provided evidence that the presence of TA on the surface caused surface reconstruction of the Cu(110) plane. STM of a saturated monolayer of L-AA on a Cu(111) single crystal was performed by
Sykes et al. to observe the phase of AA on the surface and see if the Cu (111) surface reconstructed. The left of Figure 104 shows an STM image of a Cu(111) single crystal with a saturated exposure of L-AA after heating the Cu(111) to 460 K for 1 minute. The STM image shows that the L-AA islands (yellow) and Cu step edges and islands (orange and brown) on the surface run in one of three directions. The black line indicated on the figure is parallel to one of the close packed/high symmetry directions and the blue line is parallel to one of the three directions of the Cu step edge/ L-AA islands on the surface. The directions of the Cu islands and step edges are not located directly along the close packed or high symmetry directions indicated by the inset image on the top right but instead are each rotated ~20° from the high symmetry directions. The right of Figure 104 displays the map of O at % for the X = 60 quench TPRS of L-AA on the Cu(111) S^4C seen previously. This image is rotated to align the high symmetry directions on the Cu(111) S^4C with the close packed directions on the Cu(111) single crystal of the STM image. The high symmetry directions containing crystal planes with (100) step edges are shown in black and the blue line is drawn where maxima in O at % occurs on the Cu(111) S^4C. The map shows that the L-AA remaining on the Cu(111) S^4C shows a similar ~20° rotation as the orientation of the Cu step edges and L-AA islands after surface reconstruction on the Cu(111) single crystal. This provides evidence that a similar surface reconstruction is also occurring on the Cu(111) S^4C with L-AA adsorbed and that Cu crystal planes located 20° from the (100) step edge high symmetry direction have enhanced binding of AA.
5.4 Discussion

5.4.1 Reaction Mechanism for AA decomposition on Cu(100) S\textsuperscript{4}C

A reaction mechanism shown in Equation 5.1-5.3 for AA decomposition on the Cu(100) S\textsuperscript{4}C was proposed based on the XPS and TPRS results. The ● represents an empty site on the surface and a species with a ● next to it represents an adsorbed species. In Equation 5.1, AA adsorbed on the surface desorbs into the gas phase or decomposes, creating an empty site on the surface (initiation step). In Equation 5.2, the adsorbed AA undergoes explosive decomposition on \( n \) empty sites creating 1 CO\textsubscript{2} molecule and leaving the intermediate species
\[
OOC - CH(NH\textsubscript{2}) - CH\textsubscript{2}
\]
remaining adsorbed on the surface (explosion step).
The TPRS data for L-AA-4\(^{13}\)C showed that the first carboxyl group to decompose from AA is the C4 atom. In Equation 5.3 the intermediate undergoes explosive decomposition on \(m\) empty sites creating CO\(_2\) which desorbs from the surface and \(\text{CH}(\text{NH}_2)\) \(-\) CH\(_2\) which remains adsorbed to the surface (intermediate step). From the XPS data, the presence of \(\text{CH}(\text{NH}_2)\) \(-\) CH\(_2\) adsorbed after the reaction on the Cu(100) S\(^4\)C has been confirmed. The rate constant for each reaction step is listed to the right of each step. The rate constant of Equation 5.1 (initiation step) is \(k_i\), for Equation 5.2 (explosion step) is \(k_e\), and for Equation 5.3 (intermediate step) is \(k_f\). From the TPRS data, there is strong evidence that decomposition of the first carboxyl group is explosive from the behavioral similarity with AA decomposition on Cu(110) single crystal. What is not known is whether the intermediate also undergoes explosive decomposition to form CO\(_2\) or if there is another type of reaction occurring on the surface.

\[\text{OOC} - \text{CH}(\text{NH}_2) - \text{CH}_2 - \text{COO} + \bullet \rightarrow \text{OOC} - \text{CH}(\text{NH}_2) - \text{CH}_2 - \text{COO}_{(g)} + \bullet \quad k_i \ (5.1)\]

\[\text{OOC} - \text{CH}(\text{NH}_2) - \text{CH}_2 - \text{COO} + n\bullet \rightarrow \text{OOC} - \text{CH}(\text{NH}_2) - \text{CH}_{2(n)} - n\bullet + \text{CO}_{2(g)} \quad k_e \ (5.2)\]

\[\text{OOC} - \text{CH}(\text{NH}_2) - \text{CH}_2 + m\bullet \rightarrow \text{CH}(\text{NH}_2) - \text{CH}_2 + m\bullet + \text{CO}_{2(g)} \quad k_f \ (5.3)\]

To calculate the values for \(n\) and \(m\) in the above model, a rate law was proposed from the above model listed in Equations 5.4-5.7. The rate law shows the change in the fractional coverage \(\{0,1\}\) of each species on the surface: \(\theta_{\text{Asp}}\) for AA, \(\theta_{\text{int}}\) for the intermediate \(\text{OOC} - \text{CH}(\text{NH}_2) - \text{CH}_2\) and \(\theta_{\text{C2H3N}}\) for \(\text{CH}(\text{NH}_2) - \text{CH}_2\). Equation 5.4 shows the fractional site balance on the surface.
The first assumption of the site balance is that the initial coverage of AA on the surface is 1 ($\theta_{Asp,0} = 1$). The second assumption is that $OOC - CH(NH_2) - CH_2$ occupies ¾ of the number of sites occupied by AA and that $CH(NH_2) - CH_2$ occupies ½ the number of empty sites as AA. If the coverage of each species on the surface was equal, the fraction of empty sites on the surface would always be zero which means that based on the reaction model, explosive decomposition would never occur. This rate law also assumes that $CH(NH_2) - CH_2$ remains on the surface and therefore the rate of $C_2H_3N$ desorption is always zero. Another key assumption to the rate law is that the desorption of AA from the surface is irreversible. This assumption is based on the results showing that the desorption of TA from the surface was irreversible on a Cu(110) single crystal, but this experiment for AA has not been performed yet. Using this rate law and data for coverage of each species vs. time, values for $k_i$, $k_e$ and $k_f$, can be calculated for each point on the surface and used to determine the values of $n$ and $m$.

Site Balance: $1 = \theta_{Asp} + \frac{3}{4} \theta_{Int} + \frac{1}{2} \theta_{C2H3N} + \theta_*$

$$\frac{d\theta_{Asp}}{dt} = -k_i \theta_{Asp} - k_e \theta_{Asp} \left(1 - \theta_{Asp} - \frac{3}{4} \theta_{Int} - \frac{1}{2} \theta_{C2H3N}\right)^n$$

$$\frac{d\theta_{Int}}{dt} = k_e \theta_{Asp} \left(1 - \theta_{Asp} - \frac{3}{4} \theta_{Int} - \frac{1}{2} \theta_{C2H3N}\right)^n - k_f \theta_{Int} \left(1 - \theta_{Asp} - \frac{3}{4} \theta_{Int} - \frac{1}{2} \theta_{C2H3N}\right)^m$$

$$\frac{d\theta_{C2H3N}}{dt} = k_f \theta_{Int} \left(1 - \theta_{Asp} - \frac{3}{4} \theta_{Int} - \frac{1}{2} \theta_{C2H3N}\right)^m$$

The difficulty in modeling this data is in distinguishing which one of the three species in the rate law is present on the surface at a given time and
calculating the fractional coverage of each species. It is also possible that all
three species could be present on the surface at the same time which would not be
distinguishable using the XPS data. Several simplifications were made in
calculating the fractional coverages of each species from the XPS data. The first
assumption is that only two species are present on a surface point at any given
time. This means that there are one of two possibilities for species present on the
surface. The first possibility is that there is a mixture of AA and the intermediate,
\(-CH(NH_2) - CH_2\), on the surface. The second possibility is that there is a
mixture of the intermediate, \(OOC - CH(NH_2) - CH_2\) or \(CH(NH_2) - CH_2\) on the
surface. This assumption means that at any given time, there are not three species
on the surface and also that AA and \(CH(NH_2) - CH_2\) are not present at a point
on the surface at the same time.

In general, the fractional coverages were calculated based on the peak area
of the \(O\ 1s\) signal at point \(j, I_{O,j}\), divided by the peak area of the \(Cu\ 2p_{3/2}\) signal
from the clean \(Cu(100)\ S^4C\) surface at that point, \(I_{Cu,j}\). Equation 5.8 and 5.9
shows the equations used to calculate the fractional coverage for each possibility.
Equation 5.8 shows the calculation for \(\theta_{Asp}\) and \(\theta_{Int}\) for the first possibility
(region 1) with \(\theta_{C_2H_3N_x} = 0\) and Equation 5.9 shows the calculation for \(\theta_{Int}\) and
\(\theta_{C_2H_3N}\) for the second possibility (region 2) with \(\theta_{Asp,x} = 0\). The choice of
which region to use to calculate the coverage is based on the value of \(K\) shown in
Equation 5.10. The value of \(K\) is the average peak area ratio of \(O\ 1s\) to the clean
\(Cu\ 2p_{3/2}, \frac{I_O}{I_{Cu}}\), for the intermediate species across the entire \(S^4C\) surface. It is
calculated by assuming that the average peak area ratio of the intermediate species at a given surface location, \( j \), is halfway between the ratio of the monolayer of AA, \( \frac{I_{O,j}}{I_{Cu,j}} \_0\% \), and the ratio of the fully reacted surface, \( \frac{I_{O,j}}{I_{Cu,j}} \_100\% \). For each point \( j \), if \( \frac{I_{O,j}}{I_{Cu,j}} \_x\% \geq K \), then Equation 5.8 was used, but if \( \frac{I_{O,j}}{I_{Cu,j}} \_x\% \leq K \), then Equation 5.9 was used to calculate the fractional coverages.

\[
If \ region \ 1 \ for \ point \ j: \quad \theta_{Asp,x} = \frac{\frac{I_{O,j}}{I_{Cu,j}} \_x\% - K}{\frac{I_{O,j}}{I_{Cu,j}} \_0\% - K} \quad \theta_{int,x} = 1 - \theta_{Asp,x} \quad \theta_{C2H3N,x} = 0 \quad (5.8)
\]

\[
If \ region \ 2 \ for \ point \ j: \quad \theta_{int,x} = \frac{K(\frac{I_{O,j}}{I_{Cu,j}} \_x\%)}{K(\frac{I_{O,j}}{I_{Cu,j}} \_0\%)} \quad \theta_{C2H3N,x} = 1 - \theta_{int,x} \quad \theta_{Asp,x} = 0 \quad (5.9)
\]

\[
K = \frac{\sum_{j=1}^{225} \left[ \frac{\frac{I_{O,j}}{I_{Cu,j}} \_0\% + \frac{I_{O,j}}{I_{Cu,j}} \_100\%}{2} \right]}{225} \quad (5.10)
\]

Using these equations, the coverage vs. time for each of the three species on the surface was calculated for all 225 points for both L-AA-4-\(^{13}\)C and D-AA on the Cu(100) S\(^4\)C. For D-AA there were eight values of coverage vs. time at each surface point with only seven values of coverage vs. time at each surface point for L-AA-4-\(^{13}\)C. The time that the sample was held at 460 K in each experiment was used and not the time of the peak which is the same metric used for TA decomposition on the Cu(111) S\(^4\)C. Two different methods were used to calculate values for the rate constants and determine the best fit values of \( n \) and \( m \). The first method only used the coverage of AA, \( \theta_{Asp} \), vs. time to calculate values for \( k_i \) and \( k_e \) and determine the best fit value for \( n \) only. The second method used
all three $\theta_{Asp}$, $\theta_{int}$, and $\theta_{C2H3N}$ vs. time values to calculate values of $k_i$, $k_e$, and $k_f$ and determine best fit values of both $n$ and $m$.

5.4.2 Method One Results

For method one, a modified version of Equation 5.1 was used as the rate law for $\frac{d\theta_{Asp}}{dt}$. In this equation, the coverage of the empty sites on the surface was changed from $1 - \theta_{Asp} - \frac{3}{4} \theta_{int} - \frac{1}{2} \theta_{C2H3N}$ to $1 - \theta_{Asp}$ since the coverages of $\theta_{int}$ and $\theta_{C2H3N}$ are not included in this method. The form of Equation 6.1 then becomes $\frac{d\theta_{Asp}}{dt} = -k_i \theta_{Asp} - k_e \theta_{Asp} (1 - \theta_{Asp})^n$. Only two models were fit to the data for $\theta_{Asp}(t; k_i, k_e)$: $R_1$, where $n = 1$ and $R_2$, where $n = 2$. Numerical integration was used to generate the model data of $\theta_{Asp}(t; k_i, k_e)$ using ode45 as a solver in Matlab. The lsqnonlin function was used to adjust the value of $k_i(\vec{r})$ and $k_e(\vec{r})$ to minimize the sum of squared errors in the $\theta_{Asp}(t; k_i, k_e)$ between the model and experiment. Separate values for $k_i(\vec{r})$ and $k_e(\vec{r})$ were calculated for each of the 225 points on the S$^4$C surface for both 4-$^{13}$C L- and D-AA for $R_1$ and $R_2$.

Figure 105 shows parity plots comparing $\theta_{AA}^{exp}$ and $\theta_{AA}^{model}$ for each point on the Cu(100) S$^4$C for L-AA-4-$^{13}$C and D-AA for models $R_1$ and $R_2$. The plots for $R_1$ where $n=1$ are shown on the right and the plots for $R_2$ for $n=2$ are on the left. For D-AA shown in blue, the parity plots of $R_1$ and $R_2$ are similar. Over 90% of the data points for D-AA for both models lie ± 0.1 from the black line where $\theta_{AA}^{exp} = \theta_{AA}^{model}$. The parity plots of L-AA-4-$^{13}$C in red appear to be a much
better fit to both models than the data for D-AA. Over 99% of the points for both $R_1$ and $R_2$ fall within 0.1 of the $\theta_{AA}^{exp} = \theta_{AA}^{model}$ line. However, there is a noticeable change between $R_1$ and $R_2$ for L-AA-4-\textsuperscript{13}C in the range of $\theta_{AA}^{exp} < 0.4$ where the values for $R_2$ lie much closer to the $\theta_{AA}^{exp} = \theta_{AA}^{model}$ line than for $R_1$.

Inset in each parity plot on Figure 105 the values calculated for the sum of squared errors (SSE) between the model and the experimental data for each enantiomer for the $R_1$ and $R_2$ models. The SSE values show that for both L-AA-4-\textsuperscript{13}C and D-AA, $R_2$ is a better fit to the data than $R_1$ showing that a value of $n=2$ is a better fit to the data than $n = 1$. 
\[ R_n = k_i \theta + k_e (1-\theta)^n \]

Figure 105: Parity plots of experimental vs. model data for both L-AA-4-\(^{13}\)C and D-AA decomposition for \(R_1\) and \(R_2\) models.

The top of Figure 106 shows the fit of the \(R_2\) model to the data for two points on the Cu(100) \(S^{4}\)C surface for 4-\(^{13}\)C L-AA (top left) and D-AA (top right). The two points are indicated on a map of the at \% O on the Cu(100) \(S^{4}\)C under each plot. The map under the 4-\(^{13}\)C L-AA coverage vs. time plot is the \(X=38\) experiment for 4-\(^{13}\)C L-AA and the map underneath the D-AA coverage vs. time plot is the \(X=50\) experiment for D-AA. The black point is a surface of R chirality and is shown by the black lines on each plot of \(\theta_{ASP}\) vs. time and the magenta point is a surface of S chirality indicated by the magenta lines. These points have the same surface structure; the only difference between the two points is the
chirality of the surface. For decomposition of L-AA-4-\(^{13}\)C, the S surface clearly decomposes before the R surface, while for D-AA, the R surface clearly decomposes before the S surface. The rate constants from the model for each line is shown above each plot of coverage vs. time. Both \(k_i\) and \(k_e\) for the R surface is lower than the S-surface for the decomposition of 4-\(^{13}\)C L-AA. This is not the same trend seen for D-AA decomposition. The value of \(k_i\) for the S surface is lower than the R surface but the value of \(k_e\) is higher for the S surface than the R surface. The \(R_2\) model appears to be a good fit at both of these points for both 4-\(^{13}\)C L- and D-AA.
Values for $k_i(\overline{r_j})$ and $k_e(\overline{r_j})$ were calculated for all 225 points for model R$_2$ for both D- and L-AA-4-13C decomposition on the Cu(100) S$^4$C. Some of the values of $k_i(\overline{r_j})$ and $k_e(\overline{r_j})$ were calculated from two data points or less with values $> 0$ since on some points on the S$^4$C surface, AA decomposed quickly.

Data points with two or less points $> 0$ were removed from the analysis of the rate constants. Figure 107 shows maps of $k_i(\overline{r_j})$ and $k_e(\overline{r_j})$ across the Cu(100) S$^4$C for data points with $> 2$ non-zero values for $\theta_{Asp}$ vs. time. For L-AA-4-13C...
decomposition, the largest trend observed on the surface is that $k_i(\overrightarrow{r})$ is a minimum value of $\sim 2 \times 10^{-4} \text{ s}^{-1}$ around the (100) plane at the center while $k_e(\overrightarrow{r})$ reaches maximum of $\sim 0.1 \text{ s}^{-1}$ around the (100) plane. For D-AA decomposition, values of $k_i(\overrightarrow{r})$ are the highest around the edges of the stereographic triangle with (111) step edges with values around $1 \times 10^{-2} \text{ s}^{-1}$ (black lines). Minimum values in $k_i(\overrightarrow{r})$ occur around the (100) plane and range from $5 \times 10^{-5} \text{ s}^{-1}$ to $5 \times 10^{-4} \text{ s}^{-1}$. Along the directions exposing (110) step edges (orange lines), values of $k_e(\overrightarrow{r})$ reach minimum values around $1 \times 10^{-4} \text{ s}^{-1}$ while $k_e(\overrightarrow{r})$ reaches maximum of $\sim 0.4 \text{ s}^{-1}$ on surfaces with a high density of (100) step edges. The minimum $k_e(\overrightarrow{r})$ value extends around the edge of the Cu(100) S$^4$C further in the S regions than the R regions. It appears that the overall value of $k_e(\overrightarrow{r})$ in R-regions is greater than in the S-regions around the edges of the Cu(100) S$^4$C, but there is not a clear change in the value of $k_e(\overrightarrow{r})$ between the R and S chiral regions on the surface. From the trends observed for $k_i(\overrightarrow{r})$ and $k_e(\overrightarrow{r})$ for both L-AA-4-$^{13}$C and D-AA on the Cu(100) S$^4$C, there is not a clear indication as to whether the initiation step or the explosion step is the rate limiting step in the overall reaction. However, it appears that for D-AA, the values of both $k_i(\overrightarrow{r})$ and $k_e(\overrightarrow{r})$ are significantly lower along directions exposing (110) step edges than directions exposing (111) step edges especially close to the edges of the Cu(100) S$^4$C.
Method Two Results

For method two, Equations 5.5-5.7 were used to fit four kinetic models for D-AA decomposition on the Cu(100) $S^4C$ to the data of $\theta_{\text{Asp}}, \theta_{\text{Int}},$ and $\theta_{C2H3N}$ vs. time. Each model differing the reaction order of the explosion step in the vacancy concentration for AA, $n$, and for the intermediate, $m$, $R_{n,m}$ ($n=1,2; m=0,1,2$). The set of three $\frac{d\theta_i}{dt}$ equations were solved by numerical integration to predict $\theta_{\text{Asp}}(t; k_i, k_e, k_f), \theta_{\text{Int}}(t; k_i, k_e, k_f),$ and $\theta_{C2H3N}(t; k_i, k_e, k_f)$ at each point on

Figure 107: $k_i(\overline{r})$ and $k_e(\overline{r})$ vs position on the Cu(100) $S^4C$ surface for D-AA (in blue) and $4^{-13}\text{C}$ L-AA (in red). For L-AA-$4^{-13}\text{C}$, the value of $k_i(\overline{r})$ reaches a minimum value $\sim 2 \times 10^{-4} \text{ s}^{-1}$ around the (100) plane at the center while $k_e(\overline{r})$ reaches maximum of $\sim 0.1 \text{ s}^{-1}$ around the (100) plane. For D-AA the value of $k_i(\overline{r})$ in a minimum around the (100) plane and range from $5 \times 10^{-5} \text{ s}^{-1}$ to $5 \times 10^{-4} \text{ s}^{-1}$ while $k_e(\overline{r})$ reaches maximum of $\sim 0.4 \text{ s}^{-1}$ on surfaces with a high density of (100) step edges.
the surface using the \textit{ode45} solver in Matlab. The \textit{lsqnonlin} function was again used to fit the predictions of each model to the experimental data. The input of \textit{lsqnonlin} is a vector of errors that adjusts the values of $k_1(\overline{r_j})$, $k_e(\overline{r_j})$, and $k_f(\overline{r_j})$ by minimizing the sum of squared errors in the three coverages between each model and the experimental data. Only the data for D-AA was used to determine the best fit model since there were more experimental data points for D-AA decomposition (24 per surface point) than L-AA-4-$^{13}$C decomposition (21 per surface point).

Figure 108 shows the parity plot of all of the calculated coverages for each model of the proposed rate law. The $\theta_{\text{Model}}$ versus $\theta_{\text{Exp}}$ are included separately for each species and indicated by red for $\theta_{\text{Asp}}$, green for $\theta_{\text{int}}$, and blue for $\theta_{\text{C}_2\text{H}_3\text{N}}$. Magenta lines are indicated on each figure to help show the overall trend of the majority of the coverage data. The model on the top left $R_{20}$ sets the value $m = 0$ on the empty site of the explosive decomposition of the intermediate which simplifies that term of the equation to $-k_f\theta_{\text{int}}$ which is the same form as first order desorption. This model is the worst fit to the data showing the largest deviation from the $\theta_{\text{Model}} = \theta_{\text{Exp}}$ line. The parity plots of the models for $R_{21}$ and $R_{11}$ have similar trends. While both models are better fits to the data than $R_{20}$, both models have a significant deviation from the $\theta_{\text{Model}} = \theta_{\text{Exp}}$ line at $\theta_{\text{Exp}} > 0.8$ where the model consistently under predicts the value of the coverage for $\theta_{\text{int}}$ and $\theta_{\text{C}_2\text{H}_3\text{N}}$. The parity plot of $R_{22}$ lies the closest to the $\theta_{\text{Model}} = \theta_{\text{Experiment}}$ line and does a better job of predicting the values of $\theta_{\text{int}}$ and $\theta_{\text{C}_2\text{H}_3\text{N}}$. 


for $\theta_{\text{Exp}} > 0.8$. The $R_{22}$ model does have several deviations at points where $\theta_{\text{Model}} = 1$ for $\theta_{\text{Asp}}$ and $\theta_{\text{Model}} = 0$ for $\theta_{\text{Int}}$.

The sum of squared errors between the coverages predicted by the model and experimental data for each of the models for the rate law is inset in each parity plot on Figure 108. The $R_{20}$ model has the highest value of the sum of squared errors at 185 and is the worst fit to the data as clearly displayed in the parity plot. The sum of squared errors for $R_{21}$ and $R_{11}$ are about equal but the $R_{11}$
model is a slightly better fit. The best fit model is $R_{22}$ which has a minimum in
the sum of squared errors at 145. The rest of the analysis of the trends in rate
constants with surface orientation were calculated using model $R_{22}$.

Figure 109 displays coverage vs. time plots of the $R_{22}$ model with the D-
AA experimental data for each species at three surfaces on the Cu(100) $S^4C$. The
lines represent the coverage values predicted by the model and the data points are
the experimental data: red for $\theta_{Asp}$, green for $\theta_{int}$, and blue for $\theta_{C2H3N}$. The
point labeled “R region” is a point located at the edge of the Cu(100) $S^4C$ in the R
chiral region of the surface while the point labeled “S region” is also located at
the edge of the $S^4C$ in an S chiral region. The final point is the (100) plane and is
achiral. The experimental data and the model show that both D-AA and the
intermediate remain longer on the S surface than the R surface. The peak in $\theta_{int}$
occurs at 290 seconds on the R surface while it occurs at 360 seconds for the S
surface. The value of $\theta_{Asp} = 0$ is reached by the model on the R surface at 325
seconds while on the S surface $\theta_{Asp} = 0$ isn’t reached until >400 seconds. On both
the R and the S surface, the intermediate is present on the surface for a much
longer period of time than on the (100) plane. The FWHM of the peak for $\theta_{int}$ of
the model on the (100) plane is ~50 seconds while it is 150 seconds on the S
surface at ~ 200 seconds on the R surface. This shows that the intermediate is
present on chiral surfaces for a longer period of time than the achiral surface and
that the decomposition of the intermediate is effected by the chirality of the
surface. Of the three points shown, the $R_{22}$ model predicts the data best at the
Cu(100) surface.
Figure 109: Plots of coverage vs. time for the $R_{22}$ model and experimental data for D-AA for select points on the Cu(100) S$^4$C. The model and predicted experimental data show that D-AA and the intermediate decomposes on the R surface before the S surface. The intermediate is on the (100) plane for the shortest amount of time.

Figure 110 shows the values of $k_i(\tau_j)$, $k_e(\tau_j)$, and $k_f(\tau_j)$ across the Cu(100) S$^4$C calculated for model $R_{22}$ for both L-AA-4-$^{13}$C and D-AA.
decomposition. The value of $k_i(\overline{r_j})$, the initiation rate constant, is slightly higher in S regions near the edge of the Cu(100) S^4C for D-AA while for L-AA-4-^{13}C, $k_i(\overline{r_j})$ is higher in R regions of the Cu(100) S^4C near the edge and close to the (110) step edge directions. The values of $k_e(\overline{r_j})$ vary significantly with surface orientation for both enantiomers. For D-AA, $k_e(\overline{r_j})$ has local minima in the S chiral regions of the S^4C near the edges at ~0.6 s^\text{-1} while maxima occur around the (111) step edge at ~10 sec^\text{-1}. L-AA-4-^{13}C has the opposite trend in the surface chirality as there are local minima in $k_e(\overline{r_j})$ in the R chiral regions of the S^4C near the edges ~0.3 s^\text{-1}. For D-AA decomposition, $k_e(\overline{r_j})$ is lower on S surfaces at the edge where D-AA remained for the longest time, and for L-AA-4-^{13}C, $k_e(\overline{r_j})$ is lower on R surfaces at the edge and the (100) plane where L-AA-4-^{13}C remained for the longest time. The trends in $k_e(\overline{r_j})$ with surface chirality provide evidence that there is a positive correlation between $k_e(\overline{r_j})$ and the overall rate of AA decomposition. The value of $k_f(\overline{r_j})$ has a different trend for L-AA-4-^{13}C compared to D-AA. For D-AA, $k_f(\overline{r_j})$ is a maximum at the (100) plane at the S^4C center at ~0.4 s^\text{-1} with local maxima on the S chiral regions near the edge of the S^4C. The value of $k_f(\overline{r_j})$ does not vary significantly for L-AA-4-^{13}C across the S^4C surface except for a maximum at the (100) plane of 0.1 s^\text{-1}.
Figure 110: Values of $k_i(\mathbf{r}_j)$, $k_e(\mathbf{r}_j)$, and $k_f(\mathbf{r}_j)$, vs. position on the Cu(100) $S^4C$ from $R_{22}$ model for both $4^{-13}C$ L- and D-AA decomposition. The trends in $k_e(\mathbf{r}_j)$ with surface chirality provide evidence that there is a positive correlation between $k_e(\mathbf{r}_j)$ and the overall rate of AA decomposition.

Figure 111 shows the trend in each rate constant with angle from the (111) step edge high symmetry direction for both L-AA-$4^{-13}C$ and D-AA decomposition for the $R_{22}$ model. Located at $45^\circ$ from the (111) step edge are surfaces with...
(110) step edges that are not chiral. Each point is from the outer ring of measured points on the S\(^4\)C as black for the R surfaces and orange for the S surfaces. The values in the plots of each rate constant versus angle are the average of four points as each measured surface is repeated every 90° azimuthally on the S\(^4\)C. For D-AA, \(k_i(\overline{r})\) on both the R and S surfaces has a parabolic trend with distance from the step edges with a minima located at 32.5° from (111) step edge line for the S surfaces and 20° from (111) step edges for the R surfaces. The trend in \(k_i(\overline{r})\) is much different for L-AA-4\(^{13}\)C. As the distance from the (111) step edge increases, so does the value of \(k_i(\overline{r})\) on R surfaces while \(k_i(\overline{r})\) does not change significantly on S surfaces. For D-AA, the value of \(k_e(\overline{r})\) is generally higher on R surfaces than S surfaces while the opposite is true for L-AA-4\(^{13}\)C. This shows further evidence that \(k_e(\overline{r})\) is affected by the surface chirality. For both enantiomers, \(k_e(\overline{r})\) appears to linearly increase for R surfaces as the points get closer to the (111) step edge high symmetry direction. The trend in \(k_f(\overline{r})\) with surface structure shows that the value doesn’t change significantly on R surfaces for D-AA and on both S and R surfaces for L-AA-4\(^{13}\)C. However, \(k_f(\overline{r})\) for D-AA reaches a maximum on S surfaces between 20 and 25° from the (111) step edge which is directly between the (111) and (110) step edge high symmetry directions and a maximum in kink density. The trends in the values of \(k_e(\overline{r})\) with surface chirality at the edges of the Cu(100) S\(^4\)C are closer to the trends seen in the at % maps of each enantiomer than \(k_i(\overline{r})\) and \(k_f(\overline{r})\) providing evidence that \(k_e(\overline{r})\) is sensitive to the surface chirality.
Figure 111: (Left) Average values of each rate constant as they vary with angle from the (100) step edge. The points are from the outer ring of the Cu(100) S\textsuperscript{4}C. Orange points are S surfaces and black points are R surfaces. The value of $k_e(\vec{r}_j)$ is consistently higher or R surfaces than S surfaces which matches the data that R decomposes on R regions before S regions.
5.5 Conclusions

The explosive decomposition of L-AA-4-\(^{13}\)C and D-AA was studied on the Cu(100) \(S^4C\) and L-AA explosive decomposition was studied on the Cu(111) \(S^4C\). Quench TPRS experiments and spatially resolved XPS were used to visualize the progression of the decomposition of AA across 225 points on each \(S^4C\) surface. On both \(S^4Cs\), the surface chirality played an important role in the decomposition reaction. L-AA on the Cu(111) \(S^4C\) remained longest on the R surfaces along a direction 20° from the (100) step edge high symmetry direction. For AA decomposition on the Cu(100) \(S^4C\), L-AA-4-\(^{13}\)C remained longer on R surfaces near the edge of the Cu(100) \(S^4C\) while D-AA remained longer on S surface near the edge of the Cu(100) \(S^4C\). Analysis of the XP spectra showed that an intermediate species [OOC-CH(NH\(_2\))CH\(_2\)] was present on the surface during the reaction and C\(_2\)H\(_3\)N remained on the surface after complete decomposition of AA for isothermal TPRS experiments at 460 K. A rate law was proposed based on the findings from XPS and several models were fit to the experimental data to calculate the rate constants and determine reaction order of the explosion step in the vacancy concentration for AA, \(n\), and the intermediate, \(m\). The best fit model was \(R_{22} (n = 2, m = 2)\) and \(k_e(\tilde{n})\) matched the trends in decomposition activity for both enantiomers providing evidence that the rate limiting step in the decomposition of AA on Cu(100) \(S^4C\) is the explosion of AA on the surface.
CHAPTER 6

6 CH₃CH₂OH, CD₂CD₂OD, and CF₃CH₂OH decomposition on ZnO(1 1 00)

6.1 Introduction

ZnO is a wide band-gap II-VI semiconductor that has applications in blue and UV LEDs, solar cells, catalysts, and chemiresistive sensors. ZnO has a hexagonal (“wurtzite”) structure and can expose a variety of crystal facets, each with its own unique surface chemistry. For sensor and catalytic applications of nanoscale ZnO morphologies, there has been recent interest in one-dimensional “nanorod” structures, which have high surface-to-volume ratios. ZnO nanorods grow preferentially along their c-axes, and most of their exposed surface area is composed of “non-polar” ZnO{1100} planes, with equal densities of surface O and Zn atoms. Characterization of the interactions of typical analyte and reactant species with these ZnO{1100} surfaces is important for understanding and improving ZnO-based sensors and catalysts.

A number of studies of alcohol adsorption and reaction on single crystal ZnO surfaces have been published. Mokwa et al. reported H₂, H₂O, CH₃CH=O, and CH₂=CH₂ as the primary products of thermal decomposition of CH₃CH₂OH on non-polar ZnO(1100). Shao et al. used scanning tunneling microscopy (STM) to study the intermediates formed by CH₃OH adsorption at 300 K on ZnO(1100). They observed two different surface
species on the ZnO(1100) surface; a methyl (-CH₃) species formed at a surface lattice O site upon breakage of the C-O bond in CH₃OH, and a methoxy (CH₃O-) species formed at a surface lattice Zn site upon breaking of the O-H bond. DFT calculations confirmed that the formation of both species was energetically favorable by -0.8 eV for CH₃O- formation and -0.4 eV for -CH₃ formation.

While the products of CH₃CH₂OH decomposition on the ZnO(1100) surface have been identified, little is known about the details of the reaction mechanism or its transition state(s). In this work, we use temperature programmed reaction spectrometry (TPRS) to examine the thermal decomposition of CH₃CH₂OH, CD₃CD₂OD and CF₃CH₂OH on ZnO(1100). We propose a reaction mechanism and surface intermediate species that are consistent with the observed decomposition products. Deuterium kinetic isotope effects and F substitution effects observed in TPRS of CD₃CD₂OD and CF₃CH₂OH, respectively, provide insight into the rate limiting steps and the transition states in the mechanisms for formation of CH₃CH=O and CH₂=CH₂ during CH₃CH₂OH decomposition on ZnO(1100). The reaction products, F substituent effects and kinetic isotope effects are consistent with a mechanism for CH₃CH₂OH decomposition on ZnO(1100) in which there are two parallel pathways through two distinct intermediates; an ethoxy (CH₃CH₂O-) intermediate bound to the Zn sites and leading to the formation of CH₃CH=O and an ethyl (CH₃CH₂-) intermediate bound to the lattice O sites and leading to the formation of CH₂=CH₂.
6.2 Experimental

Experiments were performed in UHV chamber 1 with a base pressure of $3 \times 10^{-10}$ Torr equipped with an Omicron NSE 10 ion gun for Ar$^+$ ion sputter cleaning of the ZnO surface, a Dycor quadrupole mass spectrometer for identification and quantification of desorption products; a Specs X-ray source and an Omicron EA125 hemispherical analyzer for performing X-ray Photoelectron Spectroscopy (XPS); a leak valve for introduction of ethanol vapor into the chamber background; and a PHI Low Energy Electron Diffraction (LEED) optics.

A $10 \times 10 \times 1$ mm$^3$ ZnO$(1\overline{1}00)$ single crystal was bonded to a Ta plate using Aremco Pyroduct 597-A, a thermally and electrically conducting Ag based paste. Two Ta wires were spot-welded to the Ta plate and then attached to the end of a sample manipulator mounted vertically in the UHV chamber. The crystal mount was in thermal contact with a liquid N$_2$ reservoir and the Ta plate was heated resistively to reach temperatures in the range 100 – 1000 K. The temperature was measured using a K-type thermocouple spot-welded to the Ta plate and was controlled using a computer.

Before each TPRS experiment, the ZnO$(1\overline{1}00)$ crystal was prepared by at least two cycles of (1) sputtering at 400 K with a 6 $\mu$A current of 2 kV Ar$^+$ ions for 50 minutes and (2) annealing for 5 minutes at 750 K. XPS analysis verified the cleanliness and the Zn:O atomic ratio of the surface. A LEED pattern of the clean ZnO$(1\overline{1}00)$ surface at 100 K is shown in Figure 112. LEED verified that the surface retained its Zn$(1\overline{1}00)$ order after the sputtering and annealing cycles (250). CH$_3$CH$_2$OH (99.6%, Sigma Aldrich), CD$_3$CD$_2$OD (99.5%, Sigma
Aldrich), and CF₃CH₂OH (>99%, Sigma Aldrich) were purified by several freeze-pump-thaw cycles before introduction into the chamber via a leak valve for background exposure of the ZnO(1̅100) surface at 300 K.

Figure 112: LEED pattern of the clean ZnO(1̅100) surface at 100 K (E = 150 eV) from UHV chamber 1.

XPS characterization of the ZnO(1̅100) crystal was performed using an Al Kα X-ray source and a seven channeltron Omicron EA 125 hemispherical energy analyzer operated with a pass energy of 100 eV in constant analyzer energy (CAE) mode. The sample was positioned 5 mm in front of the X-ray source oriented at an angle midway between the axes of the X-ray source and the lens of the hemispherical energy analyzer. This angle and sample position yielded the maximum Zn 2p₃/₂ signal. Integrated areas of the Zn 2p₃/₂, O 1s, F 1s, and C 1s peaks were used with Wagner library sensitivity factors for quantitative estimates of surface compositions (251).
TPRS experiments were performed using the quadrupole mass spectrometer to monitor species that desorbed from the ZnO(1\textsc{I}00) surface. After exposure to CH$_3$CH$_2$OH, CD$_3$CD$_2$OD, or CF$_3$CH$_2$OH, the ZnO(1\textsc{I}00) crystal was positioned in front of the mass spectrometer < 5 mm from the aperture to the ionizer and then heated from 300 to 750 K at 1 K/s in each TPRS experiment. The mass spectrometer signal for any given \( m/z \) contains contributions from multiple desorbing species and cannot be used to directly determine the relative yields of product species desorbing into the gas phase. Therefore, the mass spectrometer signals from each TPRS experiment were converted to pressures by determining the signal intensities at each \( m/z \) for each pure component species introduced into the chamber at a known pressure. Pure CH$_3$CH$_2$OH, CH$_3$CH=O, H$_2$, H$_2$O, or CH$_2$=CH$_2$ were leaked into the UHV chamber at pressures between 1\( \times \)10$^{-9}$ Torr and 5\( \times \)10$^{-8}$ Torr, measured using a Bayard-Alpert ion gauge corrected for sensitivity, (252) and the signals at \( m/z = 2, 18, 28, 29, \) and 31 were recorded. For each of the five pure components, \( i, \) introduced into the chamber and at the five \( m/z \) ratios, \( j, \) the mass spectrometer signal was measured at four different pressures, \( l_{ij}(P) \). The sensitivity of signal to pressure was calculated to yield \( \alpha_{ij} = \frac{dl_{ij}}{dp}. \) This was repeated for the five pure components to create a 5x5 matrix, \( \bar{\alpha}. \) A similar matrix was developed for TPRS of CD$_3$CD$_2$OD by leaking pure D$_2$, D$_2$O, CD$_3$CD=O, CD$_2$=CD$_2$, or CD$_3$CD$_2$OD into the UHV chamber at pressures between 1\( \times \)10$^{-9}$ Torr and 5\( \times \)10$^{-8}$ Torr and recording signals at \( m/z = 4, 20, 32, 30, \) and 34. The \( \bar{\alpha} \) matrices for CH$_3$CH$_2$OH and CD$_3$CD$_2$OD decomposition products are given in Tables 6.1 and 6.2. These
matrices were used to convert the TPRS signals at the five \( m/z \) ratios into pressures of each component desorbing from the surface. This analysis was not applied to TPRS experiments of \( \text{CF}_3\text{CH}_2\text{OH} \) due to the lack of availability of all pure component products of \( \text{CF}_3\text{CH}_2\text{OH} \) decomposition.

Table 8: Matrix of mass spectral sensitivities, \( \alpha_{ij} = \frac{dI_i}{dP} \), for ionization fragments of \( \text{CH}_3\text{CH}_2\text{OH} \) and its decomposition/desorption products \( \text{CH}_3\text{CH}_2\text{OH}, \text{CH}_3\text{CH}=\text{O}, \text{H}_2, \text{H}_2\text{O}, \) and \( \text{CH}_2\text{CH}_2 \). Each pure compound, \( i \), was leaked into the UHV chamber at 4 different pressures and the signals for ionization fragments, \( j \), at \( m/z = 2, 18, 28, 29, \) and 31 were recorded to calculate \( \alpha_{ij} \).

<table>
<thead>
<tr>
<th>( m/z )</th>
<th>( \text{CH}_3\text{CH}_2\text{OH}/\text{ZnO}(1\bar{1}00) ) TPRS Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>( \text{H}_2 )</td>
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<tr>
<td>18</td>
<td>9.2</td>
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<td>28</td>
<td>2.3</td>
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<td>29</td>
<td>1.1</td>
</tr>
<tr>
<td>31</td>
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Table 9: Matrix of mass spectral sensitivities, $\alpha_{ij} = \frac{dI_{ij}}{dp}$, for ionization fragments of CD$_3$CD$_2$OD and its decomposition products CD$_3$CD$_2$OD, CD$_3$CD=O, D$_2$, D$_3$O, and CD$_2$CD$_2$. Each pure compound, $i$, was leaked into the UHV chamber at 4 different pressures and the signals for ionization fragments, $j$, at $m/z = 4, 20, 32, 30, \text{ and } 34$ were recorded to calculate $\alpha_{ij}$.

<table>
<thead>
<tr>
<th>$m/z$</th>
<th>CD$_3$CD$_2$OD/ZnO(1100) TPRS Products</th>
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<tbody>
<tr>
<td></td>
<td>D$_2$</td>
</tr>
<tr>
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<tr>
<td>30</td>
<td>1.1</td>
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<tr>
<td>34</td>
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6.3 Results

6.3.1 XPS of clean ZnO(1100) and CH$_3$CH$_2$OH/ ZnO(1100)

XP spectra of the sputtered and annealed ZnO(1100) surface were acquired before TPRS to verify surface cleanliness and surface composition. The ratio of Zn:O was 0.95 ± 0.05, as determined from 20 cleaned surfaces. Figure 113 shows the C 1s signal from the ZnO(1100) surface before dosing, after a CH$_3$CH$_2$OH exposure of 0.4 L (sufficient to saturate the surface at 300 K), and after TPRS of the adsorbed CH$_3$CH$_2$OH. A small C 1s peak, equivalent to < 1 % of the surface composition, is visible in the XPS of the clean surface at 282 eV. The C content of the surface was < 1 % (atomic) before each TPRS experiment. After exposure of the surface to 0.4 L of CH$_3$CH$_2$OH, a larger C 1s feature,
corresponding to a saturated monolayer of CH$_3$CH$_2$OH, is observed at a binding energy of 283.5 eV. After TPRS of the adsorbed CH$_3$CH$_2$OH, the C 1s signal decreases significantly to ~15% of its original intensity, indicating that ~85% of the CH$_3$CH$_2$OH monolayer desorbed or decomposed into gas phase products.

![C 1s XPS Signal vs. Binding Energy](image)

Figure 113: C 1s XP spectra of the ZnO(1100) surface after cleaning, after exposure to 0.4 L of CH$_3$CH$_2$OH at 300 K, and after thermal decomposition of the adsorbed CH$_3$CH$_2$OH during heating to 700 K at 1 K/s. All three spectra were baseline subtracted. Over 85% of the adsorbed CH$_3$CH$_2$OH and its decomposition products desorb during TPRS, with ~15 at% C remaining on the ZnO(1100) surface.

### 6.3.2 Products of CH$_3$CH$_2$OH/ZnO(1100) TPRS

To identify the products of CH$_3$CH$_2$OH decomposition on the ZnO(1100) surface, a series of TPRS experiments were performed after exposure of the ZnO(1100) surface to 0.4 L of CH$_3$CH$_2$OH at 300 K; an exposure that saturates
the CH₃CH₂OH monolayer without leading to multilayer adsorption. TPRS was conducted by heating the surface from 300 to 700 K at 1 K/s while monitoring desorption signals at m/z ratios of 2, 18, 28, 29 and 31 with the mass spectrometer. The m/z ratios monitored were chosen based on species identified in literature reports of CH₃OH and CH₃CH₂OH decomposition on a variety of ZnO surfaces (243, 244, 253, 254). The species identified desorbing from the surfaces in those studies include: CO, CO₂, CH₄, CH₂=CH₂, CH₃CH₃, O₂, H₂, CH₃CH=O, H₂O, and CH₃CH₂OH. Among these, the primary CH₃CH₂OH decomposition products observed in our TPRS experiments were H₂, H₂O, CH₂=CH₂, CH₃CH=O, and CH₃CH₂OH.

Figure 114 displays the TPR spectra obtained following a 0.4 L exposure of CH₃CH₂OH to ZnO(11̅00) at 300 K. The product desorption curves are displayed as pressures of H₂, H₂O, CH₂=CH₂, CH₃CH=O, and CH₃CH₂OH. The baselines of the spectra have been offset for clarity in Figure 114. For H₂O, there is a sharp peak at 355 K with a two lower intensity peaks at 440 K and 550 K. For CH₂=CH₂ there is a low temperature feature at 380 K with a broad peak at 480 K. For CH₃CH=O desorption, there is a broad peak between 400 and 550 K. For H₂, there is a broad desorption feature centered at 480 K, starting at 420 K and ending at 570 K; for CH₃CH₂OH there is a large desorption feature at 375 K with a smaller shoulder at 440 K. The noise in the TPR spectra of H₂, H₂O, and CH₂=CH₂ is larger than for CH₃CH=O and CH₃CH₂OH because of contributions of the background signals at m/z = 2, 18, and 28 from the H₂, H₂O and CO in the
background of the UHV chamber.

Figure 114: TPRS of CH₃CH₂OH (exposure of 0.4 L) on ZnO(1̅100). The pressure of each species was calculated from the mass spectral signal versus temperature for $m/z = 2, 18, 28, 29,$ and 31 using the $\bar{a}$ matrix described in the experimental section. Backgrounds were subtracted from each spectrum before plotting and the spectra have been offset for clarity.

TPR spectra of CH₃CH=O and CH₃CH₂OH, after CH₃CH₂OH exposures in the range 0.005 to 30 L, are shown in Figure 115. Note that CH₂=CH₂ desorption is also observed after exposure of ZnO(1̅100) to CH₃CH₂OH, but is not shown in Figure 115 because the signal at $m/z = 28$ amu is quite noisy due to its overlap with that of CO in the UHV chamber. At exposures $\leq 0.05$ L, a broad CH₃CH=O desorption peak is observed from 400 K to 525 K, and there is no significant CH₃CH₂OH desorption. For exposures $\geq 0.4$ L, the desorption signals for both CH₃CH=O and CH₃CH₂OH saturate. From exposures of 0.05 L to 0.4 L, the CH₃CH₂OH desorption increases significantly. This pattern suggests that at low coverages CH₃CH₂OH initially populates sites or adsorption states that result in CH₃CH₂OH decomposition to yield CH₃CH=O formation.
To estimate the peak locations and widths of multiple TPRS features, Lorentzian curves were fit to the pressure versus temperature data. The left of Figure 116 shows the TPRS spectra of CH$_3$CH$_2$OH from a 0.4 L exposure of CH$_3$CH$_2$OH (black) fitted by two Lorentzian peaks in red and green. Two distinct features are present in the desorption spectrum of CH$_3$CH$_2$OH, one centered at 370 K and a second at 435 K. Whether these arise from desorption of molecularly adsorbed CH$_3$CH$_2$OH or from recombination of CH$_3$CH$_2$O and H atoms, is not determined. The right of Figure 116 displays the TPRS spectra of CH$_3$CH=O from a 0.4 L exposure of CH$_3$CH$_2$OH in black. There are also two features in the desorption spectrum of CH$_3$CH=O, peaks at 435 K and 495 K. The fitted spectra in blue on each plot is the sum of the two fitted peaks and shows that the fitted spectrum fits the raw data well for both CH$_3$CH$_2$OH and CH$_3$CH=O.
Figure 116: Peak fitted TPRS spectra (black) of CH$_3$CH$_2$OH and CH$_3$CH=O desorption from a 0.4 L exposure of CH$_3$CH$_2$OH to ZnO(1100). Two Lorentzian functions were used to fit each spectrum. The blue curve shows the fitted TPR spectrum determined from the sum of both peaks.

3.3. Products of CD$_3$CD$_2$OD/ZnO(1100) TPRS

TPR spectra following various CD$_3$CD$_2$OD exposures to ZnO(1100) were acquired at the same conditions as used for the CH$_3$CH$_2$OH experiments. Figure 117 shows TPR spectra for a 0.4 L exposure of CD$_3$CD$_2$OD at 300 K as pressures of D$_2$, D$_2$O, CD$_3$CD=O, CD$_2$=CD$_2$, and CD$_3$CD$_2$OD. The raw signal versus temperature for m/z = 4, 20, 32, 30, and 34 were converted to product pressures using the $\bar{a}$ matrix in Table 6.2. The baseline pressure of each spectrum is zero; however, they have been offset for clarity in Figure 117. The desorption and decomposition of CD$_3$CD$_2$OD on ZnO(1100) follow the same general trends as those for CH$_3$CH$_2$OH. The main feature for D$_2$O appears at 360 K, roughly the same temperature as for H$_2$O desorption observed during CH$_3$CH$_2$OH TPRS. D$_2$O also displays lower intensity, higher temperature desorption peaks at 450 K and 550 K much like H$_2$O during CH$_3$CH$_2$OH TPRS. The CD$_3$CD$_2$OD desorption spectrum has a peak at 370 K with a shoulder at 440 K, roughly the same
temperatures as for CH$_3$CH$_2$OH. CD$_3$CD=O desorption has a low temperature shoulder at 435 K, with a high temperature feature at 490 K. The CD$_2$=CD$_2$ desorption spectrum has a peak at 485 K, ~20 K higher than that observed for CH$_2$=CH$_2$ during CH$_3$CH$_2$OH TPRS. D$_2$ desorption displays a peak at 505 K, 20 K higher than that of H$_2$ from CH$_3$CH$_2$OH.

Figure 117: TPRS Spectra of a 0.4 L exposure of CD$_3$CD$_2$OD on ZnO(1 1 00). The spectra have been offset for clarity. The pressure of each species was calculated from the raw data of signal vs. temperature for $m/q = 4, 20, 32, 30,$ and 34 using the $\tilde{a}$ matrix described in the experimental section. The peak locations follow a similar pattern to TPRS of CH$_3$CH$_2$OH.

Figure 118 displays CD$_3$CD$_2$OD, CD$_3$CD=O, and CD$_2$=CD$_2$ desorption spectra for CD$_3$CD$_2$OD exposures from 0.006 to 3 L. Desorption of both CD$_3$CD=O and CD$_2$=CD$_2$ occurs at low exposures, indicating that CD$_3$CD$_2$OD initially populates the sites or states that result in CD$_3$CD$_2$OD decomposition to these two products. The amount of both CD$_3$CD=O and CD$_2$=CD$_2$ that desorbs increases with increasing exposure. CD$_3$CD$_2$OD does not desorb at exposures < 0.05 L; for higher exposures, the CD$_3$CD$_2$OD desorption yield increases with
increasing exposure until the surface becomes saturated by an exposure of ~0.4L. This is the same trend as was observed for CH₃CH₂OH/ZnO(1100) TPRS. Peaks were fit to the CD₃CD₂OD spectra using the same Lorentzian peak fitting as for CH₃CH₂OH. Figure 119 compares the Lorentzian peak fitting for the TPRS spectra of CD₃CD=O and CD₂=CD₂ from a 0.9 L exposure of CD₃CD₂OD. The spectrum of CD₃CD=O are best fit by two Lorentzian peaks centered at 432 K and 491 K while the TPR spectrum of CD₂=CD₂ is best fit by one peak centered at about 490 K. The fitted spectra for both species are a good fit to the raw data. For the other exposures, two Lorentzian peaks were fit to the CD₃CD=O data and one peak was fit to the CD₂=CD₂ data.
Figure 118: TPR spectra of CD$_3$CD$_2$OD, CD$_3$CD=O, and CD$_2$=CD$_2$ desorption from ZnO(1 1 00) after various exposures of CD$_3$CD$_2$OD. Peaks for CD$_3$CD=O and CD$_2$=CD$_2$ desorption are present even at low exposures and increase with increasing exposure. CD$_3$CD$_2$OD desorption is only observed for exposures $\geq$ 0.05 L.
6.3.3 Products of CF$_3$CH$_2$OH/ZnO(1100) TPRS

TPR spectra of CF$_3$CH$_2$OH adsorbed on ZnO(1100) were acquired at the same conditions as were used for the CD$_3$CD$_2$OD and CH$_3$CH$_2$OH experiments. Figure 120 (left) shows TPR spectra after exposure of 0.4 L of CF$_3$CH$_2$OH at 300 K. Desorption products from TPRS of CF$_3$CH$_2$OH were similar to those observed for CD$_3$CD$_2$OD and CH$_3$CH$_2$OH; they included $m/z = 18$ (H$_2$O), 29 (CF$_3$CH=O), 31 (CF$_3$CH$_2$OH), and 45 (CF$_2$=CH$_2$). The signal for $m/z = 2$ (H$_2$) was too small to be measured. The TPRS signal at $m/z = 18$ follows a trend similar to those of H$_2$O and D$_2$O from CH$_3$CH$_2$OH and CD$_3$CD$_2$OD, but with peaks shifted to ~30 K higher temperatures: the $m/z = 18$ spectrum has a peak at 380 K, with a shoulder extending to 650 K. The peak for $m/z = 45$ for CF$_2$=CH$_2$ desorption starts at 325 K and ends at 525 K. Both $m/z = 29$ and $m/z = 31$ result from ionization of CF$_3$CH$_2$OH, where $m/z = 31$ is the highest intensity signal and $m/z = 29$ signal has...
60% relative intensity; both TPRS features are broad. The broad peak for \( m/z = 31 \) after a 0.4 L exposure shows that the parent molecule, CF\(_3\)CH\(_2\)OH, desorbs from the surface.

To isolate a net signal for CF\(_3\)CH=O, the contribution from CF\(_3\)CH\(_2\)OH was subtracted from the signal at \( m/z = 29 \). Figure 120 (right) compares CF\(_3\)CH=O desorption and CF\(_2\)=CH\(_2\) desorption. The net signal from CF\(_3\)CH=O was isolated from the signal at \( m/z = 29 \) by subtracting the contribution from desorbing CF\(_3\)CH\(_2\)OH.

Figure 120: Left) TPRS of a 0.4 L exposure of CF\(_3\)CH\(_2\)OH to ZnO(1\{1\}00). Primary contributors to the signals were H\(_2\)O (\( m/z = 18 \)), CF\(_3\)CH=O (29), CF\(_2\)=CH\(_2\) (45) and CF\(_3\)CH\(_2\)OH (31). The \( m/z = 29 \) signal also has a contribution from CF\(_3\)CH\(_2\)OH. Right) Comparison of CF\(_3\)CH=O desorption and CF\(_2\)=CH\(_2\) desorption. The net signal from CF\(_3\)CH=O was isolated from the signal at \( m/z = 29 \) by subtracting the contribution from desorbing CF\(_3\)CH\(_2\)OH.

To isolate a net signal for CF\(_3\)CH=O, the contribution from CF\(_3\)CH\(_2\)OH was subtracted from the signal at \( m/z = 29 \). Figure 120 (right) compares CF\(_2\)=CH\(_2\) desorption and CF\(_3\)CH=O desorption for a 4 L exposure of CF\(_3\)CH\(_2\)OH; the peak locations differ by over 100 K. Figure 121 shows a TPR spectra form a 0.1 L exposure of CF\(_3\)CH\(_2\)OH. The TPR spectrum of \( m/z = 29 \) and \( m/ z = 45 \) more closely resembles the peak for CF\(_3\)CH=O and CF\(_2\)=CH\(_2\) in the right plot of Figure 120 and the signal from \( m/z = 31 \) is much lower than for the 0.4 L exposure. At exposures \( \leq 0.1 \) L the signal from \( m/z = 29 \) is larger than the signal from \( m/z = 31 \) suggesting that there is some limiting coverage of adsorbed species below which CF\(_3\)CH=O and CF\(_2\)=CH\(_2\) are the major reaction products. Once surface sites for
CF₂=CH₂ and CF₃CH=O formation are saturated, CF₃CH₂OH desorption occurs either through molecular desorption or recombinative desorption. The major species formed after high exposures of CF₃CH₂OH are H₂O and CF₃CH₂OH, while CF₃CH=O and CF₂=CH₂ are more prominent than CF₃CH₂OH at lower exposures. The products and desorption trends from CF₃CH₂OH are consistent with those from TPRS of both CH₃CH₂OH and CD₃CD₂OD on ZnO(1100).

Figure 121: TPR spectra obtained following a 0.1 L exposure of CF₃CH₂OH to ZnO(1100). The signal measured for H₂O is m/z =18, CF₃CH=O (29), CF₂=CH₂ (45) CF₃CH₂OH (31). For a 0.1 L exposure, the signal at m/z = 29 is greater than that at m/z = 31, while the opposite is true for the 4 L exposure. This shows that the sites for CF₃CH=O formation saturate before sites for reversible CF₃CH₂OH adsorption.

XPS was used to determine the state of the ZnO(1100) surface after each TPRS experiment was performed. Figure 122 shows the F 1s XPS spectral region for the clean ZnO(1100) and after TPRS of a 0.4 L exposure of
CF$_3$CH$_2$OH. The clean surface displays no evidence of F. After TPRS, there is a peak for F bonded to Zn at a binding energy of 684 eV in the F 1s spectrum (251). The XPS characterization was not performed before the TPRS experiment to eliminate the possibility of X-ray induced dissociation of F from CF$_3$CH$_2$OH. Residual surface F after the TPRS experiment must, therefore, come from a surface reaction and not from x-ray induced dissociation. XPS was also performed for a 0.4 L exposure of CF$_3$CH$_2$OH at 300 K on ZnO(1 1 00) in a separate experiment to determine the fraction of F deposited on the surface by the decomposition reaction. The F 1s signal in Figure 122 is ~25% of the F 1s signal of the 0.4 L exposure of CF$_3$CH$_2$OH at 300 K meaning that 25% of the adsorbed CF$_3$CH$_2$OH deposits F onto the surface as a result of CF$_2$=CH$_2$ formation or decomposition by other pathways.

![Figure 122: F 1s XPS for the clean ZnO(1 1 00) surface (black) and after TPRS of a 0.4 L exposure of CF$_3$CH$_2$OH (red). Both spectra were baseline subtracted. The clean surface has no peaks in the F 1s spectrum. A peak at a binding energy of 684 eV for F bonded to Zn is visible after the TPRS experiment.](image-url)
6.4 Discussion

6.4.1 Mechanism of CH$_3$CH$_2$OH decomposition on ZnO(1100)

In order to elucidate the mechanism of CH$_3$CH$_2$OH decomposition on ZnO(1100) we have attempted to quantify the stoichiometry of the product yield. Table 10 lists the fractional yields of the products of CH$_3$CH$_2$OH and CD$_3$CD$_2$OD decomposition for exposures that yield saturation coverages of the adsorbed CH$_3$CH$_2$OH and CD$_3$CD$_2$OD monolayers (≥ 0.4 L). The pressure fractions were calculated from the TPRS peak areas (after conversion to pressure) of each species. The fractional yield of a single component is equal to its peak area divided by the sum of the peak areas of all five components.

Table 10: Product pressure fractions for TPRS of saturated monolayers of CH$_3$CH$_2$OH and CD$_3$CD$_2$OD on ZnO(1100).

<table>
<thead>
<tr>
<th>CH$_3$CH$_2$OH Products</th>
<th>Pressure Fraction</th>
<th>CD$_3$CD$_2$OD Products</th>
<th>Pressure Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$</td>
<td>0.05 ± 0.01</td>
<td>D$_2$</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.34 ± 0.07</td>
<td>D$_2$O</td>
<td>0.25 ± 0.06</td>
</tr>
<tr>
<td>CH$_3$CH=O</td>
<td>0.18 ± 0.04</td>
<td>CD$_3$CD=O</td>
<td>0.21 ± 0.07</td>
</tr>
<tr>
<td>CH$_2$=CH$_2$</td>
<td>0.17 ± 0.03</td>
<td>CD$_2$=CD$_2$</td>
<td>0.18 ± 0.05</td>
</tr>
<tr>
<td>CH$_3$CH$_2$OH</td>
<td>0.26 ± 0.05</td>
<td>CD$_3$CD$_2$OD</td>
<td>0.3 ± 0.1</td>
</tr>
</tbody>
</table>

The uncertainties are the standard deviations of the fraction yields measured in five or six experiments. The yield of reversibly adsorbed CH$_3$CH$_2$OH is roughly equal to the fraction that decomposes into CH$_3$CH=O and CH$_2$=CH$_2$. This discussion will focus on the mechanism for decomposition of the irreversibly adsorbed CH$_3$CH$_2$OH. STM imaging has suggested that dissociative
adsorption of CH$_3$OH on ZnO(1 1 00) can yield both CH$_3$O- groups adsorbed to surface Zn atoms and CH$_3$- groups adsorbed on surface O atoms (249). The framework for our discussion of CH$_3$CH$_2$OH decomposition will be a mechanism that is consistent with the suggestion that there are two decomposition intermediates; CH$_3$CH$_2$O-Zn groups that decompose to yield CH$_3$CH=O and CH$_3$CH$_2$-O groups that yield CH$_2$=CH$_2$. The distinction between these ethoxy groups is that the former results from dissociation of the O-H bond in CH$_3$CH$_2$OH and is bound to a surface Zn atom, while the latter is formed by dissociation of the C-O bond in CH$_3$CH$_2$OH. In the latter case the CH$_3$CH$_2$- group is bonded to a surface lattice O atom and the CH$_3$CH$_2$OH dissociation yields an OH group, possibly bound to a surface Zn atom. The scheme for decomposition of the CH$_3$CH$_2$OH fraction that is irreversible bonded to the surfaces is summarized as follows:

\[
\begin{align*}
CH_3CH_2OH_{g} & \rightarrow CH_3CH_2O - Zn + H \quad (1) \\
CH_3CH_2O - Zn & \rightarrow CH_3CH = O_{g} + H \quad (2) \\
2H & \rightarrow H_{2,g} \quad (3) \\
CH_3CH_2OH_{g} & \rightarrow CH_3CH_2 - O + HO \quad (4) \\
CH_3CH_2 - O & \rightarrow CH_2CH_{2,g} + H \quad (5) \\
H + OH & \rightarrow H_{2}O_{g} \quad (6)
\end{align*}
\]

In this scheme the gas phase species are indicated with a subscript ‘$g$’ and the atoms originated in the ZnO(1 1 00) surface lattice are boldened. We have been deliberately vague regarding the adsorption sites for the H atoms and OH groups released onto the surface.
The ratio of the yields of CH$_3$CH=O (or CD$_3$CD=O) and CH$_2$=CH$_2$ (or CD$_2$=CD$_2$) formed during CH$_3$CH$_2$OH (or CD$_3$CD$_2$OD) decomposition are roughly equal, although there is nothing that constrains this to be the case. This result is different from that of the STM study of CH$_3$OH adsorbed on ZnO(1100), which suggested that the majority surface species was CH$_3$O-, the precursor to CH$_2$=O formation, while only trace amounts of CH$_3$, the precursor to CH$_4$ formation, were present (249). The pressure fraction of H$_2$O evolving from the ZnO(1100) during ethanol decomposition is significantly larger than that of H$_2$ and is twice the pressure fraction of CH$_3$CH=O and CH$_2$=CH$_2$. This is an unexpected result. Within the context of the proposed mechanism, the pressure fraction of H$_2$ should be closer to pressure fraction of CH$_3$CH=O formed. Similarly the pressure fraction of H$_2$O formed should be close to that of CH$_2$=CH$_2$. The fractional product yields from CD$_3$CD$_2$OD decomposition are similar to those obtained for CH$_3$CH$_2$OH. The CD$_2$=CD$_2$ and CD$_3$CD=O yields are roughly equal. As in the case of CH$_3$CH$_2$OH decomposition, the yield of D$_2$ from CD$_3$CD$_2$OD is significantly lower than that of D$_2$O which is slightly higher than that of CD$_2$=CD$_2$. The difference between the yields of CD$_2$=CD$_2$ (CD$_3$CD=O) and CH$_2$=CH$_2$ (CH$_3$CH=O) are not statistically significant.

Based on the products observed, we propose the mechanism for CH$_3$CH$_2$OH decomposition described by steps 1 – 6 listed above. CH$_3$CH$_2$OH adsorbs dissociatively via cleavage of either the O-H bond to form CH$_3$CH$_2$O- on a surface lattice Zn atom or cleavage of the C-O bond to form CH$_3$CH$_2$- on a surface lattice O atom. Roughly half of the adsorbed CH$_3$CH$_2$OH desorbs as
ethanol. Whether it is adsorbed intact or desorbs as a result of the recombination of CH₃CH₂O- and H, is not determined. The irreversibly adsorbed CH₃CH₂O- and CH₃CH₂- decompose by β-hydride elimination to yield CH₃CH=O and CH₂=CH₂, respectively. In this terminology the H comes from the C in the β-position with respect to the surface Zn or surface O atoms.

Within the context of the proposed mechanism, the formation of H₂O (step 6) results from the reaction of OH groups (resulting from C-O cleavage in CH₃CH₂OH) with H atoms (resulting from O-H cleavage in CH₃CH₂OH and β-hydride elimination). If this were the only source of H₂O formation, then the yield of H₂O would be equal that of CH₂=CH₂. Similarly, the yield of H₂ from recombination of H atoms would be equal to the yield of CH₃CH=O. While the excess yield of H₂O (D₂O) for decomposition of CH₃CH₂OH (CD₃CD₂OD) is not statistically significant, the yields of H₂ (D₂) are clearly lower than expected.

In the case of H₂O yield, the possible excess might be attributable to H₂O adsorption from the background of the UHV chamber, however this has been ruled out by direct measurements of the H₂O adsorption from the chamber background onto the clean ZnO(1̅100) surface. To confirm that no contamination by background H₂O occurred, TPD spectra from H₂O (m/z = 18), D₂O (m/z = 20) and a TPD of background gas were compared. For the background TPD, the ZnO(1̅100) single crystal was held in the dosing position at 300 K for 20 minutes to allow for H₂O in the background to adsorb on the surface. Then the normal TPD was performed from 300 - 700 K at 1 K/s. Figure 123 shows TPD spectra of m/z = 18 (H₂O) from a 3 L exposure of CH₃CH₂OH
compared to $m/z = 20$ ($D_2O$) from 3 L exposure of CD$_3$CD$_2$OD and a TPD of the background. There was no visible peak in the TPD of the background gas showing that there is no contamination of H$_2$O from the background. Another source of this increased pressure of H$_2$O could have been from contamination of CH$_3$CH$_2$OH in the doser. If the signal from D$_2$O and H$_2$O are the same, then contamination in the doser and background contamination can be ruled out. Both CH$_3$CH$_2$OH and CD$_3$CD$_2$OD underwent multiple cycles of freeze-pump-thaw before exposure to the chamber and the pressure of the chamber was monitored during the exposure of H$_2$O and showed no increase in the $m/z = 18$ signal other than from the ionization spectrum of CH$_3$CH$_2$OH. Also, the signal from $m/z = 18$ of a CH$_3$CH$_2$OH TPD has the same shape and features as $m/z = 20$ of a CD$_3$CD$_2$OD showing that there was not H$_2$O contamination in the doser.

These observations suggest that adsorbed H atoms can reduce the surface and extract lattice O atoms to yield H$_2$O. This step is consistent with formation of surface OH species from adsorbed H that has been observed through vibrational spectroscopies and linked to H$_2$O formation from ZnO (255-257).
In addition to the product distribution and yield, the temperatures at which various reaction steps occur and at which products are observed desorbing from the surface provides some insight into the mechanism of ethanol decomposition on ZnO(1100). Table 11 shows the peak locations for the acetaldehyde and ethylene species desorption during TPRS of CF₃CH₂OH, CH₃CH₂OH, and CD₃CD₂OD on ZnO(1100). TPRS spectra for CH₃CH=O and CD₃CD=O were best fit by two peaks while CF₃CH=O desorption was best fit by one peak. The peaks for desorption of CH₃CH=O and CD₃CD=O are, within statistical uncertainty, located at the same temperatures. The peak for desorption of CD₂=CD₂ is at a significantly higher temperature than that for CH₂=CH₂. These results reveal a significant deuterium kinetic isotope effect in CD₂=CD₂.
formation, but not in CD$_3$CD=O formation. The isotope effect in ethylene formation suggests that C-H(D) bond breaking on the β-C atom (β-hydride elimination) is the rate limiting step in CH$_3$CH$_2$- (CD$_3$CD$_2$-) decomposition (step 5). Such isotope effects have been observed in β-hydride elimination of alkyl groups on Cu surfaces (258, 259). Although β-hydride elimination is the expected reaction pathway for CH$_3$CH=O (CD$_3$CD=O) formation from ethoxy groups (step 2), this does not exhibit a deuterium isotope effect in the acetaldehyde desorption temperature. This is in contrast with results revealing a kinetic isotope effect during β-hydride elimination in ethoxy groups on Cu surfaces (260).

Table 11: TPRS peak temperatures for aldehyde and ethylene products of CH$_3$CH$_2$OH, CD$_3$CD$_2$OD, and CF$_3$CH$_2$OH decomposition on ZnO(1100).

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Product</th>
<th>Peak Temperature (K)</th>
<th>Product</th>
<th>Peak Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CH$_2$OH</td>
<td>CH$_3$CH=O (low T)</td>
<td>436 ± 4</td>
<td>CH$_2$=CH$_2$</td>
<td>468 ± 5</td>
</tr>
<tr>
<td></td>
<td>CH$_3$CH=O (high T)</td>
<td>491 ± 7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CD$_3$CD$_2$OD</td>
<td>CD$_3$CD=O (low T)</td>
<td>435 ± 8</td>
<td>CD$_2$=CD$_2$</td>
<td>487 ± 5</td>
</tr>
<tr>
<td></td>
<td>CD$_3$CD=O (high T)</td>
<td>491 ± 3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF$_3$CH$_2$OH</td>
<td>CF$_3$CH=O</td>
<td>562 ± 4</td>
<td>CF$_2$=CH$_3$</td>
<td>428 ± 10</td>
</tr>
</tbody>
</table>

6.4.2 Transition states for β-elimination on ZnO(1100)

The use of substituent effects is a classical approach to probing the characteristics of transitions states for elementary reactions and has been used in studies of surface chemistry on metals, and to a lesser extent oxides (260-263).
Our comparison of the decomposition of CF$_3$CH$_2$OH and CH$_3$CH$_2$OH (or CD$_3$CD$_2$OD) on ZnO(1̅00) reveals the same decomposition products but a significant impact of F substitution on the decomposition kinetics. The key point is that the observed F substitution effects are completely consistent with the proposed decomposition via two pathways with different reaction intermediates. Figure 124 provides a direct comparison of the product desorption kinetics for CF$_2$=CH$_2$, CH$_2$=CH$_2$ and CD$_2$=CD$_2$. This reveals the small but observable deuterium kinetic isotope effect of 15 ± 7 K reported in Table 11 and attributed to β-hydride elimination from an ethyl group adsorbed at a surface O atom (step 5). This isotope effect is less well resolved than in previous studies of alkyl group decomposition by β-hydride elimination on Cu surfaces, largely because of the large temperature range over which the reaction occurs on ZnO(1̅00) (258, 259). However, the magnitude of the temperature shift is similar to that reported
in prior studies on Cu single crystal surfaces.

The CF$_2$=CH$_2$ product of CF$_3$CH$_2$OH decomposition on ZnO desorbs at ~40 K lower temperature than CH$_2$=CH$_2$ from CH$_3$CH$_2$OH decomposition. This indicates that the barrier to β-fluoride elimination in CF$_3$CH$_2$- groups is significantly lower than that for β-hydride elimination in CH$_3$CH$_2$- groups. This is entirely consistent with the results for the same reactions on Ag(111) (264). The F deposited onto the ZnO(1100) surface by β-fluoride elimination is detected in XPS after reaction completion (Figure 122). Because the C-F bond is ~80-100 kJ/mole stronger than a C-H bond, (265) the lower barrier to β-fluoride elimination must arise from a stronger interaction of the ZnO(1100) surface with the product F atom than with a H atom.

Figure 124: TPR spectra of ethylene (left) and aldehyde (right) desorption following saturation exposures of CH$_3$CH$_2$OH, CD$_3$CD$_2$OD, and CF$_3$CH$_2$OH to the ZnO(1100) surface. The data from CF$_2$=CH$_2$ and CF$_3$CH=O is not in units of pressure and is divided by 30 for comparing peak locations. F substitution into the ethanol lowers the temperature of the ethylene formation and desorption and raises the temperature of acetaldehyde formation and desorption.

The CF$_2$=CH$_2$ product of CF$_3$CH$_2$OH decomposition on ZnO(1100) desorbs at ~40 K lower temperature than CH$_2$=CH$_2$ from CH$_3$CH$_2$OH decomposition.
Finally, Figure 124 reveals that the temperature at which CF$_3$CH=O appears during CF$_3$CH$_2$OH decomposition on ZnO(1$ar{1}$00) is ~100 K higher than that of CH$_3$CH=O appearance during CH$_3$CH$_2$OH decomposition. This is entirely consistent with F substitution effects observed for decomposition of ethoxy groups by β-hydride elimination on Cu single crystal surfaces (260, 266-269). In those studies and as modeled by DFT calculations, this increase in the barrier to β-hydride elimination is associated with a transition state in which the C atom adjacent to the CF$_3$- substituent group is cationic with respect to its initial state in the ethoxy group, R – C – H → [R – C$^{\delta+} \cdots$ H$^{\delta-}$]$^\dagger$. Substitution of R = CF$_3$ for CH$_3$ results in inductive destabilization of the cationic transition state as a result of the strong polarity of the F$^{\delta-}$–C$^{\delta+}$ bonds adjacent to the β-hydride elimination reaction center. Similar F substituent effects have been observed for CF$_3$CH$_2$OH decomposition on vanadia surfaces (263). The net observations of F substituent effects on the decomposition of ethanol to both ethylene and to acetaldehyde are consistent with a mechanism in which there are two distinct intermediates; an ethyl group that leads to the formation of ethylene and an ethoxy group that leads to the formation of acetaldehyde, both by β-hydride elimination.
6.5 Conclusions

The decomposition of CH$_3$CH$_2$OH, CD$_3$CD$_2$OD, and CF$_3$CH$_2$OH was studied on a ZnO(1 1 0 0) single crystal using TPRS and XPS analysis. All three adsorbates display both reversible desorption and decomposition to yield acetaldehyde, ethylene, water and hydrogen. Quantitative analysis of the desorbing species was used to determine the product ratios of CH$_3$CH$_2$OH and CD$_3$CD$_2$OD decomposition. The products yields, the deuterium isotope effects and the F substituent effects on the reaction kinetics demonstrate that the decomposition reaction mechanism is one in which there are two competing pathways. Ethanol deprotonation (O-H scission) to yield ethoxy results in the formation of acetaldehyde. Ethanol dehydroxylation (C-OH scission) to yield ethyl groups results in the formation of ethylene. By analogy with suggestions based on STM imaging of CH$_3$OH adsorption on ZnO(1 1 0 0), we suggest that the ethoxy groups are formed on surface lattice Zn site while the ethyl groups are formed on surface lattice O sites.
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