Manipulative Scanning Tunneling Microscopy and Molecular Spintronics

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This dissertation titled

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Abstract

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Nanoscale systems, at the intersection of bottom-up and top-down approaches to technological development, have demonstrated unique properties and applications in recent scientific studies. Scanning probe microscopy has emerged as a versatile tool for studying nanoscale interactions due to its capabilities of local measurement of spectroscopic, magneto-electric, and topographic properties in real-space with sub-nanometer resolution. Still, many physical and chemical effects have yet to be completely characterized and understood. This dissertation demonstrates the novel application of scanning tunneling microscopy to the study of local work functions through field emission resonances, surface catalyzed covalently bound chain formation, and spintronic interactions of organically coupled magnetic ions. Local work functions are found, by analyses of field emission resonances, for probe induced surface vacancies and atomic step edges on an atomically clean Ag(111) crystal. The extracted local work functions for defect locations vary significantly from the known and measured clean surface values. The local work function plays a large part in surface binding and electronic interaction of surface adsorbates. This technique for local work function measurement can be extended to more unique surface and molecular systems. A process for the formation, and topographic measurement, of covalently bound chains by surface catalysis is demonstrated with homogeneous magnetic and heterogeneous networks of molecules. The chain coupling occurs through an Ullmann-like halogen substitution and subsequent ring coupling reaction mediated by surface atoms, with application of adequate thermal energy. Individual molecules with central magnetic ions are shown to exhibit a Kondo resonance in spectroscopic measurements. Cova-
lently bound chains of these molecules maintain the Kondo interaction while develop-
ing an antiferromagnetic coupling between the central magnetic ions as demonstrated through theoretical and spectroscopic techniques. The measurements of magnetic in-
teraction and spin-communication along a covalently bound chain of molecules can be extended with transport and spin-polarized measurements. Together the techniques and results presented here demonstrate novel physical phenomena at atomic and molecular scales, by utilizing the versatility of scanning tunneling microscopic tech-
niques, with implications for both fundamental scientific principles and applications.
for Louise, now and always
and my family
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1 Introduction

Nanoscale sciences are at an exciting stage in their development as we are just beginning to see some of the possibilities and emerging applications [4–7]. Studies in nanoscience consist of a unique and interesting combination of physical, chemical, and biological properties [8–11]. There are many problems to which nano-scientific-methods are being applied. Nanoscale properties and devices are being considered for potential solutions to our growing energy and global climate issues, technological demands, tools for biological scientists, and national security applications. The energy and climate problems are being approached by researchers in solar energy conversion, energy storage, and energy efficient device engineering, all of whom are seeking applications of emerging properties of nanoscale systems. Many of these technologies would be helpful in device design, as device miniaturization, efficiency, and energy storage all lead eventually to consumer applications. Much of the work of this dissertation is approaching solutions to these problems through a bottom-up approach, where devices are formed from single or multiple molecules, or nanoscale surface and atomic features.

There are many experimental approaches to nanoscience, among the most useful being the recently developed techniques of scanning probe microscopic (SPM) methods. These methods, and in particular (for this work) the technique scanning tunneling microscopy (STM), allow for real-space imaging and spectroscopic characterization with sub-nanometer spatial resolution. STM methods rely on an atomically sharp metallic probe positioned precisely by piezoelectric actuators above a conductive surface. A bias applied between the probe (or, interchangeably, tip) and the surface results in a tunneling current of electrons that traverse the vacuum potential barrier with some probability dependent on the tip-surface displacement and the applied bias. By scanning the probe over the surface plane, a profile can be formed
of the surface topographic height at a constant feedback mediated current. Also, for a fixed probe position, differential conductance spectroscopic measurements can be made which provide a measure of the local density of states. Chapter 2 introduces many of the experimental and theoretical concepts important to ultra-high-vacuum low-temperature STM methods. In this document, STM methods are applied to study local surface work functions, formation of molecular chains by surface catalysis and self-assembly on a surface, and magnetic interaction of single molecules and molecular chains.

Chapter 3 examines how the local sample work function can be approximated by STM experimental methods. The local work function, the energy required to remove an electron from a certain position on the sample surface, is an important property as it determines the interaction energy of molecules adsorbed on surfaces by their site specific adsorption and the electron emission characteristic. For STM methods, the local work function can be found by considering image potential resonances, which appear at certain energies, depending on the probe and sample work functions and the absolute probe height. The local work function is studied by a novel method here of taking many voltage dependent images of desired features on an Ag(111) surface to acquire a three dimensional matrix of tip height, z(x,y,V), which is then differentiated numerically to acquire dz/dV(x,y,V) before extracting a linear profile that shows spatial variation in the resonances dz/dV(f(x,y),V). This method is applied to vacancies created on the surface by controlled probe crashes and voltage pulses, as well as to monoatomic surface step edges. Numerical values of the work functions for vacancies are found, as well as observation of the expected trend that the work function in holes is higher than, and the work function at steps is lower than at terraces.
After concluding studies of the surface work function, molecular chains are formed by surface catalyzed reactions in Chapter 4. There are three main motivations of this study. First, surface chemistry is considered one of the methods by which future devices may be assembled. Second, covalently bound molecular chains are interesting because they may approximate the behavior of very thin wires. And third, the molecules used in this study have magnetic ions at their centers which are shown in Chapter 5 to interact along the covalently bound chains. The chains are formed here by vapor deposition onto a clean Au(111) substrate and then annealing of the substrate above room temperature to induce an Ullmann-type ring coupling reaction where the former bromine terminations of the molecules act as placeholders for subsequent carbon-carbon coupling. The surface selected for chain formation is demonstrated to play a large role in the reaction success, whereas coupling experiments were found to fail on copper surfaces. The chapter concludes by demonstrating that ring coupling can be achieved between molecules of differing species, and that the intermolecular bond locations can be determined by voltage dependent imaging due to distinct bond energies.

Chapter 5 consists of measurements of the magnetic and electronic structure and interaction of individual molecules and synthesized chains. Observed magnetic interactions of molecules may be applicable to future devices such as data storage in magnetic molecular units and spin-dependent communication for spin-electronics (spintronics) applications. The magnetic interactions that are measured are manifestations of the Kondo effect where the spins of magnetic cobalt ions in the molecules interact with the subsurface conduction electrons to form a screened many-body state. This state is spectroscopically observed, and its energetic width is quantitatively measured. It is found that molecules maintain Kondo interactions isolated from their neighbors while the measurement in chains demonstrates some
inter-molecular-unit coupling of the spin interaction by what is determined, through DFT calculations, to be an anti-ferromagnetic interaction.

It is hoped that these studies demonstrate the versatility of STM techniques and contribute novel results to the growing field of surface science and nanotechnology. Local work function measurement by STM combined with probe induced nano-indentation can be extended to more diverse systems and utilized to access previously inaccessible or ignored properties of nanoscale structures. The demonstration here of heterogenous networks and networks of magnetically active molecules are large steps forward in a technique which may prove important for future molecule based devices. And the demonstration of spin interaction along a covalently bound network of spin centers should motivate future measurements into more complex molecular networks for spintronic applications.
2 General Scanning Tunneling Microscopy and Surface and Molecular Science

2.1 Ultra-High Vacuum Low Temperature Measurement

In order to study atomic scale systems on surfaces it is advantageous that experiments are performed under ultra-high vacuum and at low temperatures. Ultra-high vacuum equipment is needed to eliminate surface contaminants of studied atomic systems. Generally, the necessary equipment to enable ultra-high vacuum operation are a leak-proof ultra-high vacuum capable chamber which holds only UHV compatible components, pumping mechanisms to evacuate the chamber, pressure monitoring systems, and leak detection capability. Low-temperature operation is required for atomic and molecular scale measurements to reduce thermally induced drift and to immobilize atomic and molecular adsorbates which may, at room temperature, be mobile on the experimental substrate.

2.1.1 Ultra-High Vacuum

Ultra-high vacuum (UHV) requires the use of materials in construction that are non-porous for reduced outgassing times. Usually, UHV chambers are constructed of stainless steel with compressed copper gaskets to seal port flanges. With regard to chamber construction, it is desirable to minimize the internal surface area as the walls of the chamber will be coated with atmospheric gases and contaminant molecules and will outgas with time. For other required internal components for the experiment, it is important to use low-vapor pressure nonporous materials. This means that most organic compounds must be avoided and replaced with teflon, oxygen free copper, and ceramics. Necessary adhesion through glues and solder must be performed using special glues and lead-free solder. Welding must be carefully performed where
necessary as standard welds have high surface area and gas pockets, which would outgas slowly with time. The use of screws within the chamber should also be minimized as they have a high surface area to volume ratio. One very important class of components for UHV experiments is feedthroughs. These may be in the form of electrical feedthroughs with no moving parts, or of manipulator feedthroughs that allow physical interaction transferred from the external world to motion within the chamber. In the experiments to be described later, this is most commonly done in the form of sample transfers from preparation chambers to experimentation chambers. The materials used should additionally be stable under high temperatures, as to achieve an initial low pressure after exposure to atmospheric gases (including water vapor) it is necessary to “bake” the chamber to pressures over 100° C. Baking is typically done through the use of heating tapes and aluminum foil which spreads the heat over the chamber surface, and high temperature covering “blankets” used to contain and further spread the heat. No one type of vacuum pump has an operating range that extends from atmospheric pressure to the desired ultra-high vacuum, so an assortment of pumps must be used including rotary, turbomolecular, titanium-sublimation, cryogenic, and ion.

2.1.2 Low Temperature Cryogenic Experimentation

There are multiple reasons to utilize cryogenic experimentation, especially for surface and surface supported chemical and physical systems. Many surfaces and surface adsorbates are altered by available thermal energy, which allows hopping between potential wells of equal physical potential, such as is the case of a molecule moving by a quasi-random walk on a surface, enabling the site-specific placement and arrangement of molecules on a surface, such as pinning to ‘elbows’ on the Au(111) herringbone reconstruction or self-assembling as is the case of systems explored in
Chapter 4. Cryogenic temperatures also enable many processes and measurements that would otherwise be limited by thermal noise. There are many temperature limited effects, such as the Curie transition temperatures, superconductive transition temperatures, and Kondo temperatures of substances. Superconductors, in addition to their direct study by STM, may be of interest for the creation of magnetic fields for field-dependent measurements, which can be applied to spintronic or magnetic surface measurements for spin-polarized measurement.

Experimentation at cold temperatures also reduces signal noise in a tunneling loop. This occurs because the temperature-dependent Johnson current noise is unavoidable[12–14]. The Johnson current noise is given by

\[ I_{\text{noise}} = \sqrt{\frac{4k_BT\Delta f}{R}} \]

where \( R \) is the resistance along the current path, \( \Delta f \) is the bandwidth in Hertz over which the noise is to be quantified, \( T \) is the temperature in Kelvin, and \( k_B \) is the Boltzmann constant in Joules per Kelvin.

More applicable to the experimental data and interpretation is the consideration of electrons existing as fermions which obey the Fermi distribution:

\[ f(E) = \frac{1}{e^{(E-E_F)/k_BT} + 1} \]

where \( f(E) \) gives the probability that a given state with energy \( E \) will be occupied at a given temperature \( T \). This significantly changes, for appreciable temperatures, the distribution of electrons, and must be considered particularly when interpreting experimental results where this can result in a significant broadening of some spectral features and the disappearance of otherwise accessible states. Broadening of features (or, equivalently, decrease in experimental resolution) can be quantified as the spread of the energy distribution equals \( 2k_BT \) for the tunneling probe and \( 2k_BT \) for the surface, leading to a total spread of \( 4k_BT \). At room temperature, this leads to a
broadening of approximately 100 meV [12], which is significant for vibrational states localized to tens of meV and superconducting or Kondo spectroscopic signatures which are often no wider than a few mV.

Usually in cryogenic systems, the base liquid used to cool the system is nitrogen which can reach a temperature of 77 K, with nitrogen being significantly less costly than helium. While this temperature is adequate for many applications, it is often necessary to reduce the temperature further. This can be done using liquid helium in the forms of helium-4 or helium-3. Usually the less expensive helium-4 is used to reach base temperatures nearing 4.2 K, which allows for the study of many low temperature processes beyond those accessible with a purely liquid nitrogen cryogenic system. For the most sensitive experimental measurements, helium-3 may be used in systems designed to have a base measurement temperature in the mK range. Helium-4 and helium-3 are expensive, even prohibitively so for many groups.

The cryogenic systems may vary greatly between different laboratories, and so does maintenance of the cryogenic system. The systems used in the Hla group at Ohio University (which have much in common with other groups throughout the world), are based in a shielded bath-cryostat design. Figure 2.1 gives a schematic representation of the cryostat design. In the center of the cryostat, there is a chamber surrounded by vacuum, which has an inlet port and a gas outlet port at its top. This chamber can be filled with approximately 4 liters of either liquid helium or liquid nitrogen. The inner cryostat chamber housing nitrogen or helium is directly connected to the experimental apparatus, which hangs directly below it. All signal and control wires (which must be UHV compatible) are passed through the vacuum of the chamber and affixed to the base of the cryostat above the STM. The inner cryostat chamber should be shielded from thermal radiation of the ambient surroundings. To do this, after a surrounding vacuum, a cylindrical chamber is filled with liquid nitrogen to greatly
reduce radiative warming. This nitrogen chamber is again surrounded by vacuum to eliminate most of the conductive thermal warming.

![Side Cross Section of Cryostat](image1)

Figure 2.1: A schematic of the cryostat design implemented in the Hla group at Ohio University. Gaseous Helium can be reclaimed by tubing attached to the cryostat outlet. Gaseous nitrogen mixes with atmosphere after leaving the cryostat. The design here is to illustrate shielding and vacuum insulation positions, scale is approximate.

2.2 Fundamentals of Scanning Tunneling Microscopy and Spectroscopy

After describing ultra-high vacuum and basic cryogenics for precision measurement, the basics of scanning tunneling microscopy will now be explained. It is assumed in the following that the experiments take place at pressures below $10^{-10}$ torr and at temperatures at or below 77 K. This is not to say that all aspects below require these conditions, however. In order to describe STM, quantum tunneling must be
introduced as related to microscopic probes, and the necessary experimental control of probe position and relevant potentials need to be introduced. This is followed by an overview of the experimental capabilities of the STM system, including manipulation of structures on the surfaces and measurement of electronic properties by spectroscopy and spectroscopic mapping.

2.2.1 Probe-Sample Tunneling and Probe Movement Control

In the name scanning tunneling microscopy, tunneling refers to the quantum mechanical process in which particles have some probability to cross energetic barriers which would classically be insurmountable. When the tunneling probe, or tip, is brought within a few angstroms of the sample surface, the electron wave functions of the tip and surface overlap. This allows, with the application of a moderate bias between the tip and sample, electrons to tunnel through the vacuum barrier between the tip and sample. It is illustrative to consider a simple model of an electron of energy \( E \) tunneling through a potential barrier of height \( U \) [12, 15]. The wave function of the tunneling electron can be described by the one dimensional Schrödinger equation,

\[
-\frac{\hbar^2}{2m} \frac{d^2}{dz^2} \Psi(z) + U(z)\Psi(z) = E\Psi(z).
\]

In the regions outside of the tunneling region, the wave function has plane wave solutions

\[
\Psi(z) = \Psi(0)e^{\pm ikz}
\]

with

\[
k = \frac{\sqrt{2m(E - U)}}{\hbar}
\]

being the wave vector. In the vacuum region in this simple model, the electron can be described by the wave function

\[
\Psi(z) = \Psi(0)e^{-\kappa z}
\]
where the wave function exponentially decays with the decay constant

\[ \kappa = \frac{\sqrt{2m(U - E)}}{\hbar}. \]

The square of the wavefunction is proportional to the tunneling current, yielding a tunneling current that varies exponentially with the vacuum barrier width,

\[ I(z) \propto e^{-2\kappa z}. \]

This exponential dependence of the tunneling current on probe-sample separation is part of what makes STM such a sensitive tool for surface topographic characterizations. Typical tunneling sample biases are of the order of 1V, below the work functions of tip or sample so that field emission does not occur. In order to achieve atomic resolution on surfaces, the tunneling probe must be controlled with sub-Angstrom precision. This is achieved by piezoelectric elements. There are two main modes of imaging and probe control possible: constant current and constant height. In constant height mode, the probe is scanned across the surface and the corrugation of the surface causes deviations in the probe-sample tunneling barrier which induce variations in the tunneling current. An image then can be formed by producing the tunneling current measurement for each point in a grid with the desired image resolution. This method may be simplest, but is not typically used as the exponential sensitivity to tip height would result in large fluctuations in the current. The current fluctuations could surpass the operational ranges of current amplification units, and differing currents have different noise profiles. Additionally, with uncontrolled current, it is possible for the probe to crash into the sample causing large structural changes. The scanning is typically performed in a constant current mode where a computer controlled feedback unit maintains a constant tunneling current by varying the Z-piezo extension. The feedback unit relies on some integration
period to avoid responding to noise in the current, and so limits the imaging speed of the STM.

2.2.2 Probe Formation and Treatment

Spatial resolution in STM studies is limited by electronic and vibrational noise, surface cleanliness, computer control capabilities, and, perhaps most importantly, the form of the tunneling probe. The tunneling probe can be made from a few different materials. Most commonly, tips are formed from hard metals such as tungsten (W), molybdenum (Mo), or iridium (Ir). In the years following the initial development of STM, many methods have been developed to address tunneling probe engineering [12, 16, 17].

There are many difficulties encountered in the formation and maintenance of optimal tunneling probes, aside from initial sharpness for spatial resolution. The tip geometry is also extremely important in spectroscopic measurements, which rely strongly on the tip density of electronic states. The tunneling probes may also be changed by adsorption or desorption of molecules or atoms to or from the sample.

There are many methods for initial tip preparation prior to performing STM experiments. Though mechanical cutting or pulling as demonstrated by Binnig and Rohrer [16] is an accepted method of tip preparation, many groups today use electrochemical etching in which a tungsten tip may be etched in NaOH solutions of varying molarity by applying a bias between the partially submerged tip wire and cathode typically made of relatively impervious material such as stainless steel or platinum. The form of chemically etched tips depends greatly on the time-to-power-removal after the wire is fully etched through, which benefits from computer controlled etching bias for the fastest shut-down times. Tips formed ex-situ are generally coated
with contaminants, and for tungsten, a WO$_3$ oxide layer which should be removed before use as a tunneling probe.

### 2.2.3 Probe-Induced Manipulations

Besides being a necessary component of the tunneling mechanism in STM, the close proximity of the tip to the sample also involves physical interactions or forces. The forces between the tip and sample are unwanted in many cases including spectroscopic measurement and imaging, but may be utilized in planned STM manipulations. These manipulations include the induced movement of molecules or atoms on the surface and the formation or breaking of interatomic bonds. Lateral manipulation of atoms or molecules is achieved by bringing the probe closer to the surface than the distance used for imaging to increase the interaction, and then moving the tip from the molecular location to the new desired location on the surface. The tip-molecule interaction may be attractive, in which case the molecule is pulled across the surface, or repulsive, in which case the molecule would be pushed. An illustration of the pulling manipulation mode for a single adsorbed atom is presented in Figure 2.2.

In order to perform lateral manipulation, it is necessary that the molecule or atomic surface adsorbate be weakly adsorbed to minimize the potential which must be overcome to induce motion. Lateral manipulation may be used for many reasons, such as isolating molecules for individual study [3], breaking up of grouped molecules to determine the molecule-molecule interaction effects [3, 18], or to form novel structures such as quantum corrals which make use of the standing wave nature of surface electrons to provide novel effects such as confinement [19]. While lateral manipulations may be useful only for relocation of adsorbates, vertical manipulation is useful for electronic spectroscopy [20–23] bond breaking [8, 9, 24], and possibly movement of
Figure 2.2: A cartoon to illustrate pulling mode atomic manipulation by a STM tip. Tip is approached to the surface defect (an atom here) and then dragged at a constant speed to a new surface location. The resultant constant height measurement curve (here in red) corresponds to the atomic corrugation over which the atom is moved.

some surface adsorbates [25]. In vertical manipulation, the STM tip is located above a desired point on the molecule, and then a programmed tip voltage ($V(t)$) and tip vertical position ($z(t)$) are initialized. The programmed voltage may be swept through a range of energies in conjunction with the use of lock-in amplification techniques to get spectroscopic measurements, or may simply be ramped to a higher potential
supplying the electrons with sufficient energy to dissociate bonds of some chemical species. Some groups have been able, using tip extension, to attach a molecule or atom to the tip to relocate it to another location on the sample \[26–28\].

### 2.2.4 Spectroscopy and Spectroscopic Mapping

The observed tunneling current in scanning tunneling microscopic measurements depends on the density of occupied electron states in the tip (for a positively biased sample), and the density of available unoccupied electron states in the sample. If a constant tip density of states is assumed, we can, for this simple model, expect the tunneling current to be

\[ I \propto V \rho_s(z, E_F) \]  

where \( \rho_s(z, E_F) \) is the sample density of states at the Fermi level, \( E_F \), at the \( z \) position above the sample surface, \( z \). A more rigorous theoretical treatment was developed by Bardeen in 1960 \[29\] where Fermi’s Golden Rule is applied along with independent solution of the tip and sample wave functions. This approach, which involves determination of the tunnel matrix elements, leads to a full expression of the current, for Fermi energy levels \( E_F \) and sample bias \( V \), as

\[
I = \frac{4\pi e}{h} \int_{-\infty}^{\infty} \left[ f(E_F - eV + \epsilon) - f(E_F + \epsilon) \right] \rho_s(E_F - eV + \epsilon) \rho_T(E_F + \epsilon) |M|^2 \, d\epsilon
\]

where \( f(E) \) is the Fermi distribution function

\[
f(E) = \left\{ 1 + \exp[(E - E_F)/k_B T] \right\}^{-1}
\]

with \( k_B \) the Boltzmann constant, \( M \) the tunneling matrix, and \( \rho_s \) and \( \rho_T \) the sample and tip density of states, respectively. Under the assumptions that the required energy resolution of the experiment is greater than \( k_B T \) and magnitude of the tunneling matrix element \( |M| \) not varying significantly in the energy interval of interest, the
tunneling current may be reduced to

\[ I \propto \int_0^{eV} \rho_s(E_F - eV + \epsilon)\rho_T(E_F + \epsilon)d\epsilon \]

where the sample and tip density of states symmetrically influence the resultant tunneling current. Further simplification can be considered if the tip density of states is expected to be constant in the interval of interest. In this case, the sample density of states can be approximated as:

\[ \rho_s(E_F - eV) \propto \frac{dI}{dV}. \]

With these assumptions we then use an experimental measurement of the differential conductance \( \frac{dI}{dV} \) as a measure of the sample density of states, which is, in many STM experiments, a highly desired quantity.

Measure of the differential conductance can be achieved in various ways. A current-voltage characteristic curve may be measured by holding the probe at a fixed position and ramping the bias while recording the current. It is possible in some cases to simply numerically differentiate the I-V curve. In most cases, however, the current characteristic is somewhat noisy, and smoothing must be applied, further reducing the accuracy and resolution of the measurement. The most common way of achieving a measurement of the density of states is by utilizing lock-in amplification. In this method, a sinusoidal modulation is applied to the sample bias which results in a proportional modulation of the resultant tunneling current for a fixed sample bias. Most commonly, these spectra are taken at constant tip height (current feedback disengaged) to reduce signal noise, though they may also be taken in constant current mode. The lock-in amplifier unit then locks in to the resultant current modulation at the set modulation frequency to give a measure of the differential conductance. By sweeping the sample bias through some desired range, the \( \frac{dI}{dV} \) can be recorded as a function of applied bias, V. When using a lock-in amplifier with bias modulation
amplitude $V_{\text{mod}}$, the measured width of a peak with intrinsic width $W_i$ is given by [30]:

$$W = \sqrt{W_i^2 + (1.7V_{\text{mod}})^2 + \left(5.4 \frac{k_B T}{e}\right)^2}.$$ 

It is also possible during topographic imaging of a region to implement lock-in amplification techniques to record the differential conductance for a certain sample bias at each point in the imaged region. This technique, commonly called spectroscopic mapping, gives visual (and numerical) representation of the spatial variation in the density of states. Spectroscopic mapping may also be extended by sequentially imaging at multiple biases to achieve a matrix of differential conductance data which can be extracted from the individual spectroscopic maps. Lock-in amplification techniques require care in experiment set-up. The modulation frequency should be selected such that it is high enough to not affect the integrated constant-current feedback, small enough that it is not too far beyond the frequency cutoff of the current amplifier and additional low-pass filtration units, and at a frequency which is not highly affected by other electronic noise (as can be observed in a frequency spectrum). The amplitude of the modulation should be high enough to achieve a reasonable signal to noise ratio, yet small enough not to exceed the required experimental energy resolution. Additional parameters such as the time constant and sensitivity must be set to achieve a clean signal which integrates over a reasonable time period for measurement. The phase must also be set properly to ensure that the lock-in amplifier is locked into the resultant modulations in current which may be out of phase with the modulation signal directly taken at the lock-in amplifier modulation output.
2.3 General Experimental Sample Properties and Preparation

2.3.1 Clean Substrate Preparation

Experiments are typically performed using a single metal crystal as the substrate. These crystals are purchased as designed to meet our required specifications for geometry to fit our sample holders and crystallographic plane alignment to meet our required standards of terrace areas for measurements. As purchased, the crystals are mechanically polished and aligned to better than 1 degree deviation from normal to the desired surface plane. The polishing done in initial sample preparation is still inadequate for direct experimental use as a substrate for STM measurements. It is necessary for the first use of a new sample introduced to the UHV chamber that the sample is treated by repeated cycles of sputtering and annealing. Sputtering is the use of noble gases such as argon or neon along with a focused ion gas accelerator to bombard the sample with high kinetic energy particles. The sputtering procedure is performed by exposure of the UHV chamber to neon gas at pressures near $10^{-5}$ Torr. The gases, ionized by contact with a hot filament in the ion gun, are then accelerated by a potential of approximately 1 kV to achieve kinetic energies of bombarding particles near 1 keV which are focused by electric potential onto the surface area. This sputtering effectively removes the upper surface layers of contaminants and metal atoms to reveal clean, albeit slightly roughened pure sublayers. The sublayers are then smoothed by annealing the single crystal to allow for surface atom rearrangement into more energetically favorable flat crystalline terraces. In the following, it is assumed that the samples used (which are typically Au, Ag, or Cu(111)), have been cleaned by repeated cycles of sputtering and annealing and are found in STM measurements to have large flat terraces of the (111) oriented crystal plane between atomic height steps.
2.3.2 General Surface, Atomic, and Molecular Properties Measured by STM Techniques

Scanning tunneling microscopic measurements are surface measurements, as it is the wavefunctions at the sample surface which contribute to the tunneling current [12]. Bulk Bloch states terminate at the surface and quickly decay into the vacuum, and the termination of the periodic lattice of atomic potentials results in surface states localized to within a few Angstrom of the surface [31–33]. The measured electronic properties are highly dependent upon crystallographic orientation relative to the probe extension direction [34–36], which also determines the atomic lattice arrangement as observed in atomic resolution images and possible surface reconstructions due to vacuum termination [37]. The measured topography depends on the density of electronic states in the sample [38], which when probed near the Fermi energy can display standing wave patterns resulting from interaction and reflection off of surface boundaries, defects, or adsorbates [39, 40]. The addition of intended adsorbates such as adatoms or molecules greatly modifies not only the measured topography but the electronic structure as well [12]. It is possible to coat surfaces with well-determined coverages of fractional to multiple monolayers resulting in vastly changed electronic properties [41–43]. A coating of just a few monolayers of NaCl can obscure low-energy conduction bands and essentially render the sample insulating along the conduction path [43, 44]. This has important application for some measurements as molecules strongly interacting with free electrons can be placed onto the insulating layers for study more closely approximating vacuum properties. A coating of sub-monolayer coverage of the magnetic cobalt atoms provides, for some substrates, spin-polarized islands which can act as excellent calibration points for spin polarized measurements [45], or as substrates for spintronic molecular measurements if the molecules are deposited onto the formed cobalt islands [46]. Cobalt, if isolated
on a metallic surface, can interact with substrate electrons. The unpaired cobalt spin interacts with the free surface electrons in a quantum many-body interaction to form a Kondo state [47, 48] (as discussed in Section 5.2.3), where the free electrons effectively screen the bulk from the adsorbed atomic spin. When performing spectroscopic measurements near the Fermi level of the substrate this resonance appears as a Fano-shaped feature [49–51]. In addition to free atoms, molecules can be deposited onto the surface by thermal evaporation in vacuum. Molecules are chosen for study due to their possible applications or as a way to access measurements of complicated physical phenomena. Multiple molecules can be deposited to study charge transfer between species [52–54]. Molecules having designed rotational degrees of freedom can be observed as analogs to some simple machines [55, 56]. Some molecules are spin-polarized in the population of the electronic orbitals and can be observed under spin-polarized measurements [46]. Other molecules house single fixed spin atoms such as cobalt, and can effectively alter the Kondo interaction by changing the coupling of the magnetic atom to the substrate [3, 53]. Aside from electronic measurements, molecules also have vibrational degrees of freedom with energies in the spectroscopic range, so certain bonds or ligands can be identified by spectroscopic signatures [57].

2.4 Introduction to Ag(111), Cu(111), & Au(111) Substrates

This dissertation utilizes the (111) facets of three noble metal substrates: Ag(111), Cu(111), and Au(111). When these face centered cubic (fcc) metals are cut along the plane perpendicular to the [111] crystal lattice direction, the newly exposed faces exhibit a hexagonal close-packed atomic structure as shown in Figure 2.3 for Ag(111). In the case of Au(111), the surface exhibits a reconstruction of the close-packed surface [58] with partial dislocation domain boundaries between alternating
fcc and hexagonal close packed (hcp) regions. A topographic image of the Au(111) “herringbone” reconstruction is presented in Figure 2.4.

Figure 2.3: Constant current topographic image of a Ag(111) surface with atomic resolution. Hexagonal close packing of surface atoms is evident. Surface lattice directions are included in red. Image taken with applied sample bias of 20 mV.

For these close packed surfaces with an “L band gap”, a band structure gap in the direction corresponding to the (111) plane, the surface state results in a step in the local density of states at the surface state energy. The surface state is then manifest as a step in spectroscopic measurements as shown in Figure 2.5 for Cu(111). Surface state electrons are confined to the surface and behave as a two-dimensional electron gas (2DEG). The 2DEG scatters from surface defects and step edges resulting in standing wave patterns. The energy of the surface state electrons follow the dispersion relation given by

\[ k_0 = \sqrt{\frac{2m^*E'}{\hbar}} \]

where \( E' \) is the measurement energy with respect to the surface-state band edge and \( m^* \) is the effective mass of a surface-state electron [39]. It is then possible,
by measuring the wavelength of observed surface standing waves, to determine experimentally the effective mass.

Table 2.1 provides parameters of the (111) surface of noble metals used in this dissertation. Surface state energies are observed by spectroscopic measurements as shown in Figure 2.5 which gives some measure of the quality of the probe for further spectroscopic measurements. The nearest neighbor distance on the (111) plane of the noble metals can be used to calibrate the piezoelectric actuators for proper measurements of distances, and the step height can calibrate the z-extension piezo movement. The work functions play an important role in the interpretation of field emission resonances as shown in Chapter 3.
Figure 2.5: Local spectroscopic (dI/dV) measurement demonstrating surface state onset for Cu(111). Observed onset is at the known surface state energy for Cu(111) of 435 meV. The peak here near 600 mV is likely due to tip density of states.

Table 2.1: Common properties of the (111) surface of noble metals, including surface-state energy, lattice constant, nearest neighbor distance, step height, and work function, with references.

<table>
<thead>
<tr>
<th>Surface-State Energy (meV)</th>
<th>Cu(111)</th>
<th>Ag(111)</th>
<th>Au(111)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant, a (nm)</td>
<td>0.361</td>
<td>0.409</td>
<td>0.408</td>
<td>[60]</td>
</tr>
<tr>
<td>Nearest Neighbor Distance (nm)</td>
<td>0.255</td>
<td>0.289</td>
<td>0.288</td>
<td>$= \frac{a}{\sqrt{3}}$</td>
</tr>
<tr>
<td>Step Height (nm)</td>
<td>0.208</td>
<td>0.236</td>
<td>0.235</td>
<td>$= \frac{a\sqrt{3}}{3}$</td>
</tr>
<tr>
<td>Work Function</td>
<td>4.94</td>
<td>4.74</td>
<td>4.31</td>
<td>[61]</td>
</tr>
</tbody>
</table>
3 Quantized Field Emission Resonances of Tip Induced Surface Vacancies

3.1 Background

Field emission current occurs when the potential applied between two contacts exceeds the material work function, allowing emitted electrons to travel as free electrons. The work function of a material is the energy needed to separate an electron from the surface to an unbound position some distance away. Resonances in the field emission current in scanning tunneling microscope experiments were first published by the inventors of STM, Binnig and Rohrer [16]. They found that, conditions of constructive wave function interference, for electrons freed by field emission between the tip and a clean gold sample, resulted in resonances in measured tip extension versus sample bias curves. Ignoring the effects of matching wavefunctions for a constant current, the gap width \( z \) is proportional to the applied sample bias \( V \) in field emission mode

\[
z \propto V. \tag{3.1}
\]

In this field emission regime an oscillatory behavior is superimposed onto the linear Equation 3.1 as

\[
\left[ \frac{2n \pm 1/2}{0.203} \frac{(\phi_1 - \phi_2 + eV)}{z} \right]^{2/3} = eV - \phi_2 \tag{3.2}
\]

where \( n \) is a resonance index, \( \phi_1 \) and \( \phi_2 \) are the work functions of the surface and tip, \( eV \) is the sample bias, and \( \pm \) stand for the maxima and minima of the resonance oscillation, respectively. Equation 3.2, which was presented in work by Binning and Rohrer, was originally developed by Gundlach [62]. Some authors still refer to the resonances observed as Gundlach resonances. Later work presented a more complete picture of the field emission resonance mechanism including image state
modifications to the tunneling potential [43, 63–65], which modify the trapezoidal tunneling potential to include electrostatic image state corrections. There has been some discrepancy in the naming of the observed resonances, as some groups describe the discrete levels as “Stark-shifted image potential states” which arise from the screening of external charges by conduction electrons[65], while others claim these resonances are due to field emission currents[43, 64], and still others claim that what are described as Stark-shifted image-state resonances are the same as field emission resonances[66]. The description of these resonances as image-states is related to measurements by inverse photoelectron spectroscopy (IPES) and two-photon photoelectron spectroscopy (2PPES) which predate measurements by local probe tunneling methods and do not involve field emission. These previous methods do not, however, access local properties as they are bulk surface measurements. It is claimed [65] that the image potential states, which result in a Rydberg series of levels

\[ E_n = -\frac{0.85}{(n + a)^2} \]

for the image potential

\[ V(z) = -\frac{e^2}{16\pi\varepsilon_0 z} \]

are Stark shifted in STM measurements by the strong electric field between the tip and the sample. The more recent publications [43, 64] use a model potential including image charge corrections, and by numerical solution of the Schrödinger equation for multiple resonant energies to extract local work function information. Using this method, it was possible to extract an approximate two-dimensional map of the local surface potential [64]. The two main methods for measurement of field emission resonances by STM are scanning tunneling spectroscopy (STS) which maintains a constant probe-sample distance and sweeps the sample bias while recording the differential conductance \( dI/dV \), and separation-voltage spectra which maintain a
constant tunneling current. Here the latter method is used, which will be shown to provide a method of mapping resonances over a surface region by simple bias dependent imaging. The measurements that follow are performed on a clean silver sample that has manipulated vacancies (holes) in the surface. It will be shown that surface vacancies and atomic step edges between terraces significantly modify the resonance positions in energy, indicating significant shifts in the local surface potential or work function. These measurements, and the associated analysis, allow for a systematic measurement of approximate surface work function, probe work function, and absolute probe to sample heights. Of greatest interest is the measurement of surface work functions. The surface work function plays an important role in surface properties such as adsorption affinity, catalytic processes, and electron emission [64]. Although methods exist for the experimental determination of local surface work function such as photoemission of adsorbed xenon (PAX) and Kelvin probe force microscopy, none have the appreciable spatial resolution of scanning tunneling microscopy (STM) methods.

3.2 Surface Vacancy Creation

A single crystal of silver cut perpendicular to the [111] direction was studied. The Ag(111) crystal was cleaned by repeated neon sputtering and annealing cycles in ultra-high vacuum. The sample was transferred to the low-temperature STM for study at a base temperature of approximately 77 K achieved by liquid nitrogen cooling of the bath cryostat. It is assumed that the clean Ag(111) surface has the known work function of 4.74 eV. Surface vacancies, or holes, were created by various means. Figure 3.1 demonstrates the successive creation of multiple surface vacancies by application of voltage pulses of $\approx 2$ V and ramped probe approaches of $\approx 15$ Angstrom as shown
in Figure 3.3. Figure 3.1 also demonstrates the repeatability and control of surface vacancy creation.

Figure 3.1: A sequence of topographic images demonstrating the sequential creation of vacancies (holes) on a Ag(111) surface. Holes were created by controlled tip approaches as described in the main text. Each topograph is 102 nm across. Constant current STM topographs were taken at a current of 1.0 nA with an applied sample bias of 2.0 V with a probe speed of 311.3 nm/s. Note there is a slight tip asymmetry resulting in a shadow to the lower left of surface features.

Figure 3.2 shows an enlarged topographic image containing multiple holes of various sizes. The hole sizes and shapes are observed to vary significantly even with application of identical tip approaches for indentation. Figure 3.3 displays the tip extension as a function of time for the hole creation shown in Figures 3.1 and 3.2. During the tip motion shown in Figure 3.3, a constant sample bias of 2 V was applied.

For the following field emission resonance measurements, holes which appeared as symmetric in topographic images were selected. One such symmetric hole is shown in Figure 3.4 along with topographic profiles along horizontal and vertical axes from the center of the vacancy. The cross sections indicate a significantly larger breadth than depth. This was considered by Acharya [67] who developed a model based on tip geometry effects which resulted in a calibration for the volume of vacancies based on their diameters and depths. Using this diameter calibration, the volume of the
Figure 3.2: A single overview topograph of a region with multiple surface vacancies on a Ag(111) surface which were created by the z-approach shown in Figure 3.3. Topograph is 102 nm across. Constant current STM topograph was taken at a current of 1.0 nA with an applied sample bias of 2.0 V with a probe speed of 311.3 nm/s. Note that there is a slight shadow to the upper right of surface features due to asymmetric tip geometry (a multiple local probe tip).

Figure 3.3: Plot of tip extension versus time for vacancy creation events. Zero in tip extension corresponds to constant tunneling current of 1 nA and applied sample bias of 2.0 V. During tip extension for hole creation a constant sample bias of 2 V was applied.
vacancy given in Figure 3.4 is approximated to be 24 atoms and the true depth is approximated to be 10 Angstroms.

![Cross section of a symmetric single hole with corresponding cross sections.](image)

Figure 3.4: Topographic STM image of a selected symmetric single hole with corresponding cross sections. Constant current topograph was taken with applied sample bias of -1.0 V and current of 1.0 nA at a probe speed of 207.5 nm/s.

### 3.3 Voltage Dependent Imaging for Measurement of Field Emission Resonances

One of the simpler scanning tunneling microscopic methods to extract electronic information about surfaces and surface adsorbates is voltage dependent imaging. As stated in Equation 2.1 the tunneling current is proportional to the sample bias multiplied by the surface density of states for a constant probe height. If the probe height is allowed to vary and the tunneling current kept constant, as occurs in the standard topographic imaging mode, the probe height is found to be proportional to the surface density of states. This then allows electronic information to be extracted from simple tip height versus voltage curves ($z(V)$). One of the main benefits of probe height versus voltage measurements is that they can be extracted over an entire image region sequentially by taking multiple probe height topographs at varied energies for the same region. A sample of probe height versus voltage data is given in figure 3.5.
which shows that for varied biases, surface features and clean surface areas exhibit differing probe height versus sample bias responses. The main feature to be noted here is that there is a contrast inversion between the sample and the surface vacancy leading, for some biases, to topographies wherein the surface vacancies appear as “protrusions” above the surface. Also of note is the drift of the imaging region off of the surface vacancy center.

Figure 3.5: Topographic images taken by a scanning tunneling microscope at various sample biases over a region containing a single surface vacancy. The bias corresponding to each image is listed below the images. Each square topograph is 8.5 nm by 8.5 nm with resolutions of 512 pixels squared. The absolute z-scales are allowed to vary so absolute height between images is not physically relevant. The topographs were taken with 100 mV spacing, from which a selection is plotted here. All topographs taken at a constant current of 0.6 nA.

With voltage dependent images taken, it is possible to extract probe height (z) versus sample bias (V) curves for each point in the image by taking the absolute value of the probe height for a selected coordinate in the image (x,y). This is unfortunately a tedious process using standard data analysis tools as some voltage sequences with small bias increments, say 10 mV, could result in nearly a hundred sequential topographs. Doing this, then, for each or even a subset of the images manually would be prohibitively time consuming. Instead, data analysis was performed by scripting in the Matlab programming environment. This involved reading in each topograph to form a three dimensional matrix $z(x,y,V)$ with values of the tip height.
possible to extract a $z$ versus $V$ curve for each point in the topographic images. One such curve is shown in Figure 3.6.

![Figure 3.6: A single $z$ versus $V$ curve for a position in a sequence of bias dependent images that is known to be clean silver (at the periphery of the topographs). The steps in the curve are a result of field emission resonance (FER). Note $z$-scale is a relative scale and not absolute probe height from surface.](image)

To extract the energetic positions of the resonances, it is more illustrative to see the derivative of $z$ versus $V$ curves, $dz/dV(V)$. This was done by taking numerical derivatives of the $z$ versus $V$ curves in Matlab with moderate pre-derivative and post-derivative smoothing. An example of such a derivative is shown along with the original curve in Figure 3.7. Note that the differentiated curve matches resonance positions well, indicating validity of derivative processing.

In order to extract such tip height differential curves, care must be taken to correct for unavoidable thermally induced drift of the scanning region. Drift such as that in Figure 3.5 would result in extracted curves that do not correspond to the center of the surface vacancy if they were left simply extracted from the raw $z(x,y,V)$ data. In
Figure 3.7: A $z$ versus $V$ curve (in blue) extracted from a single point in a sequence of voltage dependent images and its numerical derivative $dz/dV(V)$ (in red). Note peak positions in the derivative curve match well with the corresponding steps and allow a more precise extraction of the resonance energies.

In order to correct for such drift the first and last images of a voltage dependent sequence were used to measure the total extent of the drift. The images then were each corrected for by shifting a distance determined by a linear interpolation of the drift. It should be noted that a linear interpolation of the image area drift is a rough approximation. It is possible that the time-dependent image drift is nonlinear, in which case this approximation is invalid. For the image sequences taken here, the approximation is assumed valid, yet a separate method of marking hole center features for each or a subset of images to achieve nonlinear drift correction has been developed.

It is possible, by comparing individual $dz/dV$ curves extracted from multiple points, to determine the spatial variation of the field emission resonance. It is more instructive, however, to form a two-dimensional plot of $dz/dV$ versus distance along a cross section that spans the features in question (either surface vacancy or step edge). These figures were extracted and plotted by Matlab scripting by correcting for
drift and then extracting \( z(V) \) curves by interpolation of positions along the desired line. The extracted \( z(V) \) curves were then differentiated and the figures were plotted, resulting in images such as that in Figure 3.8, where the spatial variation in field emission resonance positions is obvious.

![Figure 3.8](image.png)

Figure 3.8: For a cross section (along \( x \)) of a single surface vacancy a plot of \( \frac{dZ}{dV(x,V)} \) is presented. The hole is centered about the distance 55 Angstroms. Notice that the field emission resonances (peaks as a function of applied sample bias) are shifted at the location of the surface vacancy toward lower values.

### 3.4 Extracting Work Function Information from Field Emission Resonances

Measurements of the field emission resonances on flat, clean areas of the Ag(111) substrate were used both for tip work function calibration and as a test of methods by which work function information could be extracted. In Table 3.1, the relative probe height and sample biases for four resonances and their associated minima on a flat terrace of the sample are presented to be used in resonance fitting.
Table 3.1: Table of values for four resonance $dz/dV(V)$ peaks and associated minima measured on a defect-free location of the Ag(111) crystal surface. Applied sample biases of the resonances were determined by finding local maxima and minima in $dz/dV$ curves. Relative probe-sample distances, $z$, were extracted for the values found for the resonant applied sample biases.

<table>
<thead>
<tr>
<th>Resonance Index</th>
<th>Applied Sample Bias</th>
<th>Relative Probe-Sample Distance</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>V (mV)</td>
<td>z (Angstrom)</td>
</tr>
<tr>
<td>1 Max</td>
<td>4197</td>
<td>5.115</td>
</tr>
<tr>
<td>2 min</td>
<td>5051</td>
<td>9.106</td>
</tr>
<tr>
<td>2 Max</td>
<td>5778</td>
<td>11.96</td>
</tr>
<tr>
<td>3 min</td>
<td>6251</td>
<td>14.55</td>
</tr>
<tr>
<td>3 Max</td>
<td>6671</td>
<td>16.54</td>
</tr>
<tr>
<td>4 min</td>
<td>7024</td>
<td>18.68</td>
</tr>
<tr>
<td>4 Max</td>
<td>7352</td>
<td>20.41</td>
</tr>
<tr>
<td>5 min</td>
<td>7642</td>
<td>22.29</td>
</tr>
</tbody>
</table>
The data in Table 3.1 were fit using the Gundlach Equation 3.2 by minimizing
errors. With $eV$, $s$, and $n$ being independent measured values, the parameters $\phi_1$, $\phi_2$, and $dz$ were optimized. Including the first resonance maxima in the fitting, unphysical results were achieved with $\phi_1$ fixed at the lower bound, 0 eV, so removing the first data point was attempted. Fitting the data in Table 3.1, without the first resonance maxima to Equation 3.2 resulted in $\phi_1 = 4.3$ eV, $\phi_2 = 1.7$ eV, and $dZ = 10.6$ Angstrom. These values are more reasonable as the expected value of the work function of clean Ag(111) is 4.74 eV, which is close to the resultant value for $\phi_1$ of 4.3 eV. The resultant work function for the tip was calculated, as expected due to geometry, to be smaller than the sample work function, and the absolute probe height was extracted as a fit parameter to be the reasonable value of 10.6 Angstrom plus the measured relative probe displacements. The absolute probe height, while large in comparison to some approximations, matches well with the values found by fitting the linear function Equation 3.1 to the experimental data, and then finding the intercept.

If the surface work function is fixed at its known value of 4.74 eV the resultant tip work function is 1.8 eV and the absolute probe extension is 12.4 Angstrom in addition to the listed relative values. The value of the tip work function could then be taken as a constant when calculating the sample work function for step edges or holes. Instead, as a test of the data fit to Gundlach’s Equation 3.2 data extracted from the center of a surface vacancy was fit allowing the same three parameters, $\phi_1$, $\phi_2$, and $dZ$ to vary. Table 3.2 presents the data used in fitting. The resulting parameters from fitting were $\phi_1 = 5.8eV$, $\phi_2 = 1.7eV$, and $dZ = 15.8$ Angstrom. These values are reasonable. The tip work function is the same as extracted from fitting the defect-free surface resonances indicating some consistency, and the vacancy work function is higher than the clean sample work function. This is to be expected as positions with
positive surface gradients are more difficult to extract electrons from than those with a flat or negative surface gradient such as the tunneling probe.

Table 3.2: Table of values for five resonance peaks and four associated minima measured at the center of an induced surface vacancy on Ag(111). Local minima and maxima were extracted from the associated $dz/dV$ curve. Relative tip extensions, $z$, were taken at the applied sample bias points of extracted local $dz/dV(V)$ minima and maxima.

<table>
<thead>
<tr>
<th>Resonance Index</th>
<th>Applied Sample Bias $V$ (mV)</th>
<th>Relative Probe-Sample Distance $z$ (Angstrom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n = 1 Max</td>
<td>4222</td>
<td>4.916</td>
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<td>13.05</td>
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<tr>
<td>n = 3 Max</td>
<td>6427</td>
<td>15.24</td>
</tr>
<tr>
<td>n = 4 min</td>
<td>6745</td>
<td>17.14</td>
</tr>
<tr>
<td>n = 4 Max</td>
<td>7128</td>
<td>19.17</td>
</tr>
<tr>
<td>n = 5 min</td>
<td>7423</td>
<td>20.97</td>
</tr>
<tr>
<td>n = 5 Max</td>
<td>7766</td>
<td>23</td>
</tr>
</tbody>
</table>

3.5 Field Emission Resonances of Probe Induced Holes on Ag(111)

In order to better illustrate the data extraction for one surface vacancy, Figure 3.9 is constructed. This figure includes a topographic image with vacancy location and cross section marked and the extracted $dz/dV(V,x)$ data. Here it is more obvious that extracting resonances from the numerically differentiated $dz/dV$ values is easier than from the $z(V)$ curves. Extracted curves for the vacancy position and the defect-free surface terraces are compared in the figure. Comparison shows that although the
vacancy position and defect-free surface areas share a first resonance position of 4.197 V, the remaining resonances are shifted so that the vacancy resonance is found below the surface resonance energy. Also of interest is the fact that, as shown in Figure 3.9, at some energies the vacancy appears above the surface at the probe position (that is, a known surface vacancy appears as a protrusion above the surface due to shifting of the tunneling resonances).

For the surface region shown in (a) of Figure 3.9, the maxima and minima of each resonance for each induced surface vacancy were extracted. These data are given in Table 3.3. Also given in this table are data for a defect-free terrace of the Ag(111) surface. At the bottom of the table are approximate values for the measured hole depth and volume, which it was suspected would vary with the resonance energy locations. After listing the volumes, the fit parameters for Equation 3.2 are shown. While holes A1, A2, and A4 result in reasonable values for the surface work functions and probe heights, Hole A3, the smallest of the holes, results in a surface work function that is too large to be physically reasonable and goes against the trend of the other holes to increase work function and dz when increasing hole volume. There are a number of possible reasons for the discrepancies. First, the Gundlach equation may not be most suitable for the apparent surface resonances. The fits may also appear unreasonable due to non-exact determination of the resonance energies and minima. To form the dz/dV curves from which the energies were extracted, it was necessary to smooth data prior to, and after, numerical differentiation. Still, from the fits of data in Table 3.3, there are some rough conclusions that can be drawn. The increased work functions for holes relative to defect-free surface terraces may be expected as a deeper and wider surface ‘well’ would make it more difficult to extract electrons. This also explains the shift of tunneling resonances at surface vacancy edges, where the surface gradient would enable easier extraction of electrons. Also, at least for holes 1,2, and
Figure 3.9: An overview of data for one surface vacancy. The surface vacancy is marked in a by a red dot with a blue line through it. The red dot marks the point of extraction of dz/dV curves for the defect location and the blue line marks the cross section used in plotting b and c. The curves in d, e, and f are extracted from the original z(V) data and from the numerically differentiated dz/dV(V,x) data in b. Note shift in peak positions from the defect location to the defect-free surface (green to purple). Also note in f that at times the probe height, z, at the defect location is above the probe height on the defect-free surface area, turning the vacancy into a protrusion for some measurement biases.
4, the probe work function $\phi_2$ remained nearly constant, which is some indication of fit validity.

Table 3.3: A table of data extracted from multiple bias dependent images of four vacancies on Ag(111) surface and a clean surface area. V values are in mV, z and dz values are in Angstroms, Volume is in Angstroms$^3$, depth is in Angstroms, and the fit determined values of $\phi_1$ and $\phi_2$ are in eV. The z and V values are found by selecting minima and maxima in the $dz/dV(V)$ curves. For the holes, the $dz/dV$ curves used were those extracted from the hole centers. Fitting results in unreasonable values for two of the vacancies with overly large work functions of 8.8 and 6.6 eV.

<table>
<thead>
<tr>
<th>n Max</th>
<th>Surface A</th>
<th>Hole A1</th>
<th>Hole A2</th>
<th>Hole A3</th>
<th>Hole A4</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
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<td>4.916</td>
<td>4197</td>
<td>4.539</td>
</tr>
<tr>
<td>z</td>
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<tr>
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</tr>
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<td>23.96</td>
<td>7766</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>n Min</th>
<th>Surface A</th>
<th>Hole A1</th>
<th>Hole A2</th>
<th>Hole A3</th>
<th>Hole A4</th>
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<tbody>
<tr>
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</tr>
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</tr>
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</tr>
<tr>
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<td>13.8</td>
<td>19.8</td>
<td>19.9</td>
</tr>
<tr>
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<td>5.8</td>
<td>5.2</td>
<td>8.8</td>
<td>6.6</td>
</tr>
<tr>
<td>V</td>
<td>1.7</td>
<td>1.7</td>
<td>1.7</td>
<td>1.3</td>
<td>1.9</td>
</tr>
</tbody>
</table>

3.6 Image Potential Resonances at Surface Step Edges on Ag(111)

In addition to examining data measured above surface vacancies, image potential resonances were studied above monoatomic step edges on the Ag(111) surface. It is expected, due to geometric arguments, that the step edges would have lower local work functions than those measured at the surface or at surface defects. This can be seen by comparing the shifts in resonances between Figure 3.9 and Figure 3.10.
In Figure 3.9, for a surface vacancy, the peak positions at the vacancy location are shifted down in energy compared to the surface. As seen in Table 3.3, this results in an increase of the work function compared with the clean surface. Similarly, the position of the resonances is shifted for a step edge. However, for the step edge, as shown in Figure 3.10, the resonances are shifted to higher energies than for the clean surface. This would, it is expected, result in a lower energy work function. The structure of the $dz/dV(V,x)$ plot in Figure 3.10 shows that as the surface is approached from the top of the terrace there is a bending towards higher energies for the resonances. It seems also that approaching the step from the lower terrace results in image potential states that are shifted down in energy. It is expected that the true resonances for the step edge are those shifted to higher energies while the lower energies which appear to come from the lower terrace states are a result of the finite tunneling probe size interacting with both the lower and upper resonances. The structure of these resonances, which overlap, do not lend themselves to easy interpretation due to arbitrary choice of extraction position (as opposed to the case of clearly distinct resonances for the hole centers, shown in Figure 3.9) and so are instead explained only qualitatively here.
Figure 3.10: Extracted resonance data for a single step edge on Ag(111) with the profile shown. Five resonances are observed. The points of extraction for the single curves are marked with green and purple lines in the $dz/dV(x,V)$ figure.
3.7 Conclusions

In the preceding sections, approximations to the local work function on Ag(111) for clean terraces and tip induced surface vacancies were achieved by fitting of the Gundlach Equation 3.2 to maxima and minima in extracted \( \frac{dz}{dV} \) curves. The \( \frac{dz}{dV} \) curves were found by extracting and differentiating \( z(V) \) curves from arrays of constant current topographic images, with corrections for drift. The resultant work functions for vacancies were found to be larger than for terraces, while the work function at step edges were found to be lower. These relative comparisons of work functions are considered to match the expected behavior based on surface curvature, where protrusions (such as step edges) should have lower work functions. As a byproduct of the fitting approximations, the probe work functions were determined, resulting in values near 1.7 eV. The methods implemented in this chapter for the extraction of work functions can be extended to more novel surface systems. It may be possible in future measurements to utilize this method to measure work functions above quantum objects such as fullerenes adsorbed on a surface or manipulated into induced vacancies. The main benefit here is the accessibility of local work function information for systems that vary on the nanoscale. Additionally, the reproducible creation of surface vacancies may be applicable to nano-patterning or to creating surface sites into which molecules or atoms can be manipulated in order to determine the effect of surface work functions on their spectroscopic and possibly magnetic (such as Kondo effect) features.
4 Molecule Manipulation and Covalently Linked Chain Formation

4.1 Background

Demand for more efficient electronic devices has led many researchers to look beyond silicon based technologies. As miniaturization of current technologies progresses many are working to create functional devices using a bottom-up approach where individual elements may consist of single atoms [47], arrays of atoms [68], single molecules [6, 69, 70], or molecular conglomerates [7]. Each of these approaches to the bottom-up fabrication of functional devices has potential benefits and known and unknown limitations. Molecular systems are promising because they can be chemically tailored for specific applications, self-assembled into nanostructures, made very small, and possess useful electronic properties.

One of the goals of studies of surface-supported molecular systems is the formation of functional molecular electronic devices. Studies of single molecules do much to illuminate nanoscale interactions; however, functional devices may require the interaction of many molecular elements. Molecular superstructures, that is structures containing many molecules, are being investigated to determine intermolecular interactions and to form circuits with a bottom-up approach. There are multiple means of intermolecular interactions on surfaces [71]. Molecules may be held together in structures by covalent binding, $\pi - \pi$ stacking [72], dipole interaction [72], van der Waals forces [73–75], hydrogen bonding [42, 73, 74, 76–78], and metal-ligand interactions [76, 79].

One-dimensional molecular chains are an interesting subset of molecular networks which have enjoyed great interest in recent years. STM tip-induced bond formation of biphenyl molecules has been demonstrated [11], following reported thermally
induced biphenyl formation from phenyl radicals [80]. Some chains have been built by manipulation such as the vanadium-tetracyanoethylene (V-TCNE-V) chains[81]. Although the V-TCNE-V chains have coupled spin centers, they are not covalently bound, reducing the electronic communication through the linkers, and they do not self-form, which means they cannot be produced on the surface en masse. Other types of chains have been able to self-form on surfaces with the application of heat such as “wagons” formed by the “surface substitution” of copper atoms in place of dissociated bromine between constituent molecular units [82]. Additionally, chains have been formed through hydrogen bonding, such as in the case of twin chains of (4-[trans-2(pyrid-4-vl-vinyl)]-benzoic acid) (PVBA) on a Ag(111) substrate [76].

The most stable and conducting chains are linked by covalent bonds. Recently, much research has been done into the covalent bonding of chains on surfaces. Grill et al. have shown that a surface catalyzed reaction on Au(111) may be achieved by functionalizing the molecules with terminal bromine atoms which act as placeholders for intermolecular bonds [83]. In their experiments, chains, dimers, and 2D networks were formed on a surface by activating (dehalogenating) the molecules and then, through surface mobility, connecting molecular units by annealing the substrate. They showed that activation could be done in the molecular evaporator or on the substrate by heating the surface, and that STM manipulation could be used to demonstrate whether or not the bonds were covalent. Others have since worked on the surface-supported-covalent linking of chains, such as chains of dibromotetrafluorene [44, 84], and the forming of graphene nanoribbons using 10,10’-dibromo-9,9’-biantryl precursor monomers [85].

This chapter is focused on the formation of covalently bound chains of molecules. The central focus is on the formation of covalently bound chains of Co-(5,5′-Br2-Salophen) molecules. The formation of chains of these molecules is a significant
step forward as they are functionalized with magnetic centers for studies of spin interactions in a covalently bound network. In this chapter, Co-(5,5’-Br₂-Salophen) molecules are introduced, the attempted formation of chains on Cu(111) is outlined, clusters of dipole interacting molecules on Au(111) are observed, single molecules are manipulated and recognized as intact Co-(5,5’-Br₂-Salophen), and covalently bound chains are formed through thermal activation. Aside from the Salophen chains, a system of mixed chain elements, BrTPP and BrNDI, is studied on a Au(111) surface in an attempt to discover charge transfer between differing molecules when covalently bound.

4.2 Co-(5,5’-Br₂-Salophen) Molecules

The molecules investigated in the following sections are N,N’-bis(5-bromosalicylidene)-1,2-phenylenediaminocobalt(II), which are called here more simply Co-(5,5’-Br₂-Salophen) or shortened in the extreme to Co-Salophene. A model of the chemical structure of the molecule used is displayed in Figure 4.1. Co-(5,5’-Br₂-Salophen) is a planar mirror symmetric metal-organic molecule with bromine termination on the two phenyl group arms and a cobalt atom housed centrally. The planar phenyl head protects against dehydrogenation and removes the chirality associated with the parent Co-Salen molecules [86]. The Br termination serves to induce intermolecular interactions [87] and to act as a placeholder for phenyl ring coupling during chain formation. The central Co²⁺ ion is square-planar, tetra-coordinated with a low spin d⁷ electron configuration having one unpaired electron (S = 1/2). These molecules were synthesized by Jan-Peter Klöckner and Marc-Heinrich Prosen at the Institute of Inorganic Chemistry at the University of Hamburg in Germany.
Figure 4.1: A ball and stick model of the molecule of choice for work presented in this and the following chapter, Co-(5,5'-Br₂-Salophen). The chemical model here was prepared and optimized for geometry in the software ArgusLab [1] and rendered using the software POV-Ray for Windows [2].

4.3 Co-(5,5’-Br₂-Salophen) Chains on Cu(111)

The molecules, Co-(5,5'-Br₂-Salophen), were deposited by vapor deposition onto a clean Cu(111) substrate held near ambient temperature of 295 K. The sample with adsorbed molecules was then transferred to the cryogenic scanning tunneling microscope chamber for study at approximately 6 K. Topographic STM images revealed the existence of extended objects (chains) and isolated molecules on the surface as shown in Figure 4.2. The single molecules and molecular chains appear to nucleate at defect sites on the Cu(111) surface. The chains do not show any preference for orientation along the crystallographic axes. Within chains, the molecules may be oriented parallel relative to a neighboring molecule, or anti-parallel, with the phenyl “head” on the same or opposite side of the chain. There is no apparent or expected preference for parallel over anti-parallel arrangement of the molecules within chains, with performed analysis of each chain featured in STM topographic imaging.

Single molecules adsorbed on the Cu(111) surface appear to have had their bromine termination removed, by comparison with the chemical structure and the topography of molecules adsorbed onto Au(111). As molecules remain intact at
Figure 4.2: An overview image of Co-Salophen chains on Cu(111). Image is 101.25 nm in horizontal direction. Topographic STM image taken with applied sample bias of 500 mV at constant current of 0.1 nA and a scanning speed of 1236 nm/s. Observed chains nucleate from surface defect locations without orientation preference relative to crystallographic axes. Single molecules are observed in upper right of image.

the same deposition temperature when deposited onto a Au(111) substrate, it is postulated that the increased reactivity of the Cu surface induces debromination. The single molecules were found to be mobile on the surface under lateral manipulation, so strong surface binding of the radical phenyl arms is unlikely. A topographic image of one of the isolated molecules is shown in Figure 4.3.

A topographic image of a 20 member chain measured with a sharp probe is provided in Figure 4.4. In this image there are multiple oscillations between parallel and anti-parallel alignment of the molecules. Also evident in this image are protruding defects surrounding the chain, which are expected to be some of the dissociated bromine atoms. In addition to the bromine atoms, protrusions are evident between the molecules at the linking location. These protrusions are suspected to be surface
Figure 4.3: An image of a single Co-Salophen Molecule on Cu(111) suspected to be debrominated by structural comparison. Image is 12.66 nm in horizontal direction. Topographic STM image taken with applied sample bias of 400 mV at constant current of 0.62 nA and a scanning speed of 77.25 nm/s.

copper atoms linearly coordinated with the free bonds of the Salophen molecular units as has been previously reported [82].

Figure 4.4: An image of a single Co-Salophen Chain on Cu(111). Image is 34.61 nm in horizontal direction. Topographic STM image taken with applied sample bias of 50 mV at constant current of 0.1 nA and a scanning speed of 154.5 nm/s.

Figure 4.5 shows the chain presented in Figure 4.4 after removal of multiple molecular units by lateral manipulation. The ease at which molecules are removed from the chain indicates the non-covalent nature of the intermolecular bonding,
while the number of atomic size adsorbates which are assumed to be bromine atoms indicates complete dehalogenation of the Co-(5,5’-Br$_2$-Salophen) molecules.

Figure 4.5: An image of a single Co-Salophen Chain on Cu(111) after removal of three of the constituent molecules from the left end (formerly occupying area outlined by yellow rectangle). Apparent also are dislocated single bromine atoms. Image is 34.61 nm in horizontal direction. Topographic STM image taken with applied sample bias of 50 mV at constant current of 0.1 nA and a scanning speed of 309 nm/s. Manipulation was performed with an applied sample bias of 200 mV and a feedback mediated constant current of 50 nA with a probe speed of 6.49 nm/s.

Another strong indication that the bonding between chains is non-covalent is the ductility of the intermolecular bonds. As can be seen in Figure 4.6, the intermolecular bonds may be significantly distorted from a linear shape. Other chains could be significantly distorted and broken by similar lateral manipulations. In Figure 4.7, a single chain is bent and broken into two distinct chains. Additionally, bromine atoms could be seen in the vicinity of the broken chain on the surface.
4.4  **Co-(5,5’-Br$_2$-Salophen) Self-Assembled Clusters on Au(111)**

The Co-(5,5’-Br$_2$-Salophen) molecules were thermally deposited under ultra-high vacuum onto a clean Au(111) substrate held at room temperature. Au(111) was chosen as it has a reduced reactivity compared with the Cu(111) substrate which demonstrated strong interaction with the molecules. The sample was then transferred into the liquid helium cryostat to reach a base temperature of 6 K for study by a custom built scanning tunneling microscope. A topographic image of the molecules
adsorbed onto the Au(111) surface is given in Figure 4.8 where the supramolecular structures can be seen oriented along the herringbone reconstruction of the surface.

Figure 4.8: Co-(5,5′-Br₂-Salophen) form self assembled molecular conglomerates which are oriented along the herringbone reconstruction of the Au(111) surface. Note that the relative tip height color bar for this image is shared by many topographic images within this section, and is not reproduced. Constant current topograph having a resolution of (512 px)² taken with a current of 0.14 nA, an applied sample bias of -200 mV, and a probe speed of 154.5 nm/s. Reprinted with permission from [3]. Copyright 2012 American Chemical Society.

The molecular clusters form by dipolar interactions between the bromine termination and the central reactive site housing the cobalt ion [87]. Figure 4.9 shows an enlarged topographic image of a portion of one of the clusters with molecular structures overlaid for clarity. The most stable unit of the molecular clusters is the quad arrangement demonstrated in the upper left of Figure 4.10. All molecular clusters nucleate from this arrangement. As found by others [73, 88, 89], the nucleation sites
tend to be at the elbow discontinuity of the herringbone reconstruction of the Au(111) surface.

Figure 4.9: A closer look at a molecular cluster of Co-(5,5'-Br₂-Salophen). Molecular structure is overlaid to emphasize dipolar interaction. Constant current topograph taken with a current of 0.1 nA, an applied sample bias of -4 mV, and a scanning speed of 0.3 nm/s.

Figure 4.10: A sample graphic representation of clusters of Co-(5,5'-Br₂-Salophen) molecules. Upper left four molecules, with a background highlight here, form most stable unit found in all clusters where each molecular unit has two dipole interactions. Dipole interactions here are between the halogen (Pink - Br atom) and the metallic center (Orange - Co ion). Reprinted with permission from [3]. Copyright 2012 American Chemical Society.
4.5 Co-(5,5′-Br₂-Salophen) Isolation and Debromination on Au(111)

Individual molecules were extracted from the self-assembled clusters by lateral manipulation. This was done further support weak dipole binding within the clusters and to isolate individual molecules for further study outside of the clusters, as dipole binding and proximity is expected to alter the electronic behavior of molecules. A sequence of topographs demonstrating extraction is given in Figure 4.11. A sample manipulation z(x) curve is reproduced in Figure 4.12 to illustrate inter-site hopping and pulling mode manipulation. Individual molecules fit well with the chemical structure, as shown in Figure 4.13.

![Figure 4.11: A sequence of images demonstrating extraction of single molecules from a cluster of Co-(5,5′-Br₂-Salophen) molecules. Constant current topographs taken with current of 0.05 nA, applied sample bias of 50 mV, and probe speed of 77.25 nm/s. Lateral manipulation performed with applied sample bias of 50 mV, constant current of 10 nA, and manipulation speed of 19.31 nm/s.](image)

Theoretical calculations reveal that Co-(5,5′-Br₂-Salophen) molecules adsorb planar to the Au(111) surface with the cobalt ion situated preferentially at a bridge site between two adjacent atoms on the surface. Calculated structure and adsorption is given in Figure 4.14.

The bromine atoms attached to the phenyl arms are intended to serve as placeholders for molecule coupling. With the motivation of studying the molecules as they would appear in chains, the Co-(5,5′-Br₂-Salophen) molecules were selectively
Figure 4.12: An example tip vs. distance curve from lateral manipulation of Co-(5,5’-Br$_2$-Salophen) away from molecular clusters. Lateral manipulation was performed with an applied sample bias of 50 mV at a constant current of 20 nA and at a probe speed of 2.03 nm/s.

![Image of a graph showing a tip vs. distance curve]

Figure 4.13: STM topograph of isolated Co-(5,5’-Br$_2$-Salophen) molecule on Au(111) with overlaid chemical structure. Significant match of structure and topography indicate molecules are intact on surface. STM constant current topograph taken with applied sample bias of 28 mV and current of 0.05 nA at a speed of 19.31 nm/s. Reprinted with permission from [3]. Copyright 2012 American Chemical Society.

debrominated, as demonstrated in Figure 4.15, to access their bromine-free electronic and physical structure.

Debromination was performed by raising the applied tunneling bias with the probe situated at a fixed height above the approximate location of the Br-C bond. During debromination, the tunneling current was recorded. A significant change in the tunneling current indicates a change in the tip or the sample structure in the tip tunneling path. A sample current versus voltage curve is given in Figure 4.16. Most
Figure 4.14: Calculated top and side view of geometry of single intact Co-(5,5'-Br$_2$-Salophen) molecule on the Au(111) surface. Molecule-substrate separation indicate weak physisorption as opposed to strong chemisorption.

Figure 4.15: A sequence of images demonstrating the debromination of a Co-(5,5'-Br$_2$-Salophen) molecule. Constant current topographic STM images taken at an applied sample bias of 200 mV and a current of 0.05 nA with a speed of 154.5 nm/s. With probe positioned above the approximate C-Br bond location at a height determined by the imaging parameters the bias was ramped from 200 mV to 3000 mV over a period of 3.0 seconds. First dissociation occurred at 2715 mV.

bromine dissociations were observed with tunneling electron energies starting at 1.6 eV and extending to 3.0 eV.

When a single bromine atom is removed, the newly freed bond from the carbon atom attracts to the gold surface. This attraction to the gold surface causes a bending of the molecule which can be seen in the side view as calculated and shown in Figure 4.17. The molecules in this configuration could be rotated about the broken bond, but were unable to be moved to a new location by lateral manipulation, further supporting strong surface binding.
When both the terminal bromine atoms were removed, the molecules were immobile with both arms bending toward the surface as shown in figure 4.18. The doubly debrominated molecules, were unable to be rotated as in the case of singly debrominated molecules supporting the idea of additional surface binding.

Removal of the terminal bromine atoms appear to raise the cobalt ion above the surface, as is seen most clearly in the experimental cross sections reproduced in Figure 4.19 as well as in the bond breaking sequence of Figure 4.15. Theoretically calculated
Figure 4.18: Calculated top and side view of geometry of doubly debrominated Co-(5,5'-Br₂-Salophen) molecule on the Au(111) surface. Bending of phenyl arms toward the surface and slight movement of gold atoms indicate surface bonding.

cross sections reproduce the trend from Figure 4.19 of raising cobalt atom as seen in Figure 4.20.

Figure 4.19: Topographic cross sections extracted from experimental topographic image data. Horizontal is a straight line cross section through the Co ion center in the direction parallel to the terminal bromine atoms. Vertical is through the cobalt center and the central phenyl ring or 'head'.
Figure 4.20: Theoretically calculated topographic cross sections. Horizontal is along the arms in the direction of the terminal bromine atoms. Vertical is through the cobalt center and the central phenyl ring.

4.6 Co-(5,5’-Br₂-Salophen) Chains on Au(111)

Molecular chains are formed on the Au(111) surface by thermally inducing a surface catalyzed “aryl-aryl” coupling reaction between Co-(5,5’-Br₂-Salophen) units. The “aryl-aryl” coupling reaction is between free carbon bonds from terminal phenyl rings of debrominated radical molecular fragments. A schematic of the reaction is given in Figure 4.21. To induce chain formation, the Au(111) surface with Co-(5,5’-Br₂-Salophen) molecules adsorbed was removed from the cryogenic bath and annealed to 400 K for 10 minutes. The sample was then cooled back to 6 K and checked by STM imaging. A typical topograph of the surface after chain formation is given in Figure 4.22.

In order to confirm covalent binding, lateral manipulation of the chains was attempted. As shown in Figure 4.23, the chains move as units and remain rigidly
Figure 4.21: A schematic representation of the phenyl ring coupling reaction used to form chains of Co-(5,5′-Br₂-Salophen) molecules on a Au(111) surface. Br-aryl bonds (I) are broken when thermally activated with the formation of intermediate reactants (II) which then join to create biaryls (III). Reprinted with permission from [3]. Copyright 2012 American Chemical Society.

Figure 4.22: A topographic image of the Au(111) surface showing molecular chains of various lengths. (512 px)² STM topograph taken with an applied sample bias of 50 mV, constant current of 0.3 nA, and at a probe scanning speed of 309.0 nm/s. Single suspected bromine atom is visible in the lower portion of the image. Chains shown no apparent proclivity toward parallel or anti-parallel molecular unit orientation. Reprinted with permission from [3]. Copyright 2012 American Chemical Society.
linear under manipulation. This contrasts sharply with the case of chains on the Cu(111) substrate where they bend or break under manipulation, as demonstrated in Figure 4.7. In addition to lateral manipulation, attempted dehalogenation was performed on the end units and at intermolecular bond locations, as was done for the isolated molecules (Figure 4.15). The chain conformations were not found at any point to distort for applied tip biases which would have dissociated bromine from single molecules (3 V).

Figure 4.23: A sequence of topographic images demonstrating that chains remain intact and rigidly linear under lateral manipulation. Topographic images taken with an applied sample bias of 200 mV at a feedback mediated constant current of 1 nA with a probe speed of 77.25 nm/s. Manipulation between topographic images was performed with an applied sample bias of 200 mV, at a feedback mediated constant current of 200 nA, with a probe lateral speed of 11.03 nm/s. Cyan arrows indicate manipulation directions. Reprinted with permission from [3]. Copyright 2012 American Chemical Society.

Figure 4.24 shows an enlarged image of a single five member chain with a chemical structure overlay. The chemical structure used fits well without terminal or intermolecular bromine atoms. Density functional theory calculations were performed to better understand the properties of the engineered chains on the Au(111) surface. The calculations resulted in a molecule-to-substrate distance of 2.9 to 3.1 Angstroms which is large enough to indicate that the chains are either very weakly chemisorbed or physisorbed on the surface. Furthermore, calculations reveal that the molecular units forming the chains remain planar to the surface with no bonding between the
chains and the surface. Resulting structure from theoretical calculations is reproduced in Figure 4.25.

Figure 4.24: An enlarged image of a single molecular chain with structure overlaid. STM topograph taken with an applied sample bias of -5 mV with a constant current of 0.5 nA at a probe scanning speed of 3.09 nm/s. Note that the chemical structure overlay matches the expected shape best with no intermolecular bromine atoms. Suspected C-C bond location is highlighted with a red rectangle. Reprinted with permission from [3]. Copyright 2012 American Chemical Society.

Figure 4.25: Calculated molecular chain structure on Au(111). Upper left is a top view, bottom left is side view, and right is a zoom of the side view. Molecule to surface height indicates weak bonding.

4.7 **Br$_2$NDI and Br$_4$TPP Non-Homogenous Molecular Chains**

Functional molecular chains and networks will likely need to be non-homogenous. This section describes attempts to form mixed covalently linked networks of molecules.
The two molecules selected are brominated napthalenetetracarboxydimide (Br$_2$NDI) and Tetra(4-bromophenyl)porphyrin (Br$_4$TPP) which, as in the case of Co-(5,5’-Br$_2$-Salophen) molecules, had bromine termination to act as a bond placeholder for covalent bonding. Chemical structures of the molecules used are provided in Figure 4.26. A schematic of the chemical reaction was provided in Figure 4.21.

![Chemical Structures](image)

**Figure 4.26**: Chemical structures of the Br$_2$NDI and Br$_4$TPP molecules used in this section to form covalently bound mixed chains.

Experiments presented in this section were performed at Freie University in Berlin on a custom-built low temperature, ultra-high vacuum scanning tunneling microscope. A gold single crystal cut along the [111] plane was cleaned by repeated cycles of sputtering and annealing before molecular deposition. With the Au(111) crystal held at approximately 330 K, Br$_4$TPP molecules were vapor deposited by heating a “molecular crucible” aligned with the sample to 315 °C. The next molecular species, Br$_2$NDI, were then deposited by heating their containing crucible to 285 °C. Deposition rates (and the associated deposition time) rely heavily on the
concentration of molecules in the crucible and the distance of molecular source to sample. After deposition of both molecular species, the sample was transferred into the cryogenic chamber housing the scanning tunneling microscope which lowered the sample temperature to approximately 6 K for study. Subsequent topographic imaging reveals mixed islands of Br$_4$TPP and Br$_2$NDI molecules on the Au(111) surface. As seen in Figure 4.27 the Br$_4$TPP molecules tend to nucleate on the periphery of Br$_2$NDI clusters.

![Figure 4.27: Topographic STM image of Br$_2$NDI and Br$_4$TPP molecules on a Au(111) substrate. A few of each molecular species is marked in the image. Br$_4$TPP molecules tend to nucleate at edges of clusters of Br$_2$NDI and are of lower concentration. Constant current topograph taken with applied sample bias of 1.0 V at a current of 0.1 nA and a probe scanning speed of 122.8 nm/s.]

Mixed chain and network formation on the Au(111) surface was achieved by annealing the surface to 605 K for ten minutes. A topographic image of the surface after annealing is provided in Figure 4.28. In this figure, chains and networks of chains of various lengths are observed. Chains tended to nucleate in close proximity...
to each other and at step edges. Very few isolated bromine atoms were observed on the surface. Covalent binding between the chains was checked by lateral manipulation of the chains and by voltage dependent imaging. Under lateral manipulation the chains remained intact, indicating a strong intermolecular bond. Imaging of the chains at 3 V produced pronounced protrusions centered at the suspected bond locations, as seen in Figure 4.29. These protrusions appearing near 3 V are indications of localized orbitals representing the covalent bonding as discussed by Grill et al. [83].

Figure 4.28: Topographic STM image of mixed chains of debrominated Br$_2$NDI and Br$_4$TPP molecules on a Au(111) substrate. Chains and networks tend to cluster together. Image taken with applied sample bias of 1.0 V at a feedback mediated constant current of 0.01 nA and a probe scanning speed of 122.8 nm/s.
Figure 4.29: Two topographic STM images of a mixed chain of debrominated Br$_2$NDI and Br$_4$TPP molecules. Molecular species are marked in both topographs, along with the positions of suspected covalent bond locations. Topographic imaging at 3 V reveals protrusions at the suspected bond locations. Topographic images taken with sample biases of 1 V and 3V with feedback mediated constant current of 0.01 nA and probe scanning speed of 61.42 nm/s. Images cover a lateral distance of 10.06 nm.

4.8 Conclusion

Formation of covalently linked molecular chains has been demonstrated by STM. Attempted chain formation on a Cu(111) surface of Co-Salophene molecules successfully created chains with intermolecular Cu atoms and non-covalent bonding. The chains on Cu(111) were shown to dissociate by lateral tip manipulations. Chains were formed on Au(111) by an ring coupling reaction with intermediate metal substitution, a process originally described for molecules in solution by Ullmann and Bielecki [90]. The chains were then confirmed to be covalently bound by lateral manipulation and attempted dissociations. The method of surface catalyzed bond formation was extended from linear chains of like molecules to heterogeneous networks of molecules. The most important and new feature of the results presented here is the linking of molecules containing spin-centers (central Co atoms) into macromolecular chains. Future studies may address the formation of two-dimensional networks of magnetic molecules.
5 Molecular Electronics and Spintronics

5.1 Introduction

Experimental and theoretical studies of molecular systems are highly active as of this writing. The motivations for studies are both academic, as molecular systems often exhibit emergent behavior through many-body interactions which are at the forefront of what is theoretically calculable, and practical, as molecular systems are expected to enable unique properties of nanoscale electronic circuitry such as superconductivity and spin communication. This chapter is focused on spin communication of a molecular system with cobalt ions as spin centers. By linking molecular units together, a molecular wire is produced which results in a macromolecule having spin centers which interact both through the covalent network and through surface electrons. This, it is hoped, is a significant step towards formation of larger molecular networks with well understood spin communication which may be applied to the emerging class of spintronic devices.

5.2 Background

In the following subsections, overviews of three physical properties, which may be accessed by scanning tunneling microscopy of surface adsorbed molecules, are briefly explained. Molecular orbitals exist due to the spatial and energy distribution of electrons which make up the molecules. Molecular vibrational states emerge from non-rigid interactions between the constituent atoms of molecules. Additionally the Kondo effect which emerges as interactions between localized magnetic ions and bulk conduction electrons, which is not only seen in molecular systems, is explained.
5.2.1 Molecular Orbitals

Molecular orbitals are formed through interactions between atomic orbitals having comparable symmetries to each other, which allow orbital overlap with separation of the order of bond lengths. These molecular orbitals then describe the spatial and energy distribution of electrons in molecules. An approximate description of molecular orbitals comes from the linear combination of atomic orbitals (LCAO) in molecular orbital (MO) theory. In this theory, the resultant molecular orbital wave function includes contributions from all atomic orbitals, so electrons from the individual atoms are delocalized. Bonding in molecular orbital theory occurs when the resultant combined orbitals are lower in energy than when separated into their atomic components. The resultant molecular orbitals have distinct electron energy levels that differ from the constituent atomic orbitals. It is the reduction of energy when bonding which allows molecules to be energetically favorable and thus stable.

The molecular orbitals are experimentally analogous to the surface local density of states as they result in tunneling currents that vary as the sum of the local molecular orbital density from the Fermi level to the applied sample bias. This allows, through spectroscopic measurements as described in Section 2.2.4, extraction of the approximate molecular orbital energies. For some larger molecular systems, it is possible to measure the spatial variation using the local probe methods of scanning tunneling microscopy by taking spectra at various positions on the molecule. The technique of spectroscopic mapping may also be used to visualize the spatial distribution of molecular orbital electron energy dependent density [91–95]. In spectroscopic measurement, the highest energy feature found below the Fermi level, and the lowest energy feature above the Fermi level, are most commonly labeled, respectively, the highest occupied and lowest unoccupied molecular orbitals (HOMO/LUMO). Successive features are labeled HOMO-1, LUMO+1, etc. The
gaps between measured or calculated HOMO and LUMO levels can be thought of as a band-gap similar to the band structure of semiconductors and insulators [96]. Commonly, the HOMO/LUMO features are found to have different spatial distributions over the molecule [91–93, 95], as in the case of terthiophene (3T) molecules adsorbed on Au(111) presented by Koslowski et al. [95], where the highest occupied level is found at the ends of the linear molecule and the lowest unoccupied level is most prevalent at the centers.

Direct interpretation of molecular orbitals is complicated in STM measurements by interaction between the molecule and its supporting substrate [97]. There may [53, 92, 93, 98] or may not [81, 95] be a strong coupling between the molecules and substrate, which can result in shifts of the energies and shapes of the molecular orbitals from their vacuum values. Surface interaction is also of prime importance in electron transport through molecules, as the strength of coupling between a molecular wire and electrodes partially determines conductance. Aside from surface interaction, there may also be strong interaction between molecules on surfaces. Often this can result in shifted energies due to charge transfer between molecules of the same [99] or differing species [52] of molecule. Charge transfer between molecular species also is essential to the emergence of interesting physical properties such as superconductivity from charge transfer salts [54, 100]. In molecules with unpaired electrons, certain molecular orbitals may remain spin-polarized [46, 81, 93, 101, 102] when adsorbed on a surface. Direct imaging of the spin-split orbitals is possible with spin-polarized scanning tunneling microscopic techniques.

5.2.2 Vibrational States

Within a molecule, the interatomic bond lengths and bond angles are, in the vibrational ground state, determined by a minimization of energy. The energy, as a
function of bond length, can be most simply approximated by a harmonic potential centered on the equilibrium bond length. Much like a particle in a well, there are quantized levels of energy allowed for a given interatomic bond. The harmonic parabolic potential is not optimal to describe interatomic bonds as the true potential is asymmetric and more aptly described by a Morse or Lennard-Jones potential. For polyatomic molecules, the many bonds and inter-bond angles act together in molecular modes of vibration. The vibrational energies are typically tens to hundreds of meV. Molecular vibrational modes are quite distinct between molecules of even slightly differing structure, so spectroscopic measurement of vibrational modes can be useful for molecular identification and characterization.

Spectroscopic measurement of molecular vibrations can be performed by infrared (IR) or Raman spectroscopy on a large number of the molecules in question, often in solution [103]. Molecular vibrational spectra may also be measured by inelastic electron tunneling, as first demonstrated by Lambe and Jaklevic in 1968[104]. They purposefully doped the oxide layer during growth of a metal-oxide-metal system, and measured the second derivative current response to a varied voltage by a custom designed circuit, analogous to a lock-in amplification technique. The second derivative of the current with respect to variations in the voltage should have peaks centered at the energy of the oscillatory resonance, as a new tunneling channel becomes available once electrons have an energy comparable to the vibrational energy. The line width of peaks in $d^2I/dV^2$ are thermally broadened and depend on the amplitude of bias modulation. An important consideration for these inelastic electron tunneling spectroscopy (IETS) measurements is that the molecules are situated subsurface, and so may interact with their surrounding layer in such ways as to vary the vibrational modes.
Scanning tunneling microscopy was demonstrated by Stipe et al. to enable IETS measurements of single molecules adsorbed on surfaces [23] for chemical bond identification. Single molecule inelastic spectroscopic measurements by STM methods can show sensitivity of vibrational modes to interaction with nearby molecules, surface adsorption sites, and surface defects. When a vibrational mode is excited, the tunneling electrons lose energy ($\hbar \omega$) to the excited molecule which acts to increase the tunneling current as an additional tunneling channel is opened.

5.2.3 Kondo Resonances and Their Spectroscopic Measurement

The origin of anomalous increase in resistance with decreasing temperature in some metals containing magnetic impurities was originally explained by Kondo in 1964 [105, 106] by means of a scattering model which explicitly accounts for the spin interaction of conduction electrons with localized magnetic moments attributed to the magnetic impurities. This effect is now known as ‘the Kondo effect’. At sufficiently low temperatures, conduction electrons in the supporting metal couple via an anti-ferromagnetic exchange interaction (effectively spin screening) with the localized single electron of the magnetic impurity to form a resonance state near the Fermi energy of the system, $E_F$. In 1998, the Kondo effect was first observed by STM methods for single adatoms [22, 107], resulting in renewed interest in the Kondo effect [108]. In STM experiments, the Kondo effect manifests itself as a feature in the spectroscopically measured density of states centered at the substrate Fermi level. Electrons from the tunneling tip can tunnel by competing paths (assuming no low energy inelastic vibrational channels are available at the energies probed): (path 1) directly into an unoccupied bulk state of the substrate, (path 2) into the Fermi level Kondo resonance, or (path 3) into the localized hybrid state of the magnetic adatom through a spin-flip process [109]. The resultant tunneling current is determined by
quantum interference between the two spin preserving tunneling channels (paths 1 and 2). Weak tip-sample coupling, as is typical of STM experiments, ensures that the probe does not influence the spectral signature of the Kondo system [109].

Electron scattering can probe peaks in the excitation spectrum produced by the interference of discreet states with continuum states. It was shown by Fano [110] that this interference produces an energy density spectrum $\rho(E)$ which can be described by

$$\rho(E) \propto \rho_0 + \frac{(q + \epsilon)^2}{1 + \epsilon^2}$$  \hspace{1cm} (5.1)

where $\epsilon = E - E_K/\Gamma$ and $E_K$ is the resonance energy. In the case of resonances in spectroscopic measurements appearing due to the Kondo effect, a characteristic temperature called the Kondo temperature can be extracted as $T_K = \Gamma/k_B$, with $k_B$ being the Boltzmann constant. The Kondo effect, and its spectroscopic manifestations, do not appear at temperatures above the Kondo temperature. The parameter $q$ appearing in Fano’s equation characterizes the ratio between the direct and indirect tunneling processes in the Kondo effect [111]. $q$ takes values in the range $-\infty, +\infty$ where it is a positive Lorentzian for $q = \pm\infty$, a negative Lorentzian for $q = 0$, and asymmetric for intermediate values with maximum asymmetry at $q = \pm1$ [48].

There have been many measurements of the Kondo effect by STM techniques. The Kondo effect has been observed both in systems of single adsorbed atoms [22, 47, 48, 107, 112–114] and adsorbed molecules [18, 53, 98, 115–119]. The observed Kondo features in spectroscopic measurements can take either a peak or dip line shape dependent on coupling of the magnetic impurity to surface electrons [109, 115]. For molecular Kondo systems, the measured Kondo interaction can depend strongly on the molecule adsorption site [98], on the molecule conformation [115, 116], and on the local neighborhood of molecules [18, 53, 113]. Some molecules are found to have
Kondo interaction strengths leading to Kondo temperatures above room temperature [98], while other systems exhibit stronger Kondo signatures when measured locally at the ligands of a molecule as opposed to directly above the magnetic atom [53]. Measurements of the Kondo effect also depend on the thickness of substrate films onto which the impurities are adsorbed [118, 120]. The Kondo effect, being a magnetic interaction, exhibits spin-splitting in a magnetic field [51, 121]. Interaction with the surface state electrons is questionable, as groups have claimed both strong coupling [119] and weak coupling [122]. Theoretical approximations for description of the Kondo effect frequently utilize density functional theory (DFT) with numerical renormalization group (NRG) approaches [123] and calculations which are able to match experimentally observed Fano resonances for simple (atomic) impurities [49].

### 5.3 Electronic Structure of Co-(5,5′-Br₂-Salophene) Molecules: Isolated, In Clusters, and Debrominated

In this and the following sections the electronic and vibrational structure of the Co-salophene molecules adsorbed onto a clean Au(111) surface, which were studied for chain formation in chapter 4, are experimentally measured. Spectroscopic scanning tunneling microscopic measurements of the molecules in clusters were performed, which provide some information about the electronic structure of the molecules. Spectroscopy was performed on molecules in the dipole interacting clusters first, before manual isolation of the molecules. Spectroscopic measurement over a wide (-1.5 V to 2.5 V) range for molecules in clusters show features near ±100 mV and at approximately 1.9 V as shown in figure 5.1. The ±100 mV features are labeled as the highest occupied and lowest unoccupied molecular orbitals (HOMO/LUMO), as they are nearest to the most prominent features of the calculated local density of states.
(presented later in Figure 5.6) and calculated vacuum molecular orbitals (presented later in Figure 5.7).

Figure 5.1: Topographic STM image of Co-Br$_2$-Salophene molecules in a dipole mediated cluster arrangement taken at -1500 mV. Blue dot in image is tip stabilization position for spectroscopic measurement. Spectra taken with stabilization parameter of -1.25 nA at -1500 mV. Point of the assumed lowest unoccupied and highest occupied molecular orbitals are noted.

These spectroscopic features, for measurements directly above the cobalt ion site, do not vary between molecules by any significant measure, as seen in Figure 5.2. Being more likely shoulder features rather than peaks, and being symmetrical about the Fermi energy, these ±150 mV features could also be interpreted as vibrational states (as vibrational states are symmetric, as mentioned earlier). However, the “close” match with the theoretical levels leads us to conclude that the spectroscopic features are due to molecular orbitals.

The spatial distribution of the molecular orbitals measured is sought to determine if features are localized to the molecular center. Measurements in figure 5.3 highlight the facts that the most prominent features are localized to the cobalt ion site and there is only a very slight deviation in local density of states between a molecular arm with and without bromine termination for an isolated molecule.
Figure 5.2: Spectra measured above cobalt ion site for molecules arranged in dipole interacting clusters on Au(111) surface. Primary features in the energy range observed are shoulders at \( \pm 150 \text{ mV} \) and a steep rise to a feature below \(-800 \text{ mV}\). Spectra taken at different molecule centers do not vary significantly.

Figure 5.3: Spectroscopic measurements in the \(-200 \text{ to } +200 \text{ mV}\) range over multiple positions on singly debrominated Co-Salophene molecule. Most prominent features are found when measured above the cobalt ion site.

Although point spectroscopy demonstrates that the prominent electronic features are localized to the cobalt ion (as seen in Figure 5.3), it is useful to perform
spectroscopic mapping to visualize the distribution in real space. For molecules in a cluster, a spectroscopic map was taken at 140 mV above the Fermi level, the approximate energy of the suspected LUMO feature. The results are shown in Figure 5.4, where the greatest intensity for the measured features are centered about the cobalt ion sites.

Figure 5.4: Second derivative spectroscopic map taken at 140 mV over a single cluster of Co-Salophene molecules. Comparison of the topography (left image) to the spectroscopic map (right image) shows that the most prominent features are centered about the molecular center, the cobalt ion site.

We sought to determine whether the local density of states varied as bromine terminations were removed. To do this, we constructed areas similar to that shown in figure 5.5, which allowed probe access to each variety of molecule without any probe conformation change in between measurements. This allowed the measurements of intact, as well as singly and doubly debrominated molecules presented in figure 5.6. Here an observed increase in the slope and maximum value of the local density of states above the cobalt ion for occupied levels is correlated to bromine removal. The measured trend matches well the calculated values presented as an inset to figure 5.6.

Spin-resolved density functional theory (DFT) calculations, performed by N. Baadji and S. Sanvito at Trinity College in Dublin, Ireland, reveal more of the
Figure 5.5: Topographic STM image of an area prepared by lateral manipulation of single Co-Salophene molecules out of dipole attached clusters and subsequent bromine dissociation by applied sample bias ramps. This area enables access to molecules of each state of bromine attachment and in clusters.

Figure 5.6: Spectra measured above cobalt ion site for isolated molecules and inset with calculated local density of states for comparison. Note calculated and measured match well. Small feature at Fermi level attributed to Kondo resonance as discussed in main text.

molecular orbitals than measurements alone. The cobalt ion, due to a reduced symmetry planar coordination with the nitrogen and oxygen, has its d-orbital split
into two singlets ($xz$, $yz$). As shown in figure 5.7, a representation of the calculated orbital energies, the $d^2_z$ is the highest occupied molecular orbital and the $d_{xz}$ is the lowest unoccupied molecular orbital.

Figure 5.7: Graphic of results of spin-resolved density functional theory calculations showing orbital energies and spin distributions for single intact Co-Br$_2$-Salophene molecule. Select orbitals are labeled, and highest occupied and lowest unoccupied molecular orbitals (HOMO/LUMO) are labeled. Left and right positioning is to allow more space between levels to accommodate orbital graphics. Reprinted with permission from [3]. Copyright 2012 American Chemical Society.

5.4 Kondo effect in Co-Salophene molecules in clusters, isolated, and debrominated

As observed in figure 5.6, there exists, for measurements of isolated and debrominated molecules, a spectroscopic peak centered about the Fermi level. This peak is attributed to a Fano line shape due to quantum interference between tunneling paths including directly into a Kondo resonance and directly to the surface as described in section 5.2.3. Many of the following measurements are forward and back measurements to achieve many spectra for averaging. Figure 5.8 provides an example
of the original spectroscopic data as taken with multiple forward and back sweeps of the sample bias and the resultant averaged curve.

Figure 5.8: Topographic STM image of Co-Salophene molecules in a cluster taken at 200 mV. Horizontal image size is 4.9 nm. Spectra taken above point indicated in topographic image by a red dot. The spectrum has multiple forward and backward passes which can be averaged to result in a more acceptable signal to noise ratio. Spectra were taken with an initial current for the 28 mV sample bias of 28.4 nA. Spectra were taken in constant height mode. Red line is average of all (black) forward and back spectra taken.

For a cluster of molecules, each spectrum taken is fit to the Fano line shape (Equation 5.1) in order to extract the fitting parameters of the Kondo temperature $T_K$ and a measure of the tunneling path competition $q$. The equation used for fitting is

$$CR + B \times x + a \times \frac{(q + (x - e_K)/(T_K + k_B))^2}{(1 + (x - e_K)/(T_K * k_B))^2}$$

where the parameter $CR$ accounts for a constant offset, the parameter $B$ is an approximation which accounts for a linear background, and $a$ corrects for numerical scaling of the amplitude of the measured $dI/dV$. The $q$ and $T_K$ parameters are, as discussed in section 5.2.3, the tunneling competition ratio and the extracted Kondo temperature, respectively. The parameter $e_K$ accounts for shifts of the Fano line shape from the Fermi level. Fitting of the Fano features was performed in Matlab by
a nonlinear least squares method. A single spectrum taken above a different molecule in the cluster from Figure 5.8 is shown in Figure 5.9. Fit parameters are given in the caption with included 95% confidence bounds for the Kondo temperature and $q$ value. The fit shown here was achieved for the full range of values in the spectra. Some fits only converged when the fit energy range was reduced. It is important to note that the confidence bounds for the Kondo temperature were small, less than 5 Kelvin for a 70 Kelvin Kondo temperature, indicative of the validity of the fitting procedure.

![Figure 5.9: Topographic image of Co-salophene molecules in a cluster taken at 200 mV. Horizontal image size is 4.9 nm. Averaged multiple pass spectra (black dots) taken above the indicated point in the image (red dot). Red line is a plotted Fano fit of spectra for Kondo spectroscopic feature. Extracted fit parameters are $T_K = 70.45 \pm 2.33$ Kelvin, $B = -0.0014$, $CR = 0.011$, $a = 0.00597$, $e_K = -0.04$, $q = 12.88 \pm 4$ with $k_B$, the Boltzmann constant, of 0.08617 meV K$^{-1}$.](image)

Whether the Kondo temperature varies highly between molecules in a single cluster was considered. The Kondo temperatures extracted from the fits did not vary widely from their values near 70 Kelvin, and the variations were not more significant than the confidence values given by fitting. There is significant variation in appearance of the curves, ranging from a slight protrusion at the Fermi level, as in Figure 5.8, to prominent, as in Figure 5.9. As the spectra also vary based on exact positioning of the probe over the magnetic impurity, we chose to attempt to map out the spatial variation
of the Kondo feature as was done in Figure 5.4 for the $\approx \pm 140$ mV features. Figure 5.10 shows an area constructed with a small molecular cluster and isolated intact and debrominated molecules and its corresponding second derivative spectroscopic map. The second derivative map essentially records a two dimensional matrix of the slope of the spectroscopic measurements at a selected (here -5 mV) bias. At -5 mV the slope of the spectroscopic feature should be greatest as can be seen clearly in Figure 5.9. The spectroscopic map shown on the right of Figure 5.10 demonstrates the apparent strength of the Kondo features relative to the background. It is obvious from the map that the spectroscopic signature of the Kondo effect is strongest on the center of molecules in the cluster, though not uniform throughout the cluster, and not strong enough to observe through spectroscopic mapping on the intact isolated molecule. Variations for the cluster may be due to the bromine atom adjacent to the top molecule.

Figure 5.10: A topographic image paired with its second derivative spectroscopic map taken within the Kondo feature region at -5 mV for an area constructed with cluster, isolated, and debrominated molecules. Molecular structures are included to highlight the cluster arrangement of the molecules in the topographic image. Included also are dotted red circles to highlight Kondo center locations.
As previously mentioned, the spectrum at the isolated molecule was too weak to be observed in the spectroscopic map. As it is measurable in averaged spectra, it is not clear as to whether the Kondo temperature varies between the debrominated molecules and intact, or if the observed amplitude variation is only the signal to noise ratio. Measurements were performed on the isolated molecules and molecules in clusters. The results of those measurements are presented in Figure 5.11, where the data shows that the variation between isolated, debrominated, and clustered molecules is within the error bars of each. From this it is claimed that the average Kondo temperature of Co-Salophene molecules does not depend on bromine termination or intermolecular dipole interaction in clusters. An average of all measurements yields a Kondo temperature of $\approx 65K$ for molecules prior to chain formation.

![Figure 5.11: Spectra and their associated Fano lineshape fits for local measurements above the magnetic cobalt impurity for isolated intact molecules, singly debrominated molecules, doubly debrominated molecules, and intact molecules in dipole attracted clusters. The multiple pass averaged spectra are shown with solid colored lines, while plots of the Fano lineshape fits to the Kondo resonance are plotted with dotted black. Errors given in the figure correspond to confidence intervals of 95% from Matlab curve fitting. Differences in amplitude of Kondo features are obvious, yet extracted Kondo temperatures are within 95% confidence bounds of each other.](image-url)
5.5 Co-Salophene Chain Electronic Structure

As all forms of individual molecules demonstrated Kondo interaction, it was expected that molecules in chains would also demonstrate this effect. This was found to be true, yet the Kondo interaction had a significantly altered resonance lineshape as is seen in Figure 5.12. The Kondo feature, instead of being observed as a peak as in the case of single molecules, was now manifest as a dip. This is explained as the lineshape depends largely on competition of the tunneling path, which corresponds to the tunneling ratio $q$ as described in the section 5.2.3. Here we find that decreased coupling to the surface due to formation of the chains results in a dip feature. The spectroscopic map in Figure 5.12 demonstrates that the Kondo interaction is truly localized to the molecular centers where the Co ions are situated.

To the right on Figure 5.12, it is observed that the extracted Kondo temperatures vary between positions in a single chain. Roughly, in this figure, it is seen that the feature width is widest in energy at the center of the chain and decreases towards the periphery. To test that the Kondo effect truly depends on position within the chains, measurements were taken over approximately five chains of each length encountered on the surface, up to five members in length. A sample of the measurements and the associated Kondo fits are given in Figure 5.13.

Further proof that the measured spectra relate to Kondo interactions are given in Figure 5.14, where spectra are taken along a line leading from the magnetic center. In the resultant Fano fits to the curves presented the amplitude of the Kondo feature, extracted as an additional multiplicative scaling factor, $A$ for the Fano equation (Eq. 5.1), decreases as the inverse of the distance (1/R) from the center, determined by the location having greatest amplitude. As it is known that the Kondo interaction decreases in inverse proportion to the distance from the center, this is considered strong evidence that the measured interaction is indeed due to a Kondo resonance.
Figure 5.12: In the left of this figure is a processed three dimensional representation of the topographic image of a single five-member chain overlaid with a colored second derivative map of the same region at 5 mV sample bias. The arrows in that image correspond in colors of the spectra presented at the right. In the plots to the right the dotted black line are fits of the spectra to a Fano line shape. The Kondo temperatures are given next to their corresponding curves. The corresponding unitless \( q \) fit parameters, progressing from blue to green, are 0.22, 0.18, 0.32, 0.2, and 0.012. Note that the decrease towards the Kondo feature is centered about the cobalt ion site. Reprinted with permission from [3]. Copyright 2012 American Chemical Society.

A large number of spectra such as those shown in Figure 5.13 were taken and the average Kondo temperatures were extracted for each position in each length of chain. Plotted in Figure 5.15 are the data for all measurements averaged over these Kondo chains. There is much information to be presented in this image. First, note the general trend that the Kondo temperature is greatest at the center of the chains (as was observed in Figure 5.12). Also, observe that the average temperature of the chains increases in steps only once every two additions to the length. This is most clearly seen in the right panel of Figure 5.15. This systematic increase in Kondo temperature
Figure 5.13: Multiple spectra taken over chains of various lengths. Included as red curves are the associated fits of the curves to a Fano line shape. Points in the topographic images indicate spectra positions. Only slight variation in peak widths is discernible by eye. Reprinted with permission from the supplementary information of[3]. Copyright 2012 American Chemical Society.

is interpreted as corresponding to a magnetic interaction between the chain centers, and even/odd asymmetry (that is, pairing in average Kondo temperatures between chains of length 1 & 2 and 3 & 4) is interpreted as corresponding to antiferromagnetic (AFM) coupling between the spin centers, as monotonic increase would be indicative of ferromagnetic interaction with fixed energy for each additional unit.

Spin resolved density functional theory calculations (DFT) were performed to verify the spin localization and antiferromagnetic coupling between the molecular spin centers. After removal of terminal bromine atoms the unpaired carbon atoms
Figure 5.14: To the right are spectra taken along a line leading from a spin center of one of the molecules in a two member chain shown in the lower left. Included in green are the corresponding Fano fits to the measured spectra. In the upper left are the amplitudes \((A \text{ or } a \text{ in the fits})\) extracted from the fits plotted as a function of distance from the magnetic center. Spectra positions are indicated in the topographic image by white dots. The red line in the upper left is a plot of \(1/R\), with \(R\) being the distance from the magnetic center. Reprinted with permission from [3]. Copyright 2012 American Chemical Society.

ferromagnetically couple to the localized \(d_{xz}\) electron of the central cobalt ion. When two terminal carbon atoms pair by the formation of a singlet state composed of a covalent link between their previously free bonds, the resulting state is antiferromagnetically coupled as best observed in Figure 5.16. For a three member chain, the AFM state is determined to be 7.5 meV lower in energy than the next (non-AFM) configuration. Calculations, with results reproduced in Figure 5.17, are seen to support both the localization of spin density to the Salophene unit centers as seen in the spectroscopic map of Figure 5.12, and the antiferromagnetic correspondence between the spin centers which was concluded from Kondo energy versus chain length and position presented in Figure 5.15.

Coexistence of a Kondo resonance with antiferromagnetic linking in a Kondo lattice is somewhat controversial, as the standard interpretation would claim that the
Figure 5.15: A graphic of the resulting Kondo temperature data taken from averaging individual chain measurements. Left panel shows the resonance width as a function of molecule position within chains and chain length (as colors). Note general increase with increasing chain length. Right panel has averaged temperatures for each length of chain plotted as a function of the number of units in the chain. Note even/odd pairing with increasing temperature as a function of chain length. Reprinted with permission from [3]. Copyright 2012 American Chemical Society.

Figure 5.16: DFT calculations show antiferromagnetic coupling of central Cobalt ion with terminal Carbon atom, and subsequent antiferromagnetic coupling to neighboring Cobalt ion.

Kondo spin-flip process, which causes rapid alternation of the spin of the localized magnetic moment, cannot coexist with an antiferromagnetic coupling that relies on fixed alternate spins between molecules. Still, some such as Tsukahara et al.[124] have reported coexistence of a Kondo resonance with AFM in molecular clusters.
Figure 5.17: Result of spin sensitive DFT calculations for a three member chain of S allophone molecule units. Top portion of image is view from above while bottom unit is view along Au(111) surface parallel. Results highlight both spin density localization and antiferromagnetic coupling between the molecular centers. Reprinted with permission from [3]. Copyright 2012 American Chemical Society.

with coupling through long-range surface mediated Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions. Here we described true coexistence of the Kondo interaction and antiferromagnetism, where the spin-flip process involves flipping of the complete extended molecular spin orbitals, which are unbound by any spin-orbit interaction that would energetically bind their spins to a certain state.

5.6 Summary

This chapter has presented experimental measurements and theoretical calculations of Co-Salophene-Br$_2$ molecules adsorbed on an Au(111) surface as it relates to their electronic structure and an observed Kondo effect resonance. The intact single molecules in clusters and those isolated by manipulation have highest occupied and lowest unoccupied molecular orbitals (HOMO/LUMO) at energies of $\approx \pm 150$ mV, which match well with theoretical calculations of the local density of states. These features are well localized to the site of the cobalt ion within the molecules. Comparison of intact and debrominated molecules modifies slightly the sharpness of onset of
observed spectroscopic features, and variations in the orbital density of states which are also supported by calculations. A feature found at the Fermi level is interpreted as a Kondo resonance. This feature appears as a peak for single molecules and a dip for covalently bound chains of Salophene units. Multiple measurements of the width of this peak, correlated with the Kondo temperature, were combined to determine the variation with chain length and magnetic center position. These results supported an interpretation that the magnetic centers were antiferromagnetically linked, as supported by theoretical calculations of the spin density. The Kondo effect was localized to the magnetic centers, as was best observed through spectroscopic mapping. The central impact of this chapter, then, is the observation of seemingly isolated magnetic centers with Kondo interactions that are antiferromagnetic coupled through the covalently bound organic periphery of the molecules.
6 Summary and Outlook

In the preceding chapters, scanning tunneling microscopic (STM) methods were applied to three distinct, yet important, topics. First, in Chapter 3, it was shown that by voltage dependent imaging and programmed data analysis, local surface work functions could be extracted. This was demonstrated for a defect-free surface, probe induced surface holes, and monoatomic step edges. The results demonstrated the viability of the measurement method along with the strong deviation of the work function in holes and at steps compared to the defect-free Ag(111) surface. This method can be extended easily to non-noble metal surfaces to determine the work functions that would otherwise be impossible to probe with such sub-nanometer precision. The work function plays a large role in the site-dependent adsorption of molecules, and this method allows a direct measurement of the position dependent local surface work functions.

Chapter 4 presented a complete story of chain formation on a surface by an Ullmann-type ring coupling reaction. It was demonstrated that the choice of the substrate was highly important. More importantly, this demonstrated a method of coupling magnetic ions through an organic molecular network. There are many extensions of this technique, including studies of molecules with multiple spin centers and molecules of differing types to form networks. One such covalently bound molecular mix was demonstrated. Future experiments may build from this method to form interesting spintronic complexes.

Chapter 5 presented measurements of magnetic and molecular electronic properties of the molecules of which chains were formed as described in Chapter 4. After introducing the Kondo effect, molecules measured were shown to form, through interaction between the central magnetic cobalt ions and Au(111) surface electrons, a Kondo resonance centered about the Fermi level. Observing and
controlling the magnetic properties of molecules and their interactions on surfaces is important for the progress of molecular spintronics, which is expected to result in useful devices with further development. The magnetic interactions of the single molecules appear again after chain formation. The chains, however, are found to interact antiferromagnetically, and the Kondo temperature measured by fitting the spectroscopically measured Kondo resonances increases with increasing chain length. This discovery of interaction along an organic molecular network presents an interesting path of future studies involving heterogeneous networks. In future research, molecular networks can be studied by systems such as multi-probe STM, on insulating substrates, or by transport measurements.

Future potential studies based on those presented in this document are exciting and numerous. Surface properties may be effectively characterized by the local work function measurement methods where, for complex systems, the work function can be extracted somewhat simply. Molecular chain formation has a great deal of potential where formation on differing surfaces and with different reactants can produce novel molecular networks and molecular wires. The hurdle of connecting arrays of nanoscale systems to external electronic devices has yet to be overcome. The magnetic properties of molecules has much room for study. With the difficulty in first principles measurements of molecular systems, experimental studies by STM methods remain important. Combination of the Kondo effect with spin-polarized transport and tunneling measurements can present data that is otherwise inaccessible. The use of spintronic molecular systems in functional devices relies on still more research yet to come.
References


