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NANOSCALE CROSSED-WIRE DEVICE FOR IN-SITU ELECTRICAL AND SPECTROSCOPIC CHARACTERIZATION OF MOLECULAR JUNCTIONS

A Thesis in
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by
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ABSTRACT

Considerable attention has been devoted to developing molecular-scale devices for applications in future electronic and sensing circuits. Several recent theoretical and experimental results have shown that small variations in the structure of the molecular junction (e.g., molecular conformation, contact geometry, bonding, single molecule vs. monolayer, etc.) can cause significant changes in the electrical properties of the device. Thus, the relationship between the electronic properties and the detailed structure of the junction must be understood before it is possible to use molecules in these applications.

In order to develop an improved understanding of the structure-property relationship, this thesis developed a new nanoscale crossed-wire molecular device that is comprised of a well-ordered monolayer of several hundred molecules sandwiched between a lithographically-defined bottom Ti/Au metal bottom contact and a single Au metal nanowire top contact. This molecular device structure has several attractive features. First, the single metal nanowire top contact reduces deleterious junction artifacts that can arise during the fabrication process (e.g., metal nanofilaments). Second, many devices can be integrated in parallel on the same substrate (potentially up to 100), which allows meaningful comparisons between theory and experiment. Third, the crossed-wire device facilitates variable and low-temperature current-voltage (I-V) measurements to study the dominant conduction mechanisms of different molecular junction. Finally, the device structure is amenable to Inelastic Electron Tunneling Spectroscopy (IETS) that allows a direct and \textit{in-situ} measurement of the vibronic properties that correspond to different electronic states of the molecular junctions.
Electrical and spectroscopic measurements were conducted using three different molecules. First, saturated alkanethiol molecules were investigated to evaluate the new device structure because these σ-bonded molecules with simple structure have been studied extensively in previous experiments. Second, conjugated oligo(phenylene-ethynylene) molecular wire molecules were used to study the effect of π-conjugation on the electronic properties of molecular junction devices. Last, the bistable switching properties of thiol-substituted methylated oligoaniline SAM (self-assembled monolayer) junction devices were investigated by comparing I-V characteristics and IET spectra collected in high- and low-conductance states of the junction.
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Chapter 1

Introduction

1.1 Motivation

The concept of using molecules as nonlinear electronic devices was theoretically proposed by Aviram and Ratner in 1974 [1]. They pointed out that a properly designed single organic molecule, sandwiched between two metal contacts, can show current-voltage (I-V) characteristics similar to that of a rectifying junction. Figure 1-1 shows the proposed molecule that consists of electron-donating, bridge, and electron-accepting substituents.

![Diagram of donor-bridge-acceptor rectifier proposed by Aviram and Ratner](image)

Figure 1-1: Donor-bridge-acceptor rectifier proposed by Aviram and Ratner (after [1])

In this system, a low ionization energy donor and a high electron affinity acceptor are separated by a saturated alkyl chain acting as a tunnel barrier. Under forward bias, the electrons can tunnel from the donor to the acceptor through the alkyl tunnel barrier easily, while the reverse bias conduction requires several electron volts (eV) higher bias, which results in rectifying behavior. This concept was experimentally demonstrated in 1999.
using a very similar molecule (C$_{16}$H$_{33}$Q-3CNQ) in a monolayer of Langmuir-Blodgett (LB) films [2]. In addition, several other types of molecules have been studied that could be potentially used in molecular electronics [3] [4] [5].

However, further investigations of molecular junction devices have revealed that the electronic properties are also greatly influenced by many other factors. These include the molecular conformation, molecule/electrode contact material (e.g., metal or semiconductor) and geometry [6] [7] [8], and the environment in which the molecules reside (e.g., individual molecule vs. densely packed monolayer) [9]. Figure 1-2 illustrates different possible configurations of molecular junction sandwiched between two metal electrodes.

Figure 1-2: Possible configurations of molecular junction sandwiched between two electrodes.

A variety of metals (e.g., Au, Ag, Al, Cu, Pd, Pt, etc) as well as semiconductors [10], or carbon nanotubes [11] have been used as contact electrodes. The molecule-electrode contacts can be established via either physisorption or chemisorption, depending on the types of end groups. The molecules can have different conformations and those may be
tilted, stretched, or bent between the electrodes. The number of molecules in contact can be single (or a few) or small assemblies (thousands of molecules).

In addition, in some cases, the molecular junction can contain unintended metal filaments that are induced during the fabrication process. For example, when the top-metal electrode is thermally deposited onto a self-assembled monolayer (SAM), energetic metal atoms can degrade the molecule and often penetrate through the monolayer to form metallic current paths. Since the SAM itself contains pinhole defects, this problem may remain even using low-temperature evaporation process that can reduce the thermal energy of the metal atoms. These metal nanofilaments can cause the electronic properties of the molecular junction device to be independent of the intended molecular properties [12] [13].

The inability to quantify the detailed structure-property relation has been a large hindrance in the molecular electronics field, since a minor structural change can influence significantly the electronic properties of the molecular junction [14] [15]. For example, in the case of a biphenyl molecule, wherein two phenyl rings are linked by a single C-C bond, its conductance is expected to change with the relative twist angle between the two rings. Based on the theoretical calculations, the highest conductance would be expected in the planar conformation (Figure 1-3 (A), top), while the lowest conductance would occur for a 90° twist angle (Figure 1-3 (A), bottom) [16].
A recent experiment showed this conductance variation as a function of molecular twist angle using a Scanning Tunneling Microscopy (STM) break-junction, which characterizes a single molecular junction formed by breaking a Au point contact in a molecular solution at room temperature [17]. Specifically, the conductance of a series of biphenyl molecules with different ring substitutions that alter the twist angle of the molecules decreased as the twist angle increased just as predicted theoretically.

The STM break-junction method was also used to demonstrate the conductance variation that can be influenced by different contact geometries. The statistical histogram obtained in a single 1,8-octanedithiol junction revealed two distinct sets of conductance values (20 nS and 4 nS) [6]. Theoretical calculations suggested that connections to an on-top site or a hollow site on Au(111) give a rather similar conductance (20 nS) if the electrode surface is basically planar (Figure 1-3 (B), left) [8]. In contrast, a conical arrangement of atoms, which might be present at the end of a pulled wire (Figure 1-3 (B), right), can result in a much reduced conductance (4 nS). Thus, it is likely that the two sets
of the conductance can be associated with the tunnel transport between either planar or pointed contacts.

As discussed previously, the relationships between electronic properties and detailed molecular junction structure must be understood before it is possible to use molecules as electronic devices. In order to gain better understanding, several different analytical tools and test structures have been introduced and explored. For example, a STM (Figure 1-4, top left) has been used to analyze individual (or few) molecules in vacuum, where the topography is measured by monitoring a feedback loop that maintains a constant tunneling current [18] [19] [20]. This technique is able to image and measure the transport properties of individual molecules. In addition, it can be used to characterize isolated single (or few) molecules of interest in an insulating matrix that allows one to control and study the local environment in which the molecules reside [21] [22].

Break-junction techniques have also been used to characterize single molecules (Figure 1-4, middle left). In order to fabricate the junction, a very thin metal wire is defined using lithographic techniques (e.g., electron beam lithography) on a flexible substrate. Then, the wire is placed under tensile stress using a piezoelectric actuator until it mechanically breaks into two electrodes with a certain gap (a few nanometer) [23] [24]. Alternatively, the gap can be created by electromigration, in which a large current is forced through the wire until it breaks [9] [25]. Using a STM and an electromigrated break-junction, variable temperature measurements were conducted in single molecule junctions [20] [9].
Conducting-probe atomic force microscopy (CP-AFM), a scanning probe technique similar to STM, has been used to characterize small ensembles of molecules (<100 molecules) [26] [19]. Since the probe is in direct contact with the SAM and the contact force is controlled by a force feedback loop, this tool is useful for studying different metal-molecule contacts (e.g., physisorbed vs. chemisorbed contact). Using a CP-AFM, a previous study showed the force dependent I-V characteristics in physically contacted SAM junctions (physisorbed). In contrast, the dithiolate SAM junctions (chemisorbed) showed force insensitive I-V characteristics [27]. Moreover, this method was used to show that the conductance became larger when the contact metal work function was larger [27].

Figure 1-4: Various test structures of molecular junctions. The left panel shows single (few) molecule measurements, and the right panel shows SAM junction measurements.
Ensembles of hundreds to thousands of molecules have also been characterized with top metal contacts formed using low-temperature evaporation [28], electroless deposition [29], metal-coated microspheres [30], and crossed metal wires [31] (see right panel in Figure 1-4). These test structures give stable I-V measurements, and some cases (e.g., in-nanowire [29] and nanopore [28]) could even be used to prototype electronic circuits. Many of these structures also allow variable and low (<10 K) temperature measurements in SAM junctions, which can provide further insight into the junction conduction mechanisms [32] (e.g., hopping, direct tunneling). Additionally, in-situ spectroscopic analysis, such as inelastic electron tunneling spectroscopy (IETS), can be applied in conjunction with electrical transport measurements to characterize and identify the molecular species under study by measuring the vibrational modes that are excited during measurement [33].

As an example, a nanopore device was used to show that for the case of saturated alkyl-based junctions, the conduction mechanism is direct or non-resonant tunneling (over the range of ± 1 V applied bias) [32]. Since the Fermi levels of metal contacts lie within a large HOMO-LUMO gap (~ 8 eV) of the alkanethiol molecules, electrons are expected to tunnel through the molecules directly, rather than via hopping, as illustrated in Figure 1-5. In the experiment, I-V measurements were taken over a range of temperatures from 300 K to 80 K in steps of 20 K. The Arrhenius plot (log current vs. inverse temperature) did not show any significant temperature dependence, indicating that the direct tunneling is dominant in alkanthiol SAM junctions.
In contrast to the alkyl case, different transport mechanisms have been observed in π-conjugated molecular junctions that have smaller HOMO-LUMO gaps. Selzer et al. demonstrated that the local environment (e.g., individual vs. SAM) can influence whether tunneling or a thermally activated hopping process dominates charge transport for an oligo(phenylene ethynylene) (OPE) derivative [9]. While the current through an in-wire junction (SAM) showed a temperature-independent behavior that can be interpreted as direct tunneling transport through the molecules, there was a transition from a coherent conduction at a low temperature (T<100 K) to a thermally activated sequential hopping mechanism at a temperature higher than ~ 100 K in a break junction (individual molecule). These characteristics were, in part, attributed to the different fluctuations of the phenyl rings due to the restricted torsional rotation in a closed packed SAM junction compared to that in an individual molecule junction.

As mentioned previously, IET spectroscopy at very low temperatures (< 10 K) allows one to monitor characteristic vibrational modes of the molecular junction excited

Figure 1-5: (left) Simplified band diagram of metal-molecule-metal junction. (right) Molecular structures of alkanethiol and OPE.
during charge transport through the molecule. Thereby, it confirms the presence of the molecule inside the device, as well as providing information about the vibronic structure of the molecular junction in the non-equilibrium state [34]. Specifically, when a bias is applied between two metal electrodes across a molecular junction, most of electrons will pass through the molecule from an occupied state on the left to an unoccupied state on the right without any energy loss (elastic tunneling). However, during the process, a small fraction of the electrons (<2%) also can tunnel through the junction via inelastic tunneling, and exchange energy with one or more vibrational levels of the molecule. As a result, this opens another current path at a specific bias as illustrated in Figure 1-6. The small current variation with respect to the applied bias can be detected using a standard Lock-in amplifier technique, where the peaks (d²I/dV²) in an IET spectrum correspond to the vibrational modes of molecule [35][36].

For example, using micron-diameter freestanding crossed metal wire devices, IET spectroscopy was conducted in undecanethiol (C11) and OPE molecular junctions, which have different chemical structures [33] (shown in inset of the each spectrum in Figure 1-
The measured IET spectra show several differences. The C-H stretch at 362 mV is the most prominent for the alkyl system and several backbone deformation modes can be observed at lower biases. On the other hand, the OPE system is dominated by three intense modes, assigned to $\nu(18a)$ and $\nu(8a)$ ring modes, as well as to the C-C stretch. These measurements have shown that the characteristic vibrational modes of the molecular junction can be detected by IET spectroscopy. In addition, the observed molecular vibrations have a strong transition component (either dipole or polarizability) perpendicular to the electrode surface. This suggests that the tunneling charge carriers couple more strongly to longitudinal rather than transverse modes caused by changes in the dipole or polarizability of the molecules along their direction of travel. Such a longitudinal propensity for metal-molecule-metal junctions is supported by the recent theoretical analysis of Troisi and Ratner, which was based on non-equilibrium Green’s function and density function theory methods [37].

![Figure](image)

Figure 1-7: Measured IET spectra in crossed two wire structure. (left) C11 molecular junctions. (right) OPE molecule junctions (after [33]).
As shown in the examples above, the combination of electrical and spectroscopic characterization at variable and low (< 10 K) temperatures can be used to gain insight into how electronic transport is related to molecular structure in metal-molecule-metal junctions. In particular, in-situ IET spectroscopic measurements on the same device from which the I-V data are taken can provide further information about the vibronic structure of non-equilibrium transport in the molecular junction. This information will be useful in studying bistable switching molecules, because as expected, different molecular structures can show significantly different vibrational spectra, and this can be directly correlated to the electrical properties of the molecular junctions.

1.2 Overview of the thesis

This thesis presents the electrical and spectroscopic characterization of three types of metal-SAM-metal junctions: saturated alkanethiols, conjugated OPE molecules, and bistable thiol-substituted methylated oligoaniline (OMAn) switching molecules. In order to characterize electronic properties of the junctions, a new nanoscale molecular junction device was developed, which is comprised of a SAM junction containing thousands of molecules sandwiched between a lithographically defined lower metal contact and a single metal nanowire top contact as shown in Figure 1-8. This crossed-wire molecular junction device has three main attributes. (1) The single metal nanowire top contact reduces deleterious junction artifacts (e.g., metal nanofilament) during the fabrication process. (2) It allows both electrical and spectroscopic measurements at variable and low temperature (< 4.2 K). This can provide rich information for studying the correlation...
between electrical and structural properties of the molecular junction. (3) Electrofluidic assembly [38] can be used to align the metal nanowires allowing parallel device integration (potentially up to 100). This allows for statistical analysis, and subsequently, meaningful comparisons can be made between theory and experiment. Chapter 3 describes the details of the design and the fabrication procedure of the crossed wire molecular junction device.

Figure 1-8: (left) Schematics of crossed-wire molecular junction device. (right) FESEM image of the device.

Using this new structure, electrical and spectroscopic measurements were conducted on three types of molecular junctions. First, saturated alkanethiol molecules are investigated to evaluate the new device structure in Chapter 4, since these molecules have been studied extensively in previous experiments and they have a simple molecular structure. Second, OPE molecules are used to study the effect of \( \pi \)-conjugation on the electronic properties of the metal-SAM-metal junctions in the crossed-wire device. Last, in Chapter 5, the intriguing bistable switching properties of OMA \( \text{S} \) SAM junctions, whose characteristics were initially reported by Cai et al. using an in-nanowire structure
In-situ spectroscopic measurements were used to monitor the vibrational modes of the switching molecule to develop an improved understanding of the molecular structure changes in high and low conductance states. In Chapter 6, conclusions of this thesis work and future work are presented.

1.3 References


Chapter 2

Theoretical Background

2.1 Electronic transport in molecular junctions

A molecular junction consists of at least two entities: the molecule and the electrode. In its simplest form, a molecule is sandwiched between two metal electrodes that the electrons tunnel through from one to the other electrode under the bias. Figure 2-1 shows a simplified energy band diagram of a metal-molecule-metal junction.

![Energy band diagram of a metal-molecule-metal junction](image)

Figure 2-1: Energy band diagram of a metal-molecule-metal junction

The two metal contacts are represented by continuous electronic energy levels filled with electrons up to the Fermi level. The molecule is represented by its highest occupied molecular orbital (HOMO) level and its lowest unoccupied molecular orbital (LUMO) level. The location of the Fermi level in the molecule determines the height of the tunnel barrier, which is placed in the HOMO-LUMO gap [1]. However, generally, the absolute
location of the Fermi level in the molecular junction is unknown. Instead, the relative alignments of the HOMO and LUMO to the Fermi level of the electrodes are considered. These can be determined by surface spectroscopic techniques, such as photoemission spectroscopy [2].

Several factors determine the current-voltage (I-V) characteristics of molecular junctions, including the molecule length, molecular conformations, and the HOMO-LUMO gap. Furthermore, as discussed in Chapter 1, charge transport can be also influenced by the bonding geometry of the molecule-electrode contact and the environment of the junction (inter- and intra-molecular interaction) [3] [4]. Extensive theoretical analysis has been conducted to explain the charge transport mechanisms that are correlated to molecular length, temperature, and tunneling electron-phonon coupling dependences. Such as, in solid state molecular junctions, coherent tunneling transport occurs in short-chain alkanes [5], while hopping in single-nitro oligo(phenylene-ethynylene) (NOPE) junctions [6].

This chapter provides an overview of electronic transport mechanisms in metal-molecule-metal junctions. It includes the coherent and incoherent tunneling that will be used for interpreting experimental data in the remainder of this thesis. A brief description of the inelastic electron tunneling spectroscopy (IETS) technique is presented later in this chapter, which can provide useful information for studying the vibronic features of the molecular junctions.
2.1.1 Coherent charge transport

In coherent tunneling, electrons are transported from one electrode to the other without strongly interacting with the vibrational modes of the molecule. Thus, their initial energy and phase information are maintained during the process. Direct (or elastic) tunneling is an example of a coherent charge transport. On the other hand, incoherent effects arise when the tunneling electrons interact with the molecule (electronic or vibrational degrees of freedom) and/or its environment. These coupling effects cause energy loss and/or decoherence (loss of phase information). More details of the incoherence are described in the next subsection.

Coherent tunneling can be categorized into two types: non-resonant tunneling and resonant tunneling. Coherent non-resonant tunneling occurs when the electronic states of the molecule are far away from the energy of the tunneling electrons. In this case, the rate of electron transport is exponentially dependent on the length of the molecule. In contrast, coherent resonant tunneling occurs when the energy of the tunneling electrons is in resonance with the electronic states of the molecule, so that the rate of electron transport is independent of the length of the molecule [7].

Coherent tunneling is expected to dominate electron transport in most short (a few nanometer) molecules with a large HOMO-LUMO gap (a few eV). Tunneling electrons do not reside on the molecule long enough to initiate a strong interaction with the vibrations of the molecule (i.e., the electrons do not ‘see’ the molecule) [8] [9]. Current flow due to the coherent tunneling can be described by the Landauer model [8] [10] [11].
[12]. Using the framework of scattering theory, the model (Figure 2-2) treats the molecule as a scatterer for the incoming electrons.

The conductance \( g \) is related to the transmission probability of the scattering events in metal-molecule-metal junction, as shown in Equation 2.1, where \( e \) is the charge of an electron, \( h \) is Planck’s constant, and \( T \) is the transmission function that reflects the efficiency of electron transmission from one contact to the other.

\[
g = \frac{2e^2}{h} T
\]  

Equation 2.1

The transmission function \( T \) can be roughly divided into three components as shown in Equation 2.2: \( T_{le} \) and \( T_{re} \) give the efficiency of charge transport across the left and right contacts, and \( T_{mol} \) reflects the charge transport through the molecule [12]. In case of coherent and non-resonant tunneling, the molecule can be treated as a rectangular barrier with a width of \( d \). The tunneling decay parameter \( \beta \) is in units of \((\text{length})^{-1}\).
In practice, this model has been used to explain charge transport of simple molecules, such as saturated alkanethiols. Due to the large HOMO-LUMO gap (about 8 eV) of the alkanes, the metal-molecule-metal junction is expected to be in the coherent limit. For example, experiments conducted using several different device structures have shown that the current decreases exponentially with increasing molecule chain length ($d$), following Equation 2.2 [13] [14] [5]. By measuring current as a function of length, the decay parameter ($\beta$) for alkane junctions was typically found to be around 1 Å⁻¹.

Equation 2.2 also indicates that the direct tunneling does not have any dependence on temperature. This was demonstrated using a nanopore device [15]. In this experiment, I-
V measurements were conducted over a sufficiently wide range of temperatures (300 K – 80 K) with a step of 20 K. The Arrhenius plot (log current vs. inverse temperature) did not show any significant temperature dependence as illustrated in Figure 2-3.

Note that the Landauer transmission model using a rectangular barrier picture can provide general explanation of the coherent charge transport in metal-molecule-metal junctions (e.g., length dependence, temperature dependence). However, the detailed electronic structure of molecular junctions must be described by a quantum mechanical approach (e.g., non-equilibrium Green’s function) [16], which will be used in a description of IET spectroscopy later in this chapter.

**2.1.2 Onset of incoherence and hopping transport**

Sufficiently strong interaction between a tunneling electron and the molecule can lead to loss of coherence and a change to incoherent charge transport. Such interactions depend on the contact time that the tunneling electron has with the molecule. For
example, in case of off-resonance tunneling, the traversal time ($\tau$) for a particle of mass $m$ and energy $E_R$ to tunnel through a rectangular barrier of height $U$ and width $W$ is given by Equation 2.3 [17]. This contact time is modified for a molecule that has $N$ equivalent sites (1-dimensional lattice) within the molecule and a barrier height ($\Delta E$) separating the electrostatic potential of the electrode from the appropriate frontier orbital energy on the molecule (see Figure 2-4) [18]. The current ($I$) of this barrier height ($\Delta E$) is given by Equation 2.3, where $k_B$ is Boltzmann constant, $T$ is temperature, and $V$ is an applied bias [5].

\[
\text{Rectangular barrier: } \tau = \sqrt{\frac{m}{2(U - E_R)W}}
\]

\[
\text{Molecule with } N \text{ subunits: } \tau = \frac{Nh}{\Delta E}
\]

\[
\Rightarrow I \sim V \exp\left(\frac{-\Delta E}{k_B T}\right)
\]

**Example**

- (a) $N = 1, \Delta E = 4eV$: $\tau = \frac{Nh}{\Delta E} = \frac{1 \cdot (6.58 \times 10^{-16} eV \cdot s)}{4eV} \approx 0.2 \text{fs}$  
  (short contact time; weak interaction)

- (b) $N = 5, \Delta E = 1eV$: $\tau = \frac{Nh}{\Delta E} = \frac{5 \cdot (6.58 \times 10^{-16} eV \cdot s)}{1eV} \approx 3 \text{fs}$  
  (contact time increased)

For a molecule with small $N$ and large $\Delta E$ (example (a) above), the electron-molecule interaction time is in the sub-femtosecond range, implying that the electron-vibration interaction has a weak effect. Under this condition, one expects coherent tunneling to be
dominant. As $N$ increased and $\Delta E$ decreased, the contact time increases. When the contact time becomes comparable with the timescale of some of the molecular motions (10 fs – 1 ps), inelastic events (energy transfer or dephasing) become more important and coherent tunneling becomes less probable [8]. At the onset of the incoherent process, an electron traversing the molecule can be localized for a short time before moving to the next localized site on the molecule. In this limit, hopping is expected to replace coherent tunneling as the dominant transport mechanism as illustrated in Figure 2-4.

This transition has been observed in a junction containing a single (or few isolated) NOPE molecule(s) as shown in the Arrhenius plot in Figure 2-5. Coherent tunneling dominates at low temperature (< 100 K). A transition occurs from this direct tunneling to an activated hopping (incoherent process) above 100 K, as indicated by the strong temperature dependence. This was attributed to the decreased electronic coupling between adjacent phenyl rings, initiating dephasing. Thus increased temperature allows sequential hopping to become a more efficient mechanism of transmission than direct tunneling. On the other hand, in the case of the same molecule assembled in a densely-packed monolayer, a higher barrier to torsional rotation suppresses the transition to
hopping even at temperatures as high as 300 K, and the monolayer conducts by coherent tunneling as shown on right of Figure 2-5.

Inelastic Electron Tunneling Spectroscopy

Inelastic electron tunneling spectroscopy (IETS) is an *in-situ* spectroscopic technique for measuring the vibrational energies of molecules. First demonstrated by Jaklevic and Lambe in 1966, this technique has been long used in surface science to extract vibrational and electronic spectroscopic information about metals, insulators, and adsorbates [19] [20] [21]. Recently, this technique has been applied in molecular electronics for identifying the molecules participating in charge transport as well as studying their vibronic structure in conjunction with theoretical calculations [22]. This section will provide a general description of the IETS technique and the theoretical approach to interpret the IET spectra in molecular junction devices. A detailed
description of the experimental setup and the measurement results will be presented in Chapters 3-5 of this thesis.

2.2.1 Inelastic Tunneling

As discussed in Section 2.1, in non-resonant coherent tunneling, most of the electrons in the occupied states of one electrode tunnel through the molecular junction to the unoccupied states of the other electrode without any energy loss (elastic tunneling). However, during the process, a small fraction of the tunneling electrons (<2%) interact with the molecule, inducing an excitation of certain molecular vibrational modes. IET spectroscopy is based on this inelastic interaction, which introduces an active inelastic channel at the specific energy associated with each mode as shown in Figure 2-6.

![IETS process schematics](image)

Figure 2-6: IETS process schematics

When the applied voltage is less than $\frac{\hbar \omega_\alpha}{e}$ ($\hbar$: Plank constant; $\omega_\alpha$: frequency of the molecular vibrational mode $\alpha$; $e$: electronic charge), the inelastic channel is closed because the final states are already filled. At the bias $V = \frac{\hbar \omega_\alpha}{e}$, the inelastic channel
opens due to the excitation of the vibrational mode $\alpha$. Further increases in $V$ result in additional possible final states with an associated increase in current every time a new inelastic channel opens.

Since only a minority of electrons (<2%) are involved in the inelastic tunneling process, the current change is too small to be seen in a simple I-V plot. By taking derivatives, its change can be observed as a step in the 1$\text{st}$ derivative and as a peak in the 2$\text{nd}$ derivative (Figure 2-7). Overall, the graph of $V$ vs. $\frac{d^2I}{dV^2}$ provides information on the vibrational levels of the molecular junction [23] [22] [24] [25]. The width of the peak depends on temperature ($\sim 3.5$ T cm$^{-1}$ K$^{-1}$), thus IET spectroscopy is most often performed below 10 K.

![Graph showing IETS signal](image)

**Figure 2-7**: Model IETS signal. Additional inelastic channel can be detected as a peak in a plot of $\frac{d^2I}{dV^2}$ versus $V$. (after [22])

### 2.2.2 Comparison to IR and Raman Spectroscopy

IETS data are frequently compared to those obtained from the conventional spectroscopic techniques (e.g., infrared (IR), Raman, and high-resolution electron-energy-loss (HREEL) spectroscopies), which also measure the vibrational energies of
molecules. However, such optical spectroscopies follow their own selection rules, because absorbed phonons induce certain transitions between the energy states of the molecule, resulting in only certain vibrational modes being active [21] [22]. For example, IR spectroscopy detects a molecular vibrational mode only if the dipole moment of the specific mode changed. The asymmetric stretch in carbon dioxide (CO$_2$), for instance, is IR active, but not the symmetric stretch because the change in net dipole moment is zero, as illustrated in Figure 2-8 (top) [26].

![Figure 2-8: (top) IR active. (bottom) Raman active.](image)

On the other hand, to be Raman active requires a change in polarizability of the molecule produced by a change of the dipole moment with distance. The symmetric stretch in CO$_2$ is Raman active, because the stretching and contraction of the bond change the interactions between electrons and nuclei, thereby changing the molecular polarizability (Figure 2-8 (bottom)). Notice that this Raman active mode is not IR active. In general, for highly symmetric polyatomic molecules, the bands (vibrational modes) can be observed in the IR spectrum, but not in the Raman spectrum (and vice-versa). In
molecules with little or no symmetry, modes are likely to be active in both IR and Raman spectroscopy. Thus, it is likely that the IR and Raman spectroscopy can provide complementary and/or confirmatory information to each other on the same molecule.

The selection rules arise in these optical spectroscopies (IR, Raman) because the wavelength of light is very long relative to the size of molecules. However, in IETS, a small fraction of tunneling electrons (<2%) interact with the molecule, which opens an active inelastic channel at the specific energy associated with each vibrational mode [21] [22]. Thus, the spectroscopy is attributed to the vibronic modification of the electronic levels between the two electrodes, which can allow one to obtain the complete vibrational spectra of molecules including the optically forbidden transitions in IR and Raman spectroscopies. For example, Figure 2-9 illustrates a comparison of the results obtained from IETS, Raman, and IR of the same species, pentacyanopropenide ion (PCP-) that is shown in the inset of the figure. The bias voltage used in IETS is converted to the more conventional wavenumber through the factor of 8,066 cm$^{-1}$V$^{-1}$[25].
The IET spectrum obtained at 4 K has a similar number of bands (peaks) to that of the Raman, but is more uniform in intensity. On the other hand, the IR spectrum shows fewer strong bands but similar line width as in the IETS. The broad feature near 900 cm⁻¹ in the tunneling spectrum may be due to Al-O motion in the oxide barrier of the contact electrode. Overall, it is likely that the IET spectrum contains the bands observed in both IR and Raman spectroscopy with the different intensity distribution in this particular case.

However, it should be noted that, in some cases, the IETS may exhibit markedly different spectra that is not just a simple linear combination of conventional optical spectroscopies [21] [22]. Unlike the samples for those optical spectroscopies, IETS

---

**Figure 2-9:** Comparison of (a) IETS, (b) Raman (power), and (c) IR (in KBr) of the CsPCP (after [27])
requires two contact electrodes to sandwich the molecule of interest between them. It may introduce steric effects, which can change the conformation of the molecules. In particular, the IET spectra of a few nm-thick molecular junction can be strongly influenced by the coupling between the molecule and the electrode and the contact geometry of the junction (e.g., end-group, orientation, etc) that may modify the electronic structure of the molecule. Thus, the peak (i.e., vibrational mode) assignment and interpretation of the IET spectra is not trivial. A complete interpretation can be achieved by numerical approaches, such as quantum mechanical calculations [16]. The next section provides a brief overview of a theoretical model for IETS in molecular junctions.

2.2.3 Theoretical Model for IETS in Molecular Junction Device

The Landauer formula described in the previous Section 2.1.1 can provide a general formalism for the theoretical description of IETS [8] [10]. Using the framework of scattering theory, the model treats the molecule as a scatterer for the incoming electrons, and the current is related to the transmission probability of the scattering event. However, instead of using a rectangular barrier picture as before, the transmission function, $T(E)$, is described by non-equilibrium Green’s function/density functional methods. The inelastic current is then expressed as a perturbative derivation from the elastic current. Specifically, the elastic conductance ($g^{el}$) and the current ($I^{el}$) can be written as Equation 2.4 and Equation 2.5, respectively, following the Landauer-Imry approach:
where \( g_c \) is the quantum conductance \((2e^2/h = 1/12.8 \, k\Omega)\), \( \Gamma^{L(R)} \) are the imaginary part of the self-energy matrices coupling the molecular ends with the left (or right) electrodes, \( G \) is the retarded Green’s function, \( H \) is any electronic Hamiltonian describing the molecule and the electrodes, \( e \) is charge of an electron, and \( f_{L(R)} \) is the Fermi distribution function.

The inelastic components can be easily derived from the elastic components above using perturbation theory under the following assumptions:

(1) The molecule is in its ground vibrational state (low temperature limit).

(2) The conductance of the molecule is much smaller than the quantum conductance.

(3) The electrodes are at equilibrium during the measurement.

With the assumptions above, the Green’s function matrix elements, which are parametrically dependent on the set of normal vibrational modes, can be expanded using a Taylor series around the equilibrium position of \( \{Q_\alpha \} = 0 \) as shown in Equation 2.6.

\[
G_{ij}^\alpha (E, \{Q\}) \equiv G_{ij}^\alpha (E, 0) + \sum_\alpha \left( \frac{\partial G_{ij} (E, \{Q_\alpha \})}{\partial Q_\alpha} \right) Q_\alpha
\]

\[
G_{ij}^\alpha = \frac{\sqrt{2}}{2} \left( \frac{\partial G_{ij} (E, \{Q_\alpha \})}{\partial Q_\alpha} \right)_{\{Q_\alpha \}=0}
\]
Thus, the inelastic conductance \( g_{\text{inel}} \) and the current \( I_{\text{inel}} \) due to the inelastic channel involving the vibrational mode \( \alpha \) are given by Equation 2.7 and Equation 2.8, respectively.

\[
g_{\alpha \text{inel}} (E) = g_c \text{Tr} \left( \Gamma^L (E) G^\alpha (E) \Gamma^R (E - \hbar \omega_\alpha) G^\alpha (E)^+ \right) \quad 2.7
\]

\[
I_{\alpha \text{inel}} = \int_{-\infty}^{+\infty} \frac{g_{\text{el}} (E)}{e} f_\alpha (E) [1 - f_\hbar (E - \hbar \omega_\alpha)] dE \quad 2.8
\]

It should be noted that Equation 2.8 implies that the inelastic channel \( \alpha \) opens when the applied bias is equal to \( \hbar \omega_\alpha \) and it stays open for larger bias. Overall, the total current through the molecular junction can be expressed as a combination of the elastic and inelastic components as in Equation 2.9.

\[
I = I^\text{el} + \sum_{\alpha} I_{\alpha \text{inel}} \quad 2.9
\]

Therefore, a plot of \( d^2 I/dV^2 \) versus \( V \) will show a peak when \( V = \hbar \omega_\alpha / e \) and the area under the peak is \( g_{\text{inel}} \). Consequently, the integrated intensity \( W_\alpha \) of the peak due to mode \( \alpha \) in an IETS spectrum can be expressed as Equation 2.11 and Equation 2.10 below.

\[
W_\alpha = \frac{\hbar \omega_\alpha}{e} \int_{-\infty}^{+\infty} \left( \frac{dI_{\alpha \text{inel}}}{dV} \right)_{V = \frac{\hbar \omega_\alpha}{e} + \Delta V} - \left( \frac{dI_{\alpha \text{inel}}}{dV} \right)_{V = \frac{\hbar \omega_\alpha}{e} - \Delta V} \quad 2.10
\]

\[
W_\alpha = g_c \text{Tr} \left( \Gamma^L (E_F) G(E_F) \Gamma^R (E_F) G(E_F)^+ \right) \quad 2.11
\]

The Equation 2.11 provides an essential formalism for calculation of the IETS peak intensity, which can be compared to experimental data. However, there are a variety of approaches to describe the retarded Green’s function \( (G) \) and self-energy matrices \( (\Gamma^L/R) \) [28]. These approaches are rather complex and are outside the scope of this primarily experimental work.
2.2.4 Propensity rules for IETS

As discussed in the Section 2.2.2, IET spectroscopy does not follow rigorous selection rules, such as those seen in other vibrational spectroscopies (e.g., IR, Raman). However, it appears that selection preferences can be applied in the IET spectra features. A recent theoretical work by Troisi and Ratner [28] proposes a practical set of propensity rules based on a consideration of the molecular symmetry and the topology of the molecule in the junction. Since the detailed calculation and proof can be found elsewhere [28] [29] [30], a few primary results will be summarized in this section.

Linear symmetric tight binding chain

Figure 2-10 illustrates an idealized symmetric molecule described by four atomic orbitals (black dots). The ends of the molecule (atoms 1 and 4) are contacted to the left and right electrode (rectangles).

![Figure 2-10: Idealized (a) symmetric mode and (b) asymmetric mode (after [28])]()
atoms 2 and 3 along their bond length. The propensity rules suggest that only the symmetric vibrational mode (Figure 2-10, a) is allowed in IET spectroscopy.

Branched symmetric tight binding chain (one contact)

The propensity rules for the linear symmetry above can be expanded to the chain of atoms that contains branches or loops as long as there is a single atomic orbital interacting with each electrode. For example, Figure 2-11 illustrates three vibrational modes when atoms 1 and 6 are contacted to the left and right electrodes. All three vibrational modes can be observed in IET spectroscopy, since these modes satisfy symmetry with respect to the C₂ axis.

Figure 2-11: Branch symmetric (after [28])

However, the intensity of each mode in IET spectra can be different. Since the atom 1 and 6 are connected to the electrodes, the vibrational mode in Figure 2-11 (f) is in the most favorable transmission path. On the other hand, the vibrations in Figure 2-11 (d) and (e) are in the sideway directions, which do not influence the main tunneling path.
Thus, the vibrational signal of Figure 2-11 (f) can be stronger than those of Figure 2-11 (d) and (e) in IET spectroscopy.

Symmetric tight binding chain (more than one contact)

The conductance is the sum of the contributions of tunneling channels, including the channel due to the coupling of the left and right electrodes. For example, Figure 2-12 shows the symmetric and antisymmetric cases with two sites in contact with each electrode. Atom 1 and 6 are in contact with the left electrode, while atoms 4 and 5 are in contact with the right electrode.

Figure 2-12: (g) Symmetric and (h) anti-symmetric modes (after [28])

According to the propensity rule above, the antisymmetric vibrational mode (Figure 2-12, Left) is not allowed. However, the existence of more than one tunneling path allows the antisymmetric modes to be detected as a weak signal. While this mode can be observed in IETS, it should be noticed that the symmetric mode (Figure 2-12, g) will be much stronger.
In conclusion, these proposed propensity rules may be used to predict which molecular vibrations are expected to dominate the IET signal for a given binding geometry and molecular configuration, and thus guide interpretation of experimental results.

2.3 References


Chapter 3
Experimental Method and Control Measurement

3.1 Crossed-wire molecular junction device

One of the most fundamental issues to be addressed in molecular electronics is the relationship between the electronic properties of the device and the structural properties of the junction (e.g., molecular conformation, bending, tilting, bonding geometry to the electrode, individual molecule vs. monolayer, etc.) [1] [2] [3] [4]. As discussed in Chapter 1, several recent theoretical and experimental results have shown that seemingly minor structural variations can cause significant changes in the electrical properties of a molecular junction device. To develop an improved understanding of this structure-property relationship, several different approaches have been developed to study single [5] [6] [7] [6] or small ensembles [8] [9] [10] [11] of molecules sandwiched between two conducting electrodes. In particular, considerable attention has been devoted to studying the electronic and vibronic properties of metal-molecule-metal junctions to characterize the mechanisms that dominate conduction in the devices.

A new nanometer-scale crossed-wire molecular junction device developed during this thesis work provides a robust platform that allows both electrical and spectroscopic characterization at variable and low temperatures (300 to 4.2 K). As depicted in Figure 3-1, the device is comprised of a self-assembled monolayer (SAM) of molecules with end-groups that are chemically bonded to two metal contacts. In this thesis, optical
photolithography and metal liftoff were used to pattern 60 nm- or 1.5 μm-wide bottom thermally-evaporated Ti/Au contact electrodes (purple) on a thermally-oxidized silicon substrate. Single ~220 nm-diameter Au nanowires were then electrofluidically aligned [12] between pairs of large-area electrodes (yellow). The aligned nanowires served as the top contact of the junction.

Figure 3-1: Schematic illustration of a crossed-wire molecular junction device. The structure is comprised of a lithographically-defined 60 nm-wide Au bottom contact and a ~220 nm-diameter Au nanowire top contact. The diagram on the right shows the metal-molecule-metal junction (not to scale).

As outlined in Table 3-1, the new device structure provides several noteworthy features. First, unlike many other molecular electronic junctions, the crossed-wire device does not use evaporated metal to form the top contact. Instead, it forms a physical or chemically-bonded contact (depending on the molecule end-group) with the smooth surface of the assembled metal nanowire, which may prevent damage of the SAM that occurs during evaporation of top metal contacts (e.g., nanofilaments, see Chapter 1). The work presented in this thesis uses Au metal for both the bottom and top contacts.
However, the top electrodeposited nanowire contacts can be easily changed to other metals such as Ag, Pt, Pd, Cu, etc. Second, since a large number of devices can be integrated onto the silicon substrate in parallel, large numbers of devices can be measured and compared. Third, the crossed-wire device allows variable and low temperature measurements (300 to 4.2 K) to investigate the dominant conduction mechanisms and vibronic properties of the molecular junction device.

The next section will provide details of the device fabrication. This will be followed by a discussion of the electrical and spectroscopic characterization methods, including the measurement setup.

<table>
<thead>
<tr>
<th>Table 3-1: Key features of crossed-wire molecular junction device</th>
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<tbody>
<tr>
<td>1. Metal nanowires form top contact.</td>
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<tr>
<td>2. Low and variable-temperature measurement.</td>
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<tr>
<td>3. Parallel integration allows device-to-device comparisons.</td>
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</table>

### 3.2 Device Fabrication

Table 3-2 outlines the main steps that were used to fabricate the crossed-wire molecular junction device. First, metal nanowires were electrodeposited within the ~220 nm-diameter pores of an anodic aluminum oxide (AAO) membrane. Second, pairs of large-area alignment / probe electrodes and bottom contact electrodes were patterned on a thermally-oxidized silicon wafer using optical and/or electron-beam lithography followed by metal liftoff of a thermally-evaporated Ti/Au thin film layer. Third, the molecular monolayer was assembled from solution onto the bottom metal contact electrode, and the
nanowire top contacts were electrofluidically aligned to complete the junction fabrication. Immediately following fabrication, all of the devices were inspected using a light- and dark-field optical microscopy to select the devices that had single nanowire top contacts. The devices were loaded into a high vacuum (~10^{-6} Torr) cryogenic probe system for electrical and spectroscopic characterization. The following sections describe the details of each step.

Table 3-2: [PROCEDURE] Fabrication of a crossed-wire molecular junction device

1. Synthesize metal nanowires
2. Fabricate bottom electrode with pairs of alignment / probe electrodes
3. Assemble SAM
4. Align nanowire on SAM
5. Inspect and load into vacuum probe station

### 3.2.1 Template synthesis of metal nanowire

Nanowires were synthesized by electrodepositing metal into the pores of commercially-purchased AAO membranes (Anodisc, SPI ; ~10^{11} pores/cm^2, 60 µm-thick) [13] [14] [15]. Figure 3-2 illustrates the procedure used to grow the Au nanowires (8 to 12 µm-long and ~220 nm-diameter) used in the crossed-wire device. A 300 nm-thick silver layer was thermally evaporated onto the branched side of the membrane to form the cathode (working electrode) for electrodeposition. A Pt mesh connected to a Pt wire was used as an anode (counter electrode), and an Ag/AgCl electrode was used as a reference electrode. The electrochemical cell was completed by clamping a glass tube with an “O”-ring seal onto top of the membrane.
The disordered pore openings on the branched side (~1 µm long) of the membrane were filled with electrodeposited Ag metal. Then, 8 to 12 µm-long straight Au nanowire segments were grown using a potentiostat (EG&G PAR M273) that supplies a constant current to the electrochemical cell. Although the current and time for this
nanowire synthesis must be adjusted depending on the diameter of the membrane and the desired length of the nanowires, the conditions of -2.5 mA (~ 1 hour) for a 2 µm-long Ag segment and -1.6 mA (~5 hours) for 10 µm-long Au segment were found to be good starting parameters for a 25 mm-diameter membrane. Following growth, the nanowires were released by selectively dissolving the Ag segments and the AAO membrane in 5 M HNO₃ (~ 5 min) and 0.5 M NaOH, respectively. The nanowires were then rinsed with DI water several times, and dispersed in ethanol for device integration.

### 3.2.2 Fabrication of Bottom Electrodes

Parallel integration of the crossed-wire junctions was done on a field-by-field basis, where each field contained 100 pairs of interconnected large-area alignment / probe electrodes with a separate 60 nm or 1.5 µm-wide bottom contact electrode centered between them. In order to preferentially align single nanowires between each large-area electrode (100 × 300 µm²), the electrode design included a sharp tip (6 × 1.5 µm²) that concentrated a large electric field in the gap between the tips. As shown in Figure 3-3, a 3-inch diameter silicon substrate contained 24 fields. Thus, 2400 potential molecular junction devices were fabricated on a single substrate.
Fabrication began with a wet thermal oxidation of the silicon substrate to provide electrical isolation of the individual molecular junctions. Following growth of a 1 µm-thick oxide, pairs of interconnected nanowire alignment/probe electrodes with 3 µm-wide gaps as well as alignment marks for subsequent electron-beam lithography of the central contact electrode were patterned on the oxide surface using a double-layer optical contact lithography process (0.3 µm PMGI (polymethylglutarimide) and 1 µm 1811 (N-Methyl-2-Pyrrolidine) photoresist). Then, a Ti(10 nm)/Au(50 nm) layer was deposited in a thermal evaporator at a base pressure of $7 \times 10^{-7}$ Torr, and the metal on top of the undeveloped photoresist was lifted-off. Using the first level alignment marks, the bottom metal contact electrodes were aligned and patterned using an electron-beam lithography system (Leica EBPG-5HR). The critical 60 nm-wide lines were defined in a 120 nm-thick layer of polymethyl methacrylate (PMMA, Anisol 950K) with a beam spot size of 20 nm, a beam current of 720 pA, and an extraction voltage of 100 kV. Following patterning, a second Ti(10nm)/Au(50nm) layer was thermally evaporated using a slow deposition rate.

Figure 3-3: Left, fabricated on a 3-inch silicon substrate, showing alignment and lower electrodes. The wafer contained 24 fields and each field contained 100 potential devices.
of 1.5 Å/s and lifted-off. This typically leaves one to three Au grains spanning the width of the electron-beam defined electrodes.

Unlike the double-layer optical lithography processes, in which the re-entrant profile due to undercutting of the photoresist prevents metal deposition on the resist sidewall, the single layer method has been shown to cause flagging of the lifted-off metal film at the edges of the features. However, cross-sectional field emission scanning electron microscope (FE-SEM) images of many bottom contact electrodes fabricated using single- (Figure 3-4, left) and double-layer processes (Figure 3-4, right) do not show evidence of metal flagging. It is important to note that prior to molecule self assembly, an aqueous cleaning process (NH₄OH:H₂O₂:H₂O = 1:1:5; RCA-1) was done on the bottom electrodes. As shown in atomic force microscope (AFM) image of Figure 3-14, the grains of the as-deposited Au metal were etched slightly during the cleaning process, which gave a smoother metal surface. This cleaning process could have removed metal flags that were present along the edges of the features because both sides of the flagged metal would have been readily attacked in the chemical etchant.
Figure 3-5 (right) shows a FE-SEM image of a 60 nm-wide bottom contact electrode centered between two large-area alignment/probe electrodes with a 3 µm-wide gap. The central Au contact electrode is also connected to two large-area probe electrodes (not shown on the FE-SEM images) that allow electrical measurements of individual molecular junctions in each field.

Figure 3-5: FE-SEM images show lithographically defined lower electrodes that are 1.5 µm (left) and 60 nm-wide (right).

Alternatively, wider bottom contact electrodes were fabricated on other substrates using optical contact photolithography. The FE-SEM image in Figure 3-5 (left) shows a 1.5 µm-wide bottom contact electrode centered between large-area electrodes with a 3 µm gap. It should be noted the surface roughness (i.e., grain structure) of the bottom contact electrodes may cause significant device-to-device variations in the measured current, which will be discussed at the end of this chapter.

### 3.2.3 Self-Assembly

Depositing a densely-packed and well-ordered monolayer of molecules onto a substrate can be achieved by either the Langmuir-Blodgett (LB) technique or through the
self-assembly method. The LB technique uses molecules with hydrophilic “heads” and hydrophobic “tails.” By laterally compressing the molecules at an air-water interface, a dense monolayer can be formed and transferred onto a conducting substrate [16]. Although this approach can provide good control of the surface coverage, the electrostatic interaction between the molecule and the contact is generally weak.

On the other hand, the self-assembly method allows the formation of molecular monolayers by selective covalent attachment of the molecule’s end group to specific materials on the substrate [17] [18]. As an example, the commonly used thiol (-SH) end-group chemistry forms a covalent bond to Au (1.9 eV or 45 kcal/mol) [19] [20], Ag [21], Cu [22], Pd [23], Pt [24], or Hg [25] substrates, but not to SiO₂ substrates. Conversely, a monolayer can be formed specifically on SiO₂ surfaces via silane attachment chemistries [26] [27]. In this thesis, all of the molecules studied were assembled onto bottom lithographically-defined Au contact electrodes using the thiol end-group chemistry.

The self-assembly process is illustrated in Figure 3-6, which shows a densely-packed molecular monolayer self assembling onto the substrate surface from a solution that contains the molecules of interest. A similar result can also be achieved using vapor phase deposition methods [28] [29].
3.2.4 Integration of the device

Once the Au nanowires and bottom electrodes were fabricated, the molecular monolayer was integrated into the crossed-wire junction using the procedure shown in Figure 3-6. For handling convenience, four adjacent fields were cleaved from the substrate and wire bonded for a subsequent electroplating step. Prior to molecule assembly, the bottom Au contact electrodes were cleaned by immersing the sample into NH₄OH:H₂O₂:H₂O = 1:1:5 (RCA-1) for one minute, followed by rinsing with DI water and ethanol. The sample was immediately transferred into a 1 mM solution of monothiol molecules and incubated in an oxygen-free nitrogen glovebox for 24 hours. For dithiole molecules, a lower 0.1 mM concentration and a shorter incubation time of 3 to 5 hours were used, which allows the formation of a monolayer rather than multiple layers.
Following the incubation, ellipsometry (L116A, Gaerner Sci. Corp) was performed on a large-area control sample prepared under identical conditions to confirm the SAM thickness.

During assembly, thiol-terminated molecules were deposited on all Au surfaces, including the large-area alignment/probe electrodes and the bottom contact electrodes as illustrated in Figure 3-7 (top). If Au nanowire top contacts were aligned directly onto these probe electrodes, additional series connected metal-molecule-metal junctions would be formed between each probe electrode and the nanowire. Consequently, the current-voltage (I-V) characteristics of the molecular devices would be due to two series-connected molecular junctions with uncontrolled contact area.

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Figure 3-7: Electroplating thin Au metal on top of the alignment/probe electrodes. Top left shows a scanning tunneling microscope (STM) image of dodecanethiol SAM’s highlighting the high density of grain boundaries and pin hole defects (after [31])
In order to overcome this limitation, a 10 nm-thick layer of Au was selectively electroplated onto the large area alignment/probe electrodes prior to nanowire alignment (Figure 3-7, bottom). This thin Au layer covers the surface of the molecules and penetrates through the SAM via defect sites (e.g., vacancies, domain boundaries, step edges, etc). As a result, the top metal nanowire and the bottom large-area alignment/probe electrodes are shorted together, which removes the second parasitic molecular junction from the device. Thus, the electrically-active junction area of these devices is now equal to contact area between the bottom central metal contact electrode (60 nm or 1.5 μm-wide) and the top metal nanowire.

In order to electrodeposit the Au layer, the interconnected alignment/probe electrodes were wire bonded and connected to macroscopic electrical leads on a Teflon holder. A constant current (1.6 mV for 5 s) was applied to the alignment/probe electrodes, but not to the 60 nm-wide central bottom contact electrodes. These conditions gave a ~10 nm-thick Au layer on the probe electrodes, but not on the bottom central contact electrodes (Figure 3-8, 3). It should be noted that these conditions were optimized for a substrate containing four fields, and should be adjusted substrates containing a different numbers of fields. Following electroplating, the sample was rinsed thoroughly with DI water and blown dry using nitrogen. Since the molecular monolayer assembled on the bottom contact electrode was immersed in the Au plating solution (no bias applied), residual ions (e.g., CN⁻) still could be incorporated into the SAM by diffusion. X-ray photoelectron spectroscopy (XPS) analysis was conducted on control
samples to quantify the residual ion concentration in the SAM. The results of these experiments will be discussed later in this chapter.

The device integration was completed by aligning the nanowires between pairs of large-area alignment / probe pads to form a top contact for the crossed-wire metal-molecule-metal junctions. Nanowires suspended in Ethanol (~2 µL) were dispersed onto one field at a time, while an AC signal of 10 kHz – 1 MHz, 1.5 \( V_{\text{rms}} \) – 1.8 \( V_{\text{rms}} \) was applied to the interconnected alignment / probe electrodes. The electric field induced by

Figure 3-8: Crossed-wire molecular junction fabrication procedure
the AC voltage causes the nanowires to become polarized and attracted to regions with the highest electric field gradient – the 3 μm gap between the sharp tips (Figure 3-8, 4).

An average of 25 out of the 100 possible locations in each field was bridged by a single nanowire. The FE-SEM images in Figure 3-9 show two fully fabricated crossed-wire molecular junction devices. The devices were comprised of a Au bottom contact electrode (60 nm-wide on the left and 1.5 μm-wide on the right) with a ~220 nm diameter Au nanowire top electrode. The devices containing single nanowire top electrodes were identified using light and dark-field optical microscopy and were placed in a high vacuum cryostat for electrical characterization.

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Figure 3-9: FE-SEM images of completed crossed-wire molecular junction devices

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### 3.3 Device Characterization Methods

Since moisture at the interface of the electrode/monolayer can affect the electrical transport properties of molecular devices, all of the electrical and spectroscopic measurements were performed under high vacuum in a Desert Cryogenics TTP-6
cryogenic probe system. After placing the devices on the sample holder (Figure 3-10, b), both the radiation shield and the vacuum chamber were sealed and evacuated by pumping overnight with a Varian turbo pumped vacuum system. Low-noise triaxial probes were used to contact the top and bottom electrodes, and the test operation and data acquisition were controlled using a customized LabVIEW program. The junctions were characterized electrically as outlined in Table 3-3. The details of each measurement will be described in the following sections.

Table 3-3: Types of Characterization Methods

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Variable temperature I-V measurements (RT ~ 4.2 K)</td>
</tr>
<tr>
<td>2</td>
<td>I-V measurements (RT ~ 4.2 K)</td>
</tr>
<tr>
<td>3</td>
<td>IETS measurements (10 K ~ 4.2 K)</td>
</tr>
</tbody>
</table>

3.3.1 Variable Temperature I-V Measurement

Figure 3-10 illustrates the setup used for variable temperature measurements from room temperature to 4.2 K. The measurement was conducted following the procedure outlined in Table 3-4.

Table 3-4: [PROCEDURE] Variable Temperature Measurement

<table>
<thead>
<tr>
<th></th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Load sample in TTP-6 system</td>
</tr>
<tr>
<td>2</td>
<td>Pump down until 10^{-6} Torr (overnight)</td>
</tr>
<tr>
<td>3</td>
<td>Adjust foot valve (5 turns) and flow controller (3.0 Psi)</td>
</tr>
<tr>
<td>4</td>
<td>Connect transfer line to L He and Bayonet of TTP-6</td>
</tr>
<tr>
<td>5</td>
<td>Set the desired temperature (4.2 K ~ RT)</td>
</tr>
<tr>
<td>6</td>
<td>Conduct measurement after small temperature variation is achieved (&lt; 0.5 K, 20 minutes)</td>
</tr>
</tbody>
</table>
Samples were placed on the sample holder that is attached to a cold head, which is cooled with liquid He delivered through a transfer line. By using two temperature sensors located on the cold head (Silicon diode) and the probe arm end (100 Ohm Plat/250), the controller (Lakeshore, Model 331) balances the DC heater power being sent to the cold head to achieve the set point. The flow of liquid He can be adjusted using the foot valve on the transfer line and the flow controller box connected to the liquid He Dewar. Once the set temperature becomes stable, I-V measurements were conducted using either an Agilent 4155C semiconductor parameter analyzer or Keithley 6430 Sub-Femtoamp Remote Sourcemeters controlled by a LabVIEW program via the GPIB ports on the measurement systems.
As discussed in Chapter 2, IET spectroscopy measures the change in current at the specific bias voltage corresponding to the molecular vibration energy. However, the current contribution due to inelastic tunneling is usually very small (< 2 %), and thus it is not possible to extract it directly from the I-V data. The small change can be found by differentiating the I-V data; this is visualized as a step in first derivative \( \frac{dI}{dV} \) and a

**Figure 3-10**: (a) A schematic of a TTP-6 (Cryogenics) system. (b) A sample loaded on the sample holder of the system. (c) A custom-written LabVIEW program controls the measurements.

### 3.3.2 IETS Measurement

As discussed in Chapter 2, IET spectroscopy measures the change in current at the specific bias voltage corresponding to the molecular vibration energy. However, the current contribution due to inelastic tunneling is usually very small (< 2 %), and thus it is not possible to extract it directly from the I-V data. The small change can be found by differentiating the I-V data; this is visualized as a step in first derivative \( \frac{dI}{dV} \) and a
peak in the second derivative \( \frac{d^2 I}{dV^2} \) [32]. Experimentally, the first or second derivative can be obtained two ways: (1) numerical differentiation of the measured I-V data, or (2) direct measurement using a lock-in amplifier (LIA) technique [33] [34] [35] [36]. A direct measurement of second harmonic (proportional to \( \frac{d^2 I}{dV^2} \)) using a LIA is preferred because the signal-to-noise ratio is much smaller compared to direct numerical differentiation of the I-V data.

Figure 3-11 gives a circuit schematic of the IETS set-up used in this thesis work where the LIA was used to collect the second derivative of the current directly.

![Figure 3-11: The block diagram shows the IETS Setup. A standard lock-in amplifier technique was used to measure the \( \frac{d^2 I}{dV^2} \) signal directly.](image)

In this circuit, a DC voltage \((V_0; \text{Keithley 6430})\) was modulated with an AC signal \((A \cos(\omega t + \theta))\), where \(A\) is the amplitude, \(\omega\) is the frequency, and \(\theta\) is the phase of the AC signal, supplied from a subunit of a LIA (SRS 830) through a 1:1 isolation transformer. The sum of the DC and AC bias given by \(V_0 + A \cos(\omega t + \theta)\) was applied across the device under test (DUT), and the current passing through the DUT was fed into a trans-impedance amplifier (TIA). Due to the high resistance of molecular junction (100 k\(\Omega\) –
10 MΩ), a virtually-grounded low-noise current preamplifier (SR 570; TIA) was employed to convert the current into a voltage signal. The voltage signal was fed into the input of the LIA, which determines the second (or first) harmonic directly. As shown in Equation 3.1 – Equation 3.4, the second harmonic is proportional to $d^2I/dV^2$, while the first harmonic is proportional to $dI/dV$.

Equation 3.1 gives the Taylor series expansion of the current at a DC bias of $V_0$.

Sample Bias: $V = V_0 + A \cos(\omega t + \theta)$

$$I(V) = I(V_0) + (V - V_0)\left(\frac{dI}{dV}\right)_{V_0} + \frac{(V - V_0)^2}{2}\left(\frac{d^2I}{dV^2}\right)_{V_0} + \ldots$$

$$= I(V_0) + A \cos(\omega t + \theta)\left(\frac{dI}{dV}\right)_{V_0} + \frac{A^2}{2} \cos^2(\omega t + \theta)\left(\frac{d^2I}{dV^2}\right)_{V_0} + \ldots \tag{3.1}$$

$$= I(V_0) + A \cos(\omega t + \theta)\left(\frac{dI}{dV}\right)_{V_0} + \frac{A^2}{4} (1 + \cos 2(\omega t + \theta))\left(\frac{d^2I}{dV^2}\right)_{V_0} + \ldots$$

The voltage signal fed into the LIA was multiplied by an internal reference ($A_r \cos(\omega t + \theta_0)$) generated by the LIA as given by Equation 3.2.
Reference signal from LIA:  $A_r \cos (\omega_r t + \theta_r)$

$$I(V)A_r \cos (\omega_r t + \theta_r)$$

$$= I(V_0)A_r \cos (\omega_r t + \theta_r) + AA_r \cos (\omega t + \theta) \cos (\omega_r t + \theta_r) \left( \frac{dI}{dV} \right)_{V_0}$$

$$+ \frac{A^2 A_r}{4} \cos (\omega_r t + \theta_r) \left( \frac{d^2 I}{dV^2} \right)_{V_0}$$

$$+ \frac{A^2 A_r}{4} \left( \cos (2\omega t + 2\theta) \cos (\omega_r t + \theta_r) \right) \left( \frac{d^2 I}{dV^2} \right)_{V_0} + \ldots$$

$$= I(V_0)A_r \cos (\omega_r t + \theta_r)$$

$$+ \frac{AA_r}{2} \left[ \cos ((\omega + \omega_r) t + (\theta + \theta_r)) + \cos ((\omega - \omega_r) t + (\theta - \theta_r)) \right] \left( \frac{dI}{dV} \right)_{V_0}$$

$$+ \frac{A^2 A_r}{4} \left[ \cos (\omega_r t + \theta_r) + \frac{1}{2} \cos ((2\omega + \omega_r) t + (2\theta + \theta_r)) \right.$$ 

$$\left. + \frac{1}{2} \cos ((2\omega - \omega_r) t + (2\theta - \theta_r)) \right] \left( \frac{d^2 I}{dV^2} \right)_{V_0}$$

$$+ \ldots$$

Here $\omega_r$ is a reference frequency and $\theta_r$ is a reference phase generated by the LIA. A signal proportional to the first derivative ($dI/dV$) can be obtained by setting $\omega_r = \omega$ and adjusting the phase, $\theta_r = \theta$. The AC component was removed using a low pass filter, which leaves a DC signal that is proportional to the first derivative as shown in Equation 3.3.

[ first harmonic ]

$$\frac{AA_r}{2} \left[ \cos ((\omega + \omega_r) t + (\theta + \theta_r)) + \cos ((\omega - \omega_r) t + (\theta - \theta_r)) \right] \left( \frac{dI}{dV} \right)_{V_0}$$

if $\omega_r = \omega$,  

$$\frac{AA_r}{2} \left[ \cos (2\omega t + (\theta + \theta_r)) + \cos (\theta - \theta_r) \right] \left( \frac{dI}{dV} \right)_{V_0}$$

$$\frac{AA_r}{2} \cos (2\omega t + 2\theta) \left( \frac{dI}{dV} \right)_{V_0} \propto \frac{AA_r}{2} \left( \frac{dI}{dV} \right)_{V_0}$$
Similarly, the second derivative can be obtained by setting $\omega_r = 2\omega$ and adjusting the phase $\theta_r = 2\theta$ (Equation 3.4).

$$\frac{AA_r}{8}\left[\cos\left((2\omega + \omega_r)t + (2\theta + \theta_r)\right) + \cos\left((2\omega - \omega_r)t + (2\theta - \theta_r)\right)\right]\left(\frac{d^2I}{dV^2}\right)_{V_0}$$

If $\omega_r = 2\omega$, $\frac{AA_r}{8}\left[\cos\left(4\omega t + (2\theta + \theta_r)\right) + \cos(2\theta - \theta_r)\right]\left(\frac{d^2I}{dV^2}\right)_{V_0}$

If $\theta_r = 2\theta$, $\frac{AA_r}{8}\cos\left(4\omega t + 4\theta\right)\left(\frac{d^2I}{dV^2}\right)_{V_0}$ $\propto$ $\frac{AA_r}{8}\left(\frac{d^2I}{dV^2}\right)_{V_0}$

It should be noted that the amplitude of the measured signal does not provide an absolute measure of the peak intensity because the TIA inserts an additional proportionality constant. However, the relative intensity of the peaks at different bias voltages can be compared using this method in the low bias regime ($< 0.5$ V) [36].

The peak broadening in IETS is determined by three factors: intrinsic ($\Gamma_0$), thermal ($\Gamma_{\text{thermal}}$), and AC modulation voltage ($\Gamma_{\text{ac modulation}}$). Considering the broadening due to each factor, the full width at half maximum (FWHM) can be obtained by the relationship given in Equation 3.5 [33] [37].

$$\Gamma = \left[\left(\Gamma_{\text{thermal}}\right)^2 + \left(\Gamma_{\text{ac modulation}}\right)^2 + \Gamma_0\right]^{1/2}$$

$$\Gamma = \left[\left(5.4\frac{k_B T}{e}\right)^2 + \left(1.7V_{ac}\right)^2 + \Gamma_0\right]^{1/2}$$

- $T$: Temperature in Kelvin,
- $V_{ac}$: RMS modulation in $V$
- $\Gamma_0$: Intrinsic half width of the line in $V(\sim 2mV)$
Here, $T$ is temperature (K), $k_B$ is Boltzmann’s constant, $e$ is the charge of an electron, $V_{ac}$ is the RMS AC modulation voltage ($V$), and $\Gamma_0$ is the intrinsic FWHM of the molecular vibrational mode. Although the Fermi function at 0 K is a step function, the edge of the Fermi level is broadened at finite temperatures, resulting in peak broadening. Figure 3-12 plots the peak broadening as a function of a temperature ($5.4 \times k_B T/e$), which shows that IET spectroscopy should be performed at as low a temperature as possible to reduce thermal peak broadening.

![Figure 3-12: Thermal broadening](image)

The AC modulation signal causes a further broadening of $1.7 V_{ac}$. Thus, lower RMS amplitudes are also required to minimize the FWHM. However, as discussed in Chapter 2, the signal-to-noise ratio also decreases as $V_{ac}$ decreases, which limits the ability to resolve peaks associated with molecular vibrations from background noise.

In the IETS measurements for this thesis work, cryogenic temperatures ($< 10$ K) and small excitation voltages ($4 – 8$ mV$_{rms}$) were used to minimize peak broadening. The
measurement procedure is described in Table 3-5. Much of the initial work on the system set-up was done by Cabassi et al. [38].

Table 3-5: [PROCEDURE] IETS measurement

1. Load sample in TTP-6 system  
2. Pump down until 10^{-6} Torr (overnight)  
3. Cool down system to 4.2 K (follow the procedure in Table 3-4)  
4. Wait until the system is well stabilized at 4.2 K (about 1 hour)  
5. Start software with setting parameters  
   (a) Keithley 6430: DC bias range, current compliance  
   (b) Subunit of SRS 830: AC excitation voltage, frequency, phase  
   (c) SRS 830: harmonics, sensitivity, time constant, settling time, filters  
   (d) SR 570: sensitivity(TIA), bandwidth, filters  
6. Monitor signal on program screen and adjusting parameters

3.4 Crossed-wire Device Control Measurements

This section considers several aspects of the crossed-wire molecular junction fabrication process that may influence the electrical and spectroscopic properties of the device, and correspondingly the interpretation of the measured I-V and IETS data: surface roughness of the metal contacts, forces on the contacted molecules, and possible incorporation of unintentional ions during alignment / probe electrode electroplating. In addition, control measurements were conducted on metal-metal junctions formed by directly contacting the top nanowire contact to the bottom evaporated Ti/Au contact over the temperature range from 300 to 4 K to verify that the crossed-wire device is robust with thermal cycling, has low contact resistance, and follows the expected temperature dependence that is observed in clean metallic systems.
3.4.1 Surface roughness of metal contacts

The molecular monolayer is contacted by two metal electrodes in this crossed-wire device: a thermally-evaporated Ti/Au thin film bottom contact and a single ~220 nm diameter Au nanowire top contact. The grain structure and surface roughness of the bottom contact can result in variations in the active junction area, and hence variations in the current through different molecular junction devices. For example, Figure 3-13 plots the estimated current of dodecanethiol (C12) junctions at 0.1 V bias as a function of the contact area. A conductance of 0.5 nS/molecule [3] and a surface coverage of a 0.2 nm²/molecule [39] were used in this calculation. As shown in the graph, the current increases linearly with increasing contact area. Specifically, if the contact area is changed from 500 to 1,000 nm², the number of molecules in the junction doubles (2,500 to 5,000 molecules), as does the current (125 to 250 nA).

Figure 3-13: Calculated current of C12 molecular junction as a function of contact area.
The surface roughness of the thin film and nanowire metal electrodes was investigated using atomic force microscopy (AFM), transmission electron microscopy (TEM), and FESEM. The Ti (10 nm)/Au (50 nm) bottom contact was thermally evaporated at a rate of 2 Å/s in a high vacuum chamber (~3×10^{-7} torr). The surface roughness of an unpatterned Ti/Au thin film (1 × 1 μm² area) deposited using the same conditions is shown in the top of Figure 3-14. The average size of the Au grains was ~40 nm, and the root-mean-square (RMS) roughness of the surface was ~1 nm. However, the peak-to-valley roughness was ~3 nm, which is larger than the length of the molecules studied in this work (~2 nm). As described in Section 3.2.4, the 60 nm-wide Ti/Au evaporated bottom contact is chemically cleaned (RCA-1) prior to molecule self-assembly. The AFM images at the bottom of Figure 3-14 show that the peak-to-valley roughness of the patterned electrode is reduced slightly (~2 nm) following this cleaning process. These images also show that between one and three Au grains span the width of the bottom metal contact.
The surface roughness of the template-grown Au nanowires was analyzed using TEM and FE-SEM. Representative images collected using both techniques are shown in Figure 3-15 and demonstrate that the nanowire surface is much smoother than the thermally-evaporated Ti/Au thin film. This can be seen most clearly in the FESEM image shown in Figure 3-15 (right) where the Au nanowire is placed on top of an evaporated Ti/Au layer deposited using the same conditions as the film shown in Figure 3-14.
In the crossed-wire device, the molecular monolayer is sandwiched between the 60 nm-wide bottom Ti/Au thin film and 220 nm-diameter Au nanowire top electrodes. The images in Figures 3-14 and 3-15 indicate that variations in the active junction area for different devices is determined largely by the grain structure of the bottom evaporated Ti/Au thin film. Thus, the current is expected to vary by more a factor of three across large numbers of devices fabricated with the same nominal 60 nm-wide patterned electrode (i.e., one to three Au grains). It should also be noted that the cross-wire junction may contain non-bridging as well as bridging molecules as illustrated in Figure 3-16. As discussed in the following section, the bridging molecules may be in compression or tension due to forces induced on the SAM layer by the crossing nanowire, which may also contribute to variations in charge transport through the molecular junctions.

Figure 3-15: Surface smoothness of an Au metal nanowire that was used as a top metal contact (TEM by Hu and Liu)
As discussed in Chapter 1, the forces that are exerted on the molecular monolayer can influence charge transport in the molecular junction device. Additional experiments that used a conducting probe-AFM (CP-AFM) also showed that a loading force of ~ 150 nN can force the metal-coated tip (20 nm diameter in apex) into the SAM until it penetrates through to the metal substrate [40]. During the junction assembly and electrical measurements, several forces (e.g., van der Waals, meniscus, electrostatic, nanowire restoring, elastic/plastic deformation, etc.) can be exerted on the SAM in the crossed-wire device. Although the magnitude and direction (e.g., compressive or tensile) of the net force exerted on the molecular monolayer was not measured experimentally in this thesis work, this section attempts to estimate it by employing reasonable assumptions and using previous experimental CP-AFM data.

**Figure 3-16**: Illustration of metal-SAM-metal junction in crossed-wire device (not to scale). The junction area contains both bridging molecules and non-bridging molecules.
The contact geometry of the crossed-wire device may be simplified as a cylinder touching a flat planar surface (Figure 3-17). Here the metal nanowire is treated as a perfect cylinder due to its smooth surface (Figure 3-15). However, the surface roughness of the evaporated Ti/Au thin film bottom contact is not negligible, and thus should be considered in this analysis. To simplify the model, however, the contact geometry was first assumed to be a perfect cylinder on a flat surface, and then the parameters associated with the surface roughness of the bottom contact electrode were adjusted.

Figure 3-17 illustrates the forces exerted on the molecular monolayer in the crossed-wire device. It includes van der Waals [41] [42], meniscus [43], electrostatic [41], nanowire restoring [41], and elastic / plastic [40] deformation forces.

The net force exerted on the SAM can be estimated by combining the contributions of the individual force components. While the meniscus is present only during nanowire assembly, electrostatic forces can occur and even change during the junction I-V measurement (i.e., when a voltage is applied between the top and bottom metal electrodes). Thus, the net force on the SAM is estimated during (1) nanowire
assembly, and (2) electrical measurement. In equilibrium, the net force in both cases is given by Equation 3.6. Simple physical and mathematical models that were used to describe each component of force are provided in the following subsections.

Case 1. Junction assembly

\[
F_{\text{vdw}} + F_{\text{mec}} = F_{\text{NW}} + F_{\text{elst/plastSAM}}
\]

Case 2. Electrical measurement

\[
F_{\text{vdw}} + F_{\text{elec}} = F_{\text{NW}} + F_{\text{elst/plastSAM}}
\]

(1) Van der Waals Force

When a single nanowire (top electrode) contacts the SAM, the Van der Waals force that is due to polarization of the molecules and the metal contacts, exerts a compressive force on the SAM. For the geometry of a cylinder on a flat surface (Figure 3-18), the Van der Waals force \( F_{\text{vdw}} \) is given by Equation 3.7 [42].

Figure 3-18: Van der Waals force for the geometry of a cylinder (nanowire) on a flat surface of a SAM layer (purple)
For a 2 nm-thick molecular monolayer sandwiched between a 220 nm-diameter Au nanowire and a 60 nm-wide planar metal thin film, the estimated Van der Waals force compressing the SAM is

$$F_{vdw} = \left( \frac{3}{4\pi} A \right) \left( \frac{D^{1/2}}{16z_0^{5/2}} \right) W$$

$$= \left( \frac{3 \times (9.85 \times 1.6 \times 10^{-19} J)}{4\pi} \right) \left( \frac{(220 \times 10^{-9} m)^{1/2}}{16 \times (2 \times 10^{-9} m)^{5/2}} \right) \cdot (60 \times 10^{-9} m)$$

$$\approx 3.40 \times 10^{-9} \text{ (unit: N)}$$

$$\text{(3.7)}$$

- $A = h\sigma_{132}$: Hamaker Constant (9.86 eV)
- $z_0$ : Thickness of SAM (2 nm)
- $D$ : Diameter of NW (220 nm)
- $W$ : Width of bottom electrode (60 nm)

For a 2 nm-thick molecular monolayer sandwiched between a 220 nm-diameter Au nanowire and a 60 nm-wide planar metal thin film, the estimated Van der Waals force compressing the SAM is $F_{vdw} \sim 4$ nN.

(2) Meniscus Force

A meniscus exists when the solvent in which the nanowires are suspended (ethanol) evaporates following nanowire alignment to form the top contact. Based on the Maugis-Dugdale approximation [43] [44], the maximum meniscus force is expected when the contact angle ($\theta$) becomes zero (Figure 3-19). Considering the crossed-wire junction as an interface between two parallel surfaces (cylindrical nanowire and planar thin film) [45], a maximum meniscus force directed from the nanowire to the substrate of $F_{msc} \sim 46$ nN is estimated using Equation 3.8. It is important to note that the meniscus and corresponding meniscus force disappears when the solvent (ethanol) is removed (less than 5 s) and thus is not acting on the SAM during device electrical measurements.
(3) Electrostatic Force

In a typical I-V measurement, a bias voltage of 0 to ±1.5 V is applied across the SAM, which gives rise to a compressive electrostatic force (capacitive force) between the two metal electrodes. The electrostatic force $F_{elec}$ was estimated using a standard capacitance model as given in Equation 3.9 [41]. This model assumes that the nanowire can be approximated as a prefect cylindrical conductor and that the lower electrode is a perfectly flat conducting surface.

$$F_{elec} = \gamma_L (\cos \theta + 1)$$

$$F_{elec, max} = \left(22.8 \times 10^{-3} \text{ N/m}\right) \cdot (1 + 1) \approx 45.6 \times 10^{-9} \text{ (unit: N)}$$

- $R$: Radius of NW (110 nm)
- $\gamma_L$: Liquid-air surface tension (Ethanol: 22.8 mN/m)
- $\theta$: Contact angle of liquid
Figure 3-20 plots the estimated electrostatic force with respect to the applied voltage for a 2 nm-thick SAM layer. At an applied bias of ~ 1 V, the estimated electrostatic force is $F_{elec} \sim 6 \text{nN}$. 

\[
F_{elec} = \left\{ \frac{d}{dz} \left( \frac{1}{2} CV^2 \right) \right\} \cdot W \\
\approx \frac{\pi \varepsilon_o \varepsilon V^2 \cdot W}{R^2 \sqrt{\frac{z_0(z_0 + 2R)}{R^2} \cdot \ln^2 \left( 1 + \frac{z_0}{R} + \sqrt{\frac{z_0(z_0 + 2R)}{R^2}} \right)}} \\
\approx \frac{\pi \left( 8.85 \times 10^{-12} \text{F/m} \right) \cdot (2.5) V^2 \left( 60 \times 10^{-9} \text{m} \right)}{\left( 110 \times 10^{-9} \text{m} \right) \cdot (0.192) \cdot \ln^2 \left( 1 + \frac{2 \times 10^{-9} \text{m}}{110 \times 10^{-9} \text{m}} + 0.192 \right)} \\
\approx 5.43 \times 10^{-9} V^2 \quad (\text{unit: N; \ V: volt})
\]

\[
\sqrt{\frac{z_0(z_0 + 2R)}{R^2}} = \sqrt{\left( \frac{2 \times 10^{-9} \text{m}}{110 \times 10^{-9} \text{m}} \right) \left( \frac{2 \times 10^{-9} \text{m} + (2 \times 110 \times 10^{-9} \text{m})}{110 \times 10^{-9} \text{m}} \right)} \\
= 0.192
\]

\[
\begin{align*}
    z_0 & : \text{Thickness of SAM (2 nm)} \\
    R & : \text{Radius of NW (110 nm)} \\
    \varepsilon_o \varepsilon & : \text{Dielectric constant (2.5} \times 8.85 \times 10^{-12} \text{F/m}^2) \\
    W & : \text{Width of bottom electrode (60 nm)} \\
    V & : \text{Voltage (volt)}
\end{align*}
\]
(4) Elastic and plastic deformation of SAM

The net compressive force exerted on the SAM in the crossed-wire device may cause elastic and/or plastic deformation of the molecules (Figure 3-17). Since the SAM is only 2 nm-thick and the Ti/Au lower electrode 40 nm-diameter grains with a peak-to-valley surface roughness of ~3 nm, the geometry of a perfectly smooth cylinder on a flat surface is not accurate. Instead, the configuration can be more accurately modeled a sphere that is in contact with a cylinder. To estimate the elastic and plastic deformation of the SAM, the evaporated Ti/Au surface was modeled as a sphere with an effective radius of 68 nm as illustrated in Figure 3-21.
Before calculating the elastic deformation, the minimum force required to begin plastically deforming the SAM layer in the crossed-wire junction devices was estimated empirically from recent CP-AFM experiments. This work measured a plastic deformation of ~7 Å when a junction load of ~60 nN was applied to an alkanethiol monolayer assembled on a planar surface using an AFM tip with an apex of 20 nm [40]. Based on the correlation between the critical load and the indentation radius (R^{0.85} to R^{1.0}) [46], a ~220 nm-diameter nanowire in contact with one Au grain requires at least twice as much compressive force as the 20 nm-diameter CP-AFM tip to plastically deform the SAM. This is equivalent to ~120 nN of applied compressive force, which is considerably larger than the sum of the forces due to factors (1) – (3) discussed previously. This indicates that the SAM layers in the crossed-wire junction should remain in the elastic limit during nanowire alignment and electrical measurement.

Figure 3-21: Simplified geometry of a Au grain with a nanowire
The elastic deformation of the SAM in the crossed-wire junction was estimated using Equation 3.10 [40], and is plotted as a function of compressive force in Figure 3-22. If the sum of the compressive forces from factors (1) – (3) is exerted on the SAM, the maximum elastic deformation of the SAM would be ~ 4 Å, which is ~ 20% of the molecule length. However, this overestimates the elastic deformation during device measurement. First, the net compressive force in for the device under bias is ~ 10 nN, which is equivalent to an elastic deflection of ~0.5 Å, or only 5% of the molecule length. Second, in addition to the elastic restoring force that is considered here, the deflected nanowire itself will induce a restoring force as discussed in the following section.
The crossed-wire junction is comprised of a single 220 nm-diameter Au nanowire that is suspended from the substrate in the regions between the large-area alignment/probe electrodes and central metal contact electrode. As discussed previously, the compressive forces cause a downward deflection of the segment of the nanowire centered over the molecular junction. The nanowire deflection (bending) will induce a restoring force that acts in conjunction with the elastic restoring force to balance the sum of the compressive forces. The nanowire restoring force is estimated by modeling the nanowire using an effective spring constant ($k$), and assuming that the force varies linearly with deflection as shown in Figure 3-23.

(5) Nanowire restoring force

Figure 3-22: Estimated elastic deformation of the SAM layer
The restoring force as a function of the nanowire displacement is given by Equation 3.11 [41], and is plotted in Figure 3-24. This shows that a restoring force of ~45 nN would be exerted for the maximum nanowire displacement of 4 Å estimated during nanowire alignment (including meniscus force), and ~5 nN for the 0.5 Å estimated during junction electrical measurement (excluding meniscus force). This suggests that the actual elastic displacement of the molecules in the SAM would equilibrate somewhat below 0.5 Å during electrical measurement, which is less than 5% of the length of the molecules used in this thesis.

Figure 3-23: A model to estimate the nanowire bending force (after [41])
\[ F_{NW} = kx = \left( \frac{384EI}{L^3} \right)x \]
\[ = \left( \frac{384 \times (70 \times 10^9 \text{Pa}) \times (115 \times 10^{-30} \text{m}^4)}{(3 \times 10^{-6} \text{m})^3} \right)x \]
\[ \approx 114.5 \times (\text{unit: N}; x: \text{m}) \]

\[ I = \frac{\pi R^4}{4} \approx \frac{\pi(110 \times 10^{-9} \text{m})^4}{4} \approx 115 \times 10^{-30} \text{m}^4 \]

\[ \text{One-end Fixed: } k = \frac{8EI}{L^3} \approx 2.4 \text{ N/m} \]
\[ \text{Fixed-Fixed: } k = \frac{384EI}{L^3} \approx 114.5 \text{ N/m} \]

\[ \begin{cases} 
E: \text{Young's modulus of Au NW (70 GPa)} \\
R: \text{Radius of NW (110 nm)} \\
L: \text{Length of NW, suspended (3 } \mu \text{m)} \\
I: \text{Moment of inertia, NW} \\
x: \text{Maximum deflection of beam} 
\end{cases} \]

Figure 3-24: Estimated nanowire restoring force. A single 220 nm-diameter Au nanowire was suspended between elevated electrodes spaced 3 \( \mu \)m apart.
Determining the number of electrically-active molecules (i.e., electrically-active contact area) in the crossed-wire molecular junction device is important for the interpretation of the measured I-V characteristics of the device. However, as described in the previous sections, the microscopic details surface morphology as well as the forces that are exerted in the SAM is very complex. Thus, it is difficult to determine a precise value for the number of molecules in the crossed-wire junction. This section provides an order of magnitude estimate for the number of bridging molecules in the crossed-wire junction. It is important to note that differences may arise between junctions fabricated using monothiolate and dithiolate molecules because of the nature of the top contact (i.e., physically vs. chemically-bonded). More specifically, dithiolate molecules should form covalent bonds with the top and bottom contact during nanowire alignment, whereas monothiolate molecules will not. Thus, for the dithiolate molecules considered in this thesis, it is necessary to determine the number of molecules that are contacted during nanowire alignment when the meniscus and Van der Waals exert a net compressive force of ~ 60 nN on the SAM. Using the junction geometry of Figure 3-21, the radius of the contact area per 40 nm-diameter Au grain determined using Equation 3.12 was ~ 4 nm [40].
Assuming the 60 nm-wide bottom metal contact contains two Au grains, the estimated contact area \(2 \times \pi a^2\) is \(\sim 100 \text{ nm}^2\). The surface coverage of alkanethiol molecules is \(\sim 0.2 \text{ nm}^2/\text{molecule} \ [7]\), and thus the junction contact should contain \(\sim 500\) single molecules in parallel. The exact number will depend on many factors including the number and diameter of the grains, the nature of the molecular bond to the top contact, and the packing / ordering of the SAM.

### 3.4.3 XPS on SAM

As described previously, the crossed-wire molecular junctions are formed by sandwiching a molecular monolayer between a bottom thermally-evaporated Ti/Au contact and a top Au metal nanowire contact. The molecules that are assembled onto the large-area alignment / probe electrodes (including sharp tips) are covered with a 10 nm-
thick electroplated Au layer deposited using a constant current of 1.6 mA for 5 sec. Although the central bottom contact electrode was not biased during electroplating, the SAM on this contact was immersed in the plating solution during this step. Thus, it is possible that ions in the electrolyte could diffuse into this electrically-active SAM layer, and influence the electronic transport properties of the molecular junction by serving as counter ions to stabilize different charged conformations of the molecules. This is particularly important for the thiol-substituted N-methyl-oligoaniline (OMAn) molecular junctions that have bistable switching characteristics as discussed in Chapter 1.

To place bounds on the maximum unintentional ion concentration in the SAM, X-ray photoelectron spectroscopy (XPS) measurements were taken on samples containing dodecanedithiol (C12-dithiol) molecules self assembled onto large-area evaporated Ti/Au thin films. One such sample was exposed to the electroplating solution for 1 min., which is considerably longer than the 5 sec. time used to fabricate the crossed-wire device. A second sample that was not exposed to the plating solution was also measured as a control. The XPS analysis was performed using a monochromatic Al Kα source instrument (Kratos Axis Ultra) operating at 14 kV and 20 mA with an x-ray power of 280 Watts. Spectra were collected with a photoelectron take off angle of 90°, energy steps of 0.15 eV, and a pass energy of 80 eV for survey and 20 eV for high resolution spectra (Figure 3-25). The electrolyte used in the commercially purchased Au electroplating solution (Technic Inc, Techni-Gold 25 E S) is a potassium aurocyanide (KAu(CN)₂) salt that would incorporate CN- ions into the SAM layer. If the concentration of the CN- ions is above the XPS detection limit, a nitrogen (N) peak would be found at a binding energy of ~ 400 eV. A comparison of XPS spectra from the two samples (Figure 3-26) does not
show a quantifiable difference in the peak intensity at this energy. Thus, these data indicate that the SAM does not contain a detectable number of CN- ions following immersion into the Au electroplating solution.

3.4.4 Contact Resistance

Prior to the electrical characterization of the metal-molecule-metal crossed-wire junction devices, control measurements were performed on metal-metal junctions that excluded the SAM layer to determine the (1) contact resistance between the nanowire and the large-area alignment / probe electrodes, (2) temperature dependence of the metal-metal junction formed between the nanowire and the central metal electrode, and (3) the

Figure 3-25: XPS survey spectra of a C12-dithiol SAM. The spectrum of the C12-dithiol control sample is shown in black, and that of the C12-dithiol sample immersed into electroplating solution for 1 min and rinsed in DI water several times is shown in blue.
robustness of the device to thermal cycling from 300 to 4 K. Before this study, it was found that the leakage current measured between pairs of large-area alignment/probe electrodes that were deposited onto thermally-grown oxide was < 300 fA at ±1 V. This provides a baseline for the highest junction resistance that can be measured using this crossed-wire test structure, which is ~3 × 10^{14} \, \Omega.

The temperature dependent I-V characteristics of the crossed-nanowire junction was measured after assembling single 8 to 10 \, \mu m-long nanowires between the lower thermally-evaporated Ti/Au central contact electrode and the tips of the large-area alignment/probe electrodes. Figure 3-26 shows the measured room-temperature I-V characteristics of a junction where the bias was applied between top and bottom metal contact electrodes. Thus, this I-V is the sum of the two series connected metal-metal interfaces as shown in Figure 3-26. At room temperature, the current increased linearly with a voltage, indicating that the metal-metal contact was ohmic. The current at 1 V was 16 mA, giving a total resistance that is the sum of the metal nanowire and the metal-metal contact resistance of ~60 \, \Omega.
The same crossed-wire junction devices were thermally cycled by first cooling them down from 300 to 25 K in steps of 20 K, and then heating them up from 25 to 300 K in steps of 20 K. The junction resistance was calculated from the I-V characteristics measured at each step after the temperature stabilized. Figure 3-26 plots the total crossed-wire junction resistance as a function of temperature. The total resistance decreased linearly with decreasing temperature.

Figure 3-26: Crossed-wire junction resistance measured as a function of temperature. Contact resistance decreased linearly with decreasing temperature.
decreased linearly from 60 Ω at 300 K to 39 Ω at 50 K. This temperature dependence is expected for clean metals where the phonon vibrational modes decrease as the temperature decreases. The resistance saturates at temperatures below 50 K. This is attributed to the surface scattering and the internal grain boundary scattering, which constitute the temperature-independent part of the resistance as in most well-ordered metallic solids [47]. These data indicate that the interface between the metal nanowire and thermally evaporated electrodes forms a metal-metal contact that is free of organic contamination. Further, the contact resistance of the Au nanowire on the large-area alignment / probe is negligible compared to the expected resistance of the molecular junctions that are studied in this thesis (100 kΩ ~ 10 MΩ).

3.5 Conclusion

This chapter described the design, fabrication, and characterization of a new crossed-wire molecular junction device comprised of a self-assembled molecular monolayer sandwiched between a lithographically-defined bottom metal contact and a single nanowire top metal contact. This high-yield fabrication process provided nanoscale device junctions containing small ensembles of ~ 500 densely-packed molecules that are amenable to low and variable temperature (4 – 300 K) electrical and in-situ spectroscopic measurements. The ability to fabricate and characterize many devices at the same time and on the same substrate allows a comprehensive study of the fundamental mechanisms responsible for the observed electrical transport properties (including
bistable switching) as well as the ability to develop a meaningful comparison between experiment and theory.

In addition to providing a detailed description of the crossed-wire junction device structure and fabrication process, this chapter also quantified the surface roughness of the two metal contact electrodes. Using AFM, FESEM, and TEM, it was determined that the lithographically-defined bottom contact had an RMS roughness of ~1 nm with a peak-to-valley roughness of up to 3 nm. The typically grain size was 40 nm-diameter and one to three metal grains spanned the width of the contact. In comparison, the cylindrical metal nanowire was very smooth and lacked a clear grain structure. The implications of the surface roughness and grain structure were discussed in the context of the forces that are present on the SAM layer during nanowire assembly and junction electrical characterization. The consequences of this surface roughness will be described in more detail in Chapters 4 and 5.

The results of several control measurements to assess the cleanliness and robustness of the crossed-wire junction were described. The effect of immersing the SAM layer in electroplating solution (not under bias) following self assembly was studied using XPS. The results of this study showed that the concentration of CN- ions present in a C-12 dithiol SAM layer following exposure to the Au electroplating solution below the XPS detection limit. Additional control measurements made on metal-metal crossed-wire junctions showed that the room-temperature contact resistance was negligible compared to the resistance of the molecular junctions studied in this thesis. Moreover, the linear reduction in resistance with temperature indicates that the metal-metal junctions were
free of organic contamination that could influence the formation of metal-molecule-metal junctions and interpretation of their electrical properties.

### 3.6 References

Chapter 4
Saturated vs. Conjugated SAM Junctions

4.1 Introduction

Two types of molecules are studied in this chapter: saturated alkanethiols and conjugated oligo(phenylene-ethynylene) (OPE) molecules. The molecular structures are illustrated in Figure 4-1.

![Figure 4-1: Molecular structure of Alkanethiol (1-dodecanethiol) and OPE](image)

Saturated alkanethiols (CH$_3$(CH$_2$)$_n$SH, n: integer), depicted in Figure 4-1 (left), are comprised of alkyl chains (C$_n$H$_{2n+1}$) and a thiol (-SH) end-group that can bind to a metal substrate (e.g., Au, Ag, Pd, Pt, Hg, etc) via covalent bonding [1]. Using the self-assembly method, these molecules can be assembled into a well organized and densely packed monolayer on the metal substrate [2]. The electrical properties of saturated alkanethiol junctions are close to those of an insulator, acting as a tunneling barrier between two metal electrodes [3] [4]. This is attributed to the large HOMO-LUMO gap of about 8 eV on Au (HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital), which was determined by ultraviolet-photoelectron spectroscopy.
(UPS) [5]. Using conducting probe-Atomic Force Microscopy (CP-AFM; see Chapter I for details) data, Beebe et al., [6] suggest that the Fermi level in the metal-alkanethiol-metal junctions lies closer to the HOMO than to the LUMO, indicating that the dominant transport mechanism is hole tunneling.

On the other hand, OPE molecules are comprised of three phenyl rings connected by triple bonds as shown in Figure 4-1 (right). The molecules can also be formed in a well ordered self-assembled monolayer (SAM) [3] like alkanethiols. However, the alkanes are σ-bonded, while the OPE molecules are π–conjugated. The delocalized π-electrons along the length of the molecules enhance electron transport, resulting in a higher conductivity than in alkanethiol junctions. UPS measurements showed that the HOMO-LUMO gap of OPE molecules on Au is about 5.1 eV [7]. This work also showed that the occupied delocalized π levels (HOMO) are located approximately 1.9 eV from $E_F$ and the corresponding π* levels (LUMO) are estimated to lie about 3.2 eV above $E_F$. Note that the exact location of the Fermi level in the metal-OPE-metal junction could be different from this UPS result [8]. Unlike the metal-molecule-metal junctions, the junctions used in UPS do not have a top metal contact. Adding a top contact could change the electronic states of the molecules, resulting in change of $E_F$.

This chapter presents electrical and spectroscopic measurements conducted on nanoscale crossed-wire molecular devices that integrate monolayers of alkanethiol and OPE molecules between two Au metal contacts. Since both types of molecules have been studied extensively in previous experiments, their results can be used to evaluate the new device structure developed in this thesis work. Moreover, these data will also be used as a baseline for comparison to the more complex OMAn (thiol-substituted methylated
oligoaniline) molecular junctions that exhibit bistable switching properties as discussed in Chapter 5.

4.2 Saturated alkanethiol SAM junctions

4.2.1 Chemisorbed contact vs. physisorbed contact

While a monothiol molecule contains a thiol (-SH) at one of the ends, both ends of a dithiol molecule are functionalized with thiols. Following assembly of the monolayer on the bottom metal contact, a metallic top contact can be formed by physical contact in the monothiol junction (physisorbed) or by chemical bonding in the dithiol junction (chemisorbed). Figure 4-2 illustrates physisorbed (left) and chemisorbed contacts (right).

Figure 4-2: Illustrations of physisorbed contact (left; C12-monothiol molecule) and chemisorbed contact (right; C12-dithiol molecule)

Prior theoretical and experimental work showed that the molecule/electrode contact (i.e., physical vs. chemically-bonded contact) can influence charge transport, affecting the electrical properties of the junction. For example, as discussed in Chapter 1, the current in chemically-bonded SAM junctions was one to two orders of magnitude higher than that
in physically contacted SAM junctions [9]. In addition, force-dependent current-voltage (I-V) measurements have shown that the current variation in a chemisorbed junction is less sensitive to contact force than in physisorbed junctions [10].

In the nanoscale crossed-wire device, the molecules are in contact with a thermally-evaporated Ti/Au thin film (bottom electrode) and a cylindrically-shaped Au nanowire (top electrode). In order to evaluate the role of the contacts, SAM junctions of 1-dodecanethiol ((CH$_3$(CH$_2$)$_{11}$SH; C12-monothiol) and 1,12-dodecanedithiol ((HS(CH$_2$)$_{12}$SH; C12-dithiol) were prepared. Table 4-1 shows the assembly conditions. The details of the fabrication and electrical characterization procedures were described in Chapter 3.

| Table 4-1: Assembly conditions used to fabricate C12-SAM junctions |
|------------------|------------------|
| **C12-mono**     | **C12-dithiol**  |
| CH$_3$(CH$_2$)$_{11}$SH | HS(CH$_2$)$_{12}$SH |
| Purchased        | Sigma-Aldrich    | Narchem Corporation |
| Assembly condition | 3 mM, 24 hours | 0.1 mM, 5 hours |
| Measured thickness | ~1.5 nm | ~1.6 nm |

### 4.2.2 Room temperature I-V measurement

Figure 4-3 shows the current-voltage (I-V) characteristics of C12-monothiol and dithiol crossed-wire junction devices measured at room temperature. The SAM layer was sandwiched between a 60 nm-wide lithographically-defined Au bottom contact and a 220 nm-diameter Au nanowire top contact. Comparisons were made by analyzing more than
ten representative I-V characteristics from each type of junction. Moreover, several independent fabrication processes were completed to ensure good run-to-run reproducibility. Short and open circuited junctions were excluded from this plot.

Figure 4-3: I-V curves of ten devices of each C12-monothiol and C12-dithiol junctions (Au-SAM-Au).

The measured current at 1 V varied from 100 to 500 nA in the C12-dithiol SAM junctions, while a slightly larger distribution from 20 to 200 nA was observed in the C12-monothiol junctions. The variation in current for a single type of molecule (i.e., either monothiol or dithiol) can be attributed to differences in the number of molecules that are electrically contacted in the junction. As discussed in Chapter 3 (Section 3.4.1) and also shown again in Figure 4-4, while the Au nanowire top contact has a very smooth surface, the peak-to-valley roughness (~ 3 nm) of the evaporated Ti/Au bottom contact is comparable to the molecule length (~ 2 nm). Thus, the top metal nanowire will typically contact between one and three Au grains on the 60 nm-wide thermally-evaporated Ti/Au
bottom contacts. Considering that the C12-molecules are less than 2 nm-long, the contact area should contain bridging molecules, in which both ends of the molecule are in good contact with the top and bottom contacts, as well as non-bridging molecules as illustrated in Figure 4-4. Due to their stronger electronic coupling to the metal contacts, the electrical properties of the junction should be dominated by charge transport through the bridging molecules. However, because of the surface roughness of the Ti/Au bottom contact, the number of bridging molecules can vary by more than a factor of three from device-to-device. In addition, as discussed in Section 3.4.2, the compressive forces (e.g., van der Waals, electrostatic, and meniscus) that are exerted on the SAM junctions during the nanowire alignment and measurement may cause different numbers of bridging molecules to be in compression and tension, which can also contribute to device-to-device variations in current.
The Landauer approach, discussed in Chapter 2, states that the conductance ($G$) of a molecular junction is proportional to the transmission function, as given in Equation 4.1 [11].
Prior work using conducting probe-Atomic Force Microscopy (CP-AFM) estimated that the contact transmission constant for Au/CH₃ (physisorbed contact) is 0.6, while for Au-S-C (chemisorbed contact) it is 0.013 [9] [12]. Since the current \( I \) is directly proportional to the conductance \( G = \frac{e^2}{\pi \hbar} \mathcal{F}(E_F) \) \( (e: \text{ charge of an electron}, \hbar: \text{ reduced Planck's constant}) \)

\[
\mathcal{F}(E_F) = \mathcal{F}_{\text{lower}} \cdot \mathcal{F}_{\text{top}} \cdot \mathcal{F}_{\text{mol}} \quad \text{(4.1)}
\]

\( \mathcal{F}_{\text{lower}} \): Transmission of lower contact  
\( \mathcal{F}_{\text{top}} \): Transmission of top contact  
\( \mathcal{F}_{\text{mol}} \): Transmission of molecule

Prior work using conducting probe-Atomic Force Microscopy (CP-AFM) estimated that the contact transmission constant for Au/CH₃ (physisorbed contact) is 0.6, while for Au-S-C (chemisorbed contact) it is 0.013 [9] [12]. Since the current \( I \) is directly proportional to the conductance \( I = GV \), where \( V \) is voltage), the magnitude of the current in a dithiol junction is expected to be at least 46 times of magnitude larger than that of the monothiol. As discussed previously, the current in the C12-dithiol SAM junctions varied by approximately a factor of five, while the C12-monothiol had a larger factor of ten variation. However, the average current of C12-dithiol junction was approximately one order of magnitude larger than that of the C12-monothiol junctions, as expected from the difference in transmission constants.

Figure 4-5 shows room temperature I-V curves of C12-monothiol and C12-dithiol SAM junctions selected from the devices plotted in Figure 4-3. The nanowire top contact was grounded and a bias was applied to the thermally-evaporated bottom contact, first sweeping from 0 to 1 V and then from 0 to -1 V on each device.
Both alkanethiol junctions had slightly nonlinear I-V characteristics within the bias range of 0 to ±1 V. In the C12-dithiol junction (Figure 4-5, right), the absolute value of the current at +1 V (220 nA) was close to that at -1 V (210 nA), showing less than a 5% variation. In this case, both ends of the dithiol junctions were chemically bonded to the bottom and top contacts. On the other hand, approximately 30% of the C12-monothiol devices had asymmetric I-V characteristics. As an example, the C12-monothiol shown in Figure 4-5 (left) had a higher current of 40 nA at +1 V compared to 32 nA at -1V, which corresponds to a 20% variation. Such asymmetry could be attributed to differences in the physical coupling between the metal nanowire (top electrode) and the methyl end groups of the molecule (CH₃-Au), as suggested by previous CP-AFM measurements [9].
4.2.3 Temperature-dependent I-V measurement

Considering the large HOMO-LUMO gap in the alkanethiol SAM junctions (~ 8 eV), the dominant conduction mechanism is expected to be direct tunneling. The Simmons equation describes the tunneling current, which is given by Equation 4.2 below:

\[
J = \frac{q^2 V}{\hbar^2 d} \left(\frac{2 m \Phi_b}{h}\right)^{1/2} \exp\left[-\frac{4 \pi d}{h} \left(\frac{2 m \Phi_b}{h}\right)^{1/2}\right]
\]

Here, \( J \) is the current density, \( q \) is the electron charge, \( V \) is the applied bias, \( h \) is Planck’s constant, \( m \) is the electron mass, \( \Phi_b \) is the barrier height, and \( d \) is the barrier thickness [13] [14]. Note that the equation does not include any temperature dependent terms.

Temperature-dependent I-V measurements were conducted on several C12-dithiol SAM junction devices included in the room temperature I-V measurement of Figure 4-3.

Figure 4-6: Arrhenius plot of C12-dithiol junctions (open symbols taken while cooling, filled symbols taken while heating).
The devices were cooled from 295 to 45 K in increments of 50 K (cooling; e.g., 295 K, 245 K, 195 K, etc), and then returned to 300K (heating; e.g., 70 K, 120 K, 170 K, etc). Figure 4-6 shows the Arrhenius plot (i.e., current as a function of 1/Temperature) for one such device. The current at 1 V is 480 nA at 300 K and it does not change significantly as the temperature decreased to 45 K. The negligible temperature dependence in the C12-dithiol crossed-wire device confirms that the dominant conduction mechanism is direct tunneling.

Figure 4-7 compares Arrhenius measurements for two different C12-monothiol crossed-wire junction devices. The C12-monothiol junction shown in Figure 4.7 (top) had negligible temperature dependence over the range from 300 to 45 K, while the junction shown in Figure 4.7 (bottom) had significant temperature dependence at temperatures exceeding 170K. Specifically, in this device, the room temperature current was 80 nA at 1 V, and increased as the temperature decreased reaching a maximum of 140 nA at 170 K. The current was essentially independent of temperature at temperatures below 170 K. Approximately 90 % of the C12-monothiol junctions that were characterized exhibited a notable temperature dependence in comparison to only 20 % of the C12-dithiol junctions that form a strong chemical bond with the bottom and top metal electrodes.
It is possible that the temperature dependence exhibited in the majority of the C12-monothiol junctions could be attributed to the effect of thermal expansion on top contact to the molecules. In the crossed-wire device, the C12-monothiol molecules form a physical contact with the top nanowire contact (Au/CH$_3$) that is aligned between two

Figure 4-7: Arrhenius plot of two different C12-monothiol junction devices. The bottom device had a more significant temperature dependence than the top device (open symbol: heating, filled symbol: cooling).
large-area probe/alignment electrodes. As the temperature is changed during measurement, the nanowire bending (restoring) force could be altered due to the thermal expansion mismatch between the substrate and the metal contacts. Consequently, the number of molecules that remain in electrical contact with the top Au nanowire could change, which would result in temperature-dependent I-V characteristics.

### 4.2.4 IETS measurement

Inelastic electron tunneling spectroscopy (IETS) is an *in-situ* spectroscopic technique for measuring the vibrational energies of molecules in metal-molecule-metal junctions. This technique has been applied in molecular electronics for identifying the molecules in the junction that contribute to charge transport as well as studying the vibronic features of the molecular junctions in conjunction with theoretical calculations. Using a standard AC modulation technique, the second harmonic signal \( \frac{d^2I}{dV^2} \) that corresponds to the characteristic vibrational modes of the molecular junction was collected directly [15] [16] [17] [18]. Details of the measurement procedures were described in Chapters 2 and 3.

Figure 4-8 (top) shows the measured IET spectra of C12-dithiol junctions assembled in the crossed-wire device, consisting of a lithographically-defined 60 nm-wide bottom contact and a 220 nm-diameter Au nanowire top contact. A DC voltage ranging from 0 to 0.4 V was applied in 2 mV increments to the nanowire top contact with respect to the bottom grounded contact. This voltage step is small compared to the
thermally-broadened FWHM of 14.5 mV, and thus can be used to resolve closely-spaced peaks in the IET spectra.

Although IR, Raman, and optical spectroscopic techniques can not be used to assign the peaks in an IET spectrum directly, their information about the intrinsic vibrational modes of the molecules can be used as a reference. Based on previous alkanethiol IETS results collected using μm-diameter freestanding crossed metal-wires [19] and nanopore [20] structures, as well as optical spectroscopy of alkanethiol SAMs on planar substrates [21], the observed IET peaks of the C12-dithiol molecular junctions were assigned to specific vibrational modes (see Figure 4-9).
Figure 4-8: Top shows an IET spectrum of a C12-dithiol SAM junction. Each vibrational peak is assigned by comparison to other work (after [22] [20] [21]).

<table>
<thead>
<tr>
<th>Mode</th>
<th>References</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>v(Au-S)</td>
<td>HREELS</td>
<td>225</td>
</tr>
<tr>
<td>v(C-S)</td>
<td>Raman</td>
<td>641</td>
</tr>
<tr>
<td>CH₂ rock</td>
<td>IR</td>
<td>766</td>
</tr>
<tr>
<td>v(C-C)</td>
<td>Raman</td>
<td>1,064</td>
</tr>
<tr>
<td>CH₂ wag</td>
<td>IR</td>
<td>1,283</td>
</tr>
<tr>
<td>CH₂ Scissor</td>
<td>HREELS</td>
<td>1,455</td>
</tr>
<tr>
<td>v(S-H)</td>
<td>Raman</td>
<td>2,575</td>
</tr>
<tr>
<td>v(C-H)</td>
<td>IR</td>
<td>2,975</td>
</tr>
</tbody>
</table>

Bias (mV) | Wavenumber (cm⁻¹) | C12-dithiol
---------|------------------|--------
28       | 225              |
79       | 641              |
95       | 766              |
132      | 1,064            |
159      | 1,283            |
180      | 1,455            |
319      | 2,575            |
368      | 2,975            |

Figure 4-9: Schematics of vibrational motion of an alkane molecule (after [23])
The IET spectrum in Figure 4-8 shows that the most intense peak for this C12-dithiol junction occurred at 368 mV, which corresponds to the C-H stretch mode. By comparison to previous work [22] [21] [13], the less intense peaks at 182 mV, 136 mV, and 82 mV were assigned to CH₂ wag and scissor, C-C stretch, and C-S stretch, respectively. The motion of these vibrational modes is illustrated in Figure 4-9. The varying intensities of the peaks could be attributed to the coupling between the tunneling electron and the vibrations of the molecular junctions. However, the region of 0-50 mV shows a combination of the Au-S stretch (~30 mV) and the zero-bias feature (ZBF), which is believed to originate in phonon interactions in the gold wires and is unrelated to the molecules in the junctions [22].

Recalling the previous discussion of peak broadening (Chapter 3, Section 3.4.1), the experimental resolution of FWHM at 10 K with an AC modulation amplitude of 8 mV is ~14.5 mV, as calculated using Equation 4.4 [24] [25]. Alternatively, by fitting the measured peaks to a Gaussian curve (see next section for details), the FWHM of the C-H stretch (366 mV) and the CH₂ rock (98 mV) were determined to be 46 and 25 mV, respectively. These estimated FWHM for these peaks are larger than expected from this calculation, which suggests that the measured peaks may be a superposition of more than one closely spaced vibrational mode or increased local junction temperature. Improved energy resolution can be obtained by lowering the junction temperature and/or modulation voltage as discussed later in this chapter.
4.3 Conjugated OPE SAM junctions

4.3.1 Room temperature I-V measurement

The length of C12-dithiol and OPE molecules are very similar (C12-dithiol: 1.63 ± 0.5 nm, OPE: 1.65 ± 0.1 nm) [26]. However, saturated C12-dithiol has a σ-bonded molecular structure, whereas the OPE molecule is π-conjugated. As discussed in Chapters 1 and 2, this difference in molecular structure has a dramatic influence on the electrical properties of the junction. Specifically, the σ-bonded C-12 molecule serves as an electrical insulator, while the π-conjugated OPE is a so-called molecular wire. This section investigates the electrical and spectroscopic properties of the crossed-wire OPE junctions, and compares them to the C12-dithiol junctions examined previously (Section 4.2.2). The OPE junctions that were characterized consisted of a thermally-evaporated 60 nm-wide Au bottom contact and a single 220-nm diameter Au nanowire top contact. Similar to the C12-dithiol SAM junctions, both ends of OPE-dithiol molecule are chemically bonded to the top and bottom contacts.

Figure 4-10 shows the room temperature I-V characteristics of ten OPE and ten C12-dithiol junctions collected from devices fabricated in several different process runs. Short and open circuited junctions were excluded from this plot.
The measured current at 1 V in the crossed-wire OPE-dithiol junction devices varied from 1 to 3.5 µA as compared to 100 to 500 nA in C12-dithiol devices. As discussed in Section 4.2.2, the variation in the current in the OPE can be also be attributed to the surface roughness of the thermally-evaporated bottom contact. Despite this variation, on average, the data in Figure 4-10 show that the OPE junctions have approximately a one order of magnitude higher current than the C12-dithiol junctions. This was expected because the π-conjugation provides electron delocalization along the length of the molecule, thus giving a lower barrier for electron transport. As discussed in Chapter 2 (Section 2.1), the tunneling current ($I_{mol}$) can be written as [3],

$$I_{mol} = I_0 e^{-\beta d}, \quad \text{where } \beta = \sqrt{\frac{8m\Phi}{\hbar^2}}$$
where $I_0$ is the rate transfer constant, $m$ is the electron mass, $\Phi_b$ is the barrier height, $\hbar$ is the reduced Planck’s constant, and $d$ is the barrier thickness. Due to the lower tunneling barrier relative to saturated alkanes, the conjugated OPE junctions should have higher current for junctions with the same contact area. The data presented here are in good agreement with previous experimental data obtained using µm-diameter freestanding crossed metal-wire [27] and in-nanowire test structures [26]. Both of these device structures showed a similar one to two order of magnitude increase in the current of conjugated OPE junctions with respect to saturated C12-dithiol junctions. Figure 4-11 shows the room temperature I-V characteristic of an OPE-dithiol SAM junction device that was selected from those plotted in Figure 4-10. Here the top nanowire contact was grounded and a bias ranging from 0 to +1 V and from 0 to -1 V was applied to the thermally-evaporated bottom contact. Although, the current increased linearly with increasing voltage in the low-bias regime ($< 0.4$ V; Figure 4-11 (right)), the OPE-dithiol junction exhibited nonlinear characteristics at higher bias. The current at 1 V is 2.62 µA and a similar current of 2.61µA was observed at -1 V, showing symmetry.
4.3.2 Temperature-dependent I-V measurement

Temperature-dependent I-V measurements were performed to study the dominant conduction mechanisms in crossed-wire OPE-dithiol junction devices. The Arrhenius plot in Figure 4-12 shows negligible temperature dependence over the range of 300 to 50 K in these junctions. This suggests that the dominant transport mechanism is coherent tunneling. This temperature-independent behavior was also observed in OPE-dithiol junctions fabricated along the length of 40 nm-diameter nanowires contacted on the bottom and top Au and Pd, respectively [28].

Figure 4-11: Typical I-V characteristic of OPE-dithiol junction. Right shows the low-bias regime (< 0.4 V)
4.3.3 IETS measurement

Figure 4-13 shows an IET spectrum collected from a crossed-wire OPE junction device measured by grounding the nanowire top contact and applying a DC bias voltage to the thermally-evaporated bottom contact. The bias was first swept in the positive direction from 0 to 0.3 V in 2 mV increments, and then in the negative direction from 0 to -0.3 V in 2 mV increments. The spectrum shown in Figure 4-13 was smoothed using a five-point Fourier Fast Transform (FFT) routine.

Figure 4-12: Representative Arrhenius plot of crossed-wire OPE junction (filled symbol: cooling, open symbol: heating).
Three prominent peaks were observed at similar energies (positions) in both bias polarities. Since the structure of the OPE molecule is symmetric (Figure 4-1, right), the peaks in the IET spectrum were expected to be symmetric about zero energy [29] as shown by the measured data. Based on the IET spectra obtained from μm-diameter freestanding crossed-wire molecular junctions [19] and optical spectroscopy of planar OPE SAMs [2], the measured IET peaks of the OPE junction at 132 mV, 196 mV, and 276 mV were assigned to the $\nu(18a)$, $\nu(8a)$, and $C \equiv C$ stretch vibrational modes, respectively.

Figure 4-13: IET Spectrum of crossed-wire OPE junction device

<table>
<thead>
<tr>
<th>Measurement condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Temperature: 4.2 K</td>
</tr>
<tr>
<td>2. DC bias: (first sweep) 0 – 0.3 V, (second sweep) 0 – -0.3 V</td>
</tr>
<tr>
<td>3. DC bias step: 2 mV</td>
</tr>
<tr>
<td>4. AC signal: 6 mV, 433 Hz</td>
</tr>
</tbody>
</table>
4.3.4 Comparison to the theory

The measured IET spectrum of the OPE-dithiol junction was interpreted by comparison to theoretical calculations performed by Troisi and Ratner [30] that used non-equilibrium Green’s function and density functional theory methods to determine the dominant vibration mode energies and intensities. Figure 4-14 compares the IET spectrum that was obtained experimentally in the crossed-wire junction with the theoretically-calculated spectrum that included thermal peak broadening. The three prominent peaks found at $\nu(18\ a)$ at 138 mV, $\nu(8\ a)$ at 202 mV, and (C≡C stretching) at 274 mV were in strong agreement with the theoretical calculation.
The effect of peak broadening was experimentally investigated by lowering the AC modulation voltage. As discussed in Chapter 3 (Section 3.3.2), the relationship between the FWHM ($\Gamma$) and modulation voltage ($V_{ac}$) is given in Equation 4.4 [24] [25].

<table>
<thead>
<tr>
<th>Vibrational Mode</th>
<th>Measured Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DC Bias (mV)</td>
</tr>
<tr>
<td>$\nu$(18 a)</td>
<td>138 mV</td>
</tr>
<tr>
<td>$\nu$(8 a), ring breath</td>
<td>202 mV</td>
</tr>
<tr>
<td>C=C stretching</td>
<td>274 mV</td>
</tr>
</tbody>
</table>

Figure 4-14: Comparison of measured and calculated IET spectrum of OPE junctions
Here, $T$ is temperature (K), $k_B$ is Boltzmann’s constant, $e$ is the charge of an electron, $V_{ac}$ is the RMS AC modulation voltage ($V$), and $\Gamma_0$ is the intrinsic FWHM of molecular vibrations (about 2 mV). The experimental resolution of FWHM at 4.2 K with an AC modulation amplitude of 6 mV is ~10.6 mV, as calculated using Equation 4.4. This equation also indicates that the peak broadening should decrease as the AC modulation voltage is decreased at a fixed temperature.

The three IET spectra shown in Figure 4-15 were measured on the same OPE-dithiol device at a substrate temperature of 4.2 K using AC modulation voltages of 8, 6, and 4 mV, respectively. For comparison, the energy and intensity of each distinct vibrational mode of the molecular junction calculated excluding thermal broadening were superimposed on this figure.

\[
\Gamma = \left[ (\Gamma_{thermal}^2 + (\Gamma_{ac\ modulation}^2) + \Gamma_0^2) \right]^{1/2}
\]

\[
\Gamma = \left[ \left( \frac{5.4k_BT}{e} \right)^2 + (1.7V_{ac})^2 + \Gamma_0^2 \right]^{1/2}
\]

\[
\Gamma \approx \left[ \left( \frac{5.4(8.62 \times 10^{-5}eV/K)(4.2K)}{e} \right)^2 + (1.7(6\times10^{-3}V))^2 + (2\times10^{-3}V)^2 \right]^{1/2}
\]

\[
\approx 10.6 \text{ mV}
\]
As predicted by the theoretical calculation, the intense vibrational modes at 132, 198, and 276 mV correspond to the energies with maximum peak intensity in the measured IET spectra. In addition it is possible to resolve several lower intensity modes after lowering the AC modulation voltage. For example, the vibrational modes denoted by (A) and (B) in Figure 4-15 appear as distinct shoulders on the intense IET peaks centered at 132 and 198 mV. This experimental data suggests that improvements in the IET peak resolution can be achieved by lowering the modulation voltage to 4 mV without reaching a limit due to significant decreases in the signal-to-noise ratio.

The intense peaks in the 180 to 220 mV bias range measured at each AC excitation voltage were further decomposed into three distinct peaks represented by
Gaussian functions. Prior to the decomposition, the spectra in Figure 4-15 were smoothed using a five-point FFT routine, as shown in the top panel of Figure 4-16.

Figure 4-16: Decomposition of the peaks in the 180 to 220 mV bias range (shaded yellow) for spectra obtained using an AC excitation voltage of 4, 6, and 8 mV at 4.2 K. Each peak was fit by three Gaussian functions.
As shown in the bottom panel of Figure 4-16, the decomposed peaks of spectra collected using the 4, 6, and 8 mV AC modulation voltage had similar peak positions of 199, 197, and 200 mV. Although there are differences in the relative peak intensities, the peak at ~200 mV that was assigned to the ν(8 a) ring mode was the most intense in each spectrum. In addition, the FWHM became smaller as the AC modulation voltage was reduced.

The FWHM ($\Gamma_{\text{exp}}$) of the dominant vibrational mode at ~200 mV was fit using the Gaussian function given in Equation 4.5 [25].

$$y = y_0 + \frac{A}{w\sqrt{\pi}/2} e^{\frac{2(x-x_c)^2}{w^2}}$$

\[
\begin{align*}
  & y_0: \text{Baseline offset} \\
  & x_c: \text{Center of the peak} \\
  & w: \text{Standard deviation (2}\sigma) \tag{4.5}
\end{align*}
\]

$$\Gamma_{\text{exp}} = w\sqrt{2(\ln 2)} = 1.177w$$

Using the fitting parameter $w$ (Figure 4-17), the FWHM of this peak was determined to be 16 mV, 14.4, and 10 mV for modulation voltages of 8, 6, and 4 mV, respectively. The FWHM of this dominant vibrational mode as a function of the AC excitation voltage is plotted in Figure 4-17.
The slope extracted from experimental data is similar to that obtained from Equation 4.4, however, the difference in the magnitude of the FWHM in the experiment and the calculation is approximately 2.9 mV. Unlike the calculation that assumes a single vibrational mode, the dominant peak still may be a superposition of a several different vibrational modes that are closely spaced in energy. Alternatively, the molecular junction could also be heated locally by inelastic tunneling electrons during the measurement, which would give rise to an increase in the actual junction temperature (i.e., larger $\Gamma_{\text{thermal}}$), which would result in a larger FWHM than estimated using the measured substrate temperature.

Figure 4-17: FWHM as a function of a modulation voltage (4 mV, 6mV, and 8 mV)
4.4 Conclusion

This chapter investigated the electrical and spectroscopic properties of saturated alkanethiol and \(\pi\)-conjugated OPE SAM junctions assembled in nanoscale crossed-wire devices. Since these molecules have been studied extensively in previous experiments, their results were used to evaluate the new crossed-wire device structure developed in this thesis work. First, the effect of a chemisorbed contact and a physisorbed contact on a SAM junction was investigated using C12-dithiol and C12-monothiol junctions. The current in C12-dithiol showed approximately a one order of magnitude higher average current compared to the C12-monothiol junctions. In addition, the C12-dithiol molecular junctions showed a smaller current distribution than that in the C12-monothiol junctions. The C12-dithiol molecules showed temperature independence over the investigated bias range, indicating coherent tunneling as expected in a large HOMO-LUMO gap saturated molecular junction. The observed IET spectra of C12-dithiol junctions show peak positions and intensities similar to that in the \(\mu\)m-diameter freestanding crossed metal-wire structure, nanopore device and optical spectroscopy results.

Although OPE and C12-dithiol are very similar in length, the higher average current observed in OPE molecule is due to its \(\pi\)-conjugation, which provides delocalized \(\pi\)-electrons for improved conduction. The OPE molecular junction showed temperature independence from 300 to 50 K, indicating coherent tunneling. IET spectra were obtained with both positive and negative bias, resulting in symmetric peak positions. The three prominent peaks found at 138 mV (\(\nu(18\ a)\)), 202 mV(\(\nu(8\ a)\)), and 274 mV(C≡C stretching) were in an excellent agreement with the theoretical calculation that included
peak broadening. Furthermore, the excitation voltage-dependent IET spectra results suggest that higher resolution IET spectra can be obtained by lowering the AC modulation voltage.

4.5 References

Chapter 5

Oligoaniline SAM Junctions

5.1 Introduction

Metal-molecule-metal junctions comprised of single [1] [2] or small ensembles [3] of densely-packed oligoaniline molecules have exhibited bistable switching between high- and low-conductance states. For example, the high- and low-conductance states were observed in a hepta-aniline oligomer [2] held in an electrolyte using the Scanning Tunneling Microscope (STM)-break junction technique described in Chapter 1. As illustrated in Figure 5-1, a single junction was formed by pushing/withdrawing a Au-coated STM tip into a Au(111) film substrate that carried a sub-monolayer of hepta-aniline in 50 mM H$_2$SO$_4$ electrolyte.

Figure 5-1: Electrical characterization of single hepta-aniline oligomer junction using STM-break junction technique (after [2])
Without a substrate potential (i.e., \(E_S=0\) V), the molecule had a low conductance. This neutral molecule was then oxidized by applying a substrate potential (\(E_S=0.4\) V), resulting in a higher conductance. The magnitude of the current of the oxidized molecule was fifteen times larger than that of the neutral molecule. This measurement was conducted in an electrolyte, wherein the mobile ions (cation: \(H^+\), anion: \(HSO_4^-\)) can easily stabilize the charged molecule in the oxidized state.

A reversible switching behavior was also observed in solid-state metal-molecule-metal junctions containing small ensembles of a few thousand densely-packed thiol-substituted N-methyl-oligoaniline (OMAn) molecules as shown in Figure 5.2 [3].

In contrast to the STM-break junction device, these solid state junctions were not immersed in an aqueous electrolyte, and thus did not contain any *intentional* mobile counter ions [3]. As shown in Figure 5-3, the 40 nm-diameter nanowire device is comprised of molecular monolayers positioned between Au (or Pd) and Pd electrodeposited nanowire segments. When a bias exceeding a threshold voltage of \(\pm 1.5\) V was applied, the junctions were switched between high- and low-conductance states with a conductance ratio of up to 50 at room temperature.
Although the oligoaniline junctions formed in solution and in the solid state both showed similar bistable switching behavior, it is not clear whether the molecular conformations in the solid state would be similar to those in the electrolyte, wherein the mobile ions can easily stabilize the charged structure that results from a structural change from benzene to quinoid rings (see the next subsection) [4] [5]. This chapter uses *in-situ* Inelastic Electron Tunneling Spectroscopy (IETS) in conjunction with current-voltage (I-V) measurements to gain insight into the correlation between the molecular structure and the electrical properties of OMA n SAM junctions. As discussed in Chapters 2 and 3, by measuring the characteristic vibrational modes of molecular junctions, the IET spectra in the high- and low-conductance states can be correlated to the molecular structure in each conductance state. The observation of molecular vibrational energies in both conductance states can also be used to confirm that the dominant charge transport occurs through the molecules rather than process induced artifacts (e.g., metal filaments) as discussed in

Figure 5-3: Reversible bistable switching behavior of OMA n SAM junctions in an in-wire structure (after [3])
Chapter 1. Prior to describing the electrical and spectroscopic characterization of the crossed-wire OMAn SAM junctions, the next subsection will present a brief overview of the properties of the conducting polymer, polyaniline (PANI).

5.1.1 Polyaniline

PANI is one of the most extensively studied conducting polymers [6] [7] [8]. Due to its stability and low cost, PANI is being considered for use in various applications, such as rechargeable battery electrodes [9], chemical sensors [10], anticorrosion coatings [11], and so forth. The electrical properties of PANI and its derivatives can be controlled either by redox chemistry (i.e., electron-removal (oxidation), electron-injection (reduction)) or by Bronsted acid-base reactions (i.e., protonation, deprotonation). As shown in Figure 5-4, PANI exists in four distinct forms that differ in their oxidation state [5].
The following provides a brief overview of the four states of PANI.

(1) The fully reduced PANI is called leucoemeraldine base (LEB or poly(paraphenylene amine)), in which the phenylene rings are interconnected by amine-nitrogen atoms. This form has relatively low conductance due to its large band gap of 3.8 eV.

(2) Low conductivity has also been observed in the fully oxidized form, pernigraniline (PNB or poly(paraphenylene imine)), with which the chemical structure is characterized by alternating aromatic and quinoid rings.

(3) The intermediate emeraldine base (EB or poly(paraphenylene amine imine)) contains quinoid and aromatic rings in a 1:3 ratio in its chemical structure. The measured lowest absorption energy is about 2.0 eV in its polymer film.

(4) The emeraldine salt (ES) is the electrically conducting form of PANI that can be obtained either by protonation of EB or by oxidation of LEB. This structure contains
aromatic and radical cations, which are present on every second nitrogen atom. This degenerate form can provide a high charge-carrier mobility mainly through inter- and intra-chain hopping between the localized charge sites on the polymer backbone [12]. As a result, the non-conductive LEB can be changed to conductive ES yielding a 12 order of magnitude change in conductivity (typically from $10^{-10}$ to $10^2$ S/cm). Additional factors, such as crystallinity, can also play a crucial role in the conductivity of PANI film.

Although the rigid and planar backbone in PANI results in high conductivity, it also makes the material insoluble in most common solvents. By placing a substituent (e.g., methyl, ethyl, propyl or butyl group) on the PANI backbone, the material can be made more soluble. In addition, the electrochemistry can be less complex, because the EB-ES transition in PANI (Figure 5-4) occurs only by protonation (addition of a proton ($H^+$) to the polymer) and deprotonation on the nitrogen atom, and the addition of the substituent hinders this acid-base reaction. Figure 5-5 illustrates the oxidation/reduction process of the N-substituted derivatives of PANI.
When the LE form loses two electrons in each unit, one of the benzene rings becomes a quionon, transforming to the E structure. In a similar way, the E form can be oxidized to the PN by losing another two electrons. Note that when a benzene ring is transformed to a quinoid ring through oxidation (loss of an electron), the mobile counter anions (A^- in the figure) are attracted to the nitrogen atom in order to neutralize the charged polymer.

**5.1.2 Thiol-substituted OMAAn**

The thiol-substituted OMAAn (4-{Methyl-at-amino}-benzenethiol) molecules studied in this chapter were provided by Professor Tour’s group at Rice University (Figure 5-6). The details of the molecule synthesis can be found in the previous work by Flatt et al. [13]. The OMAAn molecule contains methylated nitrogen atoms that can limit
the oxidation process to the highly conductive ES rather than the non-conductive EB, as discussed in the N-substituted derivatives of PANI. Consequently, this compound can be oxidized reversibly between the non-conductive LE and the conductive ES.

A prior study by Cai et al., [3] measured cyclic voltammograms (CV) of OMAn monolayers assembled onto a planar Au surface that was measured using a neutral electrolyte solution of 50 mM tetrabutylammonium perchlorate (TBAP)/CH2Cl2. As shown in Figure 5-6 (left), the CV contains two reversible, one-electron oxidation/reduction peaks at 0.35/0.23 V (vs Ag+/Ag) and 0.74/0.62 V with a potential ΔE ≈ 120 mV. Over 20 cyclic scans were reproducible in the same sample, indicating that the OMAn SAM is stable and robust. This redox process seems to be consistent with a chemical change from the neutral (bottom), to the radical cationic (center), and then to the dicaticonic state (top) of the molecule as illustrated in Figure 5-6 (right).

Figure 5-6: (left) A cyclic voltammogram of OMAn monolayer on Au substrate (after [3]). (right) Possible redox mechanism of thiol-substituted OMAn SAM junctions. A- represents mobile ions (counter ions).
Assuming that the OMA\textsubscript{n} molecule follows the same oxidation/reduction process as shown in Figure 5-6, the OMA\textsubscript{n} SAM junction (bottom) would be oxidized by losing two electrons (top). The oxidized molecules then require two anions (counter ions; represented $A^-$ in the figure) to stabilize its charged structure. Unlike in an electrolyte, wherein the mobile ions (cation: $H^+$, anion: $HSO_4^-$) can easily stabilize the charged molecules, the solid state junctions do not contain any intentional mobile ions (i.e., anions and cations). Thus, this seems unlikely that this structural conformation can explain the observed bistable switching in OMA\textsubscript{n} SAM junctions, and this subject must be explored more thoroughly.

5.2 Current-Voltage (I-V) measurements

Following the standard fabrication procedure described in Chapter 3, nanoscale OMA\textsubscript{n} crossed-wire devices were fabricated that consisted of 60 nm-wide thermally-evaporated Ti/Au bottom contacts and a single ~220 nm-diameter Au nanowire top contact. The assembly procedure is described in Table 5-1.

<table>
<thead>
<tr>
<th>Table 5-1: Assembly condition for OMA\textsubscript{n} SAM</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pre-clean: diluted RCA 1 (NH\textsubscript{4}OH:H\textsubscript{2}O\textsubscript{2}:DI water = 1:1:5), 1 min</td>
</tr>
<tr>
<td>2. Preparation of molecular solution: 0.1 mM (CH\textsubscript{2}Cl\textsubscript{2}: EtOH = 1:5), 3 min sonication</td>
</tr>
<tr>
<td>3. Incubation: wrap sample container with aluminum foil to protect from the light and store for about 3.5 hour in N\textsubscript{2} glove box</td>
</tr>
</tbody>
</table>
5.2.1 Room temperature I-V measurement

Figure 5-7 (left) illustrates the molecular structure of oligo(phenylene ethynylene) (OPE) and OMA\textsubscript{N}. Both molecules are similar in that the structure is comprised of three interconnected benzene rings. However, the OMA\textsubscript{N} molecule possesses a N-methyl group between the benzene rings, while a triple-bonded carbon atom occurs in the OPE molecule. This gives rise to the different electrical properties of the junctions. Since OPE SAM junctions have been studied extensively in other work as well as in Chapter 4, their electrical and spectroscopic properties can be used for comparison to those obtained in OMA\textsubscript{N} SAM junctions measured here. For example, Figure 5-7 (right) shows the room-temperature I-V characteristics of crossed-wire OPE SAM junctions, exhibiting nonlinear I-V features with a bias sweep from 0 to ±1 V. The device did not show evidence of switching behavior.

---

Figure 5-7: (left) Molecular structure of OMA\textsubscript{N} and OPE molecules. (right) Typical room temperature I-V characteristics of a crossed-wire OPE SAM junction that does not show evidence of switching behavior
Once the applied bias exceeded 2.9 V, an irreversible breakdown occurs in the device. The estimated electric field strength using Equation 5.1 is $1.7 \times 10^7$ V/cm for a thickness of 1.6 nm and a breakdown voltage of 2.9 V.

$$E_{\text{break down}} = \frac{V}{d} = \frac{2.9V}{1.6\text{nm}} \approx 1.7 \times 10^7 \text{ V/cm} \quad (1.7 \text{ GV/m})$$ 5.1

This value is similar to that obtained in metal-insulator-metal (Hg) junctions where two metal plates are separated by a nanometer-thick dielectric (e.g., hexadecanethiol (HDT): 0.8 GV/m, polyethylene: 0.6 – 0.8 GV/m, etc) [14]. The lack of switching behavior in these crossed-wire OPE SAM junctions was also observed in the in-wire junction device [3] illustrated in Figure 5-3.

On the other hand, the OMAN molecular junctions that possess the N-methyl group redox moiety can be reversibly switched between low- and high-conductance states in a non-aqueous environment (solid state) that contains no intentional mobile counter ions. Figure 5-8 shows the room-temperature I-V characteristics of a representative crossed-wire OMAN SAM junction.
The following characteristics were observed:

(1) As the voltage was increased from 0 to 1.0 V, the current increased until a sudden jump occurred at ~ 1.0 V.

(2) Once the junction was switched to the high conductance state, it remained in this state, and the voltage could be swept back and forth in the state within a bias window of ±1.0 V.

(3) The junction was restored to its original low conductance state by sweeping the voltage to a negative threshold voltage of ~ −1.0 V.

(4) The ratio of the high- to low-conductance states at zero bias was seven for this particular device (inset of Figure 5-8).

Figure 5-8: Typical room-temperature I-V characteristics of Au-OMAn(SAM)-Au junctions exhibiting two conductance states.
Several tens of crossed-wire OMA\textsubscript{n} SAM junctions fabricated in different synthetic runs were characterized at room temperature. The junction-to-junction variation in the low-conductance state ranged from tens of nA to a few \(\mu\text{A}\) at 1 V, whereas that of the high-conductance state ranged from hundreds of nA to tens of \(\mu\text{A}\) at 1 V. The ratio of high- and low-conductance at zero bias varied from 4 to 20, and the threshold voltage varied from 1.0 to 1.5 V. As discussed in Chapter 3, the variation in current in either state can, at least in part, be attributed to a variation in the number of bridging molecules contacted in the junction area, as illustrated in Figure 5-9.

Figure 5-9: Schematic of metal-SAM-metal junction in crossed-wire device

However, the considerably larger three order of magnitude variation of the OMA\textsubscript{n} SAM junctions in comparison to the one order of magnitude variation observed for the alkane and OPE SAM junctions may be attributed to differences in the ordering of the OMA\textsubscript{n} SAM. Unlike the alkanethiol and OPE molecules that can be assembled into a well-ordered and densely-packed SAMs, recent studies conducted by Maitani \textit{et al.} have shown that the OMA\textsubscript{n} molecules have sub-configurations and that SAM formed using these molecules have small molecular domains (~ 5 nm). This can result in larger
differences in the active junction area, resulting in larger device-to-device variations in current. The details of these measurements will be discussed in Section 5.2.3.

Once a crossed-wire OMAn SAM junction was switched from the low- to high-conductance state (or high to low), it remained in that state until an opposite voltage exceeding the threshold was applied. The high-state current of several OMAn devices that were switched from the low-conductance state under vacuum ($< 4 \times 10^{-6}$ Torr) and at room temperature were measured again after a day, showing no notable decay in the current. This long retention time suggests that the switching behavior can not simply be attributed to a change in electronic state of the molecule, which would give rise to a short transient decay ($< 20$ min [15] [16]). Rather, the switching behavior in the OMAn SAM junctions may be due to reversible conformational changes in molecules between two stable structures.

### 5.19.2 Low temperature I-V characterization

This chapter uses IET spectroscopy in conjunction with I-V measurements, which allows one to monitor the vibronic energies of the molecular junction *in-situ* as the conductance state of the device is switched from low to high (and vice versa), to correlate the molecular structure and the electrical properties of the crossed-wire OMAn SAM junctions. In order to minimize peak broadening, IETS measurements were conducted at low temperatures ($< 10$ K). Thus, the low temperature I-V characteristics were also investigated in these junctions.
Figure 4-10 shows I-V characteristics of a crossed-wire OMAn junction measured at 4.2 K. The SAM junction exhibited bistable switching with a ratio of high- and low-zero bias conductance of seven and a threshold voltage of ~ 2.5 V. The first set of I-V characteristics were collected by biasing the device in the low-conductance state. Following 100 successive I-V sweeps (black: first set of 50 I-Vs, blue: second set of 50 I-Vs) from 0 to 0.7 V, the device was switched from the low-conductance to the high-conductance state by applying a voltage of 2.5 V. Then, 150 I-V sweeps were collected in the high-conductance state for the same device from 0 to 0.7 V. All of the measurements used the bottom electrode as a ground.

Figure 5-10: I-V characteristics of an OMAn crossed-wire device at 4.2 K. The high conductance state seems to be stabilized with additional voltage sweeps within the threshold voltage.

The inset of Figure 4-10 magnifies the 150 I-V sweeps within a range of 0.3 to 0.6 V in the high-conductance state. The current distribution of the first set of 50 I-V sweeps (red) became narrower and the magnitude of the current increased in the second (green) and
the third set (black) of sweeps. Compared to the low-conductance state, which seem to be less affected by additional voltage sweeps, the high-conductance state begins to reach a stable state after 10+ successive voltage sweeps.

Figure 5-11 (top) shows the current variation of the OMAn SAM junction in high- and low-conductance states measured as a function of time at different fixed biases. First, the current at 0.8 V and 1.2 V in the low-conductance state was measured at 0.1 s intervals for total duration of 120 s (1200 data points). The observed current variation was 80 to 110 nA at 0.8 V and 180 to 320 nA at 1.2 V, respectively. The device was then switched from the low- to high-conductance state and the current at 1.0 V was collected. No additional sweeps were taken in this device after switching to the high state. The observed current variation is 550 to 720 nA during the 120 s measurements. These current fluctuations indicate that there are dynamic variations in the conductance through a fraction of the molecules in the junction. This effect is considered in the next section in comparison to the OPE junctions.
Figure 5-11: (top) Current-time sampling measurements in high- and low-conductance states at different fixed biases. (bottom) Conductance histogram obtained from the current-time data.

Figure 5-11 (bottom) shows a conductance histogram that was obtained from the current versus time data (Figure 5-11, top). Following the conversion from current to conductance (conductance = current/applied bias) at a fixed bias, the number of data
points within a 10 nS range of conductance were counted and placed in the corresponding bin on the histogram. Although the magnitude of the conductance at constant voltage varied during the 120 s measurement, the conductance state (high- and low-state) was unchanged and did not revert to the other state.

5.2.3 IETS measurements

As discussed in Chapters 2 and 3, IET spectroscopy measures the characteristic vibrational energies of molecular junctions, which can be observed as peaks in a plot of $d^2I/dV^2$ versus $V$. This technique can be a useful tool for studying bistable molecular junctions in which the electrical properties may depend on the molecular conformation. Specifically, by collecting the characteristic vibrational modes in each electronic state of the device, the molecular conformations that may be responsible for the electrical properties of the junction in that conductance state can be monitored directly. In addition, the observation of clear molecular vibrational energies in both conductance states can be used to confirm that the dominant charge transport occurs through the molecules rather than process induced artifacts (e.g., metal nanofilaments) as discussed in Chapter 1.

Figure 4-13 shows measured and smoothed IET spectra collected at 4.2 K on crossed-wire OPE SAM (top) and OMA@ SAM junctions (bottom). Here the measured IET data are plotted using solid blue squares, and the five-point FFT smoothed fit to this data is shown as red lines. It can be noted that the IET spectra observed in the crossed-wire OMA@ SAM junctions had lower signal-to-noise ratio than the OPE SAM junctions even though the same temperature (4.2 K) and AC modulation voltage (8 mV) were used.
in both measurements. This can be confirmed because the FWHM of a peak due to a molecular vibration measured under these conditions is ~15 mV; thus the sharp spurious peaks in the OMan SAM junction that have line widths of < 5 mV are not due to molecular vibrational modes.

Figure 5-12: IET spectra of OPE (top) and OMan (bottom) junctions at 4.2 K. The raw data were presented in squares, while the smoothed data in red lines. The smoothed OMan IET spectra will be used in the comparisons next.
Because peaks in the IET spectrum arise from very small changes in current at a certain bias, random current fluctuations such as those shown in Figure 5-11 may produce spurious peaks in the IET spectrum. Additional current versus time measurements were conducted at in the low-bias regime used for IETS to compare the magnitude of the current fluctuations in OPE an OMAn SAM junctions. Figure 5-13 shows the current-time (I-t) characteristics of OPE (A and B) and OMAn (C and D; low-conductance state) SAM junctions that were measured at 4.2 K using a fixed bias of 0.1 or 0.5 V. The current was measured in 0.1 s intervals for a total duration of 100 s.
Figure 5-13: (left panel) I-t characteristics of OPE and OMAan SAM junctions in the low-conductance state collected at 0.1 s intervals for a total duration of 100 s; (right panel) Current histograms obtained from I-t data.
To more directly compare the OPE and OMAn SAM junctions, each I-t measurement was converted into a current histogram. The number of data points within a 25 pA (A), 100 pA (B), 50 pA (C), and 25 nA (D) range of current were counted and placed in a bin on the histogram. The right panel of Figure 5-13 shows the current histogram for each junction and bias condition. The mean, standard deviation (σ), and FWHM (2.3548 σ; discussed in Chapter 4 (Section 4.3.3) were extracted by fitting the data to Gaussian function, and are given in Table 5-2.

Table 5-2: Current fluctuation of OPE and OMAn SAM junctions with fixed biases (0.1 V and 0.5 V)

<table>
<thead>
<tr>
<th></th>
<th>OPE</th>
<th>OMA n</th>
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<tbody>
<tr>
<td></td>
<td>0.1 V</td>
<td>0.5 V</td>
</tr>
<tr>
<td>mean</td>
<td>2.35 × 10^{-8}</td>
<td>1.45 × 10^{-7}</td>
</tr>
<tr>
<td>2 σ</td>
<td>3.08 × 10^{-10}</td>
<td>1.40 × 10^{-9}</td>
</tr>
<tr>
<td>FWHM</td>
<td>7.25 × 10^{-10}</td>
<td>3.30 × 10^{-9}</td>
</tr>
<tr>
<td>current fluctuation</td>
<td>0.8 %</td>
<td>0.6 %</td>
</tr>
</tbody>
</table>

This analysis shows that the current fluctuation at a fixed bias of 0.1 and 0.5 V in the crossed-wire OPE SAM junctions was 0.8 and 0.6 % of the total current, respectively. This indicates that the IET spectra measured over the 0 to 0.3 V bias may include spurious peaks due to current fluctuations of < 1 %. As shown in Figure 4-13, further smoothing (red lines) on the OPE raw data does not seem to change the vibrational features in the IET spectra.

In contrast, the crossed-wire OMAn SAM junctions had significantly larger current fluctuations of 5.2 and 4.2 % at a fixed bias of 0.1 and 0.5 V, respectively. Consequently, this larger fluctuation indicates that the IET spectra of OMAn SAM
junctons will contain more spurious peaks than the OPE SAM junctions. Although the OMA\textit{n} spectra have lower signal-to-noise ratio than the OPE SAM junctions, analysis of IET spectra collected from many different OMA\textit{n} SAM junctions showed consistent trends in vibrational mode peak position and intensity after smoothing the measured data using a five-point FFT routine. The following sections will present the results of these measurements and analysis.

The vibronic features of OMA\textit{n} SAM junctions corresponding to the high- and low-conductance states were studied by conducting IETS on crossed-wire OMA\textit{n} SAM junctions comprised of thermally-evaporated Ti/Au bottom contacts and single \(\sim\)220 nm-diameter Au nanowire top contacts. The width of the bottom lithographically-defined contact was either 60 nm (F, H, J, B, C, and E) or 1.5 \(\mu\)m (G, I, A, and D). Figure 5-14 shows IET spectra of ten different OMA\textit{n} junctions measured at 4.2 K using a 433 Hz AC modulation voltage of 6 mV (A, C, G, and J) or 8 mV (B, D, E, F, H, and I).
The second derivative \( \frac{d^2I}{dV^2} \) was obtained by measuring the second harmonic using the LIA technique described in Chapter 3. After changing the bias set-point, a single data point was collected after allowing the current signal to stabilize for 20 s. The measured IET spectra were smoothed using a five-point FFT routine prior to analysis. Junctions (A) through (E) were measured in the low-conductance state, and junctions (F) through (J) were measured in the high-conductance state that was obtained immediately after switching the device from the low state at room temperature (i.e., no additional I-V sweeps after the device was switched to the high state).

Figure 5-14: IET spectra of ten OMAn crossed-wire devices, where (A) – (E) were in the low-conductance state and (F) – (J) were in the high-conductance. The prominent peak change was observed around the 150 – 200 mV range.
Although the OMAAn IET spectra in the low-conductance state showed small variations in peak position and intensity, each spectrum had three dominant peaks (left panel in Figure 5-15; A – E). Referring to the table of group frequencies used in the optical spectroscopy (e.g., IR and Raman) and the calculated IET spectra (next section), the peaks near 45 mV, 125 mV, and 195 mV were tentatively assigned to the C-H out-of-plane bend, C-H bend, and C=C stretch modes, respectively.

Figure 5-15: IET spectra in the low-conductance state (A – E) showed three dominant peaks. As the conductance state changed from low to high (F – J), the peak intensity of the C-N mode (170 mV) increased, while the intensity of the C=C vibrational mode decreased.
The right panel in Figure 5-15 (F – J) shows the IET spectra in the high-conductance state. The peak near 125 mV was tentatively assigned to the C-H bending mode that was also present in the low-conductance state. The peaks near 70 mV and 170 mV may be related to the C-C-N bending and C-N stretching modes, respectively. A difference in the prominent peak position between high- and low-conductance states was observed in the range of 150 to 200 mV. Specifically, an intense peak occurred near 200 mV in the low-conductance state, compared to 170 mV in the high-conductance state. Details of the peak comparisons follow.

As discussed in Chapter 4 (Section 4.3.3), the calculated FWHM of a peak collected using an AC modulation voltage of 8 mV and a substrate temperature of 4.2 K is ~ 10 mV. However, the measured IET spectra in Figure 5-15 show peaks that are significantly wider (FWHM > 40 mV) in both high- and low-conductance states. Thus, it is likely that the measured peaks may be a superposition of peaks arising from two or more different and closely-spaced vibrational modes. For example, the peak in the 150 to 200 mV bias range can be decomposed into two primary peaks (reference dotted lines in orange and green colors in Figure 5-15). Figure 5-16 shows the decomposition of this peak found by fitting to two (or three) Gaussian functions for each junction shown in Figure 5-15.
The maxima of the two decomposed peaks are located in the bias range of 166 to 185 mV (171, 177, 166, 182, and 185 mV; C-N mode) and 185 to 201 mV (195, 201, 193, 196, and 185 mV; C=C) in the low-conductance state, and in the range of 169 to 175 mV (175, 173, 173, 175, and 190 mV; C=C) in the high-conductance state.
169, 175, 173, and 175 mV; C-N) and 188 to 200 mV (198, 200, 190, 188, and 190 mV; C=C) in the high-conductance state. In each graph of Figure 5-16, the C-N mode is shown in orange, while the C=C mode is shown in green. Although the two dominant peaks (C-N and C=C) appear in both high- and low-conductance state, the intensities of the two peaks appear to be significantly different. In the low-conductance state, the intensity of the C=C mode (~190 mV) is higher than the C-N mode (~ 170 mV). When the conductance state changed from low to high, the peak intensity of C-N (~ 170 mV) increased significantly, while the C=C (~ 190 mV) vibrational mode decreased. This implies that structural changes around –N atoms of the OMA\textsubscript{2}n molecules may occur when the conductance state is switched from the low- to high-conductance states.

The variation in peak position and intensity in the OMA\textsubscript{2}n IET spectra were further investigated by comparing the results to those obtained in OPE junctions. Figure 5-17 shows four IET spectra of OPE crossed-wire devices where each spectrum was obtained from a different device with an excitation voltage of 6 mV or 8 mV at 4.2 K.
As discussed in Chapter 4, the three intense peaks near 140 mV, 200 mV, and 275 mV are the vibrational modes of $\nu(18\ a)$, $\nu(8\ a)$, and $C=\text{C}$ stretching, respectively. Although the three peaks were observed in all IET spectra, the peak position of each vibrational mode varies from device to device. For example, the peak centered near 200 mV shows a variation of $\pm\ 4$ mV within the four spectra. This variation is probably due to differences in the voltage drop across the molecule/metal contact in different OPE SAM junctions. Compared to the OPE junctions (Figure 5-17), the IET spectra of OMAn devices (Figure 5-15) show a larger variation in peak position and intensity.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5-17.png}
\caption{Four IET spectra of OPE SAM junctions that were obtained with an excitation voltage of 6 or 8 mV at 4.2 K. The peak centered near 200 mV varies $\pm\ 4$ mV in the four spectra.}
\end{figure}
Considering that both the OPE and OMA molecules were assembled into the same crossed-wire geometry, the larger current fluctuation and variations in IET peak position of the OMA SAM junctions may be attributed to at least two additional factors: sub-configurations of the OMA molecules in the SAM and the formation of domains in OMA SAM. Unlike OPE molecules, a calculation using a Density Functional Theory (DFT) and Green’s function theory suggests that the neutral OMA molecule could have three different conformations [17]. As illustrated in Figure 5-18, conformation (A) has the lowest conformational energy (0 meV; reference energy), while conformations (B) and (C) have energies of 1.5 and 54 meV, respectively, from the reference energy. Although this suggests that conformation (A) would be the dominant structure in a OMA SAM, the other conformations could also exist because the energy difference between the conformations is relatively small.

![Figure 5-18: Three possible sub-configurations of OMA molecules. Type (A) is expected to be the dominant structure of OMA SAM junctions [17]](image)

Figure 4-10 (left) shows an AFM image of a bare flat Au surface prepared by the template stripping and flame annealing methods [18] [19]. Following the SAM assembly on this flat Au surface, AFM measurements were conducted on OMA and C16-
monothiol SAMs as shown in Figure 4-10 (center) and Figure 4-10 (right), respectively. Unlike alkanethiols and OPE molecules that form a well-ordered and densely-packed SAMs, the OMAn SAM had molecular domains that were ~ 5 nm in diameter.

5.20 In-situ IETS measurement

This section discusses a series of in-situ I-V and IETS measurements that were obtained on a single crossed-wire OMAn SAM junction device in both the high- and low-conductance states. In this measurement, the conductance state was sequentially switched from high $\rightarrow$ low and then from low $\rightarrow$ high and the corresponding I-V characteristics / IETS spectra were collected immediately following each conductance state change. All measurements were done at 4.2 K with an AC modulation signal of 6 mV at 433 Hz. The
measured IET spectra were smoothed using a five-point FFT filter routine. Table 5-3 gives the detailed measurement procedure.

Table 5-3: *In-situ* IETS measurement of OMAn SAM junction in a crossed-wire device

<p>| | | |</p>
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>A.</td>
<td>I-V sweep at RT (scan 0 in Figure 5-20)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) 0 – 1.0 V, 0 – -1.0 V</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b) 0 – 1.5 V (conductance state change to high at ( V_T \sim 1.5 ) V)</td>
<td></td>
</tr>
<tr>
<td>B.</td>
<td>Cool down system to 4.2 K and stabilize the temperature (~1 hour)</td>
<td></td>
</tr>
<tr>
<td>C.</td>
<td>[High State]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) I-V sweep at 4.2 K: 0 – 0.5 V to confirm high state (scan 1 in Figure 5-20)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(b) IETS at 4.2 K: 6 mV, 433 Hz (2 mV step)</td>
<td></td>
</tr>
<tr>
<td>D.</td>
<td>[Low State]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(a) I-V sweep at 4.2 K: 0 – -2.0 V (( V_T \sim -2.0 ) V) (scan 2 in Figure 5-20)</td>
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<tr>
<td></td>
<td>(b) IETS at 4.2 K: 6 mV, 433 Hz (2 mV step)</td>
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<tr>
<td>E.</td>
<td>[High State]</td>
<td></td>
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<tr>
<td></td>
<td>(a) I-V sweep at 4.2 K: 0 – 2.0 V (( V_T \sim 2.0 ) V) (scan 3 in Figure 5-20)</td>
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<tr>
<td></td>
<td>(b) additional 10 I-V sweeps (0 – 1 V)</td>
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<tr>
<td></td>
<td>(c) IETS at 4.2 K: 6 mV, 433 Hz (2 mV step)</td>
<td></td>
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<tr>
<td>F.</td>
<td>Device damaged (scan 4 in Figure 5-20)</td>
<td></td>
</tr>
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</table>
Figure 5-20: I-V characteristics of an OMA$n$ SAM junction fabricated using a 60-nm wide lithographically-defined bottom electrode. The measurement was conducted at 4.3 K and the conductance state was switched sequentially as described in Table 5-3.

Figure 5-20 shows the I-V characteristics of the OMA$n$ SAM junction measured at 4.2 K. The low- and high-state current measured at a bias of 1 V was 80 (trace 0) and 600 nA (trace 3), respectively. For this device, the ratio of high-to-low-state conductance in the low bias regime (<0.3 V) was approximately seven. The room temperature threshold voltage for switching the device from the initial low-conductance state to the high state was ~ 1.5 V, while a larger ~ 2.0 V bias was needed to switch the same device at 4.2 K.

Figure 5-21 provides plots of in-situ IET spectra and corresponding I-V curves measured under the same conditions.
For comparison purposes, all IET spectra are plotted together in Figure 5-22. These spectra show that most prominent changes in peak intensity consistently occurred in the 150 to 200 mV bias range. By first comparing ‘Spectrum 1’ (high state following one I-V...
sweep) and ‘Spectrum 2’ (low state following one I-V sweep), it was found that the peak at ~175 mV was reduced in intensity while a new peak appeared at ~150 mV. These data are consistent with those presented in Figure 5-14, which were collected from many different devices using similar measurement procedures (i.e., one bias sweep used to switch from the low → high state).

Figure 5-22: *In-situ* IET spectra of OMAAn SAM junction device that the conductance state was sequentially switched in the same device following the procedure in Table 5-3.
However, as discussed in Section 5.19.2, the OMAn junctions required successive voltage sweeps below the threshold voltage before the high-state current reached a stable value. In order to study any potential differences in the vibronic features upon the junction reaching a stable high state, this same device was switched from the low $\rightarrow$ high states, and then the bias was subsequently swept another ten times before ‘Spectrum 3’ was collected. The I-V characteristics plotted in Figure 5-21 show that the high-state current increases and reaches a steady state following the additional I-V sweeps. The peaks in the 150 to 200 mV bias range were then decomposed into two peaks as shown in Figure 5-22. The high-state ‘Spectrum 1’ (high state following one I-V sweep) and ‘Spectrum 3’ (high state following ten I-V sweeps) show clear differences in the relative intensities of peaks near 175 mV (C-N) and 190 mV (C=C). Specifically, the peak intensity at $\sim$184 mV in the IET ‘Spectrum 3’ collected following ten additional bias sweeps is significantly stronger than the peak at $\sim$ 168 mV, whereas both peaks have similar peak intensity in ‘Spectrum 1.’ This indicates that the mode associated with the C-N vibration becomes more intense, which may be related to structural changes around the –N atoms of the OMAn molecules.
As discussed in Chapter 2, unlike other spectroscopic measurements (e.g., infrared and Raman), IET spectroscopy does not follow strict selection rules. Thus, the observed vibrational peaks can be best interpreted by comparison to theoretical simulations [20] [21] [22]. However, in the case of the OMAn junctions, the exact molecular structures that are responsible for the high- and low-conductance states are unknown. In addition, if the molecular conformations are associated with the charged
molecular structure, such as the dicationic structure in oxidized state, it is difficult to understand if or how mobile counter ions play a role in the bistable switching behavior. The following sections review recent theoretical results that propose two possible mechanisms that may explain the observed bistable switching characteristics of OMAn junctions [17].

5.21 Proposed switching mechanism

The observed IET spectra in the high- and low-conductance states suggest that the switching properties of the crossed-wire OMAn SAM junction can be related to a change in the molecular structure of the molecule. In particular, the switching behavior seems to involve a change in the characteristic vibration associated with the IETS peak near 170 mV. The long retention time (>24 hours) also implies that the molecular structure in both the high- and low-conductance states is very stable. Based on these observed properties of OMAn junctions, this section describes two types of molecular conformational changes being investigated by several theoretical groups: (1) Current-induced chemical structure change (neutral and oxidized dicationic structures), and (2) Electric field-induced structural conformation (α-state and γ-state in the neutral structure).

5.21.1 Current-induced chemical structure change

As discussed in Section 5.1, OMAn molecules can possess different chemical structures following the reduction / oxidation process. By losing two electrons in the
molecule when applying a bias exceeding the threshold voltage, the structure in neutral state (OA neutral) could be changed into an oxidized state (OA $2^+$). When the external applied bias is removed, the dications in the OA $2^+$ state must be stabilized. As illustrated in the right panel of Figure 5-24, it is possible that image charge can be induced on the metal contacts that are in close spatial proximity (several Å) to the dications [23]. Consideration of the image charge on the metal contact is not simple, because the amount of charging and relaxation of the molecules in the junction is unknown and depends on local geometry and bonding to the metal contacts [1]. This would be even more complicated in the crossed-wire device that is comprised of a cylindrical-shaped metal nanowire and a metal film with a significant surface roughness. Alternatively, it is possible that unintentionally-incorporated mobile ions could also stabilize dications. For example, it is possible that a small number of anions (e.g., CN-) could be introduced during the electroplating, which is below the XPS detection limit as discussed in Chapter 3. However, the presence or absence of this charge (dications) in the junction has not been quantified and this subject must be explored more thoroughly in the future.
Under the assumption that the OMAn junction can switch its molecular structure from the “OA neutral (low-conductance state)” to the “OA $2^+$ (high-conductance state)” by applying a bias exceeding the threshold voltage ($V_{th}$), the IET spectra in the high- and low-conductance states were calculated using non-equilibrium Green’s function and density functional theory methods. The calculations were performed by Troisi and Ratner (unpublished). The calculated spectra and the peak assignments are shown in the right panel in Figure 5-25 and Table 5-4, respectively.

Using these simulation results, the measured IET spectra of the high- and low-conductance state are compared in Figure 5-26. Although the intensities of the peaks in the two measured spectra were somewhat different, the prominent C-N vibrational mode around 170 mV was observed in both the experimental and theoretical spectra. However, in contrast to the simulation, the measured peak at about 90 mV, which corresponds to the ring breathing and the CH out-of-plane mode, was much weaker in both spectra.
Table 5-4: Peak assignment (calculated by Troisi and Ratner)

<table>
<thead>
<tr>
<th>OA Neutral State</th>
<th>Voltage (mV)</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)C-N-C bending</td>
<td>23</td>
<td>240</td>
</tr>
<tr>
<td>C-C-C bending (central ring)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S-C-C</td>
<td>43</td>
<td>349</td>
</tr>
<tr>
<td>C((sp)_2)-C((sp)_2)-N bending</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-S stretch</td>
<td>57</td>
<td>481</td>
</tr>
<tr>
<td>H(_2)C-N-C bending</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H out-of-plane bending (rings)</td>
<td>60</td>
<td>487</td>
</tr>
<tr>
<td>C-H and C-C out-of-plane (external rings)</td>
<td>88</td>
<td>690</td>
</tr>
<tr>
<td>CH out-of-plane (central ring)</td>
<td>101</td>
<td>812</td>
</tr>
<tr>
<td>C-S stretch</td>
<td>134</td>
<td>1082</td>
</tr>
<tr>
<td>Stretches of C-C connected to S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-H in-plane bending (external rings)</td>
<td>137</td>
<td>1103</td>
</tr>
<tr>
<td>C-H in-plane bending (internal rings)</td>
<td>144</td>
<td>1190</td>
</tr>
<tr>
<td>C-N stretching</td>
<td>154</td>
<td>1245</td>
</tr>
<tr>
<td>CH in-plane bending</td>
<td>184</td>
<td>1488</td>
</tr>
<tr>
<td>CH(_2) bending</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=C stretching (central ring)</td>
<td>199</td>
<td>1803</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>OA (^{2+}) State</th>
<th>Voltage (mV)</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenyl hindered motion</td>
<td>17</td>
<td>134</td>
</tr>
<tr>
<td>C-C-C out-of-plane bending (external rings twisting)</td>
<td>50</td>
<td>404</td>
</tr>
<tr>
<td>C=C-C and C=C-N out-of-plane bending</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=C-N out-of-plane bending</td>
<td>63</td>
<td>507</td>
</tr>
<tr>
<td>C-C-C out-of-plane (external rings)</td>
<td>88</td>
<td>696</td>
</tr>
<tr>
<td>C=C-C bending (ring breathing)</td>
<td>92</td>
<td>741</td>
</tr>
<tr>
<td>C-H out-of-plane bending</td>
<td>99</td>
<td>799</td>
</tr>
<tr>
<td>C=C-H in-plane bending</td>
<td>137</td>
<td>1107</td>
</tr>
<tr>
<td>C-S stretching</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=C-H in-plane bending (central ring)</td>
<td>147</td>
<td>1185</td>
</tr>
<tr>
<td>C-N stretching</td>
<td>168</td>
<td>1357</td>
</tr>
<tr>
<td>C=C stretching (central ring)</td>
<td>183</td>
<td>1472</td>
</tr>
<tr>
<td>C=C stretching (all rings)</td>
<td>198</td>
<td>1599</td>
</tr>
</tbody>
</table>

Figure 5-25: Calculated IET spectra of OMA\(_n\) junctions by Troisi and Ratner
To further investigate the molecular structure of the high-conductance state experimentally, IETS measurements were conducted on crossed-wire OMAAn SAM junctions that were chemically oxidized in 10 mM FeClO$_4$ solution for 2.5 min. This
provides a direct source of anions to stabilize the charge on the molecule in its oxidized state. In this case, a 1 μm-wide bottom contact was used instead of a 60-nm wide contact. This was necessary because a device with a 60 nm-wide bottom contact only contains about a thousand molecules within the junction area. This makes it difficult to control the oxidation time of the molecules, and excessive oxidation time can cause the molecules to desorb from the surface.

Figure 5-27 compares the IET spectra of the high-conductance state to that of the chemically oxidized device (green). Although the peak position shifted approximately 10 mV toward lower bias compared to those in the high-conductance state measured after 10 successive I-V sweeps (labeled ‘Spectrum 3’), the chemically-oxidized sample showed a similar prominent peak near 160 mV. This indicates that the high-conductance state for the junction that is switched electrically could very likely have a similar molecular structure to the chemically-oxidized molecular structure where the benzene is transformed to a quinoid ring through oxidation (loss of an electron). In this case, however, the mobile anions are present to stabilize the charged molecular structure. Interestingly, however, the chemically oxidized OMAn device did not show any switching behavior. Rather, the device showed breakdown at higher bias (> 2.7 V) and became an open device (i.e., current < 1pA at 1 V). This may be due to the strong chemical coupling between the dications and the ClO⁻ ions, and suggests that the electrically switched OMAn SAM junctions may not have very strong chemical bonding to compensate for the dications.
5.2.1.2 Electric field-induced structural conformation

Recent theoretical work from Sotelo et al., (2007) presented a study of the structural and electronic properties of the OMA\textit{n} molecular junction [17]. They proposed
three distinct types of nonplanar conformations ($\alpha$, $\beta$, and $\gamma$) for a neutral oligoaniline molecule. Each conformation has several isomers of nearly equal energies (a few meV apart in most cases). For example, Figure 4-13 depicts the configuration of the isomers obtained from each state ($\alpha$, $\beta$, and $\gamma$) by rotating one of the exterior-phenyl-N-methyl substructures by 90° around the adjacent N-C bond. This theoretical simulation reveals that, in the case of an Au-OMAn SAM-Pd junction at room temperature, the $\alpha$-state has the highest probability to be present in the junction, while the $\beta$-state has the smallest.

![Diagram of conformational structures]

Figure 5-28: Sub-conformational structure of OMAn [17]

Since the conformational energies of many of the oligoaniline isomers differ by only a few meV, an external electric field induced by a bias applied to the junction can easily cause conformational changes in the OMAn molecule, thus affecting its conformational
distribution (i.e., a favorable molecular structure at a certain voltage). As a result, switching between different conductivity values can be expected in an OMA$n$ molecular junction.

More specifically, the left side of Figure 5-29 shows the hysteric behavior of the energy of an Au-OMAn-Pd junction in an electric field, starting at point 1 and ending at point 17 (at zero electric field).

![Figure 5-29](image)

Figure 5-29: (left) Electric field effects. (right) Transmission functions of the conformers. [17]

When the field is swept from 0 to -0.0015 a.u. (-7.7×10$^6$ V/cm), the energy of the junction follows a smooth arc until taking a sharp dive at -0.001 a.u. (-5.1×10$^6$ V/cm, point 3) leading to a conformational change, from $\gamma$ to $\alpha$ at a negative threshold of 0.0015 a.u. (point 4). The junction remains in this $\alpha$ conformation state upon sweeping the field upward until 0.002 a.u. (1.0×10$^7$ V/cm, point 11), at which point its energy once again suddenly jumps down, leading to a switch back to a $\gamma$ conformation at a positive threshold field of 0.0025 a.u. (1.3×10$^7$ V/cm, point 12). Likewise, once the junction is in
the $\gamma$ conformation, it will remain in this state until the electric field is swept down to the negative field threshold. Based on the calculations, the $\gamma$ conformer has an overall higher transmission function, with a narrower band gap, than that of the $\alpha$ conformer, resulting in higher conductance.

Since this model used the structural conformation of a neutral molecule in both high- and low-conductance states, the issues related to the dications in the previous theory would not be a concern. However, this model limited the structural conformation of a single molecule in a vacuum without two metal electrodes that may cause different electronic states of the molecule. Nonetheless, in order to correlate the measured IET spectra in high- and low-conductance state to the $\alpha$ and $\gamma$ state in this model, the calculated IET spectra for both the $\alpha$ and $\gamma$ state are required. This additional data point would be useful to complete the picture of the analysis of the observed experimental results.

5.22 Conclusion

In summary, a reversible and stable molecular switching behavior was demonstrated in a nanoscale crossed-wire device comprised of OMA$n$ SAM sandwiched between a lithographically-defined 60 nm-wide Ti/Au bottom contact and a 220 nm-diameter single Au nanowire top contact. The conductance state was changed between the low and high state by applying a bias exceeding the threshold voltage in the range of 1.0 to 1.5 V at room temperature and 2.0 to 2.5 V at 4.2 K. In the low bias region (<0.3
V), the high and low conductance ratio varies from 5 and 10 for different devices, and the retention time under vacuum and at room temperature is > 24 hours.

*In-situ* IET spectra show a change in the vibrational modes of the molecular junction as it is switched from the low to high-conductance state. In particular, the most prominent peak change near 170 mV (C-N stretching mode) suggests that electron delocalization around –N atoms may be responsible for the higher current. Overall, the experiments conducted in this chapter suggest that reversible bistable switching properties in OMAn junctions could be related to two stable molecular conformations. Based on these observed properties of OMAn junctions, two sets of molecular conformations were considered. In case of the current-induced chemical structure change (i.e., neutral and oxidized di-cation structure), the simulated IETS spectrum showed trends similar to the experimentally observed changed in the prominent peak of about 170 mV (C-N stretching). In addition, the IET spectrum in the crossed-wire chemically oxidized OMAn SAM junction also showed the intense peak of the C-N mode, supporting the theory that the high-conductance state could have a similar configuration to that of the chemically oxidized one. However, the issues related to the compensation of the dications must be explored more thoroughly in the future. Alternatively, electric field-induced structural conformational changes (α-state and γ-state in neutral structure) provide an alternative explanation for the switching characteristics of the OMAn junctions. However, in order to connect the measured IET spectra to this model, it is necessary to have simulated IET spectra in the α-state and γ-state.
5.23 References

Chapter 6

Summary and Future work

6.1 Summary

This thesis presented the development of a new nanoscale crossed-wire molecular device that was used to study the electronic and vibronic properties of metal-self assembled molecular monolayer (SAM) -metal junctions. Since small changes in the structure of the molecule and junction (e.g. molecular conformation, ending, tilting, geometry of bonding to the electrode, individual molecule vs. monolayer, etc) can significantly influence the electronic properties of the junction, the relationship between the structure and the electrical properties of the junction must be understood before molecules are incorporated into future electronic devices.

The crossed-wire device developed in this work is comprised of a monolayer that containing hundreds to thousands of well-ordered molecules sandwiched between a lithographically-defined bottom Au metal contact and a single Au metal nanowire top contact. This device structure has three primary advantages over other molecular junction devices. First, unlike many other device structures, the crossed-wire device does not use evaporated metal to form a top contact. Instead, it forms a physical or chemically-bonded contact with the smooth surface of the aligned metal nanowire, which can prevent damage of the SAM during top contact formation using physical vapor deposition (e.g., thermal evaporation). Second, because a large number of molecular junctions can be
integrated in parallel on the same substrate (potentially up to 100), large numbers of devices can be measured and data sets collected for comparison to theory. Third, the robust crossed-wire device allows variable and low temperature measurements to investigate the dominant conduction mechanism of the molecular junction device. Furthermore, this device structure can be used in Inelastic Electron Tunneling Spectroscopy (IETS) to study the vibronic properties of the molecular junction by monitoring specific vibrational peaks in the spectra.

Electrical and spectroscopic measurements were conducted using three different molecules: saturated alkanethiols, conjugated oligo(phenylene ethynylene) (OPE), and thiol-substituted methylated oligoaniline (OMAn) molecules. Because saturated alkanethiol molecules have been studied extensively previously, these molecules were integrated to evaluate the new crossed-wire device structure. Differences in the electrical properties of junctions containing molecules that form physical or chemically-bonded top contacts to the Au nanowire were investigated using C12-monothiol (1-dodecanethiol) and C12-dithiol (1,12-dodecanedithiol) molecules. The average current of the C12-dithiol junctions was approximately one order of magnitude larger than the C12-monothiol junctions. In addition, the dithiol molecular junctions had a smaller device-to-device variation in the current than that in the monothiol junctions, which was related to the difference in the top contact bonding.

The current in the C12-dithiol molecules was temperature independent over the bias voltage range of 0 to +1V, which indicated that coherent tunneling was the dominant transport mechanism as expected for a saturated molecule with a large HOMO-LUMO gap (HOMO: highest occupied molecular orbital level; LUMO: lowest unoccupied
molecular orbital level). The measured IET spectra of C12-dithiol junctions showed peak at 368 mV (C-H stretch), 182 mV (CH$_2$ wag and scissor), 136 mV (C-C stretch), and 82 mV (C-S stretch), which the positions and intensities are similar to that in the μm-diameter freestanding crossed metal-wire structure and nanopore devices.

The electronic properties of a π-conjugated junction were then compared to those of a alkanethiol σ-bonded junction, both of which have a very similar molecular length. The average measured current was approximately one order of magnitude larger for the conjugated OPE-dithiol junction than the saturated C12-dithiol junction. This is due to the smaller HOMO-LUMO gap in the OPE, which is a result of delocalized electrons in the π-conjugated molecule. Temperature-dependent I-V measurements showed that coherent transport was also the dominant conduction mechanism in the crossed-wire OPE SAM junctions, which is consistent with earlier work using in-wire device structures. The three prominent peaks corresponding to the $\nu$(18 a), $\nu$(8 a), and C≡C stretching modes observed in the IET spectra were shown to be in an excellent agreement with the theoretical calculations that included thermal broadening. Furthermore, the dependence of the full width at half maximum (FWHM) of the vibrational peaks in the IET spectra was found to depend on the magnitude of the applied AC voltage, and showed that the peak resolution could be improved by lowering the excitation voltage.

The bistable switching behavior of crossed-wire OMA$\nu$ SAM junctions were also investigated. In these junctions, the conductance of the junction was switched between the low- and high-states by applying a threshold voltage of between 1.0 and 1.5 V at room temperature and 2.0 and 2.5 V at 4.2 K. At zero-bias, the ratio of the high- and low-conductance was varied from 4 to 20 and the retention time of the high conductance state
was much longer than one day at room temperature. *In-situ* IET spectra showed a change in the vibrational modes of the molecular junction when the junction was switched from the low to high-conductance state. In particular, the most prominent peak change around 170 mV (C-N stretching mode) suggests that electron delocalization around – N atoms could be responsible for the higher current. Overall, the experiments suggest that the reversible bistable switching properties of OMAn junctions could be related to two stable molecular conformations.

Based on these measured electrical and vibronic properties of OMAn junctions, two sets of molecular conformations were considered. In the case of the current-induced chemical structure change (i.e., neutral and oxidized di-cation structure), the simulated IET spectrum showed trends similar to the experimentally observed change in the prominent peak near 170 mV (C-N stretching mode). In addition, the IET spectrum in a chemically oxidized crossed-wire OMAn SAM junction also showed an intense peak corresponding to the C-N vibrational mode, which supports the theory that the high-conductance state of the OMAn SAM device could have a similar configuration to that of the chemically-oxidized molecular structure. However, the issues related to the compensation of the dications must be explored more thoroughly in the future.

Alternatively, the electric field-induced structural conformational change (α-state and γ-state in neutral structure) provides an alternative explanation for the switching characteristics of the OMAn junctions. However, in order to connect the measured IET spectra to this model, it is necessary to have simulated IET spectra in the α-state and γ-state in the future.
6.2 Suggestions for Future work

6.2.1 Improvement of surface roughness

Although the crossed-wire molecular junction device has several noteworthy features, the surface roughness of the metal electrodes in contact with the SAM could be a drawback if one intends to control the device-to-device current variations. In addition, the number of molecules in the junction area uncontrolled, and it is difficult to estimate because of the rough surface morphology of the thermally-evaporated bottom contact. The roughness could be reduced by introducing other fabrication methods. For example, an ultra flat metal surface can be achieved using the template-striping method [1] [2]. Here, a desired metal (e.g., Au) is deposited on a Si wafer that has a thin-surface oxide layer that serves as an ultra smooth template. The metal-coated surface is then bonded to a substrate, usually by means of an epoxy, to form a template-substrate sandwich. The metal that is now chemically-bonded to the substrate wafer via the epoxy, easily detaches from the template, leaving an ultra flat surface. AFM measurements of Pt and Au thin films fabricated using this technique showed that the RMS surface roughness was of 0.1 nm and 0.2 nm, respectively, over a $1 \times 1 \mu m^2$ area.

6.2.2 Investigation of switching mechanism

Chapter 5 presented the very interesting bistable switching behavior of the crossed-wire OMAn SAM junctions in crossed-wire devices. Based on the observed electrical and spectroscopic characterization results, two possible switching mechanisms
were suggested: (1) Current-induced chemical structure change (neutral and oxidized dication structures), and (2) Electric field-induced structural conformation (α-state and γ-state in the neutral structure). In the case of (1), the molecule in the high-conductance state contains charged dications that must be stabilized with mobile anions. However, unlike junctions that are formed in an electrolyte, wherein the mobile ions (anions and cations) can easily stabilize the charged molecules, these solid state junctions do not contain any intentionally introduced mobile ions. As suggested in the last part of Chapter 5, it could be possible that image charges or very small amounts of the process induced ions are present in the junction. This subject needs to be explored more thoroughly in the future. For example, measurement of the switching response time may be useful because the image charge can be created much faster than the slow ion diffusion. On the other hand, a mimic of the crossed-wire device with a larger junction area may allow more conventional optical spectroscopic measurements of junctions in the high-conductance state (e.g., Infrared, Raman, X-ray photoelectron spectroscopy). In the case of (2), it is necessary to conduct simulations to predict the IET spectra in each state (α-state and γ-state). Then, the calculated spectra can be used to interpret the experimentally observed IET spectra to gain insight of the molecular structure.
6.3 References


VITA

Heayoung Yoon

Heayoung Yoon received the B.S. degrees in Physics (major) and Computer Science (minor) from Chungnam National University (Daejon, South Korea). She also received M.S. degrees in physics from Pohang University of Science and Technology (Pohang, South Korea). Following graduation, she worked for Samsung Advanced Institute of Technology (Suwon, South Korea) as a research scientist for two years. She graduated from Penn State University with a Doctor of Philosophy Degree in Electrical Engineering in 2007.

Currently, she is a member of the Institute of Electrical and Electronics Engineers (IEEE) and a member of American Physics Society (APS). She has given multiple presentations in academic conferences. Her current research interests include micro/nano fabrications, solid-state device characterizations, and electrical and spectroscopic characterization of molecule-scale devices.