Abstract

Electrical Characterization of Self-Assembled Monolayers

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Electrical characterization of alkanethiol self-assembled monolayers (SAMs) has been performed using a nanometer-scale device structure. Temperature-variable current-voltage measurement is carried out to distinguish between different conduction mechanisms and temperature-independent transport characteristics are observed, revealing that tunneling is the dominant conduction mechanism of alkanethiols. Electronic transport through alkanethiol SAMs is further investigated with the technique of inelastic electron tunneling spectroscopy (IETS). The obtained IETS spectra exhibit characteristic vibrational signatures of the alkane molecules that are used, presenting direct evidence of the presence of molecular species in the device structure. Further investigation on the modulation broadening and thermal broadening of the spectral peaks yield intrinsic linewidths of different vibrational modes, which may give insight into molecular conformation and may prove to be a powerful tool in future molecular transport characterization.
Electrical Characterization of
Self-Assembled Monolayers

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## List of Abbreviations and Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>a</td>
<td>Lattice constant</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>α</td>
<td>Simmons equation fitting parameter</td>
</tr>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>β</td>
<td>Tunneling decay coefficient</td>
</tr>
<tr>
<td>β₀</td>
<td>Bias-independent tunneling decay coefficient</td>
</tr>
<tr>
<td>βᵥ</td>
<td>Bias-dependent tunneling decay coefficient</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CAFM</td>
<td>Conducting AFM</td>
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<tr>
<td>C₈</td>
<td>Octanethiol</td>
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<tr>
<td>C₁₂</td>
<td>Dodecanethiol</td>
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<tr>
<td>C₁₆</td>
<td>Hexadecanethiol</td>
</tr>
<tr>
<td>C₈ dithiol</td>
<td>Octanedithiol</td>
</tr>
<tr>
<td>CH₂</td>
<td>Methylene group</td>
</tr>
<tr>
<td>CH₃(CH₂)ₙ₋₁SH</td>
<td>Alkanethiol</td>
</tr>
<tr>
<td>d</td>
<td>Tunnel junction gap distance</td>
</tr>
<tr>
<td>d'</td>
<td>Barrier width at the Fermi level</td>
</tr>
<tr>
<td>dI/dV</td>
<td>Differential conductance</td>
</tr>
<tr>
<td>d²I/dV²</td>
<td>Second derivative of I(V)</td>
</tr>
<tr>
<td>DUT</td>
<td>Device under test</td>
</tr>
<tr>
<td>δᵣₛ</td>
<td>In-plane rocking (r) and scissoring (s) modes</td>
</tr>
<tr>
<td>Δ(Φₑ, α)</td>
<td>(Σ</td>
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</table>
e  Electron charge
E  Electron energy
Ec  Conduction band bottom energy
EF  Fermi energy
Eg  Energy gap
E(k)  Energy-momentum relationship
ENBW  Equivalent noise bandwidth
Ev  Valence band top energy
eV  Electronvolt
ε  Dielectric constant

fA  Femtoampere
f(E)  Fermi function
Φ₀  Parabolic barrier height at zero bias
Φ₀  Rectangular barrier height at zero bias
Φ(x)  General barrier
Φ  Mean barrier height

G  Conductance
γw,t  Out-of-plane wagging (w) and twisting (t) vibrational modes

h  Plank’s constant
HF  hydrofluoric acid
HNO₃  Nitric acid
H₂O  Water
HOMO  Highest occupied molecular orbital
Hz  Hertz

I  Current
I  Insulator
I(V)  Current-voltage characteristic
I(V,T)  Temperature-variable I(V)

J  Current density

K  Kelvin
k  Boltzman’s constant
k  Wavevector

L-B film  Langmuir-Blodgett film
LPCVD  Low pressure chemical vapor deposition
LUMO  Lowest unoccupied molecular orbital

m  Electron mass
M  Metal
meV  Millielectronvolt
mL  Milliliter
mM  Millimolar
MO  Molecular orbitals
mV  Millivolt
m*  Effective mass
µA  Microampere
µL  Microliter
µm  Micron

nA  Nanoampere
nm  Nanometer
ν  Stretching vibrational mode
ν  Vibrational mode frequency

Ω  Ohm
pA  picoampere
PMMA  Poly(methyl methacrylate)
R  Backbone of a molecule
RIE  Reactive ion etching
RTD  Resonant tunneling diode
S  Sulfur
SAM  Self-assembled monolayer
SEM  Scanning electron microscope
Si  Silicon
Si$_3$N$_4$  Silicon nitride
SiO$_2$  Silicon dioxide
SPA  Semiconductor parameter analyzer
STM  Scanning tunneling microscope
$\sigma$  $\sigma$ bond

T  Temperature
T(E)  Tunneling transmission probability
TEM  Transmission electron microscope

V  Volt
V  Voltage

$W_{\text{modulation}}$  Modulation broadening
$W_I$  Intrinsic linewidth
$W_{\text{thermal}}$  Thermal broadening
Chapter 1

Introduction

The research field of nanoscale science and technology has made tremendous progress in the past decades, ranging from the experimental manipulations of single atoms and single molecules to the synthesis and possible applications of carbon nanotubes and semiconductor nanowires [1-3]. This remarkable research trend is driven partly by human curiosity for exploring the ultimate of small matter, and partly by the microelectronics industry’s need to go beyond the traditional photolithography-based top-down fabrication limitations. As the enormous literature has shown, nanometer scale device structures provide suitable testbeds for the investigations of novel physics in a new regime, especially at the quantum level, such as single electron tunneling or quantum confinement effect [4,5]. On the other hand, as the semiconductor device feature size keeps decreasing, the traditional top-down microfabrications will soon enter the nanometer range and further continuous downscaling will become scientifically and economically challenging [6]. This motivates researchers around the world to find alternative ways to meet the future increasing computing demands.

With a goal of examining individual molecules as self-contained functioning electronic components, molecular transport characterization is an active part of the research field of nanotechnology [2,3]. In 1974 a theoretical model of a unimolecular
rectifier was proposed, according to which a single molecule consisting of an electron donor region and an electron acceptor region separated by a $\sigma$ bridge would behave as a unimolecular p-n junction [7]. However it was a proposal ahead of its time, and it might still be ahead of the time. An experimental realization of such a unimolecular device was hampered by the difficulties of both chemical synthesis of such type of molecules and microfabrication of reliable solid state test structures. A publication in 1997 reported an observation of such a unimolecular rectification in a device containing Langmuir-Blodgett (L-B) films; however it is not clear if the observed rectifying behavior has the same mechanism since it was just shown in a single current-voltage [I(V)] measurement [8]. In the mean time, instead of using L-B films, other people proposed to exploit self-assembled conjugated oligomers as the active electronic components [9,10] and started electrical characterization of monolayers formed by molecular self-assembly technique [2].

Molecular self-assembly is an experimental approach to spontaneously form highly ordered monolayers on various substrate surfaces [11,12]. Earlier research in this area includes, for example, the pioneering study of alkyl disulfide monolayers formed on gold surfaces [13]. This research field has grown enormously in the past two decades and self-assembled monolayers (SAMs) have found their modern day applications in various areas, such as nanoelectronics, surface engineering, biosensing, etc. [11].

Various test structures have been developed in order to carry out characterizations of self-assembled molecules, and numerous reports have been published in the past several years on the transport characteristics [2,3,14,15]. Nevertheless many of them have drawn conclusions on transport mechanisms without performing detailed temperature-
dependent studies [14,15], and some of the molecular effects have been shown to be premature and due to filamentary conduction in further investigations [16-21], highlighting the need to institute reliable controls and methods to validate true molecular transport [22]. A related problem is the characterization of molecules in the active device structure, including their configuration, bonding, and indeed even their very presence.

In this research work we conduct electrical characterization of molecular assemblies that exhibit understood classical transport behavior and can be used as a control for eliminating or understanding fabrication variables. A molecular system whose structure and configuration are well-characterized such that it can serve as a standard is the extensively studied alkanethiol \([\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}]\) self-assembled monolayer [11, 22-25]. This system forms single van der Waals crystal on the Au(111) surface [26] and presents a simple classical metal-insulator-metal (M-I-M) tunnel junction when fabricated between metallic contacts because of the large HOMO-LUMO gap (HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital) of approximately 8 eV [27]. Utilizing a nanometer scale device structure that incorporates alkanethiol SAMs, we demonstrate devices that allow temperature-dependent \(I(V)\) \([I(V,T)]\) and structure-dependent measurements [24]. The obtained characteristics are further compared with calculations from accepted theoretical models of M-I-M tunneling, and important transport parameters are derived [24,28].

Electronic transport through alkanethiol SAM is further investigated with the technique of inelastic electron tunneling spectroscopy (IETS) [25,29]. IETS was developed in the 1960’s as a powerful spectroscopic tool to study the vibrational spectra of organic molecules confined inside metal-oxide-metal tunnel junctions [29-31]. In our
study IETS is utilized for the purpose of molecule identification and investigation of chemical bonding and conduction mechanism of the “control” SAM. The exclusive presence of well-known characteristic vibrational modes of the alkane molecules that are used is direct evidence of the molecules in the device structure, which is the first unambiguous proof of such occurrence. The spectral lines also yield intrinsic linewidths that may give insight into molecular conformation, and may prove to be a powerful tool in future molecular device characterization [22,25].

This thesis focuses on the electrical characterization of self-assembled monolayers, especially on the elastic and inelastic tunneling transport measurement of alkanethiol SAMs. In Chapter 2 the fundamental theories of elastic and inelastic quantum mechanical tunneling processes are discussed. Chapter 3 presents the experimental methods used to characterize transport through self-assembled molecules. It first gives a review on alkanethiol SAM, followed by a detailed description of device fabrication process. The instrumentation for IETS measurement is also presented here. Chapter 4 presents the results of a tunneling study of alkanethiol SAMs. Temperature-dependent I(V) characterization is performed to distinguish between different conduction mechanisms and length-dependent measurement is carried out to further investigate the tunneling transport behavior. Comparison with theoretical calculations is also made and transport parameters such as the barrier height of the tunnel junction are deduced. Chapter 5 discusses IETS research work on an alkanedithiol SAM device. IETS measurement at 4.2 K exhibits vibrational signatures of the measured molecule bonded to gold electrodes, which demonstrates that the IETS technique can be utilized for the unique identification of molecular species contained in nanometer scale devices with self-
assembled monolayers. Modulation and temperature broadening investigations of the spectral lines are carried out to further verify that the measured spectra are indeed coming from the inelastic tunneling mechanism. Intrinsic linewidths of certain vibrational modes are also calculated from this linewidth broadening study and a qualitative explanation based on a theoretical model is included. Chapter 6 summarizes this thesis work and suggests some future directions.
References:


Chapter 2

Theoretical Background of Quantum Mechanical Tunneling

Tunneling is a purely quantum mechanical behavior [1-4]. During the tunneling process, a particle can penetrate through a barrier – a classically forbidden region corresponding to negative kinetic energy – and transfer from one classically allowed region to another. That this process could happen is because the particle also has wave characteristics. Since the development of quantum mechanics, tunneling phenomena have been studied by both theorists and experimentalists on many different systems [5,6].

In 1928 Oppenheimer attributed the auto-ionization of excited states of hydrogen atoms to tunneling [7]. In the same year Fowler and Nordheim [8] explained, on the basis of electron tunneling, the observed phenomenon of electron field emission from cold metals under the application of a high external electrical field, which had been unexplained since its observation by Lilienfield in 1922 [9]. Other major achievements in tunneling research include the explanation of α decay as a tunneling process proposed by Gamow [10], the p-n tunnel diode reported by Esaki [11], and the measurement of superconductor energy gap using tunneling method performed by Giaever [12], etc.

The next milestone in the field was the discovery by Jaklevic and Lambe in 1966 that tunneling could yield detailed vibrational spectra of organic molecules buried inside
a metal-metal oxide-metal tunnel junction [13,14]. This marked the birth of a new spectroscopic tool that utilizes inelastic electron tunneling processes. The so-called inelastic electron tunneling spectroscopy (IETS) has numerous applications such as chemical identification, surface reaction, trace substance detection, etc. [15-18]. In this chapter we will discuss elastic tunneling models and present theoretical investigations of inelastic tunneling processes.

2.1 Elastic Electron Tunneling

2.1.1 One dimensional quantum mechanical tunneling

In this and the following subsections we will discuss elastic electron tunneling, i.e., the electron’s energy is conserved during the tunneling process. The simplest example of such an elastic tunneling is the electron penetration of a one dimensional rectangular potential barrier [1-4]. Fig. 2.1 shows a rectangular barrier with a barrier height of $\Phi_B$ and a barrier width of $d$. An electron with energy $E$ is incoming from the left. According to classical physics, if $E < \Phi_B$ the electron cannot penetrate through the barrier and appear on the right side. However from the quantum mechanical point of view, due to the wave-particle dualism, the electron has a non-zero probability to tunnel through this barrier and emerge on the other side.

The time-independent Schrödinger’s equation for an electron outside the barrier ($x < 0, x > d$; Fig. 2.1) is

$$\frac{-\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi, \quad (2.1)$$

and the solutions in these two regions can be written as
Figure 2.1. An electron with energy $E$ tunnels through a rectangular barrier of height $\Phi_B$ and width $d$ ($E < \Phi_B$).

\begin{align*}
\psi_1(x) &= e^{ik_1x} + Re^{ik_1x} \quad (-\infty < x \leq 0) \quad (2.2) \\
\psi_2(x) &= Se^{ik_2x} \quad (d \leq x < \infty), \quad (2.3)
\end{align*}

where $k_1 = \sqrt{\frac{2mE}{\hbar^2}}$, and only the transmitted wave is considered in the region of $x > d$. $|R|^2$ and $|S|^2$ will give the reflection and transmission coefficients, respectively. Inside the barrier, the Schrödinger’s equation and corresponding solution are

\begin{align*}
-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \Phi_B \psi &= E\psi \quad (2.4) \\
\psi_2(x) &= Ce^{k_2x} + De^{-k_2x} \quad (0 < x < d), \quad (2.5)
\end{align*}

where $k_2 = \sqrt{\frac{2m}{\hbar^2} (\Phi_B - E)}$.

By matching the wave functions and their first derivatives at $x = 0$ and $x = d$, one can obtain the values of $R$ and $S$, and thus the reflection and transmission coefficients:
\[ |R|^2 = \frac{(k_1^2 + k_2^2)^2 \sinh^2 k_2 d}{(k_1^2 + k_2^2)^2 \sinh^2 k_2 d + 4k_1^2 k_2^2} \]  

(2.6)

\[ T = |S|^2 = \frac{4k_1^2 k_2^2}{(k_1^2 + k_2^2)^2 \sinh^2 k_2 d + 4k_1^2 k_2^2}, \]  

(2.7)

where \( |R|^2 + |S|^2 = 1 \). The transmission coefficient \( T \neq 0 \), indicating that the electron can tunnel through a potential barrier that is higher than its kinetic energy. If \( k_2 d >> 1 \), then \( \sinh k_2 d \approx \frac{1}{2} e^{k_2 d} >> 1 \), and the transmission coefficient can thus be approximated as

\[ T \approx e^{-2k_2 d} \]

\[ = \exp\left(-\frac{2d}{\hbar} \sqrt{2m(\Phi_B - E)}\right), \]  

(2.8)

which shows that \( T \) has exponential dependence on the barrier width.

The current density in quantum mechanics for a 1-D system is

\[ J = \frac{-i\hbar}{2m} \left( \psi^* \frac{\partial}{\partial x} \psi - \psi \frac{\partial}{\partial x} \psi^* \right). \]  

(2.9)

After substituting Eq. (2.3) into Eq. (2.9) one can obtain the current density of the transmitted wave:

\[ j = eTv, \]  

(2.10)

where \( v = \frac{\hbar k}{m} \).

2.1.2 Wentzel-Kramers-Brillouin (WKB) method

For the case of a barrier with an arbitrary shape, it is usually difficult to get the tunneling transmission coefficient. However if this arbitrary barrier has a gentle slope...
[Fig. 2.2(a)], i.e., \( \lambda \frac{d\Phi}{dx} \ll E - \Phi(x) \) where \( \lambda = \frac{\hbar}{p} \), then an approximation method proposed by Wentzel, Kramers, and Brillouin can be utilized to simplify the problem [1,4].

For a potential barrier of \( \Phi(x) \) [Fig. 2.2(a)], the Schrödinger’s equation is

\[
-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \Phi(x)\psi = E\psi. 
\]  

(2.11)

The wave function can be expressed as

\[
\psi(x) = e^{i S(x)},
\]

(2.12)

then \( S(x) \) is a solution of the following equation:

\[
\frac{1}{2m} \left( \frac{dS}{dx} \right)^2 + \frac{\hbar}{i 2m} \frac{d^2S}{dx^2} = E - \Phi(x).
\]

(2.13)

When \( \hbar \to 0 \) \( (\frac{d\hbar}{dx} \ll 1) \), Eq. (2.13) can be approximated as

\[
\frac{1}{2m} \left( \frac{dS_0}{dx} \right)^2 = E - \Phi(x),
\]

(2.14)

therefore

\[
S_0(x) = \pm \sqrt{2m[E - \Phi(x)]} dx.
\]

(2.15)

Thus in the region of \( \Phi(x) < E \), the solution of Schrödinger’s equation can be approximated as

\[
\psi(x) = \frac{C_1}{\sqrt{p}} e^{\frac{i}{\hbar} \sqrt{2m[E - \Phi(x)]} dx} + \frac{C_2}{\sqrt{p}} e^{-\frac{i}{\hbar} \sqrt{2m[E - \Phi(x)]} dx},
\]

(2.16)

while in the classically forbidden region \([\Phi(x) > E]\) it can be expressed as
Figure 2.2. (a) An electron with energy $E$ tunnels through an arbitrary barrier with a gentle slope. WKB method is used to obtain the tunneling transmission coefficient. (b) An alternative way to get the transmission coefficient is to subdivide the barrier into a large number of approximate rectangular barriers with infinitesimal widths. The overall transmission coefficient can be calculated by multiplying the transmission coefficients across individual barriers.
\begin{align*}
\psi(x) &= \frac{C_1}{\sqrt{|p|}} e^{\frac{i}{\hbar} \sqrt{2m[E(x) - \Phi(x)]} dx} + \frac{C_2}{\sqrt{|p|}} e^{\frac{i}{\hbar} \sqrt{2m[E(x) - \Phi(x)]} dx}.
\end{align*}

(2.17)

Again, by matching the wave functions at \( x = a \) and \( x = b \) one obtains the transmission coefficient:

\begin{align*}
T &= \exp \left[ -\frac{2}{\hbar} \int_a^b \sqrt{2m[E(x) - \Phi(x)]} dx \right].
\end{align*}

(2.18)

An alternative way [19] to deduce equation (2.18) is to subdivide the barrier into a large number of approximate rectangular barriers having infinitesimal widths of \( d_1, d_2, \ldots, d_i \) and penetration constants \( k_1, k_2, \ldots, k_i \), respectively, where \( k_i = \sqrt{\frac{2m}{\hbar^2}} (\Phi_i - E) \) [Fig. 2.2(b)]. The tunneling transmission coefficient through the \( i \)th barrier can be written as

\begin{align*}
T_i &= \exp \left[ -2k_i d_i \right].
\end{align*}

(2.19)

By multiplying the transmission coefficients across different barriers, the overall coefficient would be

\begin{align*}
T &= \prod_i T_i = \exp \left[ -\sum_i 2k_i d_i \right].
\end{align*}

(2.20)

Since the barrier widths are infinitesimal small, the summation in (2.20) can be replaced by an integral, thus the transmission coefficient can be expressed as

\begin{align*}
T &= \exp \left[ -\int_a^b 2k(x) dx \right] \\
&= \exp \left[ -\frac{2}{\hbar} \int_a^b \sqrt{2m[E(x) - \Phi(x)]} dx \right].
\end{align*}

(2.21)
2.1.3 Metal-insulator-metal tunnel junction and the Simmons model

One of the extensively studied tunneling structures is the metal-insulator-metal (M-I-M) tunnel junction. If two metal electrodes are separated by an insulating film and the film is sufficiently thin, then current can flow between the two electrodes by means of tunneling [5,6]. The purpose of this insulating film is to introduce a potential barrier between the metal electrodes. In this section we will deduce the current-voltage characteristics for such a tunnel junction following the approach proposed by J. G. Simmons [20,21]. This approach adopts the non-interacting free electron approximation and the WKB method to obtain the transmission coefficient.

Fig. 2.3(a) shows the energy band diagram of an M-I-M junction with a general barrier \( \Phi(x) \) under bias \( V \). Following Eq. (2.10) and taking the plane of the junction to lie normal to the \( x \) direction, the tunneling current density from left to right is given by [5,20]:

\[
J_{LR} = 2 \frac{eV_x}{h} \int dp_x dp_y dp_z \left( f_L(E) - f_R(E) \right) \left[ 1 - f_R(E + eV) \right],
\]

(2.22)

where the factor of 2 is from the electron spin, \( h \) is Planck’s constant, \( v_x = \frac{p_x}{m} \) is the electron’s velocity in the \( x \) direction, \( T(E_x) \) is the tunneling transmission coefficient where \( E_x = \frac{p_x^2}{2m} \), and \( f(E) \) is the Fermi distribution function

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

\( f_L(E) \) is the probability that the initial state is occupied and \( 1 - f_R(E + eV) \) is the probability that the final state is unoccupied. Similarly the
Figure 2.3. (a) Energy band diagram of a metal-insulator-metal junction with a general barrier shape under bias $V$. (b) Energy band diagram of a rectangular barrier under bias $V$ ($V < \Phi_B/e$).
tunneling current density from right to left is given by (the transmission coefficient $T(E_x)$ is the same in either direction [20]):

$$j_{RL} = 2 \int \frac{dp_x dp_y dp_z}{\hbar^3} eV_x T(E_x) f_R(E + eV) \left[ 1 - f_L(E) \right].$$  \hspace{1cm} (2.23)

Therefore the net flow of the current through the barrier is

$$j = j_{LR} - j_{RL} = 2 \int \frac{dp_x dp_y dp_z}{\hbar^3} eV_x T(E_x) \left[ f_L(E) - f_R(E + eV) \right].$$  \hspace{1cm} (2.24)

Since $dp_x dp_y = p_x dp_x d\theta = m \frac{p_y^2}{2m} d\theta = m dE_x d\theta$ and $v_x dp_x = dE_x$, the current density can be expressed as

$$j = \frac{4\pi ne}{\hbar^3} \int_{E_0}^{E} T(E_x) dE_x \int_{0}^{\infty} \left[ f_L(E) - f_R(E + eV) \right] dE_x,$$  \hspace{1cm} (2.25)

where $m$ is the mass of the electron, and the transmission coefficient can be obtained from the WKB approximation discussed in section 2.1.2 [Eq. (2.18)]:

$$T(E_x) = \exp \left[ -\frac{2}{\hbar} \int_{E_0}^{E_x} \sqrt{2m(\Phi(x) - E_x)} \, dx \right].$$  \hspace{1cm} (2.26)

For a generalized barrier shown in Fig. 2.3(a) it becomes

$$T(E_x) = \exp \left[ -\frac{2}{\hbar} \int_{E_0}^{d'} \sqrt{2m(\Phi(x) - E_x)} \, dx \right] = \exp \left[ -\frac{2d'}{\hbar} \sqrt{2m(\Phi + E_F - E_x)} \right],$$  \hspace{1cm} (2.27)

where $d'$ is the barrier width at the Fermi level of the negatively biased electrode [Fig. 2.3(a)], and $\Phi$ is the mean barrier height above the same Fermi level, which is defined by the following equation [20]:

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\[
\Phi = \frac{1}{d'} \int_0^{d'} \Phi(x)dx.
\] (2.28)

When deriving Eq. (2.27) the following approximation is used [20]:

\[
\int_{x_1}^{x_2} f^{1/2}(x)dx = \tilde{f}^{1/2}\Delta x,
\]

where \( \Delta x = x_2 - x_1 \) and \( \tilde{f} \) is defined as

\[
\tilde{f} = \frac{1}{\Delta x} \int_{x_1}^{x_2} f(x)dx.
\]

After substituting Eq. (2.27) into Eq. (2.25) and completing the integration over \( E_r \) and \( E_x \), the tunneling current density for a generalized barrier can be expressed as [20]:

\[
J = \left( \frac{e}{4\pi^2\hbar d'^2} \right) \left\{ \Phi \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} \Phi^{1/2} d' \right] - (\Phi + eV) \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} (\Phi + eV)^{1/2} d' \right] \right\}.
\] (2.29)

For a rectangular barrier with a barrier height of \( \Phi_B \) in the bias range of \( V < \Phi_B/e \) as shown in Fig. 2.3(b), \( d' = d \), where \( d \) is the junction gap distance, and

\[
\Phi = \frac{1}{d} \int_0^d (\Phi_B - \frac{eV}{d}x)dx = \Phi_B - \frac{eV}{2}.
\]

Therefore the current density for a rectangular barrier becomes

\[
J = \left( \frac{e}{4\pi^2\hbar d^2} \right) \left\{ \left(\Phi_B - \frac{eV}{2}\right) \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} \left(\Phi_B - \frac{eV}{2}\right)^{1/2} d \right] - \left(\Phi_B + \frac{eV}{2}\right) \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} \left(\Phi_B + \frac{eV}{2}\right)^{1/2} d \right] \right\}.
\] (2.30)

In the low bias range, Eq. (2.30) can be approximated as [20]:

\[
J \approx \left( \frac{e^2 (2m \Phi_B)^{1/2}}{\hbar^2 d} \right) V \exp \left[ -\frac{2}{\hbar} (2m \Phi_B)^{1/2} d \right],
\] (2.31)
which indicates that the tunneling current increases linearly with the applied bias. It also shows that the current depends on the barrier width exponentially as \( J \propto \exp(-\beta_0 d) \).

The decay coefficient \( \beta_0 \) can be expressed as

\[
\beta_0 = \frac{2(2m)^{1/2}}{h} (\Phi_g)^{1/2}.
\]  

(2.32)

2.1.4 Effective mass in a molecular system

According to solid state theory, when an electron moves in a periodical potential, the type of potential present in crystalline lattices, the allowed energy states form energy bands, which is usually described by the energy (E)-momentum (k) relationship [22,23]. The use of an electron’s effective mass accounts for the influence of the crystal structure on the motion of the electron. With the effective mass, the motion of electrons in a crystal can be visualized and described in a free-particle manner. After establishing the crystal band structure or E-k relationship, the effective mass \( (m^*) \) can be determined by the following equation [24]:

\[
m^* = \frac{1}{\int \frac{d^2 E}{h^2 \frac{dk^2}{E}}}.
\]  

(2.33)

In general, the effective mass is a function of the electron energy. However, for carriers with energies near the top or bottom of an energy band edge, the E-k relationship is typically parabolic; therefore these carriers exhibit a constant effective mass close to the band edges [24].

Theoretical investigations on the effective mass of an electron tunneling through a molecular wire have also been conducted in the past several years [25-27]. For molecular
systems that are constructed of a finite set of repeating building blocks, as for the case of n-alkane molecules [Fig. 2.4(a)], the theory of complex band structures is used to determine the propagating and non-propagating (tunneling) states. For a one-dimensional periodic system, the electron energy eigenstates can be taken to have the Bloch form of

\[ \psi(x) = e^{ikx} u(x), \]

where \( u(x) \) is a function that reflects the periodicity of the crystalline lattice and the associated periodic potential [22]. Normally for infinite systems only the real values of \( k \) are considered, which describe the propagating wavefunctions, since \( e^{ikx} \) will diverge at either \(-\infty\) or \(+\infty\) if \( k \) contains an imaginary component. However, for systems of finite size or containing breaks or defects in spatial uniformity imaginary (or complex) \( k \) solutions are also physically applicable [27]. In the energy band gap region, the imaginary part of \( k \) depicts the decay of the wavefunction along the molecular chain.

Consider a theoretical model of a one-dimensional periodical arrangement of two types of atoms A and B in a sequence of ABABABAB… [27]. The unit cell is chosen to contain an A and a B atom and the spacing between cells is \( a \). Assuming the Bloch forms for the eigenstates, the energy eigenvalues are found to be [27]

\[
E_\pm = \frac{E_v + E_c}{2} \pm \sqrt{\left(\frac{E_v - E_c}{2}\right)^2 + 2t^2 (1 + \cos ka)},
\]

(2.34)

where \( E_v \) and \( E_c \) are valence-band top and conduction-band bottom energies, respectively, and \( t \) is the coupling between orbitals on the nearest-neighbor atoms. The plot of a complex band structure for real and imaginary \( k \) values is shown in Fig. 2.4(b), with \( t \) set equal to \( \frac{E_v - E_c}{2} \) [27]. The right half of the figure is the usual real \( k \) band structure while the left half is a plot of \( |\text{Im} \ k| \) for the \( k \) solutions with an imaginary part. The
Figure 2.4. (a) N-alkane molecular system as an example of one-dimensional infinite periodic structure. The dark circular symbols represent carbon atoms and the light circular symbols represent hydrogen atoms. (b) The complex band structure calculated for the model system with $t = (E_V - E_C)/2$. The right half is the real $k$ structure while the left half is the plot of $|\text{Im} k|$ for the imaginary $k$ solutions [$|\text{Im}(k)| = \beta a/2$]. After Ref. 27.
imaginary k value determines how an electron with a given energy will tunnel through a finite region of the crystal, i.e., the wavefunction decays by a factor of $e^{-|\text{Im}k|a}$ from one unit cell to the next. Therefore the tunneling probability is $e^{-2|\text{Im}k|a} = e^{-\beta a}$, where $\beta(E) = 2|\text{Im}k(E)|$ is the decay coefficient. $|\text{Im} k|$ decreases as the energy approaches the band edge ($E_v$ or $E_c$) [Fig. 2.4(b)]. The band edges each act as the top of an effective potential barrier and they mark the crossover point from decaying waves to propagating ones.

The complex k vector for energies in the gap can be calculated by replacing $E_z$ by an input energy E and solving for $\cos ka$. The result is [27]

$$\cos ka = -\gamma(E), \quad (2.35)$$

where

$$\gamma(E) = \frac{(E - E_v)(E_c - E)}{2t^2} + 1. \quad (2.36)$$

Therefore

$$\beta(E) = \frac{2}{a} \ln \left[\gamma(E) + \sqrt{\gamma(E)^2 - 1}\right] \quad (2.37)$$

To make a connection with the case of tunneling through a barrier, we evaluate $t^2$ using the effective mass equation [Eq. (2.33)] calculated near the band edges:

$$t^2 = \frac{\hbar^2 E_g}{2m^*a^2}, \quad (2.38)$$

where $E_g$ is the band gap. Replacing $t^2$ in Eq. (2.37) by Eq. (2.38) for $\gamma(E)$ gives

$$\beta(E) = \frac{2}{\hbar} \sqrt{2m^*(E_c - E)} \quad (2.39)$$

for energies near $E_c$ and
\[
\beta(E) = \frac{2}{\hbar} \sqrt{2m^*(E-E_v)}
\]  
(2.40)

for energies near \(E_v\). \((E_C - E)\) or \((E - E_v)\) are actually the barrier height \(\Phi_B\). Comparing the Simmons decay coefficient expression Eq. (2.32) with Eq. (2.39) or Eq. (2.40) from the complex band theory, we find that the electron mass in the Simmons expression needs to be modified to account for the effective mass.

An empirical model related to the complex band theory is the so-called Franz two-band model proposed for an M-I-M junction in 1950’s [28-32]. Unlike the Simmons model, the Franz model considered the contributions from both conduction band and valence band of the insulating film by taking into account the energy bandgap of \(E_g\) [28]. Instead of giving a tunneling current expression, it empirically predicted a non-parabolic energy-momentum dispersion relationship inside the bandgap [28]:

\[
k^2 = \frac{2m^*}{\hbar^2} E \left(1 + \frac{E}{E_g}\right),
\]  
(2.41)

where \(m^*\) is the electron’s effective mass and \(E\) is referenced relative to \(E_C\). This expression is actually an approximation of the \(E(k)\) relationship [Eq. (2.37)] obtained from the complex band structure [25]. By setting \(E_C = 0\) Eq. (2.41) becomes

\[
k^2 = \frac{2m^*}{\hbar^2} \frac{(E_C - E)(E - E_v)}{E_g},
\]

which is an approximated form of Eq. (2.37).

The Franz model is useful to get the effective mass of the tunneling electron inside the band gap [29-32]. From the non-parabolic \(E(k)\) relationship of Eq. (2.41), the effective mass can be deduced by knowing the barrier height of the M-I-M tunnel junction [32]. When the Fermi level of the metal electrodes is aligned close to one energy
band, the effect of the other distant band on the tunneling transport is negligible, and the Simmons model is a good approximation of the Franz model as shown in the previous analysis [21,33].

2.2 Inelastic Electron Tunneling

Inelastic electron tunneling due to localized molecular vibrational modes was discovered by Jaklevic and Lambe in 1966 when they studied the tunneling effect of metal-oxide-metal junctions [13]. Instead of finding band structure effects due to metal electrodes as they initially hoped, they observed structures in the d²I/dV² characteristics which were related to vibrational excitations of molecular impurities contained in the insulator [13,14]. IETS has since been developed to a powerful spectroscopic tool for various applications such as chemical identification, bonding investigation, trace substance detection, etc. [16,17].

Fig. 2.5 shows the energy band diagrams of a tunnel junction and the corresponding I(V) plot. When a negative bias is applied to the left metal electrode, the left Fermi level is lifted. An electron from an occupied state on the left side tunnels into an empty state on the right side, and its energy is conserved (process a). This is the elastic process discussed in section 2.1. During this process the current increases linearly with the applied small bias [Fig. 2.5(b)]. However, if there is a vibrational mode with a frequency of ν localized inside this barrier, then when the applied bias is large enough such that eV ≥ ℏν, the electron can lose a quantum of energy of ℏν to excite the vibration mode and tunnel into another empty state (process b) [15,18]. This opens an inelastic tunneling channel for the electron and its overall tunneling probability is increased. Thus
Figure 2.5. (a) Energy band diagram of a tunnel junction with a vibrational mode of frequency \( \nu \) localized inside. \( a \) is the elastic tunneling process while \( b \) is the inelastic tunneling process. (b) Corresponding \( I(V) \), \( dI/dV \), and \( d^2I/dV^2 \) characteristics.
the total tunneling current has a kink as a function of the applied bias [Fig. 2.5(b)]. This kink becomes a step in the differential conductance (dI/dV) plot, and becomes a peak in the d²I/dV² plot. However, since only a small fraction of electrons tunnel inelastically, the conductance step is too small to be conveniently detected. In practice, people use a phase sensitive detector (“lock-in”) second harmonic detection technique to directly measure the peaks of the second derivative of I(V) [15].

After an IETS spectrum is obtained, the positions, widths, and intensities of the spectral peaks need to be comprehended. The peak position and width can be predicted on very general grounds, independent of the electron-molecule interaction details. However the peak intensity is more difficult to be calculated since it depends on the detailed aspects of the electron-molecule couplings [15].

2.2.1 Peak identification

As discussed earlier, an inelastic process can only start to occur when the applied bias reaches \( V_i = \frac{h \nu_i}{e} \) [13]. Therefore a peak at a position of bias \( V_i \) corresponds directly to a molecular vibrational mode of energy \( h \nu_i \). This conclusion is based on energy conservation and is independent of the mechanism for the electron-molecule coupling. By referring to the huge amount of assigned spectra obtained by other techniques such as infrared (IR), Raman, and high resolution electron energy loss spectroscopy (HREELS), the IETS peaks can be identified individually [14,15,18].

2.2.2 Peak width
According to IETS theoretical studies, the width of a spectral peak includes a natural intrinsic linewidth and two width broadening effects: thermal broadening that is due to the Fermi level smearing effect, and modulation broadening that is due to the dynamic detection technique used to obtain the second harmonic signals [15].

The thermal broadening effect was first studied by Lambe and Jaklevic [14,34]. Following their treatment, consider an inelastic tunneling process related to a vibrational mode with frequency \( \nu \). Assuming that the voltage dependence of the tunneling current is only contained in the Fermi functions of the metal electrodes and the energy dependence of the effective tunneling density of states is negligible, the inelastic current can be written as:

\[
I_i = C \int_{-\infty}^{\nu} dE \left( \frac{1}{1 + e^{E/kT}} \right) \left( 1 - \frac{1}{1 + e^{[E + eV - \nu]/kT}} \right),
\]

where \( C \) takes into account all the details of the electron-molecule interactions which are independent of \( E \) and \( T \) within the above assumptions. This integral simply expresses analytically the inelastic condition discussed earlier: electrons must tunnel from an occupied state in one electrode into an empty state in the other electrode. The integral can be easily evaluated:

\[
I_i = C(EV - \hbar \nu) e^{(eV - \nu)/kT} e^{-[eV - \nu]/kT} - 1.
\]

Taking derivatives,

\[
\frac{d^2 I_i}{dV^2} = C \frac{e^2}{kT} \left[ e^x \frac{(x - 2)e^x + (x + 2)}{(e^x - 1)^3} \right],
\]
where \( x = \frac{eV - h\nu}{kT} \). It describes the line expected for an extremely narrow vibrational excitation in which case the observed linewidth will be due entirely to the smearing in energy of the electron distribution in the metals. Eq. (2.44) is plotted in Fig. 2.6, and the predicted linewidth broadening at half maximum is \( 5.4\frac{kT}{e} \) [14,34]. This can be calculated as follows: the maximum value of the function is \( 0.167 \frac{e^2}{kT} \) where \( eV = h\nu \), which yields a half maximum value of \( \sim 0.084 \frac{e^2}{kT} \). Substituting it into Eq. (2.44) and solving the equation for \( V \) gives \( V_\pm \) values at half maxima as \( (h\nu \pm 2.7kT)/e \), respectively; therefore the full width at half maximum is \( V_+ - V_- = 5.4\frac{kT}{e} \). This broadening prediction has been confirmed by experimental studies [35].

The broadening effect due to the finite modulation technique was first discussed by Klein et al. [34]. Assuming a modulation voltage of \( V_\omega \) at a frequency of \( \omega \) is applied to the tunnel junction, the resulting current is then a function of time:

\[
I = f(eV_0 + eV_\omega \cos \omega t),
\]

where \( V_0 \) is the bias voltage and \( I = f(eV) \) is the junction characteristics. We call \( f''(eV) \) the exact second derivative (with no modulation broadening) and \( F''(eV) \) the function obtained experimentally. To obtain \( d^2I/dV^2 \) we compute \( I_{2\omega} \), the current at the second harmonic frequency:

\[
I_{2\omega} = \frac{2}{\tau} \int f(eV_0 + eV_\omega \cos \omega t) \cos 2\omega t dt,
\]

where \( \tau \) is the period. Substituting the new variable \( E = eV_\omega \cos \omega t \), two partial integrations give
Figure 2.6. Thermal broadening effect of the IETS peak. The full width at half maximum (FWHM) is $5.4 \frac{kT}{e}$. After Ref. 14.
\[
\frac{\pi V_0^2 I_{2\omega}}{2} = \int_{-eV_0}^{eV_0} f''(eV_0 + E) \frac{(e^2V_0^2 - E^2)^{3/2}}{3} dE.
\] (2.47)

It then appears that the experimental quantity, \(F'' = (4/V_\omega^2)I_{2\omega}\), is a convolution product of the exact second derivative, \(f''\), with an instrumental function \(\phi\):

\[
\phi(E) = \frac{8}{3\pi (eV_\omega)^4} \left( e^2V_\omega^2 - E^2 \right)^{3/2} \quad \text{for} \quad |E| < eV_\omega
\]

\[
= 0 \quad \text{for} \quad |E| > eV_\omega.
\] (2.48)

This modulation broadening is plotted in Fig. 2.7, where the full width at half maximum is 1.2 \(V_\omega\) or 1.7 \(V_{\text{rms}}\), the rms value of the modulation voltage, which is usually measured directly [15,34].

Of these two broadening contributions, the modulation broadening is more dominant [18]. By lowering the measurement temperature the thermal broadening effect can be reduced; for example, at liquid helium temperature it gives a resolution of 2 meV. In order to make the modulation broadening comparable to the thermal effect, the modulation voltage should be less than 1.18 mV. However, since the second harmonic signal is proportional to the square of the modulation voltage and the signal to noise improvements varies with the square root of the averaging time, at such a small modulation the measurement time would be impractically extended. Therefore little is gained by further lowering measurement temperature since the modulation broadening is more dominant [18].

Thus the experimentally obtained spectral peak linewidth \(W_{\text{exp}}\) consists of three parts: the natural intrinsic linewidth \(W_{\text{intrinsic}}\), the thermal broadening \(W_{\text{thermal}}\) that is
Figure 2.7. Modulation broadening effect of the IETS peak. The full width at half maximum (FWHM) is 1.7 $\Delta V$. After Ref. 34 ($\Delta V = V_{rms}$); this plot is related to $\Phi(E)$ through Eq. (2.47).
proportional to 5.4 kT, and the modulation broadening $W_{\text{modulation}}$ that is proportional to 1.7 $V_{\text{rms}}$. These three contributions add as squares [14,36]:

$$W_{\exp} = \sqrt{W_{\text{intrinsic}}^2 + W_{\text{thermal}}^2 + W_{\text{modulation}}^2}.$$  \hfill (2.49)

### 2.2.3 Peak intensity

After the experimental discovery of inelastic electron tunneling due to molecular vibrations, several theoretical models were proposed for the purpose of quantitative analysis of the IETS spectra. The first theory was developed by Scalapino and Marcus in order to understand the interaction mechanism [37]. They treated the electron-molecule coupling as a Coulomb interaction between the electron and the molecular dipole moment and considered the case where the molecule of dipole moment is located very close to one of the electrodes so that the image dipole must be included. The interaction potential was treated as a perturbation on the barrier potential that was assumed to be rectangular. Using the WKB approximation they could estimate the ratio of the inelastic conductance to the elastic one and predict that the intensities in a tunneling spectrum should be the same as in an infrared spectrum. However it is found experimentally that although large peaks in IR spectra usually correspond to large peaks in tunneling spectra, the proportionality is not exact. Furthermore, peaks that are completely absent in IR spectra also appear in tunneling spectra [15].

Lambe and Jaklevic studied other mechanisms for electron-molecule interactions and generalized the above treatment to include the Raman type of interaction, where the electron induces a dipole moment in the molecule and interacts with this induced dipole [14]. Their calculation showed that the Raman type interaction produces inelastic
conductance changes of nearly the same order of magnitude as for the IR type electron–
dipole interaction.

The above dipole approximations provided clear physical pictures of the
interaction mechanisms of the tunneling electron and the localized molecular vibration,
however the calculations were over-simplified. Using the transfer Hamiltonian formalism
[38,39], Kirtley et al. developed another theory for the intensity of vibrational spectra in
IETS [15,40-42]. Rather than making the dipole approximation, they assumed that the
charge distribution within the molecule can be broken up into partial charges, with each
partial charge localized on a particular atom. These partial charges arise from an uneven
sharing of the electrons involved in the bonding. The interaction potential between the
tunneling electron and the vibrating molecule is thus a sum of Coulomb potentials with
each element in the sum corresponding to a partial charge. This partial charge treatment
allows one to describe the interaction at distances comparable to interatomic length.

They assume the interaction potential is of the form [15]:

$$V_i(\vec{r}) = \sum_j -\frac{e^2 Z_j}{|\vec{r} - \vec{R}_j|},$$

(2.50)

where $\vec{R}_j$ is the $j$th atom’s position, $Z_j e$ is its partial charge, and $\vec{r}$ is the position of the
electron. The sum $j$ is over all atoms in the molecule. Separating out the component of the
total potential [Eq. (2.50)] that oscillates at the vibrational mode frequency and transfers
electrons inelastically and taking into account the images of the partial charges in the two
electrodes, the interaction potential becomes:

$$V_i^k(\vec{r}) = \sum_n \sum_j -\frac{e^2 Z_j^k}{\varepsilon \delta \vec{R}_j^k \cdot \vec{V}_j} \left( \frac{1}{|\vec{r} - \vec{R}_j - 2nd\hat{x}|} - \frac{1}{|\vec{r} - \vec{R}_j - (2nd - 2a_j)\hat{x}|} \right) e^{i\omega t},$$

(2.51)
where \( \delta \tilde{R}_j^k \) is the vibrational amplitude for the \( j \)th atom due to the \( k \)th normal mode of the molecule, \( d \) is the barrier thickness, \( a_j \) is the distance of the \( j \)th atom from one metal electrode, and \( \varepsilon \) is the dielectric constant. The inelastic tunneling matrix element, which corresponds to the tunneling transmission coefficient, can be calculated using the WKB wave functions and the above interaction potential [41]. Fig. 2.8 shows the calculation result of the angle averaged matrix element squared for a single dipole oriented normal (solid line) or parallel (dashed line) to the junction interface as a function of the dipole position relative to the metal electrodes [41,42]. As shown in the plot, molecular vibrations with net dipole moments normal to the junction interface have larger inelastic cross sections than vibrations with net dipole moments parallel to the interface for dipoles close to one electrode. This is because that near a metal surface the image dipole adds to the potential of a dipole normal to the interface but tends to cancel out the potential of a dipole parallel to the interface. However, the case is different for vibrational modes localized deep inside the tunnel junction, where dipoles oriented parallel to the junction interface are favored, although at a lower scattering amplitude [15,41,42].
Figure 2.8. Plot of the angle-averaged inelastic tunneling matrix element squared for a single dipole oriented normal (solid line) or parallel (dashed line) to the junction interface as a function of the dipole position for three different vibrational energies. The barrier width is 15 Å. After Ref. 41.
References:


42. J. Kirtley, The Interaction of Tunneling electrons with Molecular Vibrations, in

Chapter 3

Experimental Methods

3.1 Self-assembled monolayers of alkanethiols

Molecular self-assembly is a chemical technique to form highly ordered, closely packed monolayers on various substrates via a spontaneous chemisorption process at the interface [1-3]. Earlier research in this field includes the self-assembly of fatty acids monolayers on metal oxides [4,5], self-assembled monolayers of organosilicon derivatives on metal and semiconductor oxides [6,7], and organosulfur SAMs on metal and semiconductor surfaces [8,9]. Among them the most thoroughly investigated and characterized one is alkanethiol SAM formed on Au(111) surface [1-3], which is the focus of this research work.

Alkanethiol is a thiol-terminated n-alkyl chain molecular system [CH₃(CH₂)ₙ₋₁SH] [1]. As an example, Fig. 3.1(a) shows the chemical structure of octanethiol, one of the alkanethiol molecules. It is well known that when self-assembled on Au(111) surface alkanethiol forms densely packed, crystalline-like structure with the alkyl chain in an all-trans conformation [10]. The SAM deposition process is shown in Fig. 3.1(b), where a clean gold substrate is immersed into an alkanethiol solution and after a period of time a monolayer is formed spontaneously on the gold surface via the following chemical reaction [1,11,12]:

\[
\text{Reaction: } \text{Au(111)} + \text{CH₃(CH₂)ₙ₋₁SH} \rightarrow \text{Au(111)-SAM}
\]
Figure 3.1. (a) Chemical structure of an octanethiol molecule. Black symbols represent carbon atoms, small circular symbols represent hydrogen atoms, and the big circular symbol represents a sulfur atom. (b) Schematic of the SAM deposition process, after Ref. 11 & 12. It also shows a STM image of the SAM [see Fig. 3.2(a)].
RS-H + Au → RS-Au + 0.5 H₂,

where R is the backbone of the molecule. This chemisorption process has been observed to undergo two steps: a rapid process that takes minutes (depending on the thiol concentration) and gives ~90% of the film thickness, followed by a second, much slower process that lasts hours and reaches the final thickness and contact angles [1,3]. Research has shown that the second process is governed by a transition from a SAM lying-down phase into an ordered standing-up phase, and it is also accompanied or followed by a crystallization of the alkyl chains associated with molecular reorganization [13-16]. There are three forces believed to determine this SAM formation process and the final monolayer structure: the interaction between the thiol head group and gold lattice, dispersion force between alkyl chains (van der Waals force, etc.), and the interaction between the end groups [1,14].

Various surface analytical tools have been utilized to investigate the surface and bulk properties of alkanethiol SAMs, such as infrared (IR) and Fourier transform infrared (FTIR) spectroscopy [10,17], X-ray photoelectron spectroscopy (XPS) [18], Raman spectroscopy [19], scanning tunneling microscopy (STM) [2,12] etc. As an example, Fig. 3.2(a) shows a constant current STM image of a dodecanethiol SAM formed on Au(111) surface (adapted from Ref. 12). Fig. 3.2(b) is the schematic of the commensurate crystalline structure that alkanethiol SAM adopts, which is characterized by a \( c(4 \times 2) \) superlattice of the \( (\sqrt{3} \times \sqrt{3})R30^\circ \) lattice [2,12]. In Fig. 3.2(b) the large circular symbols represent the alkanethiol molecules and the small circular symbols represent the underlying gold atoms, and a and b are lattice vectors of the molecular rectangular unit cell with dimensions of 0.8 and 1.0 nm, respectively [12]. Investigations have also shown
Figure 3.2. (a) STM image of a dodecanethiol SAM formed on Au(111) surface. The image size is $13 \times 13$ nm$^2$. (b) Schematic of the alkanethiol SAM commensurate crystalline structure. Large circular symbols represent the alkanethiol molecules and small circular symbols represent the underlying gold atoms. $a$ and $b$ are lattice vectors of a rectangular unit cell with dimensions of 0.8 and 1.0 nm, respectively. After Ref. 12.
that the standing-up alkyl chains of alkanethiol SAMs on Au(111) surface are tilted ~ 30° from the surface normal [20] and the bonding energy between the thiolate head group and the gold lattice is ~ 40 kcal/mol (~ 1.7 eV) [1].

Studies have revealed that defects, such as pinholes or grain boundaries, exist in the self-assembled monolayers and the domain size of an alkanethiol SAM usually is on the order of several hundred Ångstroms [1,2]. In addition to the irregularities introduced during the self-assembly process, another source of such defects is the roughness of the substrate surface. For example, although frequently called “flat” gold, there are grain boundaries existing on the Au surface layer, which introduces defects into the assembled monolayer [2]. However, surface migration of thiolate-Au molecules, the so-called SAM annealing process, is found to be helpful for healing some of the defects [1,2].

Recently, electrochemical characterization of thiol-terminated self-assembled monolayers on fabricated planar gold surfaces has been conducted [21]. The studied device structure consists of lithographically exposed rough gold surfaces with areas from 1 to 10⁴ µm². Cyclic voltammetry (CV) measurement is performed with a standard three-electrode setup and potassium chloride is used as the electrolyte, thus the electrochemical system consists of three parts: the metal electrode (processed gold), SAM, and the electrolyte solution. By carrying out such CV measurement on a SAM, the normalized capacitance of the molecular layer (Cₙ) can be obtained, and the monolayer thickness can thus be deduced using \( d_{SAM} = \frac{\varepsilon}{C_n} \), where \( \varepsilon \) is the dielectric constant of the SAM. This study has found that there is a nice progression in normalized capacitance with deposition time, which shows a gradual decrease in the capacitance through the first 3 days and
remains steady from the 4\textsuperscript{th} to 5\textsuperscript{th} day. This indicates that the monolayer coverage quality becomes the best after three days of deposition time. Furthermore, characterizations of dodecane dithiol SAM versus monothiol SAM reveal that they have similar final monolayer thicknesses. The differences between the deduced SAM thicknesses and actual molecular lengths can be further improved by employing a more complicated calculation model. Nevertheless, the observed agreement between the thicknesses of dithiol and monothiol SAMs suggests that the dithiol molecules are in a stand-up configuration in the device structure just like the monothiol molecules, and they do not form double layers either.

Alkanethiols are large HOMO-LUMO gap (~ 8 eV [22-26]) molecules with short molecular lengths (~ several nanometers), therefore the electronic transport mechanism is expected to be tunneling. Electrical characterizations have been performed on alkanethiol SAMs and will be discussed in the next chapter.

3.2 Methods of molecular transport characterization

A correct understanding of the electronic transport properties through self-assembled molecules requires fabrication methods that can separate the effects of contacts from the intrinsic properties of the molecular layer. However, such transport measurements are experimentally challenging due to the difficulties of making repeatable and reliable electrical contacts to a nanometer-scale layer [27-29]. A number of experimental characterization methods have been developed to achieve this goal and in the following we briefly review some of the major techniques.
Various scanning-probe-related techniques have been utilized for the study of molecular electronic structures, which include STM and conducting atomic force microscopy (C-AFM). STM has been used widely at the early stage of molecular characterization due to its capability to image, probe, and manipulate single atoms or molecules [30-32]. Transport measurement on a single molecule contacted by STM has also been reported [33-36]. However, for such a measurement, the close proximity between the probe tip and the sample surface could modify what is being measured by tip-induced modification of the local surface electronic structure. The presence of a vacuum gap between the tip and the molecule also complicates the analysis [37]. Besides, contamination could occur if the measurement is taken in ambient condition, therefore inert gas (nitrogen or argon) filled or vacuum STM chamber is preferred [38,39].

The C-AFM technique also has been employed recently for the purpose of electrical characterizations of SAMs [40-43]. For example, Wold et al. reported C-AFM measurements on alkanethiol molecules [42]; Cui et al. bound gold nanoparticles to alkanedithiol in a monothiol matrix and measured its conductance [41]. However, in this technique the C-AFM tip might penetrate and/or deform the molecular layer as well as create a force-dependent contact junction area. Adhesion force analysis (to rule out deformation or penetration) and a complimentary temperature-dependent characterization need to be performed to make C-AFM measurements a broadly applicable method for determining molecular conductivity [29].

Another important characterization method is the mechanically controllable break junction technique [44-46]. It can create a configuration of a SAM sandwiched between two stable metallic contacts, and two-terminal I(V) characterizations can be performed on
the scale of single molecules [44]. In the fabrication process, a metallic wire with a notch is mounted onto an elastic bending beam and a piezo electric element is used to bend the beam and thus break the wire. The wire breaking is carried out in the molecular solution and after the breaking the solvent is allowed to evaporate, then the two electrodes are brought back together to form the desired molecular junction [47]. A lithographically fabricated version of the break junction uses e-beam lithography and the lift-off process to write a gold wire on top of an insulating layer of polyimide on a metallic substrate. The polyimide is then partially etched away and a free standing gold bridge is left on the substrate. The suspended gold bridge is then bent and broken mechanically using a similar technique to form a nanometer scale junction [46]. Using the break junction method Reed et al. measured the charge transport through a benzene-1,4-dithiol molecule at room temperature [44]. Using similar technique, Kergueris et al. [45] and Reichert et al. [46] performed conductance measurements on SAMs and concluded that I(V) characterizations of a few or individual molecules were achieved.

Recently, another type of break junction that utilizes the electromigration properties of metal atoms has been developed [48-50]. For this testbed, a thin gold wire with a width of several hundred nanometers is created via e-beam lithography and angle evaporation [48]. Bias is then applied and a large current passing through this nanoscale wire causes the gold atoms to migrate and thus creates a small gap a few nanometers wide. Molecules are deposited on the wire at room temperature before electro-breaking at cryogenic temperatures [49]. The advantage of this technique is that a third gating electrode can be introduced; therefore three-terminal characterizations can be achieved. Using this electromigration break junction technique Park et al. measured two types of
molecules at cryogenic temperatures and observed Coulomb blockade behavior and the Kondo effect [49]. Similar Kondo resonances in a single molecular transistor were also observed by Liang et al. using the same test structure on a different molecular system [50]. However in these measurements the molecules just serve as impurity sites [50], and the intrinsic molecular properties has yet characterized.

The cross-wire tunnel junction is a test structure reported in 1990 in an attempt to create oxide-free tunnel junction for IETS studies [51]. It is formed by mounting two wires in such a manner that the wires are in a crossed geometry with one wire perpendicular to the applied magnetic field. The junction separation is then controlled by deflecting this wire with the Lorentz force generated from a direct current [51]. Using this method Kushmerick et al. recently studied various molecules and observed conductance differences due to molecular conjugation and molecular length differences [52,53]. The drawback of this method is that it is very difficult to control the junction gap distance: the top wire might not touch the other end of the molecules or it might penetrate into the monolayer. Furthermore, temperature-variable measurement has not been reported using this test structure.

Other experimental techniques utilized in molecular transport studies include the mercury-drop junction [54,55] and the nanorod [56], among many others. For example, the mercury-drop junction consists of a drop of liquid Hg, supporting an alkanethiol SAM, in contact with the surface of another SAM supported by a second Hg drop [54,55]. This junction has been used to study the transport through alkanethiol SAMs, however the measurement can only be performed at room temperature [54].
For the research conducted in this thesis work, we mainly use the so-called nanopore technique [57-61]. Using the nanopore method, we can directly characterize a small number (~ several thousand) of self-assembled molecules sandwiched between two metallic contacts. The contact area is around 30 to 50 nm in diameter, which is close to the domain size of the SAM [1]. Thus the adsorbed monolayer is highly ordered and mostly defect free [37,47]. This technique guarantees good control over the device area and intrinsic contact stability and can produce a large number of devices with acceptable yield so that statistically significant results can be achieved. Fabricated devices can be easily loaded into cryogenic or magnetic environments; therefore critical tests of transport mechanisms can be carried out [47]. As an example, Fig. 3.3(a) shows a 3-inch silicon substrate with more than a hundred devices fabricated. Fig. 3.3(b) is a nanopore device bonded onto a 16-pin header.

3.3 Device fabrication

3.3.1 Nanopore fabrication

Fig. 3.4 shows the process flow diagram of the nanopore fabrication. The fabrication starts with double-side polished 3-inch (100) silicon wafers with a high resistivity (ρ > 10 Ω·cm). The thickness of the substrate is 250 µm. Using low pressure chemical vapor deposition (LPCVD) method, low stress Si3N4 film of 50 nm thick is deposited on both sides of the wafer. A low stress film is required in order to make the subsequent membrane less sensitive to mechanical shocks. Next a 400 µm × 400 µm window is opened on the backside of the substrate via standard photolithography processing and reactive ion etching (RIE). Before the photolithography step the topside
Figure 3.3. (a) A 3-inch wafer with 196 nanopore devices fabricated. (b) A nanopore device bonded onto a 16-pin header.
50 nm  

Si$_3$N$_4$  

250 µm  

LPCVD to grow Si$_3$N$_4$ membranes

400µm  

Photolithography & RIE to open the backside window

40 µm  

100 nm  

KOH to etch through the silicon and wet oxidation to grow SiO$_2$ on the sidewalls

E-beam lithography & RIE to open the pore on the membrane

Final metal-SAM-metal junction

Figure 3.4. Schematics of the nanopore fabrication process.
of the substrate is coated with FSC (front side coating) to protect the nitride film. This FSC is removed after RIE by first soaking in acetone and then isopropanol alcohol. The exposed silicon is then etched through by anisotropic wet etching with the bottom nitride as the etch mask. The etchant is a 85% KOH solution heated to 85-90 ºC, and during the etching a magnetic stirrer is used to help the gas byproducts escape. At the end of the KOH etching, an optically transparent membrane of 40 µm × 40 µm is left suspended on the topside of the wafer. Fig. 3.5(a) shows a Scanning Electron Microscope (SEM) picture of the membrane and the pyramid structure of the silicon substrate after this anisotropic etching and Fig. 3.5(b) is an optical image of the suspended transparent membrane.

The wafer is carefully rinsed in water and then immersed in an isotropic silicon etchant (HNO₃:H₂O:HF = 300:150:2) for 5 minutes to remove any remaining silicon nodules on the membrane and to round out the sharp edges. The wafer is subsequently cleaned with the standard RCA cleaning process to remove any organic and metallic contaminations and then loaded into a wet oxidation furnace to oxidize the exposed silicon sidewalls for the purpose of preventing future electrical leakage current through the substrate. In order to reduce the thermal stress to the membrane caused by this high temperature process, the wafer is loaded very slowly in and out of the furnace. A wet oxidation processing at 850 ºC for 60 minutes grows ~ 1000 Å SiO₂ on the sidewalls, which is enough to provide a good electrical insulation.

The last and also the most critical steps are the electron beam (e-beam) lithography and subsequent RIE etching to open a nanometer scale pore on the membrane. The e-beam tool used is the Leica VB6 at the Cornell Nanofabrication
Figure 3.5. (a) SEM image of the pyramid structure of the silicon substrate and a free-standing nitride membrane (backside view). (b) Optical image of the membrane (topside view). (c) TEM image of an etched-through nanopore.
Facility. For the e-beam patterning, the PMMA thickness is 200 nm (4% 495K in anisole spun at 3500 rpm) and the e-beam dosage is between 40 to 300 mC/cm². After the exposure the wafer is developed in MIBK:IPA of 1:1 for 60 seconds and then loaded into a RIE chamber to transfer the developed patterns. A CHF₃/O₂ plasma is used to etch the hole in the membrane and the etching time is varied from 2 to 6 minutes for a 50 nm thick nitride film. The RIE chamber has to be cleaned thoroughly by an O₂ plasma before the etching and every two minutes during the etching to remove the hydrocarbon residues deposited in the chamber. The etching is severely impeded deep in the pore due to the redeposition of hydrocarbon on the sidewalls and therefore the opening at the far side is much smaller than that actually patterned, rendering a bowl-shaped cross section. After the etching is completed the PMMA residue is striped off in the O₂ plasma.

There are several issues that make the final dry etching process difficult on a wafer scale. First of all, the thickness of the nitride film is not uniform across the wafer. For a wafer with a diameter of 3 inches, ellipsometry examination shows that the nitride thickness has a minimum variation of ± 5 nm for a 50 nm thick film. The spin-coated PMMA layer is not even either, thus even though the e-beam dosage is fixed the individual exposed pattern sizes are somewhat different. Furthermore, the RIE etching rates are not laterally uniform across the chamber. In order to obtain consistent results, one important step is to place the wafer at a fixed spot inside the RIE chamber and rotate several times during the etching to balance out the differences. Several e-beam test patterns have also been incorporated to help find optimum fabrication conditions.

SEM and TEM (Transmission Electron Microscope) examination and metallization have been used to determine if a pore is etched through. If not, further
etching is performed until the hole is completely open. As an example, a TEM picture of an etched nanopore is shown in Fig. 3.5(c). The size of the hole is roughly 50 nm in diameter, small enough to be within the domain size of both the evaporated gold film and the SAM layer. However, SEM and TEM examination is very time consuming and a more practical way to verify whether the pore is etched open is to deposit metal contacts on both sides of the membrane and measure the junction resistance. For a completely etched pore, I(V) measurement on a regular probe station usually shows a good ohmic short with a resistance of several ohms. For a non-etched-through device, I(V) measurement shows open-circuit characteristic with a current level of ~ pA at 1.0 Volt.

After the nanofabrication, 150 nm gold is thermally evaporated onto the topside of the membrane to fill the pore and form one of the metallic contacts. The device is then transferred into a molecular solution to deposit the SAM. This deposition is done for 24 hours inside a nitrogen filled glove box with an oxygen level of less than 100 ppm. The sample is then rinsed with the deposition solvent and quickly loaded in ambient conditions into an evaporator with a cooling stage to deposit the opposing Au contact. A challenging step in fabricating molecular junctions (vertical structures similar to Fig. 3.4) is to make the top electrical contact. During the fabrication of metal-SAM-metal junctions, metallic materials deposited on the top of molecules often either penetrate through the thin molecular layer or contact directly with the substrate via defect sites (such as grain boundaries) in the monolayer, causing shorted circuit problems [62,63]. Examination showed that ~ 90% of the devices were shorted with ambient temperature evaporation [37]; therefore a low-temperature deposition technique is adopted [57,64]. During the thermal evaporation under the pressure of ~ 10^-8 Torr, liquid nitrogen is kept
flowing through the cooling stage to minimize the thermal damage to the molecular layer. This technique reduces the kinetic energy of evaporated Au atoms at the surface of the monolayer, thus preventing Au atoms from punching through the SAM. For the same reason, the evaporation rate is kept very low. For the first 10 nm gold evaporated, the rate is less than 0.1 Å/s. Then the rate is increased slowly to 0.5 Å/s for the remainder of the evaporation, and a total of 200 nm of gold is deposited to form the contact.

Preliminary I(V) measurements are carried out on a probe station at room temperature to screen out the functioning devices from those exhibiting either short circuit (top and bottom electrodes are shorted together) or open circuit (the nitride membrane is not etched through). The wafer is then diced into individual chips and the working devices are bonded onto a 16-pin packaging socket for further electrical characterizations.

3.3.2 Test patterns

E-beam lithography and RIE are two critical steps for nanopore fabrication. In order to optimize the processing parameters, several types of e-beam test patterns have been developed. One of them is the test array reported previously [37], where arrays of dots with different diameters ranging from 1μm, 100 nm, 50 nm to 5 nm (minimum pixel size) are patterned on the resist. During the e-beam exposure, the beam dosages are varied from 40 to 300 mC/cm² with a step of 20 mC/cm² from die to die. The optimum dosage therefore can be estimated by examining developed test arrays. Fig. 3.6 shows a SEM image of such test array patterns. The image is taken after dry etching; therefore the actual pore sizes are larger than the e-beam design sizes.
Figure 3.6. SEM image of test patterns with arrays of dots of different diameters. This image is taken after RIE, therefore the pore sizes are larger than the design sizes.
Another type of the test patterns is the drop-off design depicted in Fig 3.7. The purpose of this design is to provide preliminary assessment of whether the membrane is etched through and roughly how big the pore is. The four outer 2 µm × 2 µm squares consist of single dots of minimum e-beam pixel size (5 nm) and the dot spacing is 15, 30, 50, and 70 nm, respectively. The two inner squares are made of 5 and 10 nm wide lines instead. During the dry etching process, these two inner squares would drop as soon as the silicon nitride is etched through. For the four outer squares, the size of the single dots would become larger and larger when etching time increases, and finally they could connect to each other and form an etched-through line and the resulting squares would drop off. For example, the square with the 15-nm dot-spacing would drop as soon as the diameters of the etched-through single pores become larger than 15 nm. This helps estimate the device size during the etching process. Fig. 3.8(a) is a TEM image of one of the un-dropped squares and Fig. 3.8(b) is a blow up of (a), which clearly shows the unfinished connecting of individual pores.

Due to the non-uniformities of the nitride film thickness, PMMA thickness, and etching rate across the etcher chamber, the dropping-off of the squares on one membrane does not always follow the expected order of 10-nm line – 5-nm line – 15-nm spacing – 30-nm spacing – 50-nm spacing – 70-nm spacing. For example, Fig. 3.9(a) shows an optical image of the drop-off pattern after etching for 6 minutes on one membrane. On this membrane the squares made of 10-nm line and single dots of 30 and 50 nm spacing have dropped off, while the squares of the 5-nm line and 15- and 70-nm dot-spacing did not. However, a statistical study of the dropping percentage of different squares on a total
Figure 3.7. Schematic of the drop-off test pattern. The designed diameters of the dots are all 5 nm.
Figure 3.8. (a) TEM image of an un-dropped square. (b) Blow-up of (a) showing the dots start to connect to each other.
Figure 3.9. (a) Optical image of a drop-off pattern after 6 minutes etching. (b) Statistical study of the pattern dropping percentage vs. pattern size for 76 membranes of 16 wafers.
of 76 membranes of 16 wafers showed that the expected order is nearly followed [Fig. 3.9(b)].

3.4 Electrical measurement at variable temperatures

A Janis Research SuperVariTemp (SVT) cryostat is used for temperature-dependent measurements. Fig. 3.10 (a) shows the schematic of such a SVT system [65]. This system consists of an outer liquid nitrogen reservoir, an inner liquid helium reservoir, and a sample chamber, separated by vacuum jackets. Temperatures between 300 and 180 K are reached by filling the liquid nitrogen reservoir with liquid nitrogen and allowing it to pre-cool overnight. The sample is indirectly cooled down to ~ 180 K through convection and radiation and the decreasing of the temperature is slow enough to allow for acquisition of data every ten degrees without significant thermal averaging. Liquid helium is then transferred into the helium reservoir and the sample is further cooled down by controlling the cryogenic helium gas flow from the helium reservoir to the sample chamber via a needle valve. Temperatures between 180 and 4.2 K can be reached by this method, and a Lakeshore electronically controlled heater mounted on the sample stage usually is used to maintain the sample temperature at a certain value. Temperatures between 4.2 and 2 K are achieved by immersing the sample in liquid helium and evacuating the sample chamber using a mechanical pump. A Lakeshore thermometer mounted on the sample stage is used to monitor the actual sample temperature.

The device is mounted onto a 16-pin socket on the sample stage [Fig. 3.10 (b)], and in order to reduce the noise level triaxial cables are used to connect the socket leads.
Figure 3.10. (a) Schematic of the Janis SuperVariTemp cryostat. After Ref. 65. (b) Picture of the sample stage of the dipstick.
to the measurement instruments outside the cryostat through vacuum electrical feedthroughs. Two-terminal DC I(V) characterizations are carried out using a HP4145B Semiconductor Parameter Analyzer (SPA). The SPA is used as a voltage source and a current meter where the current is measured through a sense resistor across a differential amplifier. HP 4145B has a voltage resolution of 1 mV and a current resolution of 50 fA. A LabView program has been developed to interface the instruments via GPIB boards and control the measurements at different temperatures.

3.5 Instrumentation for IETS measurement

3.5.1 Lock-in measurement technique

As discussed in Chapter 2, the IETS signal, which is proportional to the second derivative of I(V), is usually measured by an AC modulation method, the so-called lock-in technique [66-70]. Theoretically, the signal can also be determined by the mathematical differential approach that computes the numerical derivatives of the directly measured I(V) characteristics [71]. However this is generally not feasible in practice as illustrated by an example in Fig. 3.11. Fig. 3.11 (a) shows a I(V) characteristic of a test device measured at 4.2 K with a DC resolution of 300 µV using HP 4156B. Fig. 3.11 (b) and (C) are the first (dI/dV) and second (d²I/dV²) numerical derivatives of the I(V), which were calculated using a 11-point smoothing algorithm. As clearly shown in Fig. 3.11 (c), the mathematical differential method produces a d²I/dV² curve dominated by noise even after the smoothing treatment. In practice, because only a small portion of electrons tunnel inelastically, the change of the junction conductance is very small. The numerical differential method produces spectra with a low signal-to-
Figure 3.11. (a) $I(V)$ characteristic of a test device measured at 4.2 K with a DC resolution of 300 $\mu$V using HP 4156B. (b) The first numerical derivative of the $I(V)$ curve in (a). (c) The second numerical derivative of the $I(V)$ curve in (a).
noise ratio making it difficult to distinguish individual IETS peaks. Hence this method is not useful for IETS studies; however it can be used as a system check.

On the contrary, the lock-in second harmonic detection technique measures a quantity directly proportional to $d^2I/dV^2$ [68,69]. During the lock-in measurement, a small sinusoidal signal is applied to modulate the voltage across the device and the response of the current through the device to this modulation is studied. This can be expressed mathematically as a Taylor expansion of the current around the applied bias [72]:

$$I(V_b + V_m \cos \omega t) = I(V_b) + \frac{dI}{dV} \bigg|_{V_b} V_m \cos \omega t + \frac{1}{2} \frac{d^2I}{dV^2} \bigg|_{V_b} V_m^2 \cos^2 \omega t + \ldots$$

$$= I(V_b) + \frac{dI}{dV} \bigg|_{V_b} V_m \cos \omega t + \frac{1}{4} \frac{d^2I}{dV^2} \bigg|_{V_b} V_m^2 (1 + \cos 2\omega t) + \ldots$$

where $V_b$ is the applied bias, $V_m$ is the AC modulation voltage, and $\omega$ is the modulation frequency. From Eq. (3.1) it can be seen that the detection of the first ($\omega$) and second ($2 \omega$) harmonic signals give the scaled values of the first and second derivatives of $I(V)$, respectively.

Experimentally, this modulation detection is realized by a lock-in amplifier. A lock-in amplifier uses a phase-sensitive detector (PSD) to single out the component of the signal at a specific reference frequency and phase, and noise signals at other frequencies are rejected [73]. During the lock-in measurement, a reference signal, which has the same frequency as the AC modulation (this is commonly done by ensuring that they are derived from the same source), is provided to the lock-in amplifier. The PSD then multiplies the device signal with this reference signal and, by adjusting the phase difference to zero, a filtered DC output that is proportional to the device signal amplitude
is generated [73]. This “lock-in” process can be mathematically explained as follows. Suppose the device signal is \( V_D \cos(\omega_D t + \theta_D) \) and the reference signal is \( V_R \cos(\omega_R t + \theta_R) \). The output of the PSD is simply the product of these two cosine waves:

\[
V_{PSD} = V_D V_R \cos(\omega_D t + \theta_D) \cos(\omega_R t + \theta_R) = \frac{1}{2} V_D V_R \left\{ \cos[(\omega_D - \omega_R) t + (\theta_D - \theta_R)] \cos[(\omega_D + \omega_R) t + (\theta_D + \theta_R)] \right\} ,
\]

(3.2)

if \( \omega_D = \omega_R = \omega \), then

\[
V_{PSD} = \frac{1}{2} V_D V_R \left\{ \cos[\theta_D - \theta_R] + \cos[2\omega t + (\theta_D + \theta_R)] \right\} .
\]

(3.3)

By adjusting the phase we can make \( \theta_D - \theta_R = 0 \), therefore the PSD output consists of a DC signal and an AC fluctuation. If this output is passed through a low pass filter then the AC component is removed and a DC output that is proportional to the amplitude of the device signal is acquired.

### 3.5.2 Instrumentation

The instrumentation setup for the IETS measurements is shown in Fig. 3.12. Using this setup \( \frac{dI}{dV} \) and \( \frac{d^2I}{dV^2} \) can be measured directly. Three circuit boxes: a voltage adder, a voltage shifter, and an I-V converter were home designed and built to complete the measurement system. The circuit schematic of the voltage adder is shown in Fig. 3.13(a). The functions of the voltage divider circuits are to divide the input DC and AC voltages by certain factors to increase the measurement resolution [74]. For example, if the DC voltage source has a resolution of 1 mV, by choosing a dividing factor of 10 the resolution can be increased to 100 µV. The DC divider circuit can divide the DC input
Figure 3.12. (a) Schematic of the IETS measurement setup. (b) A picture of the actual setup.
Figure 3.13. (a) Circuit diagram of the voltage adder. (b) Front side of the adder circuit box showing DC and AC inputs, output, and op-amp control switch. (c) Back side of the adder box showing the control switches of the DC, AC, and the third dividers.
voltage by factors of 2, 10, 25, 100, and 1000 by choosing $R_1$ to be 10 K, 1 K, 420, 100, or 10 $\Omega$, respectively. Similarly the AC divider circuit divides the AC input voltage by factors of 2, 10, 100, 1000, and 10000 via choosing $R_2$ to be 10 K, 1 K, 100, 10, or 1 $\Omega$, respectively. The AC divider also has a high-pass filter to filter out any DC component, and the cut-off frequency ($f = 1/2\pi RC$) is $\sim 150$ Hz. This cut-off frequency is chosen to remove the 60 Hz noise of the power line. Next, two follower circuits are used to isolate the circuits from each other [75]. The divided DC and AC voltages are mixed together by an operational amplifier-based noninverting summer circuit [74]. LT1012 op-amps from Linear Technology are used in our circuit due to their low noise characteristics [76]. The op-amps are powered by 9 V batteries to eliminate 60 Hz power line noise. A low-pass filter is also added into this summer circuit to filter out high frequency noise and the cut-off frequency is $\sim 70$ KHz. A third divider circuit is incorporated after the summer circuit as an additional choice. The mixed DC and AC voltage is further divided by factors of 2, 10, and 100 by selecting $R_3$ to be 100, 1 K, and 10 K$\Omega$. Fig. 3.13 (b) and (c) show pictures of the front and back sides of the completed adder box with control switches specified.

Since the DC voltage source used in this work has a maximum voltage output of 30 V, and after the adder circuit box this maximum output might not be larger enough to cover the interested bias range, a voltage shifter box is built to shift the base voltage by a certain amount. The circuit schematic is shown in Fig. 3.14 (a). A 9V battery is used to provide the DC bias and a 10 k$\Omega$ potentiometer is utilized to shift the voltage from 0 to 0.9V. A similar op-amp-based summer circuit is adopted to add the voltages together.
Figure 3.14. (a) Circuit diagram of the voltage shifter. (b) Front side of the shifter circuit box showing the input, output, and the DC shift monitoring output. (c) Back side of the shifter box showing the control switches of DC shift and monitoring.
Fig. 3.14 (b) and (c) are the pictures of the front and back sides of the completed circuit box with important controls specified.

The lock-in amplifier used in this work (Stanford Research Systems 830) has a current input that can only take currents from 1 µA down to 2 fA [73]. For measurements of large source current the amplifier’s voltage input is used and a circuitry box is built to shunt the current signal and generate a voltage input. Fig. 3.15 (a) shows the schematic of this current-voltage converter. An op-amp based inverting circuit is used to convert the current to voltage and another inverting circuit is used to correct the sign [74]. R_C can be adjusted between 1 MΩ, 100 KΩ, 10 KΩ, and 1 KΩ. Fig. 3.15 (b) and (c) shows the front and back sides of the completed converter box with controls specified.

In our experiment (Fig. 3.12) a Yokogawa 7651 DC source is used as the DC voltage provider, and a Stanford Research Systems DS345 synthesized function generator is used as the AC modulation source as well as to provide the reference signal to the lock-in amplifier. The DC bias and AC modulation are attenuated and mixed together by the voltage adder and then applied to the device under test (DUT). If a higher bias range is desired the voltage shifter is included in the setup before the DUT to increase the DC base voltage. The I-V converter is used if the voltage input of the lock-in amplifier is chosen for the measurement. The output of the lock-in amplifier is read by a HP 34401A digital multimeter (DMM). A LabVIEW program has been developed to control the DC bias sweep and record the lock-in output through this multimeter. Depending on the selection of the lock-in amplifier’s time constant, the measurement speed can be controlled by setting different delay times. Fig. 3.16 shows the front panel of this program.
Figure 3.15. (a) Circuit diagram of the I-V converter. (b) Front side of the converter circuit box showing the input, output, and op-amp control switch. (c) Back side of the shifter box showing the $R_G$ selection switch.
A resonant tunneling diode (RTD) device [77] has been used routinely to check the instrumentation setup. Fig. 3.17 (a) is the I(V) characteristic of this RTD measured with a HP 4145B semiconductor analyzer, showing two negative differential resistance (NDR) peaks at positive and negative biases. Fig. 3.17 (b) shows the lock-in 1ω measurement result obtained by the aforementioned instrumentation setup (without the voltage shifter) as well as the numerical derivative of I(V). Fig. 3.17 (c) shows the lock-in 2ω measurement result, the numerical derivative of the lock-in 1ω measurement result, and the second numerical derivative of I(V), which overlap with each other. This system
Figure 3.17. Performance check of the adder and I-V converter using a semiconductor RTD device: (a) I(V) data from HP4145B. (b) lock-in 1\(\omega\) data and the first numerical derivative of the I(V) in (a). (c) lock-in 2\(\omega\) measurement data, the second numerical derivative of the I(V) in (a), and the first numerical derivative of the 1\(\omega\) data in (b).
performance check is carried out whenever necessary to ensure that the measurement will be done correctly.

A similar performance check has also been done on the system with the voltage shifter included. Fig. 3.18 (a) and (b) are the lock-in $1\omega$ and $2\omega$ test results, respectively. The DC bias sweep range was fixed from -0.5 to 0 V, and this bias was shifted by 0.44 V and 0.90 V to give a measurement range from -0.5 to 0.905 V. Fig. 3.18 (c) shows the overlap of the $2\omega$ data and the numerical derivative of the $1\omega$ data.

3.5.3 Noise consideration

One of the challenges in IETS measurement is to troubleshoot the noise. Generally, noise sources are divided into two categories: intrinsic (or random) noise and external noise [73,78]. Intrinsic noise is present in almost all electronic signals, and it is physical in origin. The instantaneous amplitude of intrinsic noise can only be predicted in terms of probability. There are three major intrinsic noise sources: Johnson noise, shot noise, and $1/f$ noise.

Johnson noise comes from thermal fluctuations of electron density within a resistor; therefore it is also called thermal noise [79,80]. It sets a lower limit on the noise present in a circuit and it is a universal function, independent of the composition of the resistor. The thermal fluctuations of the electrons give rise to an open-circuit emf noise voltage as follows:

$$V_{Johnson} = \sqrt{4kTR\Delta f} \; ,$$  \hspace{1cm} (3.4)

where $k$ is the Boltzmann’s constant, $T$ is the measurement temperature, $R$ is the resistance, and $\Delta f$ is the bandwidth. For low current lock-in measurement, the current
Figure 3.18. Performance check of the shifter: (a) lock-in $1\omega$ measurement with DC shift of 0.44 and 0.90 V. (b) lock-in $2\omega$ measurement with DC shift of 0.44 and 0.90 V. (c) lock-in $2\omega$ measurement data in (b) and the numerical derivative of the $1\omega$ data in (a).
input of the lock-in amplifier is often used, and in such case it is preferable to represent
the thermal noise in the current source form:

\[ I_{\text{Johnson}} = \sqrt{\frac{4kT\Delta f}{R}}. \]  

(3.5)

At \( T = 300 \text{ K} \),

\[ I_{\text{Johnson}}(300K) = 128.7 \sqrt{\frac{\Delta f}{R}} \text{ pA}. \]  

(3.6)

The amount of noise measured by a lock-in amplifier is determined by the
measurement bandwidth. For a time constant (\( T_C \)) of 1 second with a 12 dB/oct filter roll-
off, the equivalent noise bandwidth (ENBW) of a SR830 lock-in amplifier is [73]

\[ ENBW = \frac{1}{8T_C} = 0.125 \text{ Hz}. \]  

(3.7)

Therefore for a typical molecular device with a resistance of 10 M\( \Omega \), the Johnson current
noise is approximately 14 fA.

Shot noise is generated by the non-uniformity of the electron flow in a circuit
[78], and it can be mathematically expressed as

\[ I_{\text{shot}} = \sqrt{2qI\Delta f}, \]  

(3.8)

where \( q \) is the electron charge and \( I \) is the DC current. For a 10 M\( \Omega \) molecular device the
shot noise also has an order of magnitude of fA.

1/f noise depends on the frequency inversely and it dominates the low frequency
regime [78]. The theoretical basis for 1/f noise is still a matter of active research. The
SR830 lock-in amplifier current input has input noises depending on the selection of the
gains, and for the gain of \( 10^6 \) the input noise is 130 fA/\( \sqrt{\text{Hz}} \). This is a 1/f noise and it is
intrinsic to the lock-in amplifier. This noise can be measured by terminating the amplifier with a 2 GΩ resistor and it becomes larger than 130 fA when the frequency becomes less than 10 Hz. However since this frequency is outside the measurement frequency range the 1/f noise is tolerable in our measurements.

All the above intrinsic noise sources are incoherent and the total random noise is the square root of the sum of the squares of all the noise sources, which gives a total intrinsic noise with an order of magnitude of 100 fA. The second harmonic signal of the corresponding molecular device measured with a modulation of 10 mV has an input signal level of ~ 100 pA, therefore the signal-to-intrinsic noise ratio is close to 1000, which is sufficient to yield well resolved spectra.

In addition to intrinsic noise, there are also a variety of external noise sources that can couple to the measurement signals [73,78]. These include, but are not limited to, radios, motors, 60 Hz power line, computer screens, fluorescent lighting, and ground loops. These noise sources can affect the real signals via capacitive and inductive couplings. Measures have been taken in order to reduce these external noises during the IETS instrumentation design and real measurements. For example, capacitors have been added to the adder circuit to filter out the 60 Hz power line noise. All the measurement equipments have been grounded to the same physical point to eliminate ground loops. Tri-axial cables have been used to connect to the devices so as to insure an improved signal level. Shorter length cables are used whenever possible. During measurement, major vibration sources have been turned off and cables are tied down to reduce mechanically induced electrical noise. These measures help reduce the external noise sources and improve the system performance.
References:


21. J. P. Chen, I. Kretzschmar, and M. A. Reed, unpublished result.
23. Although the HOMO-LUMO gap of alkyl chain type molecules has been reported (see Ref. 23-25), there is no experimental data on the HOMO-LUMO gap for Au/alkanethiol SAM/Au system. 8 eV is commonly used as HOMO-LUMO gap of alkanethiol.


Chapter 4

Electronic Conduction Mechanisms in Self-Assembled Alkanethiol Monolayers

4.1 Conduction mechanisms of metal-SAM-metal junctions

In a metal-SAM-metal system, just as in a metal-semiconductor-metal junction, the Fermi level alignment is critical in determining the charge transport mechanism [1]. Created by the overlap of the atomic orbitals of a molecule’s constituents, two molecular orbitals, lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), play similar roles as conduction band and valence band in a semiconductor, respectively. The energy difference between them, the HOMO-LUMO gap, is typically of the order of several electron volts [2,3]. In general, the Fermi level of the metallic contacts does not energetically align with either the HOMO or the LUMO of the molecule, but instead lies close to the center of the gap [4]. This energy level mismatch gives rise to a contact barrier, and depending on the height and thickness of this barrier and the presence of defects, charge transport in such a metal-SAM-metal system exhibits a variety of behaviors. Table 4.1 gives a summary of possible conduction mechanisms with their characteristic behavior, temperature dependence, and voltage dependence [5-8].
<table>
<thead>
<tr>
<th>Conduction Mechanism</th>
<th>Characteristic Behavior</th>
<th>Temperature Dependence</th>
<th>Voltage Dependence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direct Tunneling</td>
<td>( J \sim V \exp\left(-\frac{2d}{h}\sqrt{2m\Phi}\right) )</td>
<td>None</td>
<td>( J \sim V )</td>
</tr>
<tr>
<td>Fowler-Nordheim Tunneling</td>
<td>( J \sim V^2 \exp\left(-\frac{4d\sqrt{2m} \Phi^{3/2}}{3q\hbar V}\right) )</td>
<td>None</td>
<td>( \ln\left(\frac{J}{V^2}\right) \sim \frac{1}{V} )</td>
</tr>
<tr>
<td>Thermionic Emission</td>
<td>( J \sim T^2 \exp\left(-\frac{\Phi - q\sqrt{qV/4\pi e d}}{kT}\right) )</td>
<td>( \ln\left(\frac{J}{T^2}\right) \sim \frac{1}{T} )</td>
<td>( \ln(J) \sim V^{1/2} )</td>
</tr>
<tr>
<td>Hopping Conduction</td>
<td>( J \sim V \exp\left(-\frac{\Phi}{kT}\right) )</td>
<td>( \ln\left(\frac{J}{V}\right) \sim \frac{1}{T} )</td>
<td>( J \sim V )</td>
</tr>
</tbody>
</table>

Table 4.1. Possible conduction mechanisms. \( J \) is the current density, \( d \) is the barrier width, \( T \) is the temperature, \( V \) is the applied bias, and \( \Phi \) is the barrier height. After Ref. 5 & 8.
Based on whether thermal activation is involved, the conduction mechanisms fall into two distinct categories: (i) thermionic or hopping conduction which has temperature-dependent I(V) behavior and (ii) direct tunneling or Fowler-Nordheim tunneling which does not have temperature-dependent I(V) behavior. Thermionic emission is a process in which carriers overcome the metal-dielectric barrier by thermal agitation, and the current has a strong dependence on temperature. The extra voltage term in the exponential is due to image-force correction and it lowers the barrier height at the metal-insulator interface. Hopping conduction usually is defect-mediated, and in a hopping process the thermally activated electrons hop from one isolated state to another, and the conductance also depends strongly on temperature. However, unlike thermionic emission, there is no barrier-lowering effect in hopping transport. Tunneling processes (both direct and Fowler-Nordheim tunnelings) do not depend on temperature (to first order), but strongly depend on film thickness and voltage [5-8]. After a bias is applied, the barrier shape of a rectangular barrier is changed to a trapezoidal form. Tunneling through a trapezoidal barrier is called direct tunneling because the charge carriers are injected directly into the electrode. However, if the applied bias becomes larger than the initial barrier height, the barrier shape is further changed from trapezoidal to a triangular barrier. Tunneling through a triangular barrier, where the carriers tunnel into the conduction band of the dielectric, is called Fowler-Nordheim tunneling (after the two physicists who studied this phenomenon first) or field emission [5,7].

For a given metal-insulator-metal system, certain conduction mechanism(s) may dominate in certain voltage and temperature regimes [5,8]. For example, thermionic emission usually plays an important role for high temperatures and low barrier heights.
Hopping conduction is more likely to happen at low applied bias and high temperature if the insulator has a low density of thermally generated free carriers in the conduction band. Tunneling transport will occur if the barrier height is large and the barrier width is thin.

Temperature-variable I(V) characterization is an important experimental technique to elucidate the dominant transport mechanism and to obtain key conduction parameters such as effective barrier height. This is especially crucial in molecular transport measurements where defect-mediated conduction often complicates the analysis. For example, previous work on self-assembled thiol-terminated oligomers illustrated that one can deduce the basic transport mechanisms by measuring the I(V,T) characteristics [9]. It has been found that the physisorbed aryl-Ti interface gave a thermionic emission barrier of approximately 0.25 eV [9]. Another study on Au-isocyanide SAM-Au junctions showed both thermionic and hopping conductions with barriers of 0.38 and 0.30 eV, respectively [8].

In this research work we investigate the charge transport mechanism of self-assembled alkanethiol monolayers. I(V,T) characterizations are performed on certain alkanethiols to distinguish between different conduction mechanisms. Electrical measurements are also carried out on alkanethiols with different molecular length to further examine length-dependent transport behavior.

4.2 Previous research on alkanethiol SAMs

Recently some reports of molecular effects in electronic devices [10-13] have been shown to be artifacts and due to filamentary conduction [14,15], emphasizing the
fabrication sensitivity of molecular structures and the need to establish reliable controls and methods to validate true molecular transport [16]. A molecular system whose structure and configuration are sufficiently well-characterized such that it can serve as a standard is the extensively studied alkanethiol \([\text{CH}_3(\text{CH}_2)_{n-1}\text{SH}]\) SAM [17]. This system is useful as a control since properly prepared alkanethiol SAM forms single van der Waals crystal [17,18]. This system also presents a simple classical metal-insulator-metal (M-I-M) tunnel junction when fabricated between metallic contacts due to its large HOMO-LUMO gap of \(\sim 8\) eV [2,19-22].

Electronic transport through alkanethiol SAMs have been characterized by STM [23,24], conducting atomic force microscopy [25-28], mercury-drop junctions [29-32], cross-wire junctions [33], and electrochemical methods [34-36]. However, due to the physical configurations of these test structures it is very hard, if not impossible, to perform temperature-variable measurements on the assembled molecular layers; therefore these investigations were done exclusively at ambient temperature, which is insufficient for an unambiguous claim that the transport mechanism is tunneling (which is expected, assuming that the Fermi level of the contacts lies within the large HOMO-LUMO gap). In the absence of \(I(V,T)\) characteristics, other transport mechanisms such as thermionic, hopping, or filamentary conduction can contribute and complicate the analysis. Previous \(I(V)\) measurements performed at room and liquid nitrogen temperatures on Langmiur-Blodgett alkan monolayers exhibited a large impurity-dominated transport component [37,38], further emphasizing the need and significance of \(I(V,T)\) measurement in SAM characterizations.
Using the nanopore test structure that contains alkanethiol SAMs, we demonstrate devices that allow \(I(V,T)\) and length-dependent measurements \([39,40]\), and show that the experimental results can be compared with theoretical calculations from accepted models of M-I-M tunneling.

4.3 Sample preparation

Electronic transport measurement on alkanethiol SAMs is performed using the nanopore testbed described in Chapter 3 [Fig. 4.1(a)]. After 150 nm of gold is thermally evaporated onto the topside of the wafer, the sample is transferred into a molecular solution to deposit the SAM layer. For our experiments, a \(~5\) mM alkanethiol solution is prepared by adding \(~10\) \(\mu\)L alkanethiols into 10 mL ethanol. The deposition is done in solution for 24 hours inside a nitrogen filled glove box with an oxygen level of less than 100 ppm. Three alkanemonothiol molecules of different molecular lengths—octanethiol \([CH_3(CH_2)_7SH;\text{denoted as } C_8,\text{ for the number of alkyl units}]\), dodecanethiol \([CH_3(CH_2)_{11}SH,\text{denoted as } C_{12}]\), and hexadecanethiol \([CH_3(CH_2)_{15}SH,\text{denoted as } C_{16}]\) were used to form the active molecular components. The chemical structures of these molecules are shown in Fig. 4.1(b). Both ethanol and the alkane molecules were purchased from Sigma-Aldrich. The sample is then rinsed with ethanol and transferred to the evaporator for the deposition of 200 nm of gold onto the bottom side. Next it is packaged and loaded into a low temperature cryostat for electrical characterizations.

In order to statistically determine the pore size, test patterns (arrays of pores) were created under the same fabrication conditions (e-beam dose and etching time) as the real devices. Fig 4.2 shows a scanning electron microscope image of one such test pattern.
Figure 4.1. (a) Schematic of the nanopore structure used in this study. (b) Chemical structures of octanethiol, dodecanethiol, and hexadecanethiol. The dark color symbols represent carbon atoms, the medium color symbols represent hydrogen atoms, and the light color symbol represents the sulfur atom.
Figure 4.2. A representative scanning electron microscope image of array of pores used to calibrate device size. The scale bar is 500 nm.
array. This indirect method for the measurement of device size is adopted because SEM examination of the actual device can cause hydrocarbon contamination of the device and subsequent contamination of the monolayer. Using SEM, the diameters have been examined for 112 pores fabricated with an e-beam dose of 100 mC/cm$^2$ and etching time of 4.5 min, 106 pores fabricated with an e-beam dose of 100 mC/cm$^2$ and etching time of 7 min, 130 pores fabricated with an e-beam dose of 200 mC/cm$^2$ and etching time of 6 min, and 248 pores fabricated with an e-beam dose of 300 mC/cm$^2$ and etching time of 6 min. These acquired diameters were used as the raw data input file for the statistics software Minitab. Using Minitab, a regression analysis has been conducted on the device size as a function of e-beam dose and etching time, and a general size relation is obtained:

$$ \text{Size}(in \ nm) = 35.0 + 0.027 \times \text{dose}(in \ mC/cm^2) + 1.63 \times \text{time}(in \ min) $$

(4.1)

Using the same software, a device size under particular fabrication conditions can be predicted via entering the fabrication dose and etching time. The error rage of the size is determined by specifying a certain confidence interval. For example, the fabrication conditions for the C8, C12, and C16 devices that are used in the length dependence study are an e-beam dose of 100 mC/cm$^2$ and etching time of 7 min, 88 mC/cm$^2$ and 4.5 min, and 85 mC/cm$^2$ and 5 min, respectively. Therefore from this regression analysis the device sizes of the C8, C12, and C16 samples are predicted as $50 \pm 8$, $45 \pm 2$, and $45 \pm 2$ nm in diameters with a 99% confidence interval, respectively. We will use these device sizes as the effective contact areas. Although one could postulate that the actual area of metal that contacts the molecules may be different, there is little reason to propose that it would be different as a function of length over the range of alkanethiols used, and at most it would be a constant systematic error.
4.4 Tunneling characteristics of alkanethiol SAMs

4.4.1 I(V,T) characterization of alkane SAMs

In order to determine the conduction mechanism of self-assembled alkanethiol molecular systems, I(V,T) measurements in a sufficiently wide temperature range (300 to 80 K) and resolution (10 K) on dodecanethiol (C12) were performed. Fig. 4.3 shows representative I(V,T) characteristics measured with the device structure shown in Fig. 4.1(a). Positive bias in this measurement corresponds to electrons injected from the physisorbed Au contact [bottom contact in Fig 4.1(a)] into the molecules. By using the contact area of 45 ± 2 nm in diameter determined from the SEM study, a current density of 1,500 ± 200 A/cm² at 1.0 Volt is obtained. No significant temperature dependence of the characteristics from V = 0 to 1.0 Volt is observed over the temperature range from 300 to 80 K. An Arrhenius plot (ln I versus 1/T) is shown in Fig. 4.4(a), exhibiting little temperature dependence in the slopes of ln I versus 1/T at different biases and thus indicating the absence of thermal activation. Therefore, we conclude that the conduction mechanism through alkanethiol is tunneling contingent on demonstrating correct molecular length dependence.

Based on the applied bias as compared with the barrier height (Φ_B), tunneling through a SAM layer can be categorized into either direct (V < Φ_B/e) or Fowler-Nordheim (V > Φ_B/e) tunneling. These two tunneling mechanisms can be distinguished by their distinct voltage dependencies (see Table 4.1). Analysis of ln(I/V²) versus 1/V [in Fig. 4.4(b)] of the C12 I(V,T) data shows no significant voltage dependence, indicating no obvious Fowler-Nordheim transport behavior in the bias range of 0 to 1.0 Volt and thus determining that the barrier height is larger than the applied bias, i.e., Φ_B > 1.0 eV.
Figure 4.3. Temperature-dependent I(V) characteristics of dodecanethiol. I(V) data at temperatures from 300 to 80 K with 20 K steps are plotted on a log scale.
Figure 4.4. (a) Arrhenius plot generated from the I(V,T) data in Fig. 4.3 at voltages from 0.1 to 1.0 Volt with 0.1 Volt steps. (b) Plot of ln(I/V²) versus 1/V at selected temperatures to examine the Fowler-Nordheim tunneling.
This study is restricted to applied biases ≤ 1.0 Volt and the transition from direct to Fowler-Nordheim tunneling requires higher bias.

I(V,T) characterizations have also been done on other alkane molecules. As an example, Fig. 4.5(a) shows the I(V,T) measurement of an octanedithiol device from 290 to 4.2 K. As the corresponding Arrhenius plot [Fig. 4.5(b)] exhibits, there is no thermal activation involved, confirming that the conduction through alkane SAMs is tunneling.

As discussed in the previous section, temperature-variable I(V) measurement is a very important experimental method in molecular transport characterizations. This importance is demonstrated by Fig. 4.6. Fig. 4.6(a) is a room temperature I(V) characteristic of a device containing C8 molecules. The shape of this I(V) looks very similar to that of a direct tunneling device. Indeed it can be fit using the Simmons model (see next subsection), which gives a barrier height of 1.27 eV and a α of 0.96 (though a larger value; see next section). However, further I(V,T) measurements display an obvious temperature dependence [Fig. 4.6(b)], which can be fit well to a hopping conduction model (Table 4.1) with a well-defined activation energy of 190 meV as illustrated by Fig. 4.6(c). Another example is shown in Fig. 4.7: Fig. 4.7(a) shows I(V) for a C12 device measured at 4.2 K and Fig. 4.7(b) is the corresponding numerical differential conductance. Instead of displaying a direct tunneling conduction, this device exhibits a Coulomb blockade behavior with an energy gap of ~ 60 meV, which corresponds to a device capacitance of 3 × 10^{-18} F. These impurity-mediated transport phenomena are indicative of the unintentional incorporation of a trap or defect level in the devices and I(V,T) characterization is needed to discover the correct conduction mechanism.
Figure 4.5. (a) I(V,T) characteristics of an octanedithiol device measured from room temperature to 4.2 K (plotted on a log scale). (b) Arrhenius plot generated from the I(V,T) data in (a) at voltages from 0.1 to 0.5 Volt with 0.05 Volt steps.
Figure 4.6. (a) I(V) characteristic of a C8 device at 270 K. (b) Temperature dependence of the same device from 270 to 180 K (in 10 K increments). (c) Plot of ln(I/V) versus 1/T at various voltages. The line is the linear fitting and a hopping barrier of 190 meV is determined from this fitting.
Figure 4.7. (a) $I(V)$ characteristic of a C12 device at 4.2 K. (b) Numerical derivative of the $I(V)$ in (a) exhibits a gap due to the Coulomb blockade effect.
4.4.2 I(V) fitting using the Simmons model

Having established tunneling as the main conduction mechanism of alkanethiols, we can now obtain the transport parameters such as the effective barrier height by comparing our experimental I(V) data with theoretical calculations from a tunneling model.

The current density ($J$) expression in the direct tunneling regime ($V < \Phi_B/e$) from the Simmons model that has been discussed in Chapter 2 is [29,41]:

$$J = \left( \frac{e}{4\pi^2 \hbar d^2} \right) \left( \frac{\Phi_B - eV}{2} \right) \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} \alpha \left( \frac{\Phi_B - eV}{2} \right)^{1/2} d \right] \left( \Phi_B + \frac{eV}{2} \right) \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} \alpha \left( \frac{\Phi_B + eV}{2} \right)^{1/2} d \right],$$

(4.2)

where $e$ is the electron charge, $\hbar (= 2\pi\hbar)$ is Planck’s constant, $m$ is the free electron mass, $d$ is the barrier width, $V$ is the applied bias, and $\Phi_B$ is the barrier height. For molecular systems, the Simmons model has been modified with a unitless adjustable parameter $\alpha$ [27,29,41]. $\alpha$ is introduced to account for the effective mass ($m^*$) of the tunneling electrons through a molecular wire. $\alpha = 1$ corresponds to the case of a bare electron, which previously has been shown not to fit I(V) data well for some alkanethiol measurements at fixed temperature (300 K) [29]. By fitting individual I(V) data using Eq. (4.2), $\Phi_B$ and $\alpha$ can be found.

Eq. (4.2) can be approximated in two limits: low bias and high bias as compared with the barrier height $\Phi_B$. In the low bias range, Eq. (4.2) can be approximated as

$$J \approx \left( \frac{(2m\Phi_B)^{1/2} e^2 \alpha}{\hbar^2 d} \right) V \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} \alpha (\Phi_B)^{1/2} d \right].$$

(4.3)
To determine the high bias limit, we compare the relative magnitudes of the first and second exponential terms in Eq. (4.2). At high bias, the first term is dominant and thus the current density can be approximated as

\[
J \approx \left( \frac{e}{4\pi^2 \hbar d^2} \right) \left( \Phi_B - \frac{eV}{2} \right) \exp \left[ - \frac{2(2m)^{1/2}}{\hbar} \alpha \left( \Phi_B - \frac{eV}{2} \right)^{1/2} d \right].
\]  

(4.4)

The tunneling currents in both bias regimes have exponential dependence on the barrier width \(d\). In the low bias regime the tunneling current density is \(J \propto \frac{1}{d} \exp(-\beta_0 d)\), where \(\beta_0\) is a bias-independent decay coefficient:

\[
\beta_0 = \frac{2(2m)^{1/2}}{\hbar} \alpha \left( \Phi_B \right)^{1/2}.
\]  

(4.5)

While in the high bias regime \(J \propto \frac{1}{d^2} \exp(-\beta_v d)\), where \(\beta_v\) is a bias-dependent decay coefficient:

\[
\beta_v = \frac{2(2m)^{1/2}}{\hbar} \alpha \left( \Phi_B - \frac{eV}{2} \right)^{1/2} = \beta_0 \left( 1 - \frac{eV}{2\Phi_B} \right)^{1/2}.
\]  

(4.6)

At high bias \(\beta_v\) decreases as bias increases, which results from barrier lowering effect due to the applied bias.

The above distinction between low and high bias in the direct tunneling regime may seem unnecessary at first. However, it is needed to clarify the confusion and misleading conclusions present in current literature and deduce the decay coefficient expressions from a solid tunneling model. For example, in previous publications [26,27], the expression of the decay coefficient \(\beta_v\) [Eq. (4.6)] has been postulated and applied in the entire bias range from 0 to 1 [26] and 3 Volt [27], which are incorrect according to
Eq. (4.2) since over these bias ranges there is no simple exponential dependence of $J \propto \exp(-\beta_v d)$. In another published report [29], the correct Simmons equation [Eq. (4.2)] has been utilized to fit the measured I(V) data, but again the $\beta_v$ expression is used for the whole bias range. Some groups [2,3,23,25-29] used the general quantum mechanical exponential law

$$G = G_0 \exp(-\beta d)$$ (4.7)

to analyze the length dependence behavior of the tunneling current, but this equation is incapable of explaining the observed bias dependence of the decay coefficient $\beta$. On the contrary, in our study the Simmons equation (4.2) is used to fit the I(V) data in the direct tunneling regime and it is reduced to Eq. (4.3) in the low bias range to yield a similar bias-independent decay coefficient as Eq. (4.7). While in the high bias range the exponential term of $e^{-C\sqrt{|\Phi_B - \frac{eV}{2}|}}$ in Eq. (4.2) dominants, and thus Eq. (4.2) is approximated by Eq. (4.4), giving a bias-dependent coefficient $\beta_v$. This distinction between the low and high biases will be seen to explain the experimental data very well in a later subsection.

Using the modified Simmons equation (4.2), by adjusting two parameters $\Phi_B$ and $\alpha$ a nonlinear least squares fitting has been performed on the measured C12 I(V) data. The tunneling gap distance is the length of the adsorbed alkanethiol molecule, which is determined by adding an Au-thiol bonding length of 2.3 Å to the length of the free molecule [25]. For C12, the length (therefore the gap distance) is calculated as 18.2 Å. By using a device size of 45 nm in diameter, the best fitting parameters (minimizing $\chi^2$) for the room temperature C12 I(V) data were found to be $\Phi_B = 1.42 \pm 0.04$ eV and $\alpha = 0.65 \pm 0.01$, where the error ranges of $\Phi_B$ and $\alpha$ are dominated by potential device size
fluctuations of 2 nm. Fig. 4.8(a) shows this best fitting result (solid curve) as well as the original I(V) data (circular symbol) on a linear scale. A calculated I(V) for $\alpha = 1$ and $\Phi_B = 0.65$ eV (which gives the best fit at low bias range) is shown as the dashed curve in the same figure, illustrating that with $\alpha = 1$ only limited region of the I(V) curve can be fit (specifically here, for $|V| < 0.3$ Volt). The same plots are shown on a log scale in Fig. 4.8(b). The value of the fitting parameter $\alpha$ obtained from above corresponds to an effective mass $m^* (= \alpha^2 m)$ of 0.42 m.

Likewise, I(V) measurements have also been performed on octanethiol (C8) and hexadecanethiol (C16) SAMs. The Simmons fitting on C8 with an adsorbed molecular length of 13.3 Å (tunneling gap distance) and a device diameter of 50 ± 8 nm yields values of $\{\Phi_B = 1.83 \pm 0.10$ eV and $\alpha = 0.61 \pm 0.01\}$. Same fitting on C16 with a length of 23.2 Å and a device diameter of 45 ± 2 nm gives a data set of $\{\Phi_B = 1.40 \pm 0.03$ eV, $\alpha = 0.68 \pm 0.01\}$. The I(V) data and fitting results are shown in Fig. 4.9(a) and (b) for C8 and C16, respectively.

Nonlinear least square fittings on C12 I(V) data at different measurement temperatures allow us to determine $\{\Phi_B, \alpha\}$ over the entire temperature range (300 to 80 K) and the fitting results show that $\Phi_B$ and $\alpha$ values are temperature-independent. From these fittings average values of $\Phi_B = 1.45 \pm 0.02$ eV and $\alpha = 0.64 \pm 0.01$ are obtained [1σM (standard error)].

In order to investigate the dependence of the Simmons model fitting on $\Phi_B$ and $\alpha$, a fitting minimization analysis is undertaken on the individual $\Phi_B$ and $\alpha$ values as well as their product form of $\alpha\Phi_B^{1/2}$ in Eq. (4.5). $\Delta(\Phi_B, \alpha) = (\sum |I_{exp,V} - I_{cal,V}|^2)^{1/2}$ is calculated
Figure 4.8. Measured C12 I(V) data (circular symbol) is compared with calculation (solid curve) using the optimum fitting parameters of $\Phi_B = 1.42$ eV and $\alpha = 0.65$. The calculated I(V) from a simple rectangular model ($\alpha = 1$) with $\Phi_B = 0.65$ eV is also shown as the dashed curve. Current is plotted on (a) linear scale and (b) log scale.
Figure 4.9. (a) Measured C8 I(V) data (symbol) is compared with calculation (solid curve) using the optimum fitting parameters of $\Phi_B = 1.83$ eV and $\alpha = 0.61$. (b) Measured C16 I(V) data (symbol) is compared with calculation (solid curve) using the optimum fitting parameters of $\Phi_B = 1.40$ eV and $\alpha = 0.68$. 
and plotted, where $I_{\text{exp},V}$ is the experimental current value and $I_{\text{cal},V}$ is the calculated one from Eq. (4.2). 7500 different \{\Phi_B, \alpha\} pairs are used in the analysis with \Phi_B ranging from 1.0 to 2.5 eV (0.01 eV increment) and \alpha from 0.5 to 1.0 (0.01 increment). Fig. 4.10(a) is a representative contour plot of $\Delta(\Phi_B, \alpha)$ versus $\Phi_B$ and $\alpha$ generated for the C12 I(V) data where darker regions represent smaller $\Delta(\Phi_B, \alpha)$ and various shades correspond to $\Delta(\Phi_B, \alpha)$ with half order of magnitude steps. The darker regions also represent better fits of Eq. (4.2) to the measured I(V) data. In the inset in Fig. 4.10(a) one can see that there is a range of possible \Phi_B and \alpha values yielding good fittings. Although the tunneling parameters determined from the previous Simmons fitting \{\Phi_B = 1.42 \text{ eV and } \alpha = 0.65\} lie within this region, there is also a distribution of other possible values.

A plot of $\Delta(\Phi_B, \alpha)$ versus $\alpha\Phi_B^{1/2}$ is shown in Fig. 4.10(b). As it exhibits, except the minimum point of $\Delta(\Phi_B, \alpha)$, different \Phi_B and \alpha pairs could give a same $\Delta(\Phi_B, \alpha)$ value. For this plot the $\Delta(\Phi_B, \alpha)$ is minimized at $\alpha\Phi_B^{1/2}$ of 0.77 (eV)$^{1/2}$, which yields a $\beta_0$ value of 0.79 \text{ Å}^{-1} from Eq. (4.5). The C8 and C16 devices show similar results, confirming that the Simmons fitting has a strong $\alpha\Phi_B^{1/2}$ dependence. For the C8 device, although $\Phi_B$ obtained from the fitting is a little larger, combined $\alpha$ and $\Phi_B$ give similar $\beta_0$ value within the error range as the C12 and C16 devices. The values of $\Phi_B$ and $\alpha$ for C8, C12, and C16 devices are summarized in Table 4.2, as well as the $\beta_0$ values calculated from Eq. (4.5).
Figure 4.10. (a) Contour plot of $\Delta(\Phi_B, \alpha)$ values for the C12 device as a function of $\Phi_B$ and $\alpha$, where the darker region corresponds to a better fitting. Inset shows detailed minimization fitting regions. (b) Plot of $\Delta(\Phi_B, \alpha)$ as a function of $\alpha \Phi_B^{1/2}$. 
In order to further investigate the dependence of the Simmons fitting on the barrier shape, we consider a generalized barrier with a parabolic form of

$$\Phi(x) = \Phi_0 - \frac{4}{d^2} \Phi_0 (x - \frac{d}{2})^2$$

and use the Simmons equation for a general barrier [Eq. (2.29) in Chapter 2] to fit the measured I(V) data:

$$J = \left( \frac{e}{4\pi^2 \hbar d''} \right) \left\{ \Phi \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} \Phi^{1/2} d'' \right] - (\Phi + eV) \exp \left[ -\frac{2(2m)^{1/2}}{\hbar} (\Phi + eV)^{1/2} d'' \right] \right\} ,$$

where $d'$ is the barrier width at the Fermi level of the negatively biased electrode and $\Phi$ is the mean barrier height above the same Fermi level:

$$\Phi = \frac{1}{d'} \int_0^{d''} \Phi(x) dx .$$

<table>
<thead>
<tr>
<th>Molecules</th>
<th>$J$ at 1V (A/cm²)</th>
<th>$\Phi_B$ (eV)</th>
<th>$\alpha$</th>
<th>$m^*$ (m)</th>
<th>$\beta_0$ (Å⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8</td>
<td>31,000 ± 10,000</td>
<td>1.83 ± 0.10</td>
<td>0.61 ± 0.01</td>
<td>0.37</td>
<td>0.85 ± 0.04</td>
</tr>
<tr>
<td>C12</td>
<td>1,500 ± 200</td>
<td>1.42 ± 0.04</td>
<td>0.65 ± 0.01</td>
<td>0.42</td>
<td>0.79 ± 0.02</td>
</tr>
<tr>
<td>C16</td>
<td>23 ± 2</td>
<td>1.40 ± 0.03</td>
<td>0.68 ± 0.01</td>
<td>0.46</td>
<td>0.82 ± 0.02</td>
</tr>
</tbody>
</table>

Table 4.2. Summary of alkanethiol tunneling parameters obtained using Simmons model.
Fig. 4.11(a) shows the energy band diagram of this barrier when the applied bias is zero, where $d$ is the junction gap distance and $\Phi_0$ is the maximum barrier height. When a bias of $V$ is applied across the junction the barrier is changed to [Fig. 4.11(b)]:

$$\Phi(x, V) = \Phi_0 - \frac{4}{d^2} \Phi_0 \left( x - \frac{d}{2} \right)^2 - \frac{V}{d} x,$$

where we assumed a linear voltage drop. $d'$ can be obtained from Eq. (4.11) by setting $\Phi(x, V) = 0$, which gives

$$d' = d - \frac{V}{4\Phi_0} d.$$

The mean barrier height can thus be calculated by substituting Eqs. (4.11) and (4.12) into Eq. (4.10) and performing the integration:

$$\overline{\Phi}(V) = \frac{2}{3} \Phi_0 - \frac{1}{3} V + \frac{V^2}{24\Phi_0}.$$

Hence the tunneling current through a parabolic barrier is expressed as

$$J = \left[ \frac{e}{4\pi^2 \hbar (d - eV/4\Phi_0)^2} \right] \left[ \frac{2}{3} \Phi_0 - \frac{1}{3} eV + \frac{e^2V^2}{24\Phi_0} \right] \exp \left[ -\frac{2(2m)^{1/2} (d - eV/4\Phi_0)}{\hbar} \left( \frac{2}{3} \Phi_0 - \frac{1}{3} eV + \frac{e^2V^2}{24\Phi_0} \right) \right] \left[ -\left( \frac{2}{3} \Phi_0 - \frac{1}{3} eV + \frac{e^2V^2}{24\Phi_0} + eV \right) \exp \left[ -\frac{2(2m)^{1/2} (d - eV/4\Phi_0)}{\hbar} \left( \frac{2}{3} \Phi_0 - \frac{1}{3} eV + \frac{e^2V^2}{24\Phi_0} + eV \right)^{1/2} \right] \right].$$

Using Eq. (4.14), by adjusting two parameters $\Phi_0$ and $\alpha$ a nonlinear least squares fitting is performed on the alkanethiol data to determine the parabolic barrier height and corresponding $\alpha$ value. A representative fitting result of the C12 device is shown in Fig. 4.12(a), which exhibits little difference between the calculated $I(V)$ and the experimental data, and the best fitting gives $\Phi_0 = 2.97 \pm 0.06$ eV and $\alpha = 0.56 \pm 0.01$. However, further
Figure 4.11. (a) Band diagram of a parabolic barrier when the applied bias is 0.  
(b) Band diagram of the parabolic barrier under a bias of V.
Figure 4.12. (a) NLSQ fitting on the measured C12 I(V) data using a parabolic potential barrier. The best fitting gives $\Phi_0 = 2.97$ eV and $\alpha = 0.56$. (b) F-N plot of the experimental I(V) in (a). (c) F-N plot of the theoretical I(V) in (a).
analysis shows that while the experimental data reveal no Fowler-Nordheim tunneling behavior [Fig. 4.12(b)], the Simmons fitting result from Eq. (4.14) demonstrates curvatures in the ln(I/V^2) vs. 1/V plot [Fig. 4.12(c)], which indicates that the calculated I(V) has Fowler-Nordheim tunneling. This observation agrees with the energy band diagram plot in Fig. 4.11(b).

The above study demonstrates that a parabolic barrier does not fit our measured data. The rectangular barrier height obtained in previous Simmons fitting could also represent the mean barrier height of a barrier with an arbitrary shape, as long as its mean barrier height has no bias dependence other than the 1/2 eV from the linear voltage drop (i.e., a non-Fowler-Nordheim picture).

The case of a nonlinear potential drop across the molecular junction [42] can also be considered. However since from the Simmons fitting only a mean barrier height can be obtained [Eq. (4.9)], detailed voltage profiles across the junction cannot be derived from the fitting result. First-principle calculations are needed to fully understand this issue.

4.4.4 Length dependence of the tunneling current through alkanethiols

As discussed in subsection 4.4.2 [Eqs. (4.3) and (4.4)] the tunneling currents in the low and high bias ranges have exponential dependence on the molecular length as

\[ J \propto \frac{1}{d} \exp(-\beta_0 d) \]  
\[ J \propto \frac{1}{d^2} \exp(-\beta_V d) \]

respectively, where \( \beta_0 \) and \( \beta_V \) are the decay coefficients. In order to study this length-dependent tunneling behavior, I(V) characterizations are performed on three alkanethiols of different molecular length: C8,
C12, and C16 [Fig. 4.1(b)]. The adsorbed molecular length of C8, C12, and C16 are 13.3, 18.2, and 23.2 Å, respectively, as used in the Simmons fitting. To define the boundary of the high and low bias ranges, the relative magnitudes of the first and second exponential terms in Eq. (4.2) are evaluated. Using $\Phi_B = 1.42$ eV and $\alpha = 0.65$ obtained from nonlinear least squares fitting of the C12 I(V) data, the second term becomes less than ~10 % of the first term at 0.5 Volt, which is chosen as the bias boundary.

Fig. 4.13 is a semi-log plot of the tunneling current density multiplied by molecular length – $J_d$ at low bias and $J_d^2$ at high bias – as a function of the molecular length for these alkanethiols. As seen in this figure, the tunneling currents (symbols) show exponential dependence on molecular lengths. The decay coefficient $\beta$ can be determined from the slopes of the linear fittings (lines in Fig. 4.13) on the measured data. The obtained $\beta$ values at each bias are plotted in Fig. 4.14(a) and the error bar of an individual $\beta$ value in this plot is determined by considering both the device size uncertainties and the linear fitting errors.

As Fig. 4.14(a) shows, in the low bias range ($V < 0.5$ V) the $\beta$ values are almost independent of bias, while in the high bias range ($V > 0.5$ V) $\beta$ has bias dependence: $\beta$ decreases as bias increases due to the barrier lowering effect. From Fig. 4.14(a) an average $\beta_0$ of $0.77 \pm 0.06$ Å$^{-1}$ can be calculated in the low bias region. According to Eq. (4.6), $\beta^2V$ depends on bias $V$ linearly in the high bias range. Fig. 4.14(b) is a plot of $\beta^2V$ versus $V$ in this range (0.5 to 1.0 Volt) and a linear fitting of the data. $\Phi_B = 1.35 \pm 0.20$ eV and $\alpha = 0.66 \pm 0.04$ are obtained from the intercept and slope of this fitting, respectively, which are consistent with the values acquired from the nonlinear least squares fitting on the I(V) data in the previous subsection.
Figure 4.13. Log plot of tunneling current densities (symbols) multiplied by molecular length $d$ at low bias and by $d^2$ at high bias versus molecular length. The lines through the data points are linear fittings.
Figure 4.14. (a) Plot of $\beta$ versus bias in the low bias range (square symbol) and high bias range (circular symbol). (b) $\beta^2$ versus bias plot (symbol) with a linear fitting (solid curve).
Table 4.3 is a summary of previously reported alkanethiol transport parameters obtained by different techniques [16]. The current densities (J) listed in Table 4.3 are for C12 monothiol or dithiol devices at 1 V, which are extrapolated for some techniques from published results of other length alkane molecules using the exponential law of Eq. (4.7). The large variation of J among reports can be attributed to the uncertainties in device contact geometry and junction area, as well as complicating inelastic or defect contributions. The $\beta_0$ value (0.77 ± 0.06 Å$^{-1}$ ≈ 0.96 ± 0.08 per methylene) for alkanethiols obtained in our study using the Simmons model is comparable to previously reported values as summarized in Table 4.3.

Length-dependent analysis using the exponential equation (4.7) in the entire applied bias range (0 to 1.0 V) has also been performed in order to compare with these reported $\beta$ values. This gives $\beta$ values from 0.84 to 0.73 Å$^{-1}$ in the bias range from 0.1 to 1.0 Volt, which are similar to the reported values. For example, Holmlin et al. reported a $\beta$ value of 0.87 Å$^{-1}$ by mercury drop experiments [29], and Wold et al. have reported $\beta$ of 0.94 Å$^{-1}$ and Cui et al. reported $\beta$ of 0.64 Å$^{-1}$ for various alkanethiols by using a conducting atomic force microscope technique [27,28]. However, these reported $\beta$ were treated as bias-independent quantities, contrary to the results from our study and those observed in a slightly different alkane system (ligand-encapsulated nanoparticle/alkane-dithiol molecules) [42]. Since all of these experiments were performed at room temperature, the reported parameters have not been checked with a temperature-dependent analysis and non-tunneling components can dramatically affect the derived values.
Table 4.3. Summary of alkanethiol tunneling parameters obtained by different test structures.

<table>
<thead>
<tr>
<th>Junction</th>
<th>( \beta (\text{Å}^{-1}) )</th>
<th>( J (\text{A/cm}^2) ) at 1V</th>
<th>( \Phi_B (\text{eV}) )</th>
<th>Technique</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>(bilayer) monothiol</td>
<td>0.87±0.1</td>
<td>25-200(^{a)})</td>
<td>2.1(^{e)})</td>
<td>Hg-junction</td>
<td>29</td>
</tr>
<tr>
<td>(bilayer) monothiol</td>
<td>0.71±0.08</td>
<td>0.7-3.5(^{a)})</td>
<td></td>
<td>Hg-junction</td>
<td>31</td>
</tr>
<tr>
<td>monothiol</td>
<td>0.79±0.01</td>
<td>1500±200(^{b)})</td>
<td>1.4(^{e)})</td>
<td>Solid M-I-M</td>
<td>39</td>
</tr>
<tr>
<td>monothiol</td>
<td>1.2</td>
<td></td>
<td></td>
<td>STM</td>
<td>23</td>
</tr>
<tr>
<td>dithiol</td>
<td>0.8±0.08</td>
<td>3.5-5×10^5(^{c)})</td>
<td>5±2(^{f)})</td>
<td>STM</td>
<td>24</td>
</tr>
<tr>
<td>monothiol</td>
<td>0.73-0.95</td>
<td>1100-1900(^{d)})</td>
<td>2.2(^{e)})</td>
<td>CAFM</td>
<td>25</td>
</tr>
<tr>
<td>monothiol</td>
<td>0.64-0.8</td>
<td>10-50(^{d)})</td>
<td>2.3(^{e)})</td>
<td>CAFM</td>
<td>26</td>
</tr>
<tr>
<td>dithiol</td>
<td>0.46±0.02</td>
<td>3×10^5(^{c)})</td>
<td>1.3-1.5(^{e)})</td>
<td>CAFM</td>
<td>27</td>
</tr>
<tr>
<td>monothiol</td>
<td>1.37±0.03</td>
<td></td>
<td>1.8(^{f)})</td>
<td>Tuning fork AFM</td>
<td>44</td>
</tr>
<tr>
<td>monothiol</td>
<td>0.97±0.04</td>
<td></td>
<td></td>
<td>Electrochemical</td>
<td>34</td>
</tr>
<tr>
<td>monothiol</td>
<td>0.85</td>
<td></td>
<td></td>
<td>Electrochemical</td>
<td>35</td>
</tr>
<tr>
<td>monothiol</td>
<td>0.91±0.08</td>
<td></td>
<td></td>
<td>Electrochemical</td>
<td>36</td>
</tr>
<tr>
<td>monothiol</td>
<td>0.76</td>
<td>2×10^4(at 0.1V)</td>
<td>1.3-3.4(^{b)})</td>
<td>Theory</td>
<td>45</td>
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<tr>
<td>monothiol</td>
<td>0.76</td>
<td></td>
<td></td>
<td>Theory</td>
<td>46</td>
</tr>
<tr>
<td>monothiol</td>
<td>0.79</td>
<td></td>
<td></td>
<td>Theory</td>
<td>47</td>
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</table>

Note:
1. Some decay coefficients \( \beta \) are converted into the unit of \( \text{Å}^{-1} \) from the unit of per methylene.
2. The junction areas are estimated by an optical microscope\(^{a)}\), SEM\(^{b)}\), assuming a single molecule\(^{c)}\), and Hertzian contact theory\(^{d)}\).
3. Current densities (J) for C12 monothiol or dithiol at 1 V are extrapolated from published results of other length molecules using the exponential law of \( G \propto \exp(-\beta d) \).
4. Barrier height values are obtained from Simmons equation\(^{e)}\), bias-dependence of \( \beta \)\(^{f)}\), and theoretical calculation\(^{g)}\).
4.4.5 I(V) fitting using the Franz model

We can also analyze our experimental data using the Franz two-band model [48-53]. By considering the contributions from both the conduction band and valence band, the Franz model empirically predicted a non-parabolic E(k) relationship inside the bandgap as discussed in Chapter 2 [Eq. (2.41)] [48]:

$$k^2 = \frac{2m^*}{\hbar^2} E(1 + \frac{E}{E_g}).$$ (4.15)

Using Eq. (4.15), the effective mass of the tunneling electron can be deduced by knowing the barrier height of the tunnel junction [52]. However, since there is no reliable experimental data on the Fermi level alignment in the Au-alkanethiol SAM-Au system, $\Phi_B$ is unknown and it is thus treated as an adjustable parameter together with $m^*$ in our analysis. The imaginary k value is related to the decay coefficient $\beta$ [$k^2 = -(\beta/2)^2$] obtained from the length-dependent study. Using an alkanethiol HOMO-LUMO gap of 8 eV, a least squares fitting has been performed on the experimental data and Fig. 4.15 shows the resultant E(k) relationship and the corresponding energy band diagrams. The zero of energy in this plot is chosen as the LUMO energy. The best fitting parameters obtained by minimizing $\chi^2$ are $\Phi_B = 1.49 \pm 0.51$ eV and $m^* = 0.43 \pm 0.15$ m, where the error ranges of $\Phi_B$ and $m^*$ are dominated by the error fluctuations of $\beta$. Both electron tunneling near the LUMO and hole tunneling near the HOMO can be described by these parameters. $\Phi_B = 1.49$ eV indicates that the Fermi level is aligned close to one energy level in either case. The $\Phi_B$ and $m^*$ values obtained here are in reasonable agreement with previous results deduced from the Simmons model.
Figure 4.15. $E(k)$ relationship generated from the length-dependent measurement data of alkanethiols. Solid and open symbols correspond to electron and hole conductions, respectively. The solid curve is the Franz two-band $E(k)$ plot for $m^* = 0.43 m$ and $E_g = 8 eV$. The insets show the corresponding energy band diagrams.
References:


19. Although the HOMO-LUMO gap of alkyl chain type molecules has been reported (see Ref. 20-22), there is no experimental data on the HOMO-LUMO gap for Au/alkanethiol SAM/Au system. 8 eV is commonly used as HOMO-LUMO gap of alkanethiol.


Chapter 5

Inelastic Electron Tunneling Spectroscopy of Alkanethiol SAMs

5.1 A brief review of IETS

As discussed in Chapter 2, inelastic electron tunneling spectroscopy was discovered by Jaklevic and Lambe in 1966 when they studied tunnel junctions containing organic molecules and the vibrational modes of the molecules were detected by electrons that tunneled inelastically through the barrier [1,2]. In the earlier stage of IETS, the tunnel barrier was usually made of a metal oxide, therefore the choice of the metallic material was crucial since it must be capable to form a coherent and stable oxide layer with a thickness of several nanometers [3-6]. For this purpose aluminum was often utilized because of its good oxide quality. The molecular species were then introduced by either vapor phase exposure or liquid solution deposition on the surface of the barrier. Care also needed to be taken for top electrode deposition since high temperature evaporation may destroy the adsorbed molecular layer [6]. IETS has been mostly used in the spectra range of 0 – 500 meV (0 – 4000 cm⁻¹), which covers almost all molecular vibrational modes [3,6].
In the 1990’s another type of tunneling barrier was reported for IETS measurements [7]. This so-called cross-wire structure (see the description in Chapter 3.1) replaces the metal oxide barrier with an inert gas film. In order to form the tunnel junction, molecular species are mixed with the inert gas at a predetermined composition, and then they are introduced into the vacuum chamber and condense on the wire surfaces [7,8]. Recently this test structure has been used again for the investigation of vibronic contributions to charge transport across molecular junctions [9]. However, due to the difficulties in controlling the exact position of the top wire, it might not touch the other end of the molecules to form a perfect metal-SAM-metal junction or it might penetrate into the monolayer. Besides, no temperature-dependent measurement has been reported using this structure.

Another important advance in this field is the realization of single molecular vibrational spectroscopy by STM-IETS [10]. The possibility of performing IETS studies utilizing STM was discussed soon after its invention [11]. However, due to the difficulties in achieving the extreme mechanical stability that is necessary to observe small changes in tunneling conductance, this technique has only been realized recently [10]. In the STM implementation of IETS, the metal-oxide-metal tunnel junction is replaced by a STM junction consisting of a sharp metallic tip, a vacuum gap, and a surface with the adsorbed molecules. Using STM-IETS, imaging and probing can be performed at the same time, and vibrational spectroscopy studies on a single molecule can be achieved [10].

The advantage of inelastic tunneling spectroscopy over conventional optical vibrational spectroscopy such as IR and Raman is its sensitivity [3]. IR spectroscopy is a
well developed technology and has been used widely for studies of adsorbed species. It
does not require cryogenic temperature measurement and can be applied to a variety of
substrates [4]. Raman spectroscopy is used when IR is difficult or impossible to perform,
such as for seeing vibrations of molecules in solvents that are infrared opaque or for
vibrations that are not infrared active [4]. Both IR and Raman have lower sensitivities
compared with IETS: they require $10^3$ or more molecules to provide a spectrum. Since
the interaction of an electrons with molecular vibrations is much stronger than that of a
photon, as small as one monolayer of molecules is enough to produce good IETS spectra
[3,6]. Additionally, IETS is not subject to the selection rules of infrared or Raman
spectroscopy. There is orientational preference in IETS as discussed in Chapter 2, but
there are no rigorous selection rules. Both IR and Raman active vibrational modes appear
in IETS spectra with comparable magnitudes [6].

After its discovery IETS found many applications in different areas such as
surface chemistry, radiation damage, trace substance detection, among many others [4,5].
It is a powerful spectroscopic tool for chemical identification purposes: the vibrational
spectra can be used as fingerprints to identify the molecular species confined inside a
tunnel junction. It can also be used for chemical bonding investigations – in a solid state
junction, the breaking of various bonds can be monitored by the decrease in intensities of
the corresponding vibrational peaks and the formation of new bonds can be monitored by
the growth of new vibrational peaks [4,5]. The application of IETS has branched out to
the modern silicon industry as well, where it is utilized to study phonons in silicon, the
nature of the SiO$_2$ tunneling barrier, interface states in metal-oxide-semiconductor (MOS)
systems, and high-k dielectrics [12,13].
In our study IETS is utilized to identify the molecular species confined inside a solid state junction [14]. The measurement is performed using the nanopore test structure discussed in Chapter 3. Unlike earlier tunnel junctions, the nanopore uses the self-assembled molecules themselves as the tunnel barrier; thus it creates oxide-free junctions and intrinsic molecular properties can be investigated. Because the tunneling current depends exponentially on the barrier width, in the cross-wire and STM tunnel junctions a small change in the tunneling gap distance caused by vibration of the top electrode can produce a large change in the junction conductance, which can mask the conductance change associated with the inelastic channels. Compared to these systems, the nanopore structure has direct metal-molecule contacts and a fixed top electrode, and ensures intrinsic contact stability and eliminates the above problems. The molecular species used are the “control” molecules – alkane SAMs, which have been shown to form good insulating layers and present well-defined tunnel barriers in previous studies.

5.2 Alkanethiol vibrational modes

Various spectroscopic techniques have been developed to help chemists investigate the chemical structures of molecules and to study their interactions. These include mass spectrometry, nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectroscopy, ultraviolet (UV) spectroscopy, and Raman spectroscopy [15-19]. The majority of these spectroscopic tools analyze molecules based on the differences in how they absorb electromagnetic radiation [16].

The energy of a molecule consists of its electronic energy, vibrational energy, rotational energy, and translational energy. To a first approximation, these energy
contributions can be treated separately [17]. Electronic energy transitions generate absorption or emission in the ultraviolet and visible regions of the electromagnetic spectrum, while pure rotation gives rise to absorption in the microwave or the far-infrared regions. Molecular vibrations yield absorption bands throughout most of the infrared region of the spectrum and the vibrational frequencies can be studied by IR and Raman spectroscopy [16-19]. Molecular vibrational spectra depend on the masses of the atoms, their geometrical arrangement, and the strength of their chemical bonds. These factors can yield characteristic vibrations that are typical of certain groups of atoms and are defined by specific frequency ranges and intensities in the IR or Raman spectra. These characteristic spectra are used in the elucidation of molecular chemical structure [19].

Because the IETS study only concerns the molecular vibrational movement, we will only focus on the vibrational spectroscopic studies.

As a simple model, molecules consist of atoms that have certain masses and are connected by elastic bonds, and as a result they can perform periodic motions. The simplest example of a molecular vibration can be envisioned by thinking of two atoms, for example H and Cl, linked by a bond acting as two weights on a spring that stretches and compresses at a certain frequency \( \nu \). This frequency only depends on the masses of the atoms and the strength of the chemical bond, and the vibrational energy is quantized. If this HCl molecule is irradiated with a range of infrared frequencies, it will increases its vibrational energy by absorbing the energy of an infrared photon that has the frequency \( \nu \). This process will produce an IR spectrum. In order for an IR absorption to happen, the molecular vibration must change the dipole moment of the molecule, which leads to the selection rule of the IR process [16-19]. In the HCl molecule, the hydrogen atom has a
slight excess of positive charge and the chlorine atom has a slight excess of negative charge, and these two atoms create a simple dipole. The oscillating electrical field of the radiation exerts forces on the two atoms in opposite directions and therefore changes the dipole moment and induces a vibration. It will excite the molecular vibration if the radiation frequency matches the vibration frequency [17].

If a vibration does not produce a change in the molecular dipole moment then it is IR inactive; however this type of vibrations can be studied by Raman spectroscopy. Raman spectroscopy utilizes the Raman effect, where a molecular sample can produce scattered light with new frequencies differing from the incident radiation. These additional frequencies are located symmetrically below and above the frequency of the incident radiation, and the frequency difference gives the frequency of the molecular vibrational mode [16-19]. In order for a molecular vibration to be Raman active, the vibration must be accompanied by a change in the polarizability of the molecule [17]. IR and Raman spectra do not duplicate but rather complement each other, and together they yield valuable information about the molecular chemical structure.

Besides IR and Raman spectroscopy, another spectroscopic tool that has been employed to study molecular vibrations is high-resolution electron energy loss spectroscopy (HREELS) [20,21]. HREELS uses a monoenergetic well-collimated electron beam to irradiate the substrate surface and measures the intensity of backscattered electrons as a function of the energy loss transferred to the material surface [20]. The obtained spectrum exhibits energy losses due to molecular vibrational excitations, therefore yields characteristic group frequencies. In HREELS all vibrational
modes – IR active, Raman active, and optically silent modes – can be observed in the spectra.

A very important concept in molecular spectroscopies is the so-called group frequency. A molecule usually consists of many atoms, and even though these atoms will move during a normal mode of vibration, most of the motion can be localized within a certain molecular fragment that will vibrate with a characteristic frequency. For example, molecules containing a C=O group always show an absorption band in the wavenumber range of 1600 to 1800 cm\(^{-1}\). This is because the normal mode producing this band is dominated by a stretching motion of the C=O group. The remaining parts of the molecule also move but the atomic displacements are negligible and do not contribute significantly to this frequency \[17\]. Similarly, other bonds, such as C-C, CH\(_2\), etc., also produce characteristic frequencies. Therefore the existence of a functional group can be inferred by the appearance of an absorption band in a particular frequency range. In other words, we can detect the presence of a specific functional group in a molecule by identifying its characteristic frequency \[16-19\]. By identifying individual functional groups in a molecule, we can determine the molecule’s chemical composition. In addition to the fundamental vibrations, other frequencies can be possibly generated due to anharmonic effects. Anharmonicity causes the appearance of overtone absorption (integer multiples of the fundamental frequency) and also the sum and difference bands. However, these anharmonic features are usually quite weak and can be ignored to a reasonably good first approximation \[16,17\].

As for the case of alkanethiol molecules, the important vibrational modes include the stretching modes of C-C and C-S groups and various vibrations of the CH\(_2\) group.
Fig. 5.1 illustrates the available CH\(_2\) group vibrational modes, which include the symmetric and antisymmetric stretching modes, in-plane scissoring and rocking modes, and out-of-plane wagging and twisting modes [14,16]. Each of the different vibrational modes gives rise to a characteristic frequency in a spectroscopic spectrum.

Vibrational structures of self-assembled alkanethiols on Au(111) surface have been investigated by spectroscopic tools such as IR, Raman, and HREELS, and a large literature exists on the subject. References 20-23 are representative publications in this field. For example, IR measurement was conducted at the earlier stage to characterize the packing and orientation of the alkanethiol SAMs formed on Au(111) surface and the results suggest that they are densely packed in a crystalline arrangement [24-25]. It has also been used by Castiglioni et al. to study the CH\(_2\) rocking and wagging vibrations and to obtain related characteristic group frequencies [22]. Using Raman spectroscopy, Bryant et al. have investigated the C-C stretching bands of alkanethiols on Au surfaces since these bands are weak in the IR spectra. They have also characterized other vibrational features such as the C-S, S-H, and C-H stretching modes [23]. Duwez et al. and Kato et al. utilized HREELS to study various vibrational structures of alkanethiol SAMs and the Au-S bonding [20,21].

Research has also been conducted to compare the Raman or IR spectra of alkanethiols in solution to those on a substrate. For example, Bryant et al. have studied the peak frequency shift for the alkanethiol C-S stretching mode, C-C stretching mode, and some CH\(_2\) vibrations by comparing the Raman spectra of alkanethiols in solution and those adsorbed on a gold surface [23]. It was found that upon adsorption of the alkanethiols on the gold surface, the frequency of the C-S stretching mode decreases by ~
Figure 5.1. CH$_2$ vibrational modes. After Ref. 15.

- **Stretching modes for CH$_2$**
  - Symmetric
  - Antisymmetric

- **In-plane deformation modes**
  - Scissoring
  - Rocking

- **Out-of-plane deformation modes**
  - Twisting
  - Wagging
16 cm\(^{-1}\) (~ 2 meV), which is consistent with the suggestion that the C-S vibrational frequency would be lowered due to the bonding of the S atom to Au [23]. However, such frequency lowering was not universally observed for other vibrational modes of different alkanethiol molecules. For instance, in the same study, the C-C stretching frequency of dodecanethiol (1064 cm\(^{-1}\)) was found to be the same for the molecules in solution and on the Au surface [23]. In our study we mainly refer to the vibrational spectroscopic data obtained for alkanethiol SAMs formed on Au surfaces.

Table 5.1 is a summary of the alkanethiol vibrational modes obtained using aforementioned spectroscopic methods [20-23]. In this table the symbols of \(\delta_{s,r}\) and \(\gamma_{w,t}\) denote in-plane scissoring (s) and rocking (r) and out-of-plane wagging (w) and twisting (t) modes, respectively. \(\nu\) and \(\nu_{s,as}\) denote stretching and CH\(_2\) group symmetrical (s) and antisymmetrical (as) stretching modes, respectively. These characteristic group frequencies will be compared to the signal peaks in our acquired IETS spectra to identify the molecular species confined in the device junction.

### 5.3 IETS of octanedithiol SAM

Electrical measurements on octanedithiol SAM are performed with the nanopore structure discussed in Chapter 3. The sample preparation procedure is the same as that described in Section 4.3. The molecular solution is prepared by adding \(\sim 10\) \(\mu\)L octanedithiol to 10 mL ethanol. SAM formation is done for 24 hours inside a nitrogen filled glove box with an oxygen level of less than 5 ppm. Fig. 5.2(a) shows the schematic of the device configuration. I(V,T) measurement from 4.2 to 290 K shows a tunneling transport behavior (see Fig. 4.5 in Chapter 4). Fig. 5.2(b) is the room temperature I(V)
<table>
<thead>
<tr>
<th>Modes</th>
<th>Methods</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>(meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu(\text{Au-S}))</td>
<td>HREELS</td>
<td>225</td>
<td>28</td>
</tr>
<tr>
<td>(\nu(\text{C-S}))</td>
<td>Raman</td>
<td>641</td>
<td>79</td>
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<td></td>
<td>Raman</td>
<td>706</td>
<td>88</td>
</tr>
<tr>
<td>(\delta_{\text{t}(\text{CH}_2)})</td>
<td>HREELS</td>
<td>715</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>IR</td>
<td>720</td>
<td>89</td>
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<td>IR</td>
<td>925</td>
<td>115</td>
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<tr>
<td>(\nu(\text{C-C}))</td>
<td>HREELS</td>
<td>1050</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>Raman</td>
<td>1064</td>
<td>132</td>
</tr>
<tr>
<td></td>
<td>Raman</td>
<td>1120</td>
<td>139</td>
</tr>
<tr>
<td>(\gamma_{\text{w,t}(\text{CH}_2)})</td>
<td>IR</td>
<td>1230</td>
<td>152</td>
</tr>
<tr>
<td>(\delta_{\text{r}(\text{CH}_2)})</td>
<td>HREELS</td>
<td>1265</td>
<td>157</td>
</tr>
<tr>
<td></td>
<td>IR</td>
<td>1283</td>
<td>159</td>
</tr>
<tr>
<td></td>
<td>IR</td>
<td>1330</td>
<td>165</td>
</tr>
<tr>
<td>(\nu(\text{S-H}))</td>
<td>Raman</td>
<td>2575</td>
<td>319</td>
</tr>
<tr>
<td>(\nu_{\text{s}(\text{CH}_2)})</td>
<td>Raman</td>
<td>2854</td>
<td>354</td>
</tr>
<tr>
<td></td>
<td>HREELS</td>
<td>2860</td>
<td>355</td>
</tr>
<tr>
<td>(\nu_{\text{as}(\text{CH}_2)})</td>
<td>Raman</td>
<td>2880</td>
<td>357</td>
</tr>
<tr>
<td></td>
<td>Raman</td>
<td>2907</td>
<td>360</td>
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<tr>
<td></td>
<td>HREELS</td>
<td>2925</td>
<td>363</td>
</tr>
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</table>

Table 5.1. Summary of alkanethiol vibrational modes obtained from IR, Raman, and HREELS. The symbols of \(\delta_{\text{sr}}\) and \(\gamma_{\text{wt}}\) denote in-plane scissoring (s) and rocking (r) and out-of-plane wagging (w) and twisting (t) modes, respectively. \(\nu\) and \(\nu_{\text{as}}\) denote stretching and CH\(_2\) group symmetrical (s) and antisymmetrical (as) stretching modes, respectively. After Ref. 20 - 23.
Figure 5.2. (a) Schematic of an octanedithiol device. (b) I(V) measurement data at room temperature (circular symbols) and the fitting from Simmons equation (solid curve).
measurement result with the fitting from the Simmons equation. Using a junction area of 51 ± 5 nm in diameter obtained from statistical studies of the nanopore size with SEM, a current density of \((9.3 \pm 1.8) \times 10^4\) A/cm\(^2\) at 1.0 Volt is calculated. Using the modified Simmons model [Eq. (4.2)], the transport parameters of \(\Phi_B = 1.20 \pm 0.03\) eV and \(\alpha = 0.59 \pm 0.01\) (\(m^* = 0.34\) m) are obtained for this C8 dithiol device. As a comparison, the C8 monothiol device used in the length-dependent study has a current density of \((3.1 \pm 1.0) \times 10^4\) A/cm\(^2\) at 1.0 Volt, a barrier height of 1.83 ± 0.10 eV, and a \(\alpha\) of 0.61 ± 0.01 (\(m^* = 0.37\) m). That the observed current density of the C8 dithiol device is ~ 3 times larger than that of monothiol is consistent with previously published theoretical calculation and experimental data [26-31]. For example, Kaun et al. have performed first-principle calculation on alkane molecules in a metal-SAM-metal configuration using nonequilibrium Green’s functions combined with density functional theory [26]. They found that in an Au-alkanedithiol-Au device, although both Au leads are contacted by a sulfur atom, the transport behavior is essentially the same as that of alkanemonothiol device where only one Au lead is contacted by sulfur. However, the current through alkanedithiols is found to be ~ 10 times larger than that through alkanemonothiols, which, they suggest, indicates that the extra sulfur atom provides a better coupling between the molecule and the lead [26]. Experimental measurement on alkanedithiol molecules has also been performed by Cui et al. using the conducting AFM technique, and the result shows that alkanedithiol has ~ 100 times larger current than alkanemonothiol has [27,28].

IETS measurements are performed on the molecular devices using the setup introduced in Chapter 3. The second harmonic signal (proportional to \(d^2I/dV^2\)) is directly
measured with a lock-in amplifier, which has also been checked to be consistent with the numerical derivative of the first harmonic signal. As an example, Fig. 5.3(a) shows the lock-in first harmonic measurement data compared with the numerical derivative of the I(V) of the C8 dithiol device, while Fig. 5.3(b) is the 2nd harmonic measurement result checked with the numerical derivative of the first harmonic signal (all of the data are taken at 4.2 K). As Fig. 5.3(b) demonstrates, the IETS spectrum calculated from numerical differential method is compatible with that obtained from the lock-in 2nd harmonic measurement; however, the lock-in measurement yields a much more resolved spectrum.

Fig. 5.4 shows the inelastic electron tunneling spectrum of the same C8 dithiol SAM device obtained at T = 4.2 K. An AC modulation of 8.7 mV (rms value) at a frequency of 503 Hz is applied to the sample to acquire the second harmonic signals. The spectra are stable and repeatable upon successive bias sweeps. The spectrum at 4.2 K is characterized by three pronounced peaks in the 0 to 200 mV region at 33, 133, and 158 mV. From comparison with previously reported IR, Raman, and HREEL spectra of alkanethiol SAMs on Au(111) surfaces (Table 5.1) [20-23], these three peaks are assigned to Au-S stretching, C-C stretching, and CH2 wagging modes of a surface bound alkanethiolate. The absence of a strong S-H stretching signal at ~ 329 mV suggests that most of the thiol groups have reacted with the gold bottom and top contacts. Peaks are also reproducibly observed at 80, 107, and 186 mV. They correspond to C-S stretching, CH2 rocking, and CH2 scissoring modes. The stretching mode of the CH2 groups appears as a shoulder at 357 meV. The peak at 15 mV is due to vibrations from either Si, Au, or δ(C-C-C) since all three materials have characteristic frequencies in this energy range.
Figure 5.3. (a) Lock-in 1\(\omega\) data and the numerical \(dI/dV\) obtained from \(I(V)\) measurement data. (b) Lock-in 2\(\omega\) data and the numerical derivative of the lock-in 1\(\omega\) data in (a). All measurement data are taken at 4.2 K.
Figure 5.4. Inelastic electron tunneling spectrum of a C8 dithiol SAM obtained from lock-in second harmonic measurements with an AC modulation of 8.7 mV (rms value) at a frequency of 503 Hz (T = 4.2 K). Peaks labeled * are most probably background due to the encasing Si$_3$N$_4$. 
We note that all alkanethiol peaks without exception or omission occur in the spectra. Peaks at 58, 257, 277, and 302, as well as above 375 mV are likely to originate from Si-H and N-H vibrations related to the silicon nitride membrane [29,32,33], which forms the SAM encasement. Measurement of the background spectrum from Si₃N₄ of an “empty” nanopore device with only gold contacts is hampered by either too low (open circuit) or too high (short circuit) currents in such a device.

According to the IETS theory (Chapter 2) [34], molecular vibrations with net dipole moments perpendicular to the tunneling junction interface have stronger peak intensities than vibrations with net dipole moments parallel to the interface. In our device configuration [Fig. 5.2(a)] the vibrational modes of Au-S, C-S, and C-C stretching and CH₂ wagging are perpendicular to the junction interface, while the vibrations of the CH₂ group rocking, scissoring, and stretching modes are parallel to the interface. In the obtained IETS spectrum (Fig. 5.4) the vibrations perpendicular to the junction interface produce peaks of stronger intensities, while those vibrations parallel to the interface generate less dominant peaks. This experimental observation of the relative IETS peak intensities is in good agreement with the theory.

Fig. 5.5 shows the spectra of both positive and negative biases at T = 4.2 K acquired with an AC modulation of 8.7 mV at the frequency of 503 Hz. The DC biases are applied from 0 to ± 0.5 V, and the positive bias is applied to the second evaporated Au contact (physisorbed contact), which follows the “normal bias” convention in IETS measurement [3,35]. From comparison with the IR, Raman, and HREELS results (Table 5.1) the negative bias peaks at -29, -82, and -131 mV are identified as the Au-S, C-S, and C-C stretching modes, respectively. The peaks at -109 and -355 mV and the shoulder at
Figure 5.5. Spectra at both negative and positive biases obtained with an AC modulation of 8.7 mV at 4.2 K. The DC biases are applied from 0 to ± 0.5 V.
-159 mV are originated from CH$_2$ group rocking, stretching, and wagging vibrations. Other peaks at -209, -231, and -248 mV and those above -373 mV are possibly produced by Si-H and N-H vibrations [29-33]. Compared with the spectrum at positive bias, same characteristic group frequencies appear at the negative bias as well, however the relative peak intensities are different.

Different IETS peak intensities at opposite biases have been reported previously, where the bias dependence is explained as a natural consequence of the barrier asymmetry because a metal oxide was used to form the tunnel junctions [3-5,35]. In such an electrode1-oxide-molecule-electrode2 device configuration, an electron tunneling from electrode1 to electrode2 does not lose energy by inelastic scattering until it tunnels through the oxide barrier. However for an electron tunneling in the opposite direction it will lose energy to excite the molecular vibrational mode first and then tunnel through the barrier. As a result it has a reduced tunneling probability, which causes the difference in the peak intensities.

In our device configuration the tunneling barrier is introduced by the self-assembled molecules themselves, thus the aforementioned barrier asymmetry does not exist. However the fabrication processes to form the two electrical contacts in the nanopore structure are different, i.e., one contact is made by a spontaneous chemisorption process (molecular self-assembly), while the other one is formed by physical metal evaporation. In our IETS measurement the positive bias corresponds to electrons tunneling from the chemisorbed contact to the physisorbed contact. These two different fabrication processes would not produce totally symmetrical electrical contacts to the
molecules, and this contact asymmetry could be a source of the asymmetrical spectra at opposite biases.

5.4 Spectra linewidth study

In order to verify that the obtained spectra are indeed valid IETS data, the peak width broadening effect is examined as a function of temperature and applied modulation voltage. IETS measurements have been performed with different AC modulations at a fixed temperature, and at different temperatures with a fixed AC modulation. Fig. 5.6 shows the modulation dependence of the IETS spectra obtained at $T = 4.2$ K, and the modulation voltages used are 11.6, 10.2, 8.7, 7.3, 5.8, 2.9, and 1.2 mV (rms values). According to theoretical analysis, AC modulation will bring in a linewidth broadening ($W_{\text{modulation}}$) of 1.7 V rms for the full width at half maximum (FWHM) (Chapter 2) [36]. Besides, the Fermi level smearing effect at finite temperature will also produce a thermal broadening ($W_{\text{thermal}}$) of 5.4 kT [37], and these two broadening effects add as squares [37,38]. Table 5.2 gives the calculated values of the linewidth broadening due to the applied modulation as well as the final FWHMs after considering the thermal effect at 4.2 K. In order to determine the experimental FWHMs, a Gaussian distribution function is utilized to fit the spectra peaks [38,39] and an individual peak is defined by its left and right minima. As an example, Fig. 5.7 shows the fitting analysis performed on the C-C stretching peak at 133 meV obtained with a modulation of 8.7 mV at 4.2 K. The fitting is performed using the Microcal Origin 6.0 software that uses a mathematical model of the form

\[ W_{\text{FWHM}} = W_{\text{modulation}} + W_{\text{thermal}} \]
Figure 5.6. Modulation dependence of IETS spectra obtained at 4.2 K.
### Table 5.2

<table>
<thead>
<tr>
<th>AC modulation (mV)</th>
<th>Broadening of 1.7 V_{rms} (mV)</th>
<th>FWHM after adding thermal effect (mV)</th>
</tr>
</thead>
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<tr>
<td>11.62</td>
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<td>19.85</td>
</tr>
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<td>10.16</td>
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</tr>
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</tr>
<tr>
<td>2.91</td>
<td>4.95</td>
<td>5.33</td>
</tr>
<tr>
<td>1.18</td>
<td>2.01</td>
<td>2.80</td>
</tr>
</tbody>
</table>

Table 5.2. Calculated FWHM values of the modulation and thermal (4.2 K) broadenings.

**Figure 5.7.** Gaussian fitting on the C-C stretching peak to determine the experimental FWHM.
to fit the data, where $y_0$ is the baseline offset, $A$ is the total area under the curve from the baseline, $x_0$ is the center of the peak, and $w$ is $2\sigma$ (standard deviation). FWHM of a Gaussian distribution is related to $w$ by $FWHM = w\sqrt{2\ln 2}$ [40].

Fig. 5.8 shows the modulation broadening analysis of the C-C stretching mode at $T = 4.2$ K. The circular symbols are FWHMs of the experimental peaks obtained from the Gaussian fitting and the square symbols are calculated values (Table 5.2). The error range of the experimental data is also determined by the Gaussian fitting. As shown in Fig. 5.8, the agreement is excellent over most of the modulation range; however the saturation of the experimental linewidth at low modulation bias indicates the existence of a non-negligible intrinsic linewidth.

Taking into account the known thermal and modulation broadenings and including the intrinsic linewidth ($W_I$), the measured experimental peak width ($W_{exp}$) is given by Eq. (2.49) (Chapter 2) [38]:

$$W_{exp} = \sqrt{W_I^2 + W_{thermal}^2 + W_{modulation}^2}. \tag{5.1}$$

By treating $W_I$ as a fitting parameter, a nonlinear least squares fitting using Eq. (5.1) on the AC modulation data can be performed. Fig. 5.9 shows the fitting result, and from this fitting an intrinsic linewidth of $3.73 \pm 0.98$ meV can be obtained for the C-C stretching mode (the error range is determined by the NLS fitting). The shaded bar in Fig. 5.9 denotes the expected saturation due to this derived intrinsic linewidth (including a $5.4$ kT thermal contribution).
Figure 5.8. Line broadening of the C-C stretching mode as a function of AC modulation. The circular symbols are experimental FWHMs and the square symbols are theoretical calculations including both thermal and modulation broadenings.
Figure 5.9. Nonlinear least squares fitting (solid line) on the modulation broadening data (circular symbol) to determine the intrinsic linewidth of the C-C stretching mode. The shaded bar indicates the expected saturation due to this intrinsic linewidth and the thermal contribution at 4.2 K.
The broadening of the linewidth due to thermal effect can also be independently checked at a fixed modulation voltage. Fig. 5.10 shows the temperature dependence of the IETS spectra obtained with an AC modulation of 8.7 mV (rms value) at temperatures of 4.2, 20, 35, 50, 65, and 80 K. Fig. 5.11 shows the thermal broadening analysis of the same C-C stretching mode. The circular symbols (and corresponding error bars) are experimental FWHM values determined by the Gaussian fitting (and error of the fitting) to the experimental lineshapes. The square symbols are calculations included thermal broadening, modulation broadening, and the intrinsic linewidth of 3.73 meV determined from the modulation broadening analysis. The error ranges of the calculation (due to the intrinsic linewidth error) are approximately the size of the data points. The agreement between theory and experiment is very good, spanning a temperature range from below (x 0.5) to above (x 10) the thermally broadened intrinsic linewidth.

Similar linewidth investigation has also been carried out on other vibrational modes. For example, Fig. 5.12 shows the modulation broadening analysis on the Au-S stretching mode at 33 meV and the CH$_2$ wagging mode at 158 meV. For the Au-S stretching mode, the deviation of experimental data from calculated values is little, indicating that its intrinsic linewidth is small. A linewidth upper limit of 1.69 meV is determined for this vibrational mode. For the CH$_2$ wagging mode, nonlinear least squares fitting using Eq. (5.1) [solid curve in Fig. 5.12(b)] gives an intrinsic linewidth of 13.5 ± 2.4 meV. For other vibrational modes because of the weak spectral peaks the obtained FWHMs from the lineshape fitting have large error ranges, thus the intrinsic linewidths cannot not be very well resolved.
Figure 5.10. Temperature dependence of the IETS spectra obtained at a fixed modulation of 8.7 mV.
Figure 5.11. Line broadening of the C-C stretching mode as a function of temperature. The circular symbols are experimental FWHMs and the square symbols are calculations including thermal and modulation broadenings and the intrinsic linewidth.
Figure 5.12. Line broadening as a function of AC modulation obtained at 4.2 K for (a) the Au-S stretching mode and (b) the CH₂ wagging mode. The circular symbols are experimental FWHMs and the square symbols are calculations including both modulation and thermal contributions. A nonlinear least squares fitting using Eq. (5.1) to determine the intrinsic linewidth is shown as the solid curve in (b).
The inspection of intrinsic linewidth was not generally considered in the classical IETS literatures [4,5]. Linewidth broadening effects due to thermal and modulation contributions have been explored; however the intrinsic linewidth was usually treated as negligible [3]. A recent report of the IETS intrinsic linewidth comes from the STM-IETS study on the C-H stretching peak of a single HCCH molecule adsorbed on Cu(001) surface [38]. The reported value of \(4 \pm 2 \text{ meV}\) is found to be consistent with the value of \(6 \pm 2 \text{ meV}\) estimated for the hindered rotation of CO on Cu(001) from similar STM-IETS studies of the same research group [38,39]. Nevertheless, by comparing to the intrinsic linewidth value of \(\sim 6 \text{ cm}^{-1} \sim 0.75 \text{ meV}\) obtained from an IR study on the same type of molecules [41], the authors argue that the natural linewidth is negligible and this intrinsic linewidth may be dominated by instrumental broadening originating from control electronics or the environment [38].

The above STM-IETS study reported only one intrinsic linewidth from the obtained spectrum [38]. Our nanopore-based IETS characterization produces a spectrum with multiple peaks originated from different vibrational modes. The obtained intrinsic linewidths are different for the various peaks; therefore they cannot be attributed to one systematic broadening effect, but are rather due to intrinsic molecular device properties. Furthermore, analysis on Raman or IR spectra of alkanethiols on gold shows that the spectral linewidths could be much larger than 1 meV and different spectral peaks could have similar linewidths. For example, linewidth fittings using both Lorentzian and Gaussian distribution functions on a Raman spectrum [42] containing both Au-S stretching and CH\(_2\) wagging peaks yield linewidths of \(\sim 6 \text{ meV}\) and \(\sim 5 \text{ meV}\),
respectively. Therefore such comparison provides little help in the understanding of the origin of the intrinsic line widths in our case.

A recent theoretical study by Galperin et al. on the line widths of vibrational features in inelastic electron tunneling spectroscopy proposes that the intrinsic IETS line widths are actually dominated by the couplings of molecular vibrations to electron-hole pair excitations in the metallic electrodes [43]. Using a nonequilibrium Green’s function (NEGF) approach, the authors have investigated a junction consisting of two electrical leads bridged by a single molecule. The free particle Hamiltonian for this system contains terms that correspond to the electronic states representing the two electrodes, the electrons on the bridge molecule, a primary molecular harmonic mode of frequency $\Omega_0$, and a subset of harmonic modes representing the thermal environment. The interaction Hamiltonian consists of terms representing the couplings between the bridge electronic system and the electrodes, on-bridge coupling of the primary phonon to the electronic system, and interaction of this primary phonon with the thermal environment [43-48]. After self-consistently solving the related Green’s functions and self-energies, important junction characteristics such as the total tunneling current and intrinsic linewidth of the vibrational feature can be estimated. It is found that the interaction of the bridge phonon and the thermal environment contributes little (less than 0.1 meV) to the linewidth and the dominant part ($\gamma_{el}$) of the intrinsic linewidth comes from the coupling between the bridge phonon and the electronic states of the electrodes [43]. Physically meaningful values of $\gamma_{el}$ are obtained at the threshold voltage of $V = \hbar \Omega_0 / e$, at which the vibrational feature is observed. Calculations show that $\gamma_{el}$ (thus the intrinsic linewidth) has a dependence on the bridge-electrode electrical couplings. For
coupling parameters corresponding to the nanopore structure, the calculated $\gamma_{el}$ value exceeds 1 meV, which has the same order of magnitude as that obtained from the experiment. The calculation also suggests that $\gamma_{el}$ has dependence on the on-bridge phonon-electron interaction [43].

Most importantly, according to the above theoretical investigation $\gamma_{el}$ exhibits dependence on the threshold voltage, which can be compared to our experimental observation directly. Reproduced from Ref. 43, Fig. 5.13(a) is the $\gamma_{el}$ versus threshold bias plot generated for the aforementioned model junction with asymmetric couplings. In this figure the solid line is calculated from self-consistent Born approximation while the dashed line is obtained from second order perturbation theory [43]. Although the junction parameters chosen to make this plot do not represent the nanopore structure exactly, it still has some qualitative relation to our experimental observation. In Fig. 5.13(a), both calculations indicate that $\gamma_{el}$ (therefore the intrinsic linewidth) increases when the threshold voltage at which the inelastic tunneling happens becomes large. Fig. 5.13(b) is the plot of our obtained intrinsic linewidths of the Au-S stretching, C-C stretching, and CH$_2$ wagging vibrations versus corresponding peak positions (threshold voltages). As illustrated by Fig. 5.13(b), the measured intrinsic width increases when the peak position moves to a higher voltage, which agrees qualitatively with the calculated trend from the above simplified model.

One might assume that an inhomogeneous contribution would be a dominant part of the measured intrinsic linewidths because the nanopore junction contains several thousand molecules; however it is very unlikely that such a contribution based on the number of molecules would give different linewidths for different vibrational modes.
Figure 5.13. (a) $\gamma_{el}$ (dominant part of the intrinsic linewidth) versus bias plot for a metal-molecule-metal junction with asymmetric couplings. The solid line is calculated from self-consistent Born approximation while the dashed line is obtained from second order perturbation theory. After Ref. 43. (b) Plot of the experimental intrinsic linewidths vs. corresponding threshold voltages.
Furthermore the characterized linewidths from the nanopore method have similar order of magnitude to the STM-IETS measurement results where only a single molecule is examined [38,39].

The asymmetric line shapes and negative values of our IETS spectra such as those at 33 mV (Au-S stretching) and 133 mV (C-C stretching) can also be explained by the same theoretical model [43-48]. Asymmetric features in IETS spectra have been observed in several cases in an aluminum oxide tunnel junction and STM-IETS studies [49-51]. Theoretical investigations based on the same molecule-induced resonance model found that the inelastic channel always gives positive contribution to the tunneling conductance, while depending on the junction energetic parameters the contribution from the elastic channel could be negative and, furthermore, could possibly overweight the positive contribution from the inelastic channel and result in a negative peak in the IETS spectra [43,45,46]. The source of the negative contribution of the elastic channel, which only happens at the threshold voltage of $V = \hbar\Omega_0 / e$, is the interference between the purely elastic current amplitude that does not involve electron-phonon interaction and the elastic amplitude associated with the excitation and reabsorption of virtual molecular vibrations.

By setting certain values of the couplings of the bridging molecular state with the electrodes in the previously discussed model, numerical calculations have been performed to examine the change of the IETS spectrum as a function of the molecular energy level [43,46]. Fig. 5.14 is the calculation result adopted from Ref. 46, which shows the asymmetric shapes and negative peaks of the spectra because of the resonance coupling and the evolution of the spectra at different molecular energy levels. Line shapes at 33 and 133 mV in our measured IETS spectra are similar to those shown in Fig.
5.14; however an analytical expression is needed from theoretical studies in order to fit the experimental data and better understand such features. Furthermore, a gated IETS experimental inspection could help understand this resonant energy level.

In conclusion, our observed intrinsic linewidths of spectral peaks of different vibrational modes are dominated by intrinsic molecular properties. Theoretical inspections using nonequilibrium Green’s function formalism on a simplified metal-single bridge molecule-metal model suggests that the coupling of the molecular vibrational modes to the electronic continua of the electrodes makes a substantial contribution to the spectral line shape and linewidth. The observed intrinsic linewidth differences can be qualitatively explained by the linewidth dependence on the threshold voltage. By choosing appropriate junction parameters, a quantitative comparison between theory and experiment is expected.
Figure 5.14. Asymmetric line shapes and negative peaks of the IETS spectra due to the resonance coupling to a bridging molecular state. The spectra are calculated using a numerical method for several positions of the molecular energy level $\varepsilon_a$. The IETS peak (molecular vibrational energy $\hbar \Omega_0$) is at 100 meV. The solid, dashed, dot-dashed, and double-dot-dashed lines represent $\varepsilon_a$ at the Fermi level ($E_F$) of the electrodes, and 1, 1.5, and 2 eV above the Fermi level of the electrodes, respectively. After Ref. 46.
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Chapter 6

Conclusion and Outlook

In this work we have investigated electronic transport through alkanethiol SAMs, with the intent of having a fully understood system that can serve as a simple control for the development of molecular junctions. Electrical transport through alkanethiol SAMs has been reported previously using various device structures, and the conduction mechanism has been prematurely claimed as tunneling – all of these measurements were exclusively performed at ambient temperature, which is insufficient for an unambiguous determination of the tunneling transport. In the absence of temperature-dependent characterization, other conduction mechanisms such as thermionic, hopping, or even filamentary conduction cannot simply be excluded in the data analysis, thus such a claim is premature. A further related question is the identification of the measured molecular species in the device area. Although numerous claims of “molecular transport studies” have been made, there was no unequivocal evidence of such a measurement. By far, the field lacked a tool to verify the existence of the desired molecules in the prepared molecular devices.

Using a nanometer-scale device structure, we have performed temperature-dependent I(V) characterization for the first time on alkanethiol SAMs, and demonstrated unambiguously that tunneling is the dominant conduction mechanism. Comparing to a
standard model of metal-insulator-metal tunneling, important transport parameters such as the barrier height have been derived, which qualitatively described the tunneling process. In addition, the inelastic electron tunneling spectroscopy technique has been applied to the study of molecular transport. This technique is used to fingerprint the chemical species inside the molecular junction. The obtained spectra exhibit characteristic vibrational signatures of the confined molecular species, presenting direct evidence of the presence of molecules in a molecular transport device for the first time.

The field of “molecular electronics” is rich in proposals and promises of plentiful device concepts, but unfortunately has a dearth of reliable data and characterization techniques upon which to test these ideas. As our results have shown, a well-prepared self-assembled alkanethiol monolayer behaves as a good, thin insulating film and shows understood “canonical” tunneling transport behavior. This molecular system should be used as a standard control structure for any molecular transport characterizations. The IETS technique has been proven to be a dependable tool for the identification of chemical species. It has especially indispensable applications in solid state molecular devices, where other spectroscopic tools such as IR or Raman are hard, if not impossible, to employ. The spectroscopic study conducted in this research verified the characterization of intrinsic molecular properties; therefore it should be generally utilized for any future molecular transport investigations.

The importance of carefully prepared control measurements in transport studies cannot be overemphasized – the most glaring example being the alleged “molecular switching effect” reported by the HP/UCLA groups using L-B films [1-4], which has been exposed to be due to filamentary conduction [5,6]. These careless claims of intrinsic
molecular conduction lacked any significant control characterization – indeed, tunneling transport has yet to be demonstrated in an alkane L-B film (such as reported here for a SAM), which instead is dominated by defect conduction [5,7,8]. This thesis has shown that definitive controls can not only be shown for a given fabrication protocol, but it is necessary to responsibly determine transport mechanisms, and if omitted, can lead to dreadful misleading claims (http://www.hpl.hp.com/news/2002/oct-dec/beyond_silicon.html). In light of this, the claim of “unimolecular rectification” [9] using an L-B film is thus highly suspect until appropriate controls and temperature-dependent studies are performed.

As has been discussed previously, another crucial issue this research work has raised is the application of the IETS technique as a reliable characterization method in molecular transport studies. Researchers have claimed that intrinsic molecular conduction has been observed, however there was no unambiguous evidence that the molecules of interest actually existed in the junction. The IETS results presented in this thesis are the first definite affirmation of the presence of the desired molecular species in a molecular device and could yield valuable information regarding the intrinsic molecular properties.

This thesis also has raised some interesting questions. One of them is the origin of the asymmetrical lineshape and the negative peaks in our obtained IETS spectra. As discussed in Chapter 5, theoretical investigations based on a molecule-induced resonance model have attributed this asymmetry to the interference between the elastic current amplitude that does not involve electron-phonon interaction and the elastic amplitude associated with two electron-phonon interaction events involving virtual phonon emission and absorption processes [10-12]. By setting different values of the molecular
energy level, the evolution of the spectral lineshape can be calculated [Fig. 5.14]. However, what is the physical nature of this resonant energy state? A theoretical study on the CH$_3$NC molecule that had shown an asymmetrical experimental lineshape and a negative peak of the C≡N stretching mode in its IETS spectra obtained using an aluminum oxide tunnel junction [13] proposed that the resonant level came from the orbital structure of the N≡C, which is assumed to be located 2 ~ 3 eV above the Fermi energy of the electrodes [11]. According to this explanation, a theoretical investigation of the energy levels of the Au-S and C-C orbitals could help explain the lineshape of our two spectral peaks. Furthermore, experimental design and realization of a measurement that can tunably change the molecular energy level would be useful to quantitatively locate the resonant states and further understand their characteristics.

Another interesting question is to find out if the charge transport in a SAM is through the LUMO or the HOMO energy level. It seems that this question could be easily answered if we know the energy level alignment in a metal-SAM-metal system. However, the location of the Fermi energy relative to the molecular levels in such a system is poorly understood and controversial [14]. As we have discussed in Chapter 4, theoretical fittings on measured I(V) characteristics could not give a definite answer either. Nevertheless, a recent theoretical investigation on this subject suggests that by creating a temperature difference between the two metal electrodes and measuring the thermoelectric current through the junction this question could be answered [14]. A temperature gradient gives rise to a current in a metal-SAM-metal junction because there is a difference between the Fermi functions of the electrodes and calculations show that this thermoelectric current depends on the derivative of the transmission coefficient times
the temperature difference. For the phenyl-dithiol molecule studied by this model a 10 K temperature difference could produce a thermoelectric voltage of 0.1 to 0.5 mV. According to the theoretical expectation, this thermoelectric voltage should be insensitive to the contact geometry and quality and should be easy to measure and interpret [14]. However an experimental realization of such a measurement in a test structure such as the nanopore is not trivial due to the difficulties of establishing a stable thermal gradient in the device configuration. STM is more suitable for performing this type of measurement because of the thermal isolation of the STM tip and the substrate.

Study of the transition behavior from direct tunneling to other conduction mechanisms of a monolayer is another appealing topic. The I(V) characterization performed in our research work was restricted to applied bias of \( \leq 1.0 \) V since higher bias causes device degradation. The obtained barrier height of alkanethiol SAM is actually larger than 1 V, therefore the transition from direct tunneling to Fowler-Nordheim tunneling was not observed. However, a molecular tunneling structure with a barrier height less than 1 V could be designed and measured, and the obtained results could be used to inspect this transition behavior. Creating systems with low barrier heights would involve an interesting study of various different functional endgroups (instead of thiol) and/or metals (or degenerate semiconductors). If achieved, one could study not only the FN transition but perhaps even the inelastic scattering of carriers and the transition from tunneling to hopping as the molecular length increases.

The IETS technique can also be applied to other molecular systems to examine chemical bonding issues. For example, in our study we characterized a dithiol alkane structure, and the S-H stretching mode at \( \sim 329 \) mV is very weak in our acquired spectra,
indicating that most of the thiol groups have reacted with the gold bottom and top contacts. An IETS characterization of a monothiol alkane SAM can further clarify this matter, i.e., whether the thiol end group would react completely with the gold surface during the self-assembly process. Furthermore, we have also observed asymmetrical spectra at opposite bias even though we used a symmetrical molecule. This spectral asymmetry could be attributed to the asymmetrical contacts formed during the device fabrication process. A measurement on an alkanemonothiol SAM could provide more information about this contact issue. Another application of the IETS method is to help understand the switching behavior observed in the nanopore structure with molecules containing a nitro side group. Possible IETS characterization of the vibrational frequency shift or spectral intensity change of the two conducting states could provide valuable information regarding the switching mechanism.

In summary, understanding the fundamental charge transport processes in self-assembled monolayers is a challenging task. However, the model control system and the reliable characterization methods presented in this research work should assist in guiding future research work toward more interesting and novel molecular transport systems.
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