New Measurement Techniques and Their Applications
in Single Molecule Electronics

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A Dissertation Presented in Partial Fulfillment
of the Requirement for the Degree
Doctor of Philosophy

Approved April 2012 by the
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May 2012
ABSTRACT

Studying charge transport through single molecules tethered between two metal electrodes is of fundamental importance in molecular electronics. Over the years, a variety of methods have been developed in attempts of performing such measurements. However, the limitation of these techniques is still one of the factors that prohibit one from gaining a thorough understanding of single molecule junctions.

Firstly, the time resolution of experiments is typically limited to milli to microseconds, while molecular dynamics simulations are carried out on the time scale of pico to nanoseconds. A huge gap therefore persists between the theory and the experiments. This thesis demonstrates a nanosecond scale measurement of the gold atomic contact breakdown process. A combined setup of DC and AC circuits is employed, where the AC circuit reveals interesting observations in nanosecond scale not previously seen using conventional DC circuits. The breakdown time of gold atomic contacts is determined to be faster than 0.1 ns and subtle atomic events are observed within nanoseconds.

Furthermore, a new method based on the scanning tunneling microscope break junction (STM-BJ) technique is developed to rapidly record thousands of I-V curves from repeatedly formed single molecule junctions. 2-dimensional I-V and conductance-voltage (G-V) histograms constructed using the acquired data allow for more meaningful statistical analysis to single molecule I-V characteristics. The bias voltage adds an additional dimension to the conventional single molecule conductance measurement. This method also allows one to
perform transition voltage spectra (TVS) for individual junctions and to study the correlation between the conductance and the tunneling barrier height. The variation of measured conductance values is found to be primarily determined by the poorly defined contact geometry between the molecule and metal electrodes, rather than the tunnel barrier height.

In addition, the rapid I-V technique is also found useful in studying thermoelectric effect in single molecule junctions. When applying a temperature gradient between the STM tip and substrate in air, the offset current at zero bias in the I-V characteristics is a measure of thermoelectric current. The rapid I-V technique allows for statistical analysis of such offset current at different temperature gradients and thus the Seebeck coefficient of single molecule junctions is measured. Combining with single molecule TVS, the Seebeck coefficient is also found to be a measure of tunnel barrier height.
DEDICATION

To my beloved parents for nurturing and education,

and to my wife for never-ending love and support.
ACKNOWLEDGEMENTS

I would like to thank my advisor, Dr. Nongjian Tao, for five years of continuous encouragement and mentoring.

Also I have learned a great deal from Dr. Francis Tsow and Dr. Joshua Hihath on circuit designing and troubleshooting, Dr. Zhifeng Huang and Dr. Ismael Diez-Perez on Conducting AFM, Dr. Joshua Hihath and Dr. Ismael Diez-Perez on STM break junction technique, electrochemistry, LabView coding. In addition, I would like to express my gratefulness to all the members in Dr. Tao’s group for their informative discussions and feedback. I enjoyed my time with them all, and I would like to explicitly thank Mr. Christopher Bruot, Mr. Thomas Hines, Mr. Limin Xiang and Miss Yueqi Li.

Finally, I greatly appreciate the valuable time and feedback from my committee members: Dr. Nongjian Tao, Dr. Peter Bennett, Dr. Cun-Zheng Ning and Dr. Hongbin Yu.
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1 INTRODUCTION TO MOLECULAR ELECTRONICS

1.1 Why molecular electronics

Molecular electronics is an idea of building circuits using functional blocks based on one molecule or a group of molecules. This idea was originated from a seminal paper published back in 1974 by Aviram and Ratner in which a single molecular rectifier was proposed. (1) In the last two decades, the thriving of complementary metal-oxide-semiconductor (CMOS) technology has lead to exponentially increasing computational capability, which follows the famous Moore’s law. However, quantum physics places an impassable limit when the devices eventually reach the size of one or a few atoms, and Moore’s law is seeing its end of the road. Among all the proposed alternatives to CMOS technology, molecular electronics has been considered as one of the most promising candidates and is thus receiving dramatically increasing attention from researchers all around the world. Meanwhile, the advance in organic syntheses, the development in theoretical computation, the invention of scanning probe microscopes (SPM) and the dramatically improved micro/nano fabrication capability have enabled in-depth study of single molecular devices. (2-20) This is a highly interdisciplinary field that has brought physicists, chemists, biologists as well as engineers all together.

It is of fundamental importance to understand the charge transport through single or assemble of molecules at nanometer scale. (21-25) And direct transport measurements of different molecules tethered between metal electrodes – such as single molecule conductance and current-voltage characteristics measurements –
are crucial in such study. Over the years, researchers with different fields of expertise have developed a variety of methods and tools (3, 4, 26-46) in order to make such direct transport measurements possible. Although it is intrinsically difficult for molecules to stably bind to metals via chemical bonds, a quite wide selection of linker groups have been successfully utilized in forming metal-molecule-metal junctions, including thiol(14, 47, 48), amino(49), pyridine(3), carboxyl(49), cyanide (50) and so on. Meanwhile, quite a few tools have been developed in the attempt of fabricating metal-molecule-metal (MMM) junctions effectively, given the short lifetime of molecule-metal contact (typically seconds or even less). For example, the scanning tunneling microscope based break junction (STM-BJ) technique(3, 51-53) and mechanically controlled break junction (MCBJ) setup(26, 27, 54-59) have been proved extremely useful in terms of reproducing thousands of nano size junctions down to single molecule level within a short period of time, thus allow for statistical analyses with large quantity of data. In the next section, a brief introduction of these two techniques will be provided. The electrochemical gate (8, 9, 16, 60) and oxide-semiconductor based back gate (61-63) are also introduced to make three-terminal measurements possible. Furthermore, by using a cryostat system, amazing stability and extremely high signal to noise ratio can be achieved and thus more subtle measurement can be performed(27, 59), such as inelastic electron-phonon tunneling spectroscopy measurements (19, 59, 64) and molecular spintronics(65-68).
Along the same pathway, researchers are also looking for analogies between conventional basic electronic functional blocks and single molecules. To date, various properties of different molecules have been reported, in which single molecules are proposed to perform like wires (3, 4, 10, 35, 40, 51, 53, 57, 69-71), diodes (31, 72-82), switches (83-90) and transistors (8, 91-94).

Meanwhile, there are also other places where molecular electronics can potentially make a profound impact – for instance in the field of biology. There have been several reports on single molecule conductance measurements of DNA molecules in the recently years (7, 95, 96). The capability of determining the conductance and other electronic properties of particular DNA molecules quickly and reliably could profoundly impact the field of DNA study.

Admittedly, the field of molecular electronics is a field that is far from well developed. For example, apart from a very limited number of simple molecules such as alkanedithiols (14, 47, 48, 97-100), the accurate conductance values of most molecules are still under debate. Also a wide discrepancy persists between theory and experiments over the years (101, 102). More complicated molecular systems are still beyond our understanding capability. Furthermore, the practical application of single molecular devices into complicated circuit systems is still in the far future. The techniques of forming robust molecule-electrode interface and inter-molecular contacts haven’t been developed. This is a field that still requires extensive work. And this report is to follow all those footprints of the predecessors, and to continue exploring unknown electronic properties of single
molecules as well as new methods and techniques that could potentially benefit this field.

1.2 The history of single molecule conductance measurement and techniques

As mentioned above, the ability of quickly and reliably measuring single molecule conductance is one of the most critical requirements in the field of molecular electronics\cite{21, 22}. As a result, many groups around the world have developed many techniques in order to measure multiple or even single molecule junctions over the years. Generally, the techniques that made profound impact went from early application of scanning probe microscope (SPM) \cite{35, 38, 103-112}, microfabricated fixed electrodes with various techniques to create nanosized gaps \cite{61-63, 70, 113-123} to the most commonly used break junction techniques which includes STM break junction (STM-BJ) technique \cite{3, 51-53} and mechanically controlled break junction (MCBJ) technique \cite{26, 27, 54-59}.

1.2.1 Early scanning probe techniques and STM break junction technique

The ultra high resolution and great flexibility that SPM can achieve has attracted worldwide attention. One naturally thinks about placing a scanning tunneling microscope tip or a metal coated AFM tip over a molecule, measuring current by applying a bias voltage\cite{36, 103-106, 124} and moving single molecules around on the substrate surface\cite{107}. In order to better define the junction, a mixed matrix of self assembled monolayer (SAM) is often prepared where molecules of interest are often dispersed into a matrix of much less conducting reference molecules\cite{35, 108, 110}. Sometimes metal nanoparticles are
used to covalently attach to the top end of the target molecules in order for the tip to locate easily (110). More complicated assemble techniques such as attaching one end of the molecule to a step edge on a metal substrate (109) and assembling target molecules bound to two gold atomic chains (38) have also successfully demonstrated the possibility of single molecule conductance measurement.

However, due to the large variation of contact geometries that the molecules have when tethered to metal, above techniques encountered great challenges in terms of getting reliable conductance values. The STM-BJ technique allows for quick reproduction of large quantities of metal-molecule-metal (MMM) junctions. By the aid of computer technology, massive data logging and processing provide meaningful statistical analysis. Similarly to previous cases, the target molecules with both ends reactive with metal electrodes are absorbed onto a metal surface to form a SAM before the measurement is carried out (Fig. 1.1a). During the measurement, instead of kept stationary or made scan the surface, the SPM tip is first brought close enough to or into contact with the sample surface, where MMM junctions can be formed (Fig. 1.1b). And then the tip is pulled away at a constant ramp rate (typically nanometers per second), during which the current-distance traces are recorded (Fig. 1.1c-d). The steps in the recorded traces are the signature of one or multiple molecules bridging between the electrodes (Fig. 1.1e). Such process is repeated for thousands of times, and the recorded traces can be projected onto the conductance axis to obtain a histogram with peaks indicating the most probable conductance values (Fig. 1.1f).
Fig. 1.1 Measurement of single molecule conductance using STM break junction. (a-d) Schematic representation of STM break junction applied in the single molecule measurement: (a) approach, (b) formation of molecular junctions, (c) pulling and (d) breaking. (e) Sample conductance traces recorded during pulling process in the presence of 4, 4’-bipyridine molecules. (f) A histogram consisting 1000 curves like the ones shown in (e)(3).

The STM-BJ technique has achieved great success due to its simplicity and effectiveness. In Chapter 3 of this report, a more advanced algorithm based on this technique will be presented which allows for rapid acquisition of large amount of current-voltage characteristics of MMM junctions. Such technique reveals more statistical results of great significance.

1.2.2 Microfabricated fixed electrodes and mechanically controlled break junction technique

Huge progress has been made in the development of microfabrication over the years. The capability of made micro/nano size electrodes with ultra-fine
precision also facilitates the fabrication of MMM junctions. A critical challenge though, is to fabricate a small gap of the size of single molecules between the electrodes, which typically is only a few nanometers. A few tricks – such as electron migration (61, 113), electrochemical etching or deposition (114-117) and other unconventional methods (62, 70, 118-120) – have been used to create such gaps. Also, metal nanoparticles have been used as bridges to avoid the necessity of creating nanosize gaps (88, 121, 122) Due to the fine precision of such fixed electrodes on a substrate, the fabricated molecular junctions are mechanically more stable, making it ideal to study charge transport properties over a much longer period of time. Together with cryostat, many interesting phenomena – such as single-electron charging and Kondo effects in molecules – have been studied (61-63, 113, 123).

However, the complication in the fabrication process often results in low yield. Due to the same need of statistical analysis, this becomes a drawback (117, 118). The MCBJ setup (54, 55), with a similar lateral layout of the electrodes, also managed to create thousands of junctions reproducibly within short time window. In the simplest scenario, a thin metal wire is notched in the center and supported on a solid substrate. It is then broken into a pair of electrodes by bending the substrate with a mechanical actuator mounted underneath it (Fig. 1.2a). (55, 125) By controlling the same actuator, the separation between the electrodes can be modulated so electron tunneling can be studied. When the electrodes are exposed to a solution containing molecules with linker groups on both ends (e.g. thiols etc) (26, 57, 126), MCBJ is able to create and break MMM junctions in the gap.

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repeatedly so that large amount of data can be collected. To improve the junction stability, electron beam lithography (EBL) has been used to fabricate a nanobridge between a pair of microfabricated electrodes on a substrate with ultra-fine precision.\(^{(56)}\) The nanobridge can be broken and the resulting gap can then open and close by controlling the mechanical actuator in a similar way (Fig. 1.2b).

![Mechanical controlled break junction (MCBJ) setup. (a) Principle of the MCBJ.\(^{(125)}\) (b) Scanning-electron-microscope picture of the lithographically fabricated break junction.\(^{(127)}\)](image)

**Fig. 1.2** Mechanical controlled break junction (MCBJ) setup. (a) Principle of the MCBJ.\(^{(125)}\) (b) Scanning-electron-microscope picture of the lithographically fabricated break junction.\(^{(127)}\)

Compared to the STM-BJ technique, although similarities can be found, the MCBJ technique is generally more complicated and difficult to setup. Owing to the poor stiffness of most metal, MCBJ made by breaking a single metal wire experiences mechanical instability especially when a liquid cell is involved. MCBJ fabricated using EBL can achieve good stability but involves complicated clean room work and is thus restricted by low yield. Meanwhile, STM-BJ is generally easy to setup, also compatible to liquid environment so that electrochemical gating experiments can be easily carried out.
1.3 Charge transport mechanisms of single molecule junctions

As stated above, understanding charge transport mechanisms of single molecule junctions is one of the most important goals of molecular electronics study. Although the exact mechanisms are not well understood, there are several models that have received worldwide recognition. In this section, we will start with the very basic Landauer Formula. And then we will discuss two well-received transport models, namely, coherent non-resonant tunneling and incoherent hopping. A useful technique will be introduced to determine the energy alignment between the electrode Fermi level and the nearest molecular orbital, which is one of the most important features in understanding the charge transport mechanism.

1.3.1 Landauer Formula

The Landauer Formula\(^{(128, 129)}\) describes the conductance of small dimension samples where conventional Ohm’s Law does not hold. In such systems, the conductance depends on the number of transverse modes in the sample as well as the interface resistance that is independent of the length of the sample. The charge transport process can be viewed as a transmission process and the general representation can be derived using scattering approach\(^{(125, 129)}\).

The following shows a simplified but more straightforward way to see how Landauer formula interprets such electron transport process. In an ideal one-dimensional sample of length \(L\), the density of states between \(k\) and \(k + dk\), including electron spin, is given by

\[
n(k)dk = \frac{1}{L} \frac{L}{2\pi} dk. \quad (1.3.1)
\]
From the basic quantum theory, the electron group velocity is given by

\[ v = \frac{\hbar k}{m}, \quad (1.3.2) \]

where \( \hbar \) is the reduced Plank constant. From the basic electrodynamics, the current is given by

\[ I = nev, \quad (1.3.3) \]

where \( n \) is the number of charge carriers, \( e \) is the electric charge of each carrier, and \( v \) is the velocity of carriers. The current flow through above one-dimensional system is thus an integration over all electrons occupying energy states in electrodes 1 and 2 following Fermi-Dirac distribution \( f_1 \) and \( f_2 \), given by

\[ I = e \int_0^\infty n(k)f_1(k)v(k)dk - e \int_0^\infty n(k')f_2(k')v(k')dk'. \quad (1.3.4) \]

Combining Equation 1.3.1, 1.3.2 and 1.3.4, the current is given by

\[ I = e \int_0^\infty \frac{\hbar k}{m \pi} \left( f_1(k) - f_2(k) \right) dk. \quad (1.3.5) \]

Converting momentum space to energy space, one obtains

\[ I = e \int_{-\infty}^\infty \frac{\hbar k}{m \pi} \left( f_1(E) - f_2(E) \right) \frac{dk}{dE} dE = e \int_{-\infty}^\infty \frac{\hbar k}{m \pi} \left( f_1(E) - f_2(E) \right) \frac{1}{\hbar \hbar k} dE, \quad (1.3.6) \]

and thus one gets

\[ I = \frac{e}{\pi \hbar} \int_{-\infty}^\infty \left( f_1(E) - f_2(E) \right) dE. \quad (1.3.7) \]

The above derivation assumes perfect transmission of 1. For non-perfect transmission, a transmission function \( \tau(E) \) of energy \( E \) is added. And the complete Landauer Formula of a single channel becomes

\[ I = \frac{e}{\pi \hbar} \int_{-\infty}^\infty \tau(E) \left( f_1(E) - f_2(E) \right) dE. \quad (1.3.8) \]

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Assuming perfect transmission and zero temperature, \( f_1 \) and \( f_2 \) reduce to two step functions, the current is now

\[
I = \frac{e}{\pi \hbar} (\mu_1 - \mu_2) = \frac{e^2}{\pi \hbar} V, \tag{1.3.9}
\]

where \( \mu_1 \) and \( \mu_2 \) are the Fermi energy levels of electrodes 1 and 2 respectively and \( V \) is the voltage different between electrodes 1 and 2. Now, \( \frac{e^2}{\pi \hbar} \) is the conductance of one perfect transmission channel (~77.5µS or ~12.9kΩ in resistance), which is defined as the conductance quantum and normally denoted as \( G_0 \). Such conductance quantization phenomenon can be observed in a gold quantum point contact experiment using as simple as a pair of cross wires.

In the molecular junction systems, where there are multiple modes resulting in multiple possible transmission channels, the conductance can be given by

\[
G = \frac{e^2}{\pi \hbar} \sum T_{ij}, \tag{1.3.10}
\]

where \( T_{ij} \) is the transmission probability from mode \( i \) in electrode 1 to mode \( j \) to electrode 2. This gives the complete representation of the Landauer formula.

### 1.3.2 Coherent non-resonant tunneling and incoherent hopping

The Landauer formula provides the most important framework for understanding charge transport in general mesoscopic systems. However, in single molecule junctions particularly, the transmission probability \( \sum T_{ij} \) is normally far from perfect. Over the years, several models have been developed to understand the mechanism behind the measured values of the transmission probability. A well accepted model consists two electron reservoirs denoted by
the donor $|D\rangle$ and the acceptor $|A\rangle$, which are bridged by a molecular bridge denoted by a series of $N$ single electron states $|1\rangle$, $|2\rangle$, … $|N\rangle$ with energy $E_n$ (Fig. 1.3). The charge carriers go from donor to acceptor and see a set of molecular states. Usually only interactions between the neighboring states are taken into account in such system. Depending on the difference between the Fermi levels in the electrodes and molecular states $\Delta E$, this process can be either coherent non-resonant tunneling, which is commonly modeled by tight binding superexchange theory(130), or incoherent hopping, which is usually a thermally activated process(131).

Fig. 1.3 A simple level structure model for electron transmission in metal-molecule-metal junction. A pair of metal electrodes is bridged by a molecule represented by a series of localized molecular states. (130) Depending on difference between the bridge states and Fermi levels in the electrodes, denoted by $\Delta E$, the electron transport mechanism can be coherent tunneling or incoherent hopping.
When $\Delta E$ is far beyond the thermal energy ($\sim 25 \text{ meV}$), the charge carriers transport by means of tunneling without physically residing on the molecule. The first order time dependent perturbation theory in quantum mechanics gives rise to the transition rate from $k'$ to $k$ states, given by

$$w = \frac{2\pi}{\hbar^2} |H'_{k'k}|^2 \rho(E_k). \quad (1.3.11)$$

where $H'_{k'k}$ is $\langle k'|H'|k \rangle$ and measures the coupling strength between $k'$ and $k$ states, and $\rho(E_k)$ is the Franck Condon weighted density of nuclear states. This is the famous Fermi’s Golden Rule.

In the single molecule junction system (Fig. 1.3), $H'_{k'k}$ is replaced by $T_{DA}$, the total coupling between donor and acceptor, where the $T$ operator is defined as

$$T = V + VGV, \quad (1.3.12)$$

where the operator $V$ denotes the coupling the donor, acceptor and the bridge states, and $G$ is the Green function of the bridge and given by

$$G(E) = \frac{1}{E - H + (1/2)\Gamma}, \quad (1.3.13)$$

with $\Gamma$ being the inverse lifetime matrix of bridge levels. Assuming the bridge states are localized in space and only the coupling between nearest neighbors exists, $T_{DA}$ can be simplified as,

$$T_{DA} = V_{DA} + V_{D1} G_{1N} V_{NA}. \quad (1.3.14)$$

Making tight-binding approximation and in the weak coupling limit, meaning $\max|V| \ll \min(E_n - E)$, where $E$ is the energy of the transmitted electrons and equal to $E_D$ and $E_A$, the Green function term $G_{1N}$ is given by

$$G_{1N}(E) = \frac{1}{E - E_N} \prod_{n=1}^{N-1} \frac{V_{n,n+1}}{E - E_n}. \quad (1.3.15)$$
In many cases, the molecule of interest consists identical bridge elements, such as alkane-chains, $E_n$ and $V_{n,n+1}$ are reduced to constants $E_B$ and $V_B$. The resulting $G_{1N}$ is now

$$G_{1N}(E) = \frac{1}{V_B} \left( \frac{V_B}{E_B-E} \right)^N.$$ (1.3.16)

In fact, $T_{DA}$ and $\sum_{i,j} T_{ij}$ in the Landauer formula 1.3.10 are related by

$$\sum_{i,j} T_{ij} (E) = 4\pi^2 \sum_{D,A} |T_{DA}|^2 \delta(E-E_D) \delta(E-E_A).$$ (1.3.17)

The first term in Equation 1.3.14 can be disregarded if we assume that $V$ couples the states $|D\rangle$ and $|A\rangle$ only via states of the molecular spacer. Therefore, $\sum_{i,j} T_{ij}$ is given by

$$\sum_{i,j} T_{ij} (E) = |G_{1N}(E_F)|^2 \Gamma^{(D)}_1(E_F) \Gamma^{(A)}_N(E_F).$$ (1.3.18)

This directly relates conductance $G$ to transition rate $w$, both of which are proportional to $|G_{1N}|^2$, given by

$$|G_{1N}(E)|^2 = \left( \frac{1}{V_B} \right)^2 \left( \frac{V_B}{E_B-E} \right)^{2N} \propto \left( \frac{E_B-E}{V_B} \right)^{-2N} = \exp \left[ -2 \alpha \ln \left( \frac{E_B-E}{V_B} \right) N \right] = \exp(-\beta d),$$ (1.3.19)

where $\alpha$ is the length of each bridge element so $d = N\alpha$ is the length of the entire bridge. So the superexchange model indicates that the electron transfer rate, or the conductance, follows an exponential decay over the distance, with the decay constant $\beta = \frac{2}{a} \ln \left( \frac{E_B-E}{V_B} \right)$. Sometimes $\beta$ is also defined as $2\ln \left( \frac{E_B-E}{V_B} \right)$ so the conductance is proportional to $\exp(-\beta N)$. $\beta$ is an important parameter which indicates the height of molecular states over the Fermi level of the electrodes. For
instance, a $\beta$ value of $\sim10$ per C-C bond for alkane-chain molecules has been experimentally found by several groups around the world(14, 47, 99).

The superexchange model discussed above is based on the assumption that the bridge states are all virtual states, meaning the electron does not reside on any of these states but tunnel directly through. On the opposite side, if the electron does occupy the bridge states, this is when phenomena such as diffusion or sequential hopping come into play and the electron transfer rate is now determined by the rate of such phenomena.(131) In this limit, the electron transfer rate is characterized by Ohm’s law. Furthermore, such process is often considered to be thermally activated with a low donor-bridge energy gap $\Delta E$. Therefore the electron transfer rate follows

$$k_{ET} \propto \frac{1}{N} \exp \left( -\frac{\Delta E}{k_BT} \right), \ (1.3.20)$$

where $N$ is the number of bridge states units. An equivalent expression is given in terms of resistance, which also takes contact resistance $R_0$ into account, given by(133)

$$R = R_0 + \alpha L \exp \left( \frac{\Delta E}{k_BT} \right), \ (1.3.21)$$

where $\alpha$ defines a prefactor unit in the resistance per unit length.

According to both Equation 1.3.20 and 1.3.21, one can see that the way to experimentally explore the thermally activated hopping mechanism for specific molecules is to examine length dependence and temperature dependence. Moreover, the transition from tunneling to hopping has attracted wide attention. The earliest attempts were made by photoinduced charge transfer kinetics
measurements(134, 135). Direct conductance measurements were carried out in molecular thin films(136) and single molecule junctions(137) only recently.

1.3.3 Current-voltage characteristics and transition voltage spectroscopy

The current-voltage characteristics are also crucial to understanding transport properties of single molecule junctions. Based on WKB approximation in quantum mechanics theory, Simmons(138) developed a model for the current-voltage behavior of a direct tunneling process through an arbitrary tunnel barrier, which is given by

\[
I = \frac{qA}{4\pi^2h^2d^2} \left\{ \left( \phi - \frac{qV}{2} \right) \exp \left( - \frac{2d\sqrt{2m_e}}{\hbar} \sqrt{\phi - \frac{qV}{2}} \right) - \left( \phi + \frac{qV}{2} \right) \exp \left( - \frac{2d\sqrt{2m_e}}{\hbar} \sqrt{\phi + \frac{qV}{2}} \right) \right\}, \quad (1.3.22)
\]

where \( A \) is the junction area, \( d \) is the barrier width, \( m_e \) is the electron effective mass, \( \phi \) is the barrier height, and \( q \) is the electronic charge. By fitting the measured current-voltage curve of single molecule junction to this model, the tunnel barrier height can be estimated(14).

Based on Simmons model, Beebe et al(139) developed a technique that can quickly estimate the tunnel barrier height without doing the fitting. In the zero bias limit, Equation 1.3.22 reduces to

\[
I \propto V \exp \left( - \frac{2d\sqrt{2m_e}\phi}{\hbar} \right). \quad (1.3.23)
\]

In the large bias limit,

\[
I \propto V^2 \exp \left( - \frac{4d\sqrt{2m_e}\phi}{3hqV} \right). \quad (1.3.24)
\]
Converting both equations in terms of the variables $\ln(I/V^2)$ and $1/V$, we obtain
\[
\ln(I/V^2) \propto \ln(1/V) - \frac{2d\sqrt{2m_e\phi}}{\hbar} \quad \text{and} \quad \ln(I/V^2) \propto -\frac{4d\sqrt{2m_e\phi^3}}{3\hbar q} (1/V), \quad (1.3.25)
\]
for zero bias and high bias limits, respectively. Therefore, when plotting measured current-voltage curves in terms of the variables $\ln(I/V^2)$ and $1/V$, a minimum can be found and the corresponding voltage is a good approximation of the tunnel barrier height (Fig. 1.4). This voltage is referred as transition voltage and the method is called transition voltage spectroscopy (TVS). In fact, such plot is often used in solid state junctions to study the transition from tunneling to field emission, named Fowler-Nordheim plot. The energy barrier shape changes from trapezoidal to triangular at the transition voltage, which causes the nonlinearity in high bias range.

![Graph](image)

**Fig. 1.4** Transition voltage spectroscopy of Au-anthracenethiol-Au junctions.

The self assembled monolayer junction was measured by conducting probe
atomic force microscope (CP-AFM). The solid curve in the inset represents the average of 100 I-V curves measured. The dashed line marks out the minimum point in the transition voltage spectroscopy plot.

Transition voltage spectroscopy has been popular in interpreting current-voltage data recently (140-142). In Chapter 3 of this report, this technique will also be used to in large quantities of single molecule I-V curves.

1.4 Implementation of radio frequency circuits in STM systems

1.4.1 Basic concepts of radio frequency circuits

Broadly speaking, radio frequency (RF) refers to alternating electric current with a frequency that covers the spectrum from 3 kHz from 300 GHz. In particular, however, radio frequency technology deals with signals with frequencies typically in the megahertz to gigahertz range. In this range, the wavelength of the electric signals is smaller than the length of the transmission cables, and therefore all signals transmitted have to be considered as waves that obey the basic electromagnetic theory. Radio frequency technology is widely used in wireless communication because the energy of an RF signal can radiate off a conductor into space, through air or dielectric insulators, and be collected also by a conductor into electric circuits. When carefully tuned, the RF signal is also able to travel very long distance in specialized cables with very low loss.

Maximum Power Transfer Theorem and Impedance Matching

One of the basic requirements of RF technology is to maximize the power transfer or minimize reflections from the load. To do this, the impedance
matching technique is used to make the load impedance equal to the complex conjugate of the source impedance,

\[ Z_{\text{load}} = Z_{\text{source}}^* \] (1.4.1)

The power transfer efficiency achieves a maximum percentage of 50\% in this case. In the presence of reactive components, the resulting simple matching network usually only achieve a perfect match at a single frequency because the added capacitors or inductors are frequency dependent. A wide bandwidth application usually involves more complicated matching network and needs to be carefully designed. The following L-network matching (Fig. 1.5) is one of the most commonly used matching networks due to its simplicity(143).

The source impedance is represented as a resistive component \( R_S \) in series with a reactive component \( X_S \), while the load impedance is represented as a resistive component \( R_L \) in parallel with a reactive component \( X_L \). Obviously, \( jX_L//R_L \) has to have resistive component \( R_S \) and reactive component \(-X_S\) to satisfy Equation 1.4.1.

![Fig. 1.5 L-matching network.](image)

After simple math, one finds
\[ R_S = \frac{X_L R_L}{R_L^2 + X_L^2} \text{ and } X_S = -\frac{X_L R^2}{R_L^2 + X_L^2}. \] (1.4.2)

Note that if \( X_L \) is capacitive, the L-network behaves as a low-pass filter and as a high-pass filter if \( X_L \) is inductive. The choice depends on concerns in other frequency range than the designated matching frequency.

There are other types of matching networks such as \( \pi \)- and T-networks, which are all based on the same principle. Due to different configuration, the network can behave as band-pass filter or other types of filters in terms of its frequency response. More complicated matching network can be done by using the Smith Chart, which will be discussed in below.

The RF and microwave industry uses a 50 \( \Omega \) (75 \( \Omega \) in some cases such as CATV) impedance as the standard impedance that every other piece of equipment has to be matched to. This value originates from the development of coaxial cable in early days, and is a compromise between power handling and signal loss per unit length of coaxial cable for air dielectric.

**Transmission Line Model**

![Equivalent circuit model used in the transmission line theory.](image)

**Fig. 1.6** Equivalent circuit model used in the transmission line theory.
Coaxial cables are widely used in RF and microwave signal transmission. Unlike in low frequency applications, they cannot be treated as simple conduction wires shielded from external noise but transmission lines(143). Using a lumped component model (Fig. 1.6), for every small piece of coaxial cable $\Delta z$, by applying Kirchhoff's voltage and current law and in the limit of $\Delta z \to 0$, we obtain two equations for AC current $i$ and voltage $v$, given by

$$\frac{\partial v}{\partial z} = -L \frac{\partial i}{\partial t} \quad \text{and} \quad \frac{\partial i}{\partial z} = -C \frac{\partial v}{\partial t}, \quad (1.4.3)$$

where $L$ and $C$ are the inductance and capacitance per unit length and can be calculated if the permittivity $\varepsilon$, permeability $\mu$ and the geometric parameters of the cable are known. Equations 1.4.3 give rise to two wave equations

$$\frac{1}{c^2} \frac{\partial^2 v}{\partial t^2} - \frac{\partial^2 v}{\partial z^2} = 0 \quad \text{and} \quad \frac{1}{c^2} \frac{\partial^2 i}{\partial t^2} - \frac{\partial^2 i}{\partial z^2} = 0, \quad (1.4.4)$$

where $c = 1/\sqrt{LC}$ is the propagation speed. Equation 1.4.4 indicates that the voltage and current will behave as combinations of waves traveling in the negative and positive $z$ directions, $v_+$ and $v_-$ for voltage and $i_+$ and $i_-$ for current.

Equation 1.4.3 yields

$$\frac{\partial v_\pm}{\partial z} = \pm cL \frac{\partial i_\pm}{\partial z}, \quad (1.4.5)$$

and therefore

$$v_\pm = \pm Z_0 i_\pm, \quad (1.4.6)$$

where $Z_0 = \sqrt{L/C}$ is defined as the characteristic impedance of the transmission line, normally 50 Ω as mentioned above.
For the propagation of harmonic waves on a transmission line with length of \( l \) with load impedance \( Z_L \) (Fig. 1.7), using Equation 1.4.6, one finds the voltage and current amplitudes along the transmission line given by

\[
V(z) = V^+(z) + V^-(z) \quad \text{and} \quad \phi(z) = I^+(z) - I^-(z), \quad (1.4.7)
\]

where \( V^+(z), V^-(z), I^+(z) \) and \( I^-(z) \) are the voltage and current waves that are travelling in the positive and negative \( z \) direction, respectively. The current is thus given by

\[
I(z) = \frac{1}{Z_0} \left( V^+(z) - V^-(z) \right). \quad (1.4.8)
\]

Since the load impedance is given by \( Z_L = V(I)/I(I) \), one further obtains

\[
V^-(l) = \frac{Z_L - Z_0}{Z_L + Z_0} V^+(l). \quad (1.4.9)
\]

If one defines the reflection coefficient as \( \Gamma(z) = V^-(z)/V^+(z) \), one finds

\[
\Gamma(l) = \frac{Z_L - Z_0}{Z_L + Z_0} = \frac{z^{-1}}{z + 1}. \quad (1.4.10)
\]

where \( z \) is the normalized impedance \( z = Z/Z_0 \).

It can be seen that when \( Z_L = Z_0 \), reflection of zero is achieved, which is consistent with the above maximum power transfer argument.

![Fig. 1.7 A transmission line terminated by a load impedance.](image-url)
One can further find that the impedance looking into the line at \( z = 0 \) is given by
\[
Z_{\text{in}} = \frac{V(0)}{I(0)} = \frac{Z_L \cos \beta l + jZ_0 \sin \beta l}{Z_0 \cos \beta l + jZ_L \sin \beta l} Z_0, \quad (1.4.11)
\]
where \( \beta \) is the propagation constant \( \beta = \omega \sqrt{L/C} \). This is a very important equation when analyzing circuits in which transmission lines are involved. It can also be applied to transforming the impedance values when designing RF circuits simply using microstrip lines, such as the \( \lambda/4 \) transformer(143).

**The Smith chart(144)**

For complex \( \Gamma = U + jV \) and \( z = r + jx \), one can separate the real part from the imaginary part of Equation 1.4.10 and obtain
\[
U = \frac{r^2 - 1 + x^2}{(r+1)^2 + x^2} \quad \text{and} \quad U = \frac{2x}{(r+1)^2 + x^2}, \quad (1.4.12)
\]
Eliminating \( x \) and \( r \) from Equation 1.4.12 respectively results in two circular equations
\[
\left( U - \frac{r}{r+1} \right)^2 + V^2 = \left( \frac{1}{r+1} \right)^2 \quad \text{and} \quad (U - 1)^2 + \left( V - \frac{1}{x} \right)^2 = \left( \frac{1}{x} \right)^2. \quad (1.4.13)
\]
Equation 1.4.13 gives rise to constant resistance and reactance circles on the \( UV \) plane (or the \( \Gamma \) plane). A chart with such circles is the impedance (\( Z \)) Smith chart (Fig. 1.8a and black grids in Fig. 1.8b).

A similar derivation leads to the admittance (\( Y \)) Smith chart (red grids in Fig. 1.8b). Both Smith charts can be combined into the \( ZY \) Smith chart (Fig. 1.8b), which is extremely useful in various aspects of radio frequency circuit design, such as impedance matching, power gain design, stability and noise analysis.
Fig. 1.8 Examples of Smith chart. (a) A Z Smith chart with constant resistance and reactance circles (courtesy of Agilent.com). (b) A ZY Smith chart (courtesy of ece.queensu.ca).

S parameters

Based on the concept of reflection coefficients, the scattering matrix ($S$ matrix) can be used to describe RF circuits as two-port (or higher) networks. Fig. 1.9 shows the $S$ matrix and $Z$ matrix description of two-port network. The $S$ matrix is defined as

$$V^- = SV^+, \quad (1.4.14)$$

where

$$V^\pm = \begin{pmatrix} V_1^\pm \\ V_2^\pm \end{pmatrix}. \quad (1.4.15)$$

Similarly, the $Z$ matrix relates the total voltage and current by

$$V = ZI, \quad (1.4.16)$$
where

\[ V = \begin{pmatrix} V_1 \\ V_2 \end{pmatrix} = V^+ + V^- \quad \text{and} \quad \begin{pmatrix} I_1 \\ I_2 \end{pmatrix} = I^+ + I^- = (V^+ - V^-)/Z_0 . \quad (1.4.17) \]

The \( Z \) and \( S \) matrix can thus be related through

\[ S = (Z + Z_0 I)^{-1}(Z - Z_0 I) . \quad (1.4.18) \]

**Fig. 1.9** The \( S \) matrix and \( Z \) matrix representation of two-port network. (Left) \( S \) matrix. (Right) \( Z \) matrix.

The \( S \) matrix has been widely used in RF circuit designs and is the basics of a lot of advanced CAD software such as ADS from Agilent.

### 1.4.2 General RF amplifier design

The most important concerns when designing an RF amplifier are the power gain, stability and noise.

**The power gain equation**

The transducer power gain \( G_T \) is the most commonly used, which is defined as

\[ G_T = \frac{\text{power delivered to load}}{\text{power available from source}} . \quad (1.4.19) \]

For a general RF amplifier with source and load (Fig. 1.10), using the \( S \) matrix defined in Equation 1.4.14, one obtains the power gain equation as

\[ G_T = \frac{1-|\Gamma_L|^2}{|1-\Gamma_{in}\Gamma_S|^2} |S_{21}|^2 \frac{1-|\Gamma_L|^2}{|1-\Gamma_{22}\Gamma_L|^2} \quad \text{or} \quad G_T = \frac{1-|\Gamma_L|^2}{|1-\Gamma_{11}\Gamma_S|^2} |S_{21}|^2 \frac{1-|\Gamma_L|^2}{|1-\Gamma_{out}\Gamma_L|^2} . \quad (1.4.20) \]
where
\[
\Gamma_{\text{in}} = S_{11} + \frac{S_{12}S_{21}\Gamma_{L}}{1-S_{22}\Gamma_{L}} \quad \text{and} \quad \Gamma_{\text{out}} = S_{22} + \frac{S_{12}S_{21}\Gamma_{S}}{1-S_{11}\Gamma_{S}}, \quad (1.4.21)
\]
are the reflection coefficients seen into the input and output ports of the amplifier, respectively.

**Fig. 1.10** The diagram of a general two-port amplifier connected to a source and a load.

For simplicity and practical cases, the network is assumed to be unilateral, that is, when \( S_{12} = 0 \), Equation 1.4.20 is now the unilateral transducer power gain, given by
\[
G_{TU} = \frac{1-|\Gamma_{S}|^2}{|1-S_{11}\Gamma_{S}|^2}|S_{21}|^2 \quad \text{and} \quad G_{L} = \frac{1-|\Gamma_{L}|^2}{|1-S_{22}\Gamma_{L}|^2}. \quad (1.4.22)
\]
If one defines \( G_{TU} = G_{S}G_{0}G_{L} \), one gets
\[
G_{S} = \frac{1-|\Gamma_{S}|^2}{|1-S_{11}\Gamma_{S}|^2}, \quad G_{0} = |S_{21}|^2 \quad \text{and} \quad G_{L} = \frac{1-|\Gamma_{L}|^2}{|1-S_{22}\Gamma_{L}|^2}. \quad (1.4.23)
\]
It is obvious that only by optimizing \( G_{S} \) and \( G_{L} \), can one obtain maximum unilateral transducer power gain, denoted as \( G_{TU,\text{max}} \). It turns out that when \( \Gamma_{S} = S_{11}^* \) and \( \Gamma_{L} = S_{22}^* \), (1.4.24)

one obtains
\[
G_{TU,\text{max}} = \frac{1}{1-|S_{11}|^2}|S_{21}|^2 \frac{1}{1-|S_{22}|^2}. \quad (1.4.25)
\]
Stability concerns

The unconditional stability of the two-port network shown in Fig. 1.10 at a designated frequency in terms of reflection coefficients requires

\[ |\Gamma_S| < 1, |\Gamma_L| < 1, |\Gamma_{in}| = \left| S_{11} + \frac{s_{12}s_{21}\Gamma_L}{1-s_{22}\Gamma_L}\right| < 1 \text{ and } |\Gamma_{out}| = \left| S_{22} + \frac{s_{12}s_{21}\Gamma_S}{1-s_{11}\Gamma_S}\right| < 1. \]  

(1.4.26)

One can use the Smith chart to plot the circle centered at origin and of a radius of 1 for \( |\Gamma_S| = 1 \) and \( |\Gamma_L| = 1 \). The circles for \( |\Gamma_{in}| = 1 \) and \( |\Gamma_{out}| = 1 \) can also be plotted in terms of \( \Gamma_S \) and \( \Gamma_L \) (normally referred as the \( \Gamma_S \) and \( \Gamma_L \) plane)

respectively. By manipulating Equation 1.4.26, one obtains

\[ \left| \Gamma_S - \frac{(S_{11}-\Delta S_{22})^*}{|S_{11}|^2-|\Delta|^2} \right| = \left| \frac{S_{12}S_{21}}{|S_{11}|^2-|\Delta|^2} \right| \text{ and } \left| \Gamma_L - \frac{(S_{22}-\Delta S_{12})^*}{|S_{22}|^2-|\Delta|^2} \right| = \left| \frac{S_{12}S_{21}}{|S_{22}|^2-|\Delta|^2} \right|. \]  

(1.4.27)

where \( \Delta = S_{11}S_{22} - S_{12}S_{21} \).

Whether the outside or the inside area of these circles is the stable region is determined by \( |S_{11}| \) and \( |S_{22}| \), which follows Fig. 1.11. Note that when there is no overlap between the circles, there can be no unconditionally stable configurations for the circuits in Fig. 1.11b and 1.11b.

Analytically, a lengthy derivation from Equation 1.4.27 results in the following necessary and sufficient conditions for unconditional stability:

\[ K = \frac{1+|\Delta|^2-|S_{11}|^2-|S_{22}|^2}{2|S_{12}S_{21}|} > 1 \text{ and } |\Delta| = |S_{11}S_{22} - S_{12}S_{21}| < 1. \]  

(1.4.28)
Fig. 1.11  Unconditional stability circles. The areas of unconditional stability (a, b) for source and (c, d) for load.

**Constant power gain circles**

For unilateral case, from Equation 1.4.23, the normalized gain factor for the source, denoted by $g_S$, can be defined as

$$g_S = \frac{g_S}{g_{S,\text{max}}} = G_S(1 - |S_{11}|^2). \ (1.4.29)$$

Let $\Gamma_S = U_S + jV_S$ and $S_{11} = A_{11} + jB_{11}$. One obtains

$$
\left[U_S - \frac{g_{SA_{11}}}{1-|S_{11}|^2(1-g_S)}\right]^2 + \left[V_S - \frac{g_{SB_{11}}}{1-|S_{11}|^2(1-g_S)}\right]^2 = \left[\frac{\sqrt{1-g_S}(1-|S_{11}|^2)}{1-|S_{11}|^2(1-g_S)}\right]^2, \ (1.4.30)
$$
which leads to a family of constant power gain circles on the $\Gamma_S$ plane on the Smith chart with $g_S$ as a parameter.

Similarly, one obtains a family of constant power gain circles on the $\Gamma_L$ plane on the Smith chart, given by

$$
\left[ U_L - \frac{g_L A_{22}}{1-|S_{22}|^2(1-g_L)} \right]^2 + \left[ V_L - \frac{g_L B_{22}}{1-|S_{22}|^2(1-g_L)} \right]^2 = \left[ \frac{\sqrt{1-g_L(1-|S_{22}|^2)}}{1-|S_{22}|^2(1-g_L)} \right]^2,
$$

where $g_L = \frac{G_L}{G_{L,\text{max}}} = G_L (1 - |S_{22}|^2)$ is the normalized gain factor for load,

$\Gamma_L = U_L + jV_L$ and $S_{22} = A_{22} + jB_{22}$. For bilateral case where $S_{12}$ cannot be neglected, bilateral transducer power gain equation has to be used:

$$
G_T = \frac{1-|\Gamma_S|^2}{|1-\Gamma_{in}\Gamma_S|^2} |S_{21}|^2 \frac{1-|\Gamma_L|^2}{|1-S_{22}\Gamma_L|^2} = G'_S G_0 G_L,
$$

where $G'_S = \frac{1-|\Gamma_S|^2}{|1-\Gamma_{in}\Gamma_S|^2}$, and $G_0$ and $G_L$ are the same as in Equation 1.4.23.

The maximum transducer power gain requires simultaneous conjugate match, meaning

$\Gamma_{in} = \Gamma_S^*$ and $\Gamma_{out} = \Gamma_L^*$.

The optimal configuration is generally difficult to get. A practical procedure, however, starts with the $G_L$ constant power gain circles in Equation 1.4.31. The desired $\Gamma_L$ and $G_L$ can be selected, and $\Gamma_{in}$ as well as $G'_S$ can thus be calculated using Equation 1.4.32.

By replacing $S_{11}$ with $\Gamma_{in}$, the $G'_S$ circles are then plotted using Equation 1.4.30 so that $\Gamma_S$ can be decided for a given $G'_S$. $\Gamma_L$ needs to be selected over and over if the $G'_S$ value is not satisfactory.

Constant noise figure circles
The noise figure \((NF)\) describes the noise performance of an RF amplifier. It is defined as the ratio of the signal to noise power ratio at the input and that at the output, given as

\[
NF = \frac{PS/PNI}{PSO/PSo} \quad (1.4.34)
\]

The noise figure analysis of a general two-port amplifier leads to the following expression for constant noise figure circles on the \(\Gamma_s\) plane:

\[
\left| \Gamma_s - \frac{\Gamma_0}{1+N_l} \right|^2 = \frac{N_l^2+N_l(1-|\Gamma_0|^2)}{(1+N_l)^2} \quad (1.4.35)
\]

where \(\Gamma_0\) is the source reflection coefficient that results in minimum noise figure \(NF_{min}\). \(N_l\) is a parameter defined by

\[
N_l = \frac{|\Gamma_s-\Gamma_0|^2}{1-|\Gamma_s|^2} \quad (1.4.36)
\]

**General RF amplifier design using the Smith chart**

As discussed above, the areas of unconditional stability for source and load, constant power gain circles and constant noise figure circles can all be plotted on the \(\Gamma\) plane of the Smith chart. The circuit design now becomes basically looking for an operating point on the Smith chart that is in the area of unconditional stability, with an optimal combination of high power gain and low noise figure. The matching network circuits are then designed using the corresponding reflection coefficients obtained at this point.

**1.4.3 Radio frequency circuit implementation in STM**

There have been several attempts in the literature of implementing RF circuits into the conventional STM system. In 2006, Kemiktarak et al.(145) developed an RF-STM system based on impedance transform discussed above.
By feeding RF power into the system and measuring change in the power reflected from the impedance between the tip and the substrate (Fig. 1.12a), the displacement between the tip and the substrate can be precisely controlled and maintained constant during imaging (Fig. 1.12d). In this system, the RF portion of the circuit is couple to the conventional system through a bias-T circuit (or an L-C tank circuit) closely placed to the tip. The bias-T circuit consist a capacitor and an inductor with the resonance frequency at 115MHz (Fig. 1.12c inset). The RF power is input into the system by a directional coupler and the output RF power is amplified by an RF amplifier. This application enhances the sensitivity of conventional STM due to the increase of its operation frequency. However, the calibration curve of the reflection coefficient $\Gamma$ as a function of the tunnel junction resistance $R_T$ in Fig. 1.12c shows that the effective range of this RF-STM is limited to $\sim 0.2$-$2$ M$\Omega$. This limits its capability of studying structures with large resistance, such as single molecule junctions. Furthermore, the fastest detectable tunnel impedance change is on the order of 10 MHz, which also limits its capability of studying various interesting ultra fast events – such as atomic rearrangement and chemical bond breaking and forming.
Fig. 1.12 Radio frequency scanning tunneling microscope. (a) The schematics of the radio frequency STM setup. (b) Calibration curve of the reflection coefficient of the entire system as a function of tunnel resistance. (inset) Calibration curve of the tank circuit. (c) STM image acquired using low frequency circuit. (d) STM image acquired using RF setup.

Another attempt was done by Messina et al at Argonne National Laboratory in 2009 (146). In this system, a bias-T circuit closed placed to the tip is also used to integrate the AC part of the circuit with the conventional DC circuit. Different from the previous system, instead of inputting RF power into the system and measuring the reflected power, this particular system aim to measure directly
the fluctuations in the tip-substrate resistance. Three stages of high gain wide band RF amplifiers are carefully designed and stacked onto the AC output. The bandwidth of this system can reach as high as GHz, making it possible to measure phenomena that take place in the time scale of nanoseconds.

In 2010, a similar measurement approach using MCBJ setup was also applied to the study of shot noise suppression in gold quantum point contact at room temperature using MCBJ by Wheeler et al (147). A lock-in amplifier was employed to measurement average wide band power over a time scale of milliseconds. The shot noise suppression in gold quantum point contact has been studied before under cryogenic ultra-low noise condition before by Ruitenbeek and colleagues (148) using low frequency circuits. The significant increase in operation frequency reduces the contribution from 1/f noise and other noise sources dramatically. This greatly enhances the signal to noise ratio, making possible the room temperature measurement that will otherwise be very difficult using low frequency circuits.

In Chapter 2 of this report, a transient measurement of the breakdown process of the gold quantum point contact using RF approach will be discussed. Interesting nanosecond scale phenomena – such as bond breakdown and reforming, atomic rearrangement – can be seen. And also an upper limit of the time scale of gold quantum point contact breakdown process is pinned down at 0.1 ns.
1.5 Thermoelectric effects in molecular junctions

1.5.1 The thermoelectric effect and the Seebeck coefficient

The thermoelectric effect, also referred as the Seebeck effect, is the effect of electric voltage developed due to thermal gradient in the materials. It was first discovered by Seebeck. The reverse effect, commonly referred as the Peltier effect, also exists, in which a charge current induces temperature gradient in the materials. Such effects are the basics behind most commonly seen devices such as thermocouple thermometer and semiconductor heater or cooler.

The Seebeck coefficient \( S \) is a measure of the temperature to voltage conversion efficiency, which is defined as in

\[
\Delta V = V_2 - V_1 = \int_{T_1}^{T_2} -S(T) \,dT, \quad (1.5.1)
\]

where \( S \) is generally a function of absolute temperature. However, within small temperature difference \( \Delta T = T_2 - T_1 \), \( S \) is normally treated as a constant, given by

\[
S = -\frac{\Delta V}{\Delta T}, \quad (1.5.2)
\]

In real applications (e.g. the thermocouple in Fig. 1.13a), several materials are used in the circuit that connects the inputs of the voltage meter that measures the thermoelectric voltage. A general form of the voltage measured is given by

\[
V = \sum_i \int_{T_{i1}}^{T_{i2}} -S_i(T) \,dT, \quad (1.5.3)
\]

where \( T_{i2} \) and \( T_{i1} \) are the temperatures applied to material \( i \) and \( S_i \) is its Seebeck coefficient.
Fig. 1.13 Thermoelectric devices. (a) Typical schematic of a thermocouple. Several materials can be used to form the entire circuit. (b) A simplified scenario of thermoelectric voltage measurement. (courtesy of efunda.com and Wikipedia)

In the simplest scenario, only two materials $A$ and $B$ and two temperatures $T_1$ and $T_2$ are present (Fig. 1.13b). When $T_2 - T_1$ is small, the voltage measured is given by,

$$V = (S_B - S_A) \cdot (T_2 - T_1). \ (1.5.4)$$

It can be seen that materials with different Seebeck coefficient have to be used in order for a measurable voltage seen by the meter.

1.5.2 Mechanisms of thermoelectric energy conversion devices

The thermoelectric voltage is basically due to accumulation of charge carriers moving from one side of the material to the other. In bulk materials, this is either caused by charge carriers diffusion or phonon drag. Both the charge carriers and the phonons in the materials will diffuse or move along the thermal
gradient. The diffusion of charge carriers results directly in the generation of electric field. And the phonons tends to push electrons by losing momentum along the way of their moving, which causes an electric field too and is especially significant in the temperature region where phonon-electron scattering is predominant.

A typical example of utilizing charge carrier diffusion is the thermocouples made of semiconductor junctions (Fig. 1.14), which are commonly seen in power generation devices nowadays. A thermal gradient is applied between the metallic interconnect in the center of the junction and the metal contacts at the ends. Due to the different types of major charge carriers in n-type and p-type elements, the thermoelectric current flows through the n-type element in the opposite direction of the electron diffusion, crosses the metallic interconnect, and passes into the p-type element in the same direction of the hole diffusion and thus provides power to the external circuit (Fig. 1.14a). On the other hand, if an external power source is provided, the thermoelectric device may act as a cooler (Fig. 1.14b). This is the Peltier effect as described above. Electrons in the n-type element will move opposite the direction of current and holes in the p-type element will move in the direction of current, both removing heat from one side of the device.
1.5.3 Thermoelectric effect in molecular junctions

In molecular junctions, the charge carriers also move along the thermal gradient. Differently from bulk materials, instead of diffusion, the charges transport through the junction either via tunnel or thermally activated hopping depending on the transport mechanism of the molecule as discussed above. Also depending on the alignment of molecular energy levels and electrode Fermi energy, the charge carriers can be electrons for LUMO dominated transport or holes for HOMO dominated transport. Fig. illustrates the two scenarios. For LUMO dominated transport, due to higher transmission probability of the electrons, more electrons transport from the hot side to the cold side than holes, resulting in a net negative thermoelectric current or higher electric potential on the
hot side (Fig. 1.15a). Similarly for HOMO dominated transport, a net positive current flows from the hot side to the cold side, leading to higher electric potential on the cold side (Fig. 1.15b).

![Energy diagrams of thermoelectric effect in molecular junctions with direct tunneling transport.](image)

**Fig. 1.15** Energy diagrams of thermoelectric effect in molecular junctions with direct tunneling transport. (a) LUMO dominated. (b) HOMO dominated.

In a simplified theory model, such effect can be analytically seen by deriving from Landauer formula. For LUMO transport, the Landauer formula is given by

\[
I_{H\to C} = -\frac{|e|}{\pi \hbar} \int_{-\infty}^{\infty} \tau(\varepsilon)[f_H(\varepsilon, \mu_H, T_H) - f_C(\varepsilon, \mu_C, T_C)]d\varepsilon . \tag{1.5.5}
\]
For HOMO transport, note that $1 - f$ instead of $f$ should be used for holes, which gives rise to

$$I_{H \rightarrow C} = \left| e \right| \pi h \int_{-\infty}^{\infty} \tau(\epsilon)[(1 - f_H(\epsilon, \mu_H, T_H)) - (1 - f_C(\epsilon, \mu_C, T_C))] d\epsilon. \quad (1.5.6)$$

After simplification, this results in the exact same expression as Equation 1.5.5.

When applying Taylor’s expansion to the Fermi function like equation with respect to temperature, one obtains the Sommerfield Expansion given by

$$\int_{-\infty}^{\infty} \frac{H(\epsilon)}{e^{\beta(\epsilon - \mu)} + 1} d\epsilon = \int_{-\infty}^{\mu} H(\epsilon)d\epsilon + \frac{\pi^2}{6} \left( \frac{1}{\beta} \right)^2 H'(\mu) + O\left( \frac{1}{\beta^4} \right). \quad (1.5.7)$$

Applying this to Equation 1.5.5, and assuming low bias difference, one obtains

$$I_{H \rightarrow C} \approx \frac{|e|^2}{\pi h} \tau(E_f) \Delta V - \frac{|e|^2 k_B^2 T}{3} \frac{\partial \tau(\epsilon)}{\partial \epsilon} \bigg|_{\epsilon = E_f} \Delta T, \quad (1.5.8)$$

where $\Delta V = V_H - V_C = -\frac{\mu_H - \mu_C}{|e|}$, $\Delta T = T_H - T_C$ and $T = \frac{1}{2} (T_H + T_C)$. Note that small bias and temperature difference applies to the above approximation. Now,

$$\Delta V\bigg|_{H \rightarrow C = 0} = \frac{\pi^2 k_B^2 T}{3|e|} \frac{\partial \ln(\tau(E))}{\partial E} \bigg|_{E=E_f} \Delta T. \quad (1.5.9)$$

And thus,

$$S_{\text{junction}} = -\frac{\Delta V}{\Delta T} = -\frac{\pi^2 k_B^2 T}{3|e|} \frac{\partial \ln(\tau(E))}{\partial E} \bigg|_{E=E_f}. \quad (1.5.10)$$

In simplified models, the transmission peaks (namely, HOMO and LUMO peaks) are normally fitted by Lorentzian distributions (Fig. 1.16). This indicates that the alignment between the molecular energy level and the electrode Fermi
level determines not only the sign but also the magnitude of the Seebeck coefficient.

![Logarithmic plot of the transmission as a function of energy.](image)

**Fig. 1.16** Logarithmic plot of the transmission as a function of energy. Thin solid and dash lines represent the transmission calculated from the Extended Hückel model through the 1,4-bezenedithiol molecule strong and weakly bound to both electrodes, respectively. Thick solid and dash lines represent the Lorentzian distribution fitting. The position of Fermi energy $E_f$ determines the sign and magnitude of the thermopower $S_{junction}$. (149)

The thermoelectricity in molecular monolayer was firstly measured by Majumdar and colleagues in 2007 (150). A combination of DC current preamplifier and voltage amplifier is used in an STM break junction setup to fulfill the measurement (Fig. 1.17a). The measurement is carried out in ambient condition. The current preamplifier is used to monitor the current when the cold tip is being approached toward the heated substrate functionalized with molecules of interest (e.g. 1,4-benzenedithiol). Once the tip-substrate conductance reaches a set point where the tip is close enough to the substrate to form molecular junctions,
the tip is retracted, the bias is turned off and the circuit is switched to the voltage amplifier at the same time. Therefore, the thermoelectric voltage can be measured (Fig. 1.17b-c). Note that the gold electrodes are involved in the measurement. Similarly to Equation 1.5.4, the Seebeck coefficient of the molecular junctions can be extracted by using

$$S_{\text{junction}} = S_{\text{Au}} - \frac{\Delta V_{\text{measured}}}{\Delta T_{\text{applied}}}, \quad (1.5.11)$$

where the Seebeck coefficient of bulk gold is used for $S_{\text{Au}}$.

**Fig. 1.17** Experimental setup and results of thermoelectric voltage measurement of molecule junctions. (a) Experimental setup based on STM-BJ system. (b) Typical thermoelectric voltage traces during tip retracting process at different temperature gradients. (c) Statistical results of measured thermoelectric voltage at different temperature gradients.

The same group also studied the effect of electron-withdrawing and donating groups on the thermopower by measuring benzenedithiol derivatives monolayer(151). It is proposed that the difference in the thermopower is due to the shift of the HOMO and LUMO levels with respect to the electrode Fermi level.
The voltage amplifier approach directly measures the thermoelectric voltage and provides a more straightforward method of calculating the Seebeck coefficient. However, detailed information is not included such as the number of molecules bridged between the electrodes and correlation between the Seebeck coefficient and molecular conductance. Vankataraman and colleagues measured the single molecule thermopower by direct current measurement in an STM break junction setup in ambient condition (Fig. 1.18a). Conventional single molecule conductance measurement is performed to determine the conductance range of the molecule first (Fig. 1.18b). Then when measuring the thermopower, the cold tip is approached to the heated substrate functionalized with target molecules until close enough to form molecular junctions and then retracted by a predefined distance. The tip is then held stationary for a certain period of time during which the bias is turned off and back on. The current of such process is measured using an electrometer. The bias-on portion of the current provides conductance and the bias-off portion measures the thermoelectric current (Fig. 1.18c-e). By comparing such measured conductance with the value measured in single molecule conductance measurement (Fig. 1.18f), the data with conductance in the range is selected and its corresponding thermoelectric current is used to extract the Seebeck coefficient using Equation 1.5.11 (Fig. 1.18g).
**Fig. 1.18** Experiment setup and results of thermoelectric current measurement of single molecule junctions. (a) Diagram of setup. (b) Conventional conductance measurement using STM-BJ technique. (c-e) Thermoelectric current measurement procedure. (f) Measured conductance. (g) Measured thermoelectric current.

Such current measurement approach to some extend allows simultaneous measurement of single molecule conductance and thermopower. However, the tip retraction of a predefined constant distance annihilates the signature of bridging of the single molecule between the electrodes, namely, the steps in the current traces. Even though careful data selection is carried out in the post-processing, there’s no direct evidence of such measured conductance corresponding to single molecule junctions. In Chapter 4 of this thesis, an alternative approach based on the rapid I-V curve measurement method will be discussed.
2 BREAKDOWN OF ATOMIC-SIZED METALLIC CONTACTS
MEASURED ON NANOSECOND-SCALE

2.1 Introduction

Studying electron transport in nanoscale-structures and devices, including
atomic point contacts(125) and molecular junctions(22, 24), is critical for
understanding many fundamental phenomena and developing potential device
applications. Electron transport measurements to date are limited to relatively
slow time scales (mili- to micro-seconds). Extending the measurements to faster
time scales will open the door to the study of atomic scale structural
rearrangement, molecular conformational changes, charge transfer, and many
other fast processes in nanostructures.(153) An important example is the
mechanical breakdown process of an atomic sized contact created by pulling two
electrodes in contact apart. It has been shown that during the last stage of pulling
a neck-shaped wire connects the two electrodes, and the diameter of the wire
reduces to a single atom before breakdown.(154-156) The conductance of the
contact recorded during the breakdown process decreases in a stepwise fashion,
and the steps for metals, such as gold, are multiples of the conductance quantum,
G0=2e2/h, where e is the electron charge and h is the Planck constant. The
formation and breakdown of atomic scale contacts have been predicted and
modeled by molecular dynamic simulations.(157, 158) However, the time scales
in first-principle simulations are typically limited to picosecond or nanosecond
time scales due to computational constraints, in contrast to μs-ms time scales that
typical experiments can measure. Fast transport measurements are needed to
bridge the wide time gap between the simulations and real world experiments, but building an electronic circuit with a broad frequency bandwidth to cover fast physical processes has been a difficult task. In this chapter, we report on a study of atomic scale contacts with nanosecond time resolution. (145)

2.2 Method and circuit design and analysis

We overcome the experimental difficulties of measuring fast processes by developing a circuit including a conventional DC current amplifier and an AC-coupled GHz amplifier inspired by literature (145, 146) (Fig. 2.1). The DC amplifier measures slow processes, which allows us to compare the results with previous studies, and the AC-coupled amplifier probes fast transient processes that cannot be measured by the DC amplifier. The separation of the DC and AC components of the signal from an atomic sized contact formed with a scanning tunneling microscope (STM) break junction is achieved by using an LC network consisting of an inductor and a capacitor, commonly referred to as a “bias-T” in microwave terminology. The inductor feeds the low frequency components of the current signal into a DC current amplifier and the capacitor couples the AC component to a radio frequency (RF) amplifier. Due to the large ratio of the single atom contact resistance (1/G0 ~12.9 kΩ) to the standard characteristic impedance (50 Ω) used in RF systems, the AC current coupled to the RF circuit is small. To overcome this difficulty, we have built three RF amplification stages to increase the gain of the circuit in order to measure the small AC current occurring at high frequencies. Previous studies on quantum point contacts at RF frequencies have focused on measuring the average power in the RF frequency range over a time
scale of ms with a lock-in amplifier(147). Such time averaged studies demonstrate an additional technique to study quantum transport. Whereas the current experiment is focused on the transient breakdown process of Au-Au bond measured on sub-ns scale.

**Fig. 2.1** Schematic of experimental setup. A bias-T is used to separate DC and AC components of the current signal from an atomic sized contact formed with a STM break junction. After the separation, the DC component is fed into a DC amplifier and the AC component into 3 RF amplification stages. When a step shows up on the DC output as a response to sudden change in the junction conductance, a corresponding spike will also appear on the RF output, of which the amplitude represents both the magnitude and rate of the conductance change.

To analyze and characterize the entire circuit, we first carried out numerical transient circuit analysis of the “bias-T”, and then we introduced 3 digital filters to simulate the 3 RF amplification stages.

**The Bias-T circuit**
Fig. 2.2a shows a diagram of Bias-T without the DC and RF amplifiers. This is basically a high-pass filter configuration in which the DC (inductor $L_M$) branch is directly grounded the AC (capacitor $C_M$) is terminated with a load resistance of $R_L$, normally 50 Ω. The resistance (capacitance) between the two electrodes is modeled as $R_T$ ($C_T$). The concern is that whether $C_T$ will significantly cut off the response due to the sudden change of $R_T$ seen at the AC output $U_{out}$. For the breakdown process of a gold quantum point contact, we model its resistance $R_T$ changes as a function of time given by

$$R_T = R_{T0} \exp(t/\tau), \quad (2.2.1)$$

where $\tau$ is the time constant of the gap opening between the electrodes. The total capacitance $C_T$ between the two electrodes is modeled to be constant since it is determined by the bulk electrodes. Note that the Laplace transform does not apply to exponentially changing resistance in transient circuits. Therefore, a numerical transient analysis was performed. Based on the intrinsic properties of capacitors and inductors, the numerical equations based on a time increment of $h$ are given by

$$I = C \frac{dV}{dt} \Rightarrow I_{n+1} = \frac{C}{h} V_{n+1} - \frac{C}{h} V_n$$

and

$$V = L \frac{dI}{dt} \Rightarrow V_{n+1} = \frac{L}{h} I_{n+1} - \frac{L}{h} I_n. \quad (2.2.2)$$

Therefore, a capacitor (inductor) can be equivalently transformed to a resistor in parallel (series) with a current source (voltage source) shown in Fig. 2.1b. The complete circuit is then transformed to Fig. 2.2c. At time $t(0) = 0$, the initial conditions are given by

$$I = I_0, \quad V = 0.$$

Therefore, a capacitor (inductor) can be equivalently transformed to a resistor in parallel (series) with a current source (voltage source) shown in Fig. 2.1b. The complete circuit is then transformed to Fig. 2.2c. At time $t(0) = 0$, the initial conditions are given by
\[ R_T(0) = R_{T_0}, \ U_1(0) = 0, \ U_{out}(0) = 0 \] and \[ I_L(0) = \frac{U_{in}}{R_{T_0}}. \] (2.2.3)

At time \( t(n) = nh \), using results from time \( t(n-1) = (n-1)h \) we get

\[ I_{eqT}(n) = \frac{U_{in} - U_1(n-1)}{R_{eqT}}, \ I_{eqC}(n) = \frac{U_1(n-1) - U_{out}(n-1)}{R_{eqC}} \] and

\[ U_{eqL}(n) = I_L(n-1) \cdot R_{eqL}, \] (2.2.4)

where \( R_{eqT} = \frac{h}{C_T}, \ R_{eqC} = \frac{h}{C_M} \) and \( R_{eqL} = \frac{L_M}{h} \) are constants.

From basic circuit relations, we obtain

\[ \frac{U_1(n)}{R_2} + \frac{U_{out}(n)}{R_L} = -I_L(n-1) + \frac{U_{in}}{R_1} - I_{eqT}(n), \ \frac{U_1(n)}{R_{eqC}} - \frac{U_{out}(n)}{R_3} = I_{eqC}(n) \] and

\[ I_L(n) = \frac{U_1(n)}{R_{eqL}} + I_L(n-1), \] (2.2.5)

where \( R_1 = R_T(n) / R_{eqT}, \ R_2 = R_T(n) / R_{eqL} \) and \( R_3 = R_{eqC} / R_L \). Note that \( R_T \) is a function of time given by \( R_T(n) = R_{T_0} \cdot e^{-\frac{nh}{\tau}} \). And thus we can solve \( R_T(n), U_1(n), U_{out}(n) \) \( \text{and} \) \( I_L(n) \) for the next iteration.

The responses seen at \( U_{out} \) at different \( C_T \) are shown in Fig. 2.2d inset.

And the dependence of response amplitude with respect to \( C_T \) (Fig. 2.2d) indicates that \( C_T \) doesn’t not cut of the response up to 20 pF, which is much higher than measured capacitance in the modified CSTM setup (typically ~50fF).
Fig. 2.2 Transient circuit analysis of Bias-T circuit. (a) Circuit diagram with parameters. (b) Equivalent circuits for a capacitor and a inductor in numerical transient analysis. (c) Equivalent circuit for the entire circuit in (a). (d) Simulated AC output to sudden conductance changes with different $C_T$ values, showing that the output is insensitive to $C_T$ up to $\sim 20$ pF.

**Frequency response of bias-T circuit with DC current preamplifier**

We understand the performance of the bias-T together with the DC current preamplifier by printing every component shown in Fig. 2.3 on a PCB board. The black color in the diagram represents the real components and the green color represents the parasitic capacitances. $K$ is the open loop gain of the operational amplifier (OPA129), which is a function of the frequency. According to Miller’s
theorem, the feedback resistance $R_F$ and capacitance $C_{F,p}$ can be transformed to that shown in Fig. 2.3b. The transfer function is given by

$$H(s) = \frac{Z_3}{Z_3 + R_S} \times \frac{Z_2}{Z_2 + Z_T} \times \frac{R_L}{Z_1}$$ \hspace{1cm} (2.2.6)

where

$$Z_F = R_F // \frac{1}{sC_F}, \quad Z_T = \frac{1}{sC_T} // R_T, \quad Z_1 = \frac{1}{sC_M} + R_L, \quad Z_2 = \left( sL_M + \frac{Z_F}{1 - K} // \frac{1}{sC_{input}} \right) // Z_1 \hspace{1cm} (2.2.7)$$

and $Z_3 = Z_2 + Z_T$. (2.2.7)

Fig. 2.3c shows the comparison of measured AC frequency response and simulation. A sharp dip at ~100MHz was found to be induced by the resonance of $L_M$ and $C_{input} + C_F/(1 - K)$. Since the RF amplifiers are designed to work at 900MHz, $L_M$ is set to be 300 nH so that this dip is out of the frequency range of interest. Also, the increase of RF gain at frequencies higher than 100MHz is induced by $C_T$. But this is mainly due to the response of $C_T$ to the AC voltage.

According to the simulation in the last section, the AC response due to a sudden exponential increase of $R_T$ with constant bias should be insensitive to $C_T$ up to a fairly large value (~20pF). Furthermore, the measured fluctuations in the high frequency range may be due to the parasitic effects on the surface mount circuit board, as well as the transmission line effect in the presence of imperfect impedance match, which can be largely reduced by using shorter coaxial cables where possible. This same calibration method was also used to measure the capacitance $C_T$ in the modified CSTM setup, typically of ~30-70fF.
**Fig. 2.3** Frequency response of Bias-T circuit with DC current preamplifier. (a) Circuit diagram with parameters. (b) Equivalent circuits after applying Miller’s theorem. (c) A comparison (red) of measured AC frequency response and simulation (blue and green).

**The single stage RF amplifier**

SKY65050 high electron mobility transistor (HEMT) is used for the RF amplifier. We followed the recommended design from the datasheet which is shown in Fig. 2.4a. And Fig. 2.4b shows the small signal equivalent circuit, in which blue components represent the testing source and load, green components represents parasitic capacitance of the HEMT and the components in each green dashed rectangle can be combined into $Z_S$, $Z_L$ and $Z'_L$ respectively for simplification. $Z_{pwr}$ is the impedance induced by the power line. The entire circuit can be separated into 3 stages according to the red dash lines. Fig. 2.4c
shows the comparison between frequency response measurement and simulation.

Parasitic parameters are obtained by fitting to the simulation to the measurement.

Since the transfer function is sensitive to parasitic effects in the source lead suggested by the datasheet, a source parasitic inductance $L_S$ in series with $Z_S$ is also induced as a fitting parameter. In high frequency range, $C_2$, $C_5$, $C_7$ and $C_8$ can be considered as directly shorted to ground. This leads to

$$Z_S \approx sL_S, \quad Z_{pwr} \approx sL_3, \quad Z_L \approx sL_3//\frac{1}{sC_6} \quad \text{and} \quad Z'_L = R_2//R_L. \quad (2.2.8)$$

The transfer function of first stage is given by

$$H_1 = \frac{(sL_2+Z_{in})/sL_3}{R_5+(sC_1+(sL_2+Z_{in})/sL_1)} \times \frac{Z_{in}}{Z_L+sL_2+Z_{in}}, \quad (2.2.9)$$

where $Z_{in}$ is the input impedance of the second stage seen at the left red dash line, given by

$$Z_{in} = \frac{1}{s(C_3+C_{gd})} - \frac{sC_3}{sC_3^2+g_m} - \frac{g_m}{Z_S+g_m}. \quad (2.2.10)$$

The transfer function of the second stage is given by

$$H_2 = \frac{sC_{gd}Z_L[1+(sC_3+g_m)Z_S]-g_mZ_L}{(1+sC_{gd}Z_L)[1+(sC_3+g_m)Z_S]}. \quad (2.2.11)$$

The transfer function of the third stage is given by

$$H_3 = \frac{Z'_L}{Z_{out}+\frac{1}{sC_4}+Z'_L}, \quad (2.2.12)$$

where $Z_{out}$, the output impedance of the second stage seen at the right red dash line, given by

$$Z_{out} = Z_L//\frac{1}{sC_{gd}}. \quad (2.2.13)$$

The transfer function of the entire amplifier is then
\[ H = H_1 \times H_2 \times H_3 \times 2. \] (2.2.14)

Note that due to the 50 Ω standard impedance for all equipments used, the power generated by the source is actually twice of the power by direct measurement. A factor of 2 is thus included in Equation 2.2.14.

**Fig. 2.4** Frequency response of single stage RF amplifier. (a) Circuit diagram with parameters. (b) Small signal equivalent circuit. (c) A comparison of measured RF frequency response (green) and simulation (blue).

**Simulation of entire circuit response to a breakdown process of a single atom contact**

After characterizing the RF amplifier, we transformed the transfer function into a digital filter using Z transform in MatLab. Using the numerical method for
bias-T discussed above and three of such digital filters for RF amplifiers, we were able to simulate the response of the circuit to a breakdown process of a single atom contact that was modeled with an exponential decay in the conductance starting from a fixed number to zero (Fig. 2a). In the simulation, each breakdown process leads to a wavelet (or a brief oscillation) output from the RF amplifier with a duration of ~5 ns (Fig. 2b). The amplitude of the wavelet depends on the time constant (τ) of the conductance decay (Fig. 2c), as well as the change in the conductance, ΔG (Fig. 2d). However, since we focused on clear breakdowns of the last step in the conductance decay, for modeling purposes we used a conductance change of 1G₀. For a slow breakdown process (τ>10 ns), the AC output is small, which is expected for an AC coupled circuit. The amplitude increases as the time constant decreases and eventually reaches a plateau of ~0.3 at ~0.02 ns. It should be noted that, the wavelet amplitudes quoted throughout this letter are unitless because the output measured from the RF amplifier is in volts, and this value is divided by the input bias to be able to compare measurements performed under different bias conditions. The monotonic dependence of the amplitude on the time constant between the two limits (~0.02 and ~10 ns) allows for sub-nanosecond measurement precision (Fig. 2d). This is ~4 orders of magnitude faster than the previously studied time scales using conventional DC amplifiers.
Fig. 2.5  Numerical simulation of dependence of spike amplitude on the magnitude and rate of conductance change. Results are normalized by applied bias and thus unit-less. (a) Conductance changes from 1 G0 to 0 modeled by exponential functions with time constants (τ) of 100 ps, 500 ps and 1 ns (blue, green and red, respectively). (b) Simulated RF outputs of the entire setup (normalized by applied bias, URF/UBias) corresponding to conductance changes in (a) (colors matched respectively). Spike amplitude is defined as the negative maximum amplitude of the RF output signal. (c) Normalized spike amplitude dependence on conductance change time constant. (d) Normalized spike amplitude dependence on conductance change magnitude.

Similar modeling has also been carried out for the formation of an atomic sized contact, in which the conductance increases from zero to a finite value, such as 1 G0. The output of the AC circuit also produces a wavelet but with a 180° phase shift (vertical inversion). Also, if one fixes the time constant, and models different conductance changes, the amplitude of the wavelet is proportional to the magnitude of the conductance change (Fig. 2.5d), allowing us to determine the conductance values of the atomic sized contacts. Note that simple exponential
decay curves were used in the simulation for simplicity, but the basic findings of the circuit response are insensitive to the choice of the decay curves. These findings were further verified by tests discussed in later sections.

2.3 Instruments, software and control system

Using the circuit described above, we studied atomic sized contacts created with a break junction approach(3, 14). The pulling rate was fixed at ~600 nm/s. We note that the rate accessible with the piezoelectric actuator is much slower than the breakdown time of Au-Au contact, and should not directly affect the transient breakdown studied here. To minimize parasitic capacitance of the electrodes while maintaining good controllability, we built an STM-break junction setup, based on a previous design(100), in which a gold tip (cut from 0.25 mm gold wire) and a gold ball (~1-2 mm in diameter) are mounted onto the open ends of two SMA coaxial cables (Fig. 2.6a inset). In addition, we ensured that a constant bias was applied to the larger electrode side (gold ball side) to further reduce the possible parasitic capacitance effects. The tip was driven into contact with the gold ball until the DC conductance reached a preset value, and then withdrawn, by ramping the voltage applied to the piezoelectric transducer. Both the DC conductance and AC response measured by the amplifier circuit were recorded by a Lecroy WavePro 950 oscilloscope with 1 GHz bandwidth and 8 GHz sampling frequency (2 channels). The DC amplifier has a bandwidth of ~40 kHz and therefore introduces a delay into the DC signal. We determined this delay to be ~0.25 µs by using a clock generator (Stanford Research Systems CG635), to simulate the breakdown of a junction and properly calibrate the delay.
time. This ~0.25 µs delay was observed in all of the curves featured with a clean 1 G0 DC step. The oscilloscope records a maximum of only 50 µs of data at a time due to memory constraints. So we also recorded the entire DC conductance curve in parallel with a National Instruments PCIe-6259 Data Acquisition card (100 kHz sampling rate), while using the Lecroy oscilloscope to capture the last conductance step.

2.4 Experimental results and discussions

Fig. 2.6 RF response due to the breakdown of a gold atomic sized contact compared to that of a sudden bias decay in a dummy test. (a) A typical DC conductance trace of breaking a gold atomic sized contact shows step-wise decrease, recorded by a LabVIEW program (100 kHz sampling rate). Pulling speed ≈ 600 nm/s. Inset: the gold tip and ball electrode configuration. (b)
Simultaneous DC conductance trace and RF response captured by LeCroy WavePro 950 oscilloscope (1 GHz bandwidth, 8 GHz sampling frequency for 2 channels). Due to the slow response of DC amplifier (10 μA/V, ~40kHz bandwidth), a 0.25 μs offset was introduced for synchronization purposes. (c) Close-up details of the RF response shows a spike with a typical amplitude of ~0.3 and a duration time of (< 9 ns). (d) Sudden bias step-down (0.2 V → -0.2 V, τ < 300 ps) is applied on a 10 kΩ dummy resistor. Both bias and dummy RF response are recorded by the LeCroy oscilloscope. (e) Close-up details of the dummy RF response. Inset: simulation using the actual applied bias step-down (red line) is in good agreement with the measured response (blue line). (f) Comparison of conductance step-down and bias step down simulation shows similar spikes in shape and duration.

Fig. 2.6a displays a typical DC conductance trace showing a stepwise decrease in the conductance. The last step is close to 1G0, corresponding to the breakdown of a single atomic gold contact, which is in agreement with previous studies(159, 160). The simultaneously recorded AC response (blue curve in Fig. 2.6b) shows a spike with an amplitude of ~0.3 associated with the DC conductance step (black curve in Fig. 2.6b). Such curve composes over 40% of all recorded data. Note that the DC conductance (black curve) on the short time scale shows a gentle decay on the order of μs, which is due to the finite bandwidth of the DC amplifier. Zooming-in on the AC spike reveals a wavelet-like signal with a duration of ~8 ns (Fig. 2.6c). The observed wavelet is not due to random noises.
because it has a distinct waveform and it is accompanied with a stepwise change in the DC conductance. Also, it is not possible to observe these wavelets when the tip is not in contact with the substrate. There is a small difference in the time duration of the wavelet between simulation and experiment. This difference may be due to the fact that the conductance change occurring during the breakdown of the last gold atom is not exactly an exponential decay. A possible impedance mismatch or interference between different stages of the circuit may also contribute to this small discrepancy.

To further validate the finding, we measured the RF amplifier output due to a fast step-down input signal applied to the bias with the clock generator described above with 80 ps rise and fall times and observed a wavelet output that is in excellent agreement with the wavelet observed in real experiments (Figs. 2.6d and e). We note that the test used a step-down bias signal to simulate the abrupt drop in the conductance associated with the breakdown of an atomic contact, and the circuit responses to the two situations are not necessarily identical. To examine this difference we simulated the circuit responses due to two different inputs, an exponential decay in the bias and an exponential decay in the conductance. As shown in Fig. 2.6f, both produce wavelets with similar shape and duration. However, there is a small difference in the phase between the two inputs, which is due to parasitic capacitance.

Performing the break junction measurements repeatedly resulted in many individual traces similar to those shown in Figs. 2.6a-c, and allowed for a detailed statistical analysis. Fig. 2.7a is a DC conductance histogram constructed with
1810 traces recorded by the Lecroy oscilloscope, which shows a peak near $1G_0$, a feature that has been identified as a single atom quantum point contact. We varied the bias between 400-700 mV, and obtained similar results. Bias voltages much lower than 400 mV resulted in more noise due to the limited gain of the AC amplifier. Each wavelet from the AC circuit can be characterized with two parameters, amplitude and duration. The former is the maximum amplitude while the latter is extracted from the time at which the amplitude drops to one half of the maximum value. Analysis of the amplitude and duration allowed us to construct a two dimensional histogram in which the color scale represents the counts, and the vertical and horizontal axes represent the duration and amplitude of the wavelets, respectively (Fig. 2.7d). An important finding is that most wavelets have amplitude near ~0.3 and duration of ~9 ns. According to the model simulation using the measured circuit response function, this peak amplitude corresponds to $1G_0$, which is consistent with the DC conductance histogram. So the two dimensional histogram shows that most breakdown events measured here involve a change of $1G_0$, corresponding to a single atom contact. Based on the observation that the most probable wavelets have time duration of ~9 ns and amplitude of ~0.3, and the response curve shown in Fig. 2.5c, we conclude that the single atom contact breakdown processes are faster than ~0.1 ns.
Fig. 2.7  Statistical analysis of all 1810 traces recorded with bias of 400-700mV. (a) DC conductance histogram shows clear peak at ~1 G0 representing single gold atom quantum point contact, which is consistent with previous studies. (b) Duration histogram showing most spikes have duration of ~9 ns. (c) Normalized spike amplitude histogram showing most spikes have amplitude near ~0.3. (d) 2-D histogram constructed from amplitude and duration of spikes, showing most spikes have amplitude near ~0.3 and duration of ~9 ns.

The breakdown time of a single metallic bond under a mechanical strain has not been previously measured. We may expect that the fastest time scale be close to the vibration frequency of a gold atom, which is on the order of picoseconds. However, if the breakdown or formation process involves the
collective motion of multiple atoms, such as clusters of atoms moving together, the time scale should be substantially slower \((161)\). Such collective motion is evident in molecular dynamic simulations and in the observation of the formation of shell structures in metallic nanowires \((162-164)\). Our experiment places an upper limit of \(\sim 0.1\) ns on the most probable breakdown time, which is consistent with the findings by the molecular dynamic simulations \((165)\). If the time scale for the breakdown of a single Au-Au is determined by the vibrational frequency of Au-Au bond, which is on the order of \(\sim 1\) ps, then the collective motion involving \(N\) atoms, should be \(N\) times slower. The observation that the breakdown time is shorter than \(\sim 0.1\) ns suggests that the breakdown should involve less than \(\sim 10^4\) atoms (\(\sim 5\) nm gold clusters).

The breakdown of a single atom contact typically results in multiple AC wavelets. Fig. 2.8 shows such an example. The DC conductance trace (Fig. 2.8a) shows a rather clean breakdown of a single gold atom contact, but the simultaneously recorded AC trace (Fig. 2.8b) reveals several interesting features. First, associated with the breakdown of the last gold atom contact (marked by a filled arrow, an AC wavelet (marked with a “1”) with amplitude \(\sim 0.3\) is observed, which is similar to the AC wavelet in Fig. 2.6b. However, before the breakdown a small stepwise decrease in the DC conductance occurs (marked by an unfilled arrow). This stepwise decrease is accompanied by two spikes marked “2” and “3” (Fig. 2.8b, d) in the AC response, showing that at least two discrete atomic scale structural rearrangements are involved in the single stepwise DC conductance decrease. While every stepwise change in the DC conductance is accompanied by
one or more AC wavelets, we also found occasions where AC wavelets occur with no obvious DC conductance changes. Spikes “4” and “5” shown in Fig. 2.8b, e-f are such examples, which can be attributed to the occurrence of processes faster than the DC circuit response time. The two spikes have amplitudes significantly different from 0.3, which, as we will discuss later, are attributed to two or more events taking place within very short time scale (<1 ns). Due to the inability to record the complete conductance plateaus with the LeCroy oscilloscope, it is difficult to correlate the plateau length to the number of wavelets or the amplitude of wavelets with the current setup, which would otherwise provide us with further insight into the processes responsible for single atom contact breakdown.

Fig. 2.8  RF response due to the breakdown of a gold atomic sized contact showing different types of spikes. (a) DC conductance trace recorded by
LabVIEW program. (b) Simultaneous DC conductance trace and RF response captured by LeCroy WavePro 950 oscilloscope. A 0.25 μs correction is induced for synchronization purpose. (c-f) Close-up details of the spikes corresponding to the ones in (b) labeled with numbers.

Figs. 2.6a-b and 2.8a-b show rather clean single step breakdown processes in both the DC and AC measurements. In many cases, the breakdown of the last gold atom contact involves complex atomic scale structural fluctuations. One such example is given in Fig. 2.9. The DC conductance trace reveals several steps in the conductance before dropping to zero (Figs. 2.9a-b). However, due to the finite response time of the DC circuit, these steps are round and not well resolved. In contrast, the AC traces allow us to observe many spikes with different amplitudes associated with the DC steps. Detailed close-up view of individual spikes is shown in Fig. 2.9.
Fig. 2.9 (continued on next page)
Fig. 2.9  An example of multiple conductance switching processes during the breakdown of a single atom contact. (a) DC conductance curve while stretching the atomic sized junction until it breaks. (b) Simultaneous DC conductance change and AC response. Multiple switching events can be observed in the DC signal but detailed features are rounded. In contrast, the AC response resolves more details that are well correlated with the DC changes. (c-p) Close-up views of each of the spikes labeled in (b).

The two-dimensional histogram in Fig. 2.7d shows most AC wavelets have time durations of ~9 ns. However, there are a small number of breakdown events with durations longer than ~9 ns. These events can be more clearly
identified in the duration histogram created by projecting the two-dimensional histogram onto the vertical axis, revealing a distribution in the wavelet duration regardless of the amplitude (Fig. 2.7b). The appearance of events with longer time durations is not because these breakdown events are slower than 9 ns. As we have discussed earlier, the AC response of slow events leads to smaller amplitudes, rather than longer time duration. This is the characteristic of the AC coupled amplifier, which is shown in Figs. 2.6b-c. The long durations of some of the breakdown events are due to the consecutive breakdown and reformation of atomic sized contacts taking place within a short time interval (see spikes #3, 4, 6, and 11 in Fig. 2.9).

Fig. 2.10 shows some examples of consecutive events. There are three AC spikes, marked by “1”, “2” and “3” near the breakdown of the last atom contact (Figs. 2.10a-b). Spike “1” is a clean single process at the DC conductance breakdown edge showing the ~9 ns wavelet in a close-up examination (Fig. 2.10c). In contrast, spike “2” is actually two closely spaced spikes (Fig. 2.10d). Zooming-in on spike “3” also reveals double spikes (Fig. 2.10e). Such double spikes were frequently observed. Furthermore, the DC conductance trace shows no overall conductance change over “2” and “3” region. The presence of these double spikes without any conductance change indicates that such events could be attributed to a switching event, in which the conductance switches back and forth between two levels, corresponding to a breakdown and reformation of an atomic contact or switching between two atomic configurations of a contact. We have simulated such a process using the same experimental response function as in Fig.
2.6a and reproduced the experimental result (Fig. 2.10f). When a series of switching events occur with time intervals longer than ~ 4ns, the individual wavelets can be well resolved. However, if two switching events take place within a shorter time interval, a broad wavelet results, which is the reason for the broad duration distribution shown in Fig. 2.7 (see Fig. 2.9).

**Fig. 2.10** RF response due to the breakdown of a gold atomic sized contact showing consecutive switching events occurring in fast succession. (a) DC conductance trace recorded with a LabVIEW program. (b) Simultaneous DC conductance trace and RF response captured by Lecroy WavePro 950 oscilloscope. A 0.25 μs correction is induced for synchronization purpose. (c-e) Close-up details of the spikes corresponding to the ones in (b) labeled as “1”, “2” and “3”, respectively. (f) Simulation reproduces the scenario of two spikes with a separation time of 4 ns.
While most of the AC responses show wavelet amplitudes close to ~0.3, which are due to the breakdown or formation of a single gold atom contact, we have also observed wavelet amplitudes either greater or smaller than ~0.3. For example, the wavelet marked with “4” in Fig. 2.10b and 2.10e has amplitude ~0.6, and that marked with “5” in Fig. 2.10b and 2.10f has amplitude only ~0.17. Projecting the two-dimensional histogram onto the horizontal axis produces an amplitude histogram, which shows the amplitude distribution regardless the time durations (Fig. 2.7c). The amplitude histogram shows more clearly a pronounced peak near 0.3 with low but finite counts of wavelets with amplitude either greater or smaller than the peak value. Wavelets with amplitude smaller than 0.3 may be attributed to small but abrupt atomic scale rearrangements near the contact, which would lead to conductance jumps smaller than $1G_0$. Likewise, wavelets with amplitude greater than 0.3 may be associated with conductance jumps greater than $1G_0$. However, the DC trace in these regions shows no “net” conductance change, as such an alternative explanation is necessary. An alternative reason for these spike amplitudes is the interference of wavelets due to consecutive switching events. The simulation described in the Supporting Information shows that two consecutive events taking place within ~1 ns of one another result in interference, which can lead to the measurement of a single wavelet with an amplitude either greater or smaller than 0.3 depending on if the interference is constructive or destructive (Figs. 2.11c-d). Despite the uncertainty for the low amplitude switching events, the pronounced peak in the histogram indicates that the most
probable conductance change is $1G_0$ and the time duration of the breakdown is faster than 0.1 ns.

**Fig. 2.11** Response of the AC circuit to two consecutive conductance-switching events: a step-down followed by a step-up after certain time duration. If the duration is large, two distinct wavelets are resolved (a). However, if the duration is short, only a single wavelet is observed. The amplitude of the wavelet depends on the duration. For example, if the duration is 0.5 ns, the amplitude is close to 0.6 V, due to constructive interference of the two overlapping wavelets (b). If the duration is 0.1 ns, the amplitude of the resultant wavelet is small, due to destructive interference of the two overlapping wavelets (c). The normalized amplitude of the resultant wavelet vs. duration is plotted in (d). It shows that when the duration $> \sim 2$ ns, the two wavelets associated with two consecutive
conductance-switching events are well separated and the amplitude of each
wavelet becomes constant 0.3.

2.5 Further concerns and preliminary design

For further applications, the RF system needs to be carefully designed in
terms of stability, gain and noise figure. Conventional RF circuit design typically
focuses on 50 Ω systems ($\Gamma_5 = 0$). However, the $\Gamma_5$ in this particular setup
depends on the impedance between the two electrodes in our situation ($R_T$ and $C_T$
in Fig. 2.12a), which can be determined by several factors (e.g. molecular bridge,
experimental media). Fig. 2.12b plots $\Gamma_5$ as a function of $R_T$ for $C_T$ of 50fF and
4pF (representing ambient and aqueous conditions, respectively). $\Gamma_5$ is typically
close to 1, which indicates large reflection. Using the MATLAB RF toolbox, we
then performed a stability analysis to the RF amplifier from calculated $\Gamma_5$ for open
circuit ($R_T = \infty$) under ambient condition (Fig. 2.12d). Since both $|S_{11}|$ and $|S_{22}|$
are less than 1(Fig. 2.12c), the unconditional stability area follows Fig. 1.11a and
c. As shown in Fig. 2.12d, when $\Gamma_5$ is represented as the black marker, the

$\Gamma_{out}$ corresponding $\Gamma_{out}$ is out of the unconditional stability area (red asterisk). This
indicates that the circuit is not unconditionally stable. In fact, although the circuit
is stable in the gold quantum point contact measurement under ambient condition,
the instability was seen in our test in aqueous media. To really make such circuit
suitable for all condition, the circuit needs to be stable for all impedances.

Therefore, a modified design for the first stage RF amplifier is proposed below.
A common way of stabilizing the circuit is introducing a shunt resistor on the drain of the HEMT. A 27 \( \Omega \) resistor is therefore used. The stability analysis is shown in Fig. 2.13. Now the input and output stability circles are all outside the \( |\Gamma_S| < 1 \) and \( |\Gamma_L| < 1 \) respectively (Fig. 2.13b), meaning that for all input impedance, the shunted HEMT will be stable. The optimal operation point can
thus be selected using the constant gain circles (red) and NF circles (green) based on a compromise between gain and NF. The impedance matching networks on the input and output are then designed accordingly.

**Fig. 2.13** Stability analysis of SKY65050 HEMT shunted by a 27 Ω resistor. (a) Plot of $S_{11}$ and $S_{22}$ as a function of frequency. Inset: diagram of circuit analyzed. (b) Smith chart showing constant gain circles, NF circles and unconditional stability areas for input and output.

**Fig. 2.14a** shows a potential design of unconditionally stable RF amplifier. Impedance matching networks are designed to match to standard 50 Ω. The introduction of shunt resistor stabilizes the circuit but at the expense of reducing maximum gain from 25 dB to 20 dB.
A potential design of an unconditionally stable RF amplifier. (a) Diagram of the RF amplifier with parameters. (b) Plot of transducer power gain $G_T$ and available power gain $G_A$.

Another concern of applying this system for single molecule measurement is the low conductance of molecules (typically below 0.01 $G_0$). This requires an additional gain of 40 dB or more, which can be potentially achieved by stacking more RF amplification stages. A potential issue, however, is the noise caused by multiple stages. As mentioned above, compromise is normally made between maximum gain and minimum noise figure for single stage amplifier design. However, due to the possible mismatch between stages in the real cases, very careful design, tests and calibration will be needed.

2.6 Conclusions

In summary, we have developed a method to measure electron transport in atomic sized contacts with nanosecond resolution. It uses a circuit that can simultaneously measure DC and AC conductance. The DC signal determines the formation and conductance of an atomic sized contact on slow time scales ($>\mu s$),
and serves as a feedback signal for the STM break junction. The AC signal measures the fast transient breakdown, reformation, and atomic scale structural rearrangements of a single atom contact. Every conductance change observed in the DC signal is accompanied with one or multiple wavelets in the AC output. However, the AC circuit also detects many fast atomic scale structural rearrangement events that cannot be resolved by the DC circuit. Statistical analysis of the AC wavelets from multiple atomic sized contacts reveals that most breakdown processes of a single atom contact are faster than 0.1 ns. In addition, the multiple spike features in the AC signals reveal that the atomic scale behavior predicted by molecular dynamics does happen at least in nanosecond scale. The study bridges the wide gap in the time scale between the molecular dynamic simulations and previous experimental works. We anticipate that the method can be further improved and applied to study fast transport and conformational changes in other nanoscale devices including molecular junctions.(166) after carefully considering stability, gain and noise figure issues. Further improvements could include simultaneous force and conductance measurements, room and low temperature capabilities, and high gain for studying devices with small conductance.
3 MEASUREMENT AND STATISTICAL ANALYSIS OF SINGLE MOLECULE CURRENT-VOLTAGE CHARACTERISTICS, TRANSITION VOLTAGE SPECTROSCOPY AND TUNNEL BARRIER HEIGHT

3.1 Introduction

Measuring electron transport in a single molecule bridged between two electrodes is a basic task in understanding the electronic properties of single molecules and designing molecular junctions with desired device functions.\(^{(22-25)}\) Due to the large variability in the molecule-electrode contact geometry and the sensitive dependence of the electron transport properties on the atomic-scale details of the contact, the repeated formation and measurement of single molecule junctions and statistical analyses of these individual junctions have been introduced and used to characterize the conductance of a single molecule. The mechanically controllable break junction (MCBJ),\(^{(27, 167, 168)}\) and the Scanning Tunneling Microscope (STM) break junction methods\(^{(3, 91, 169)}\) have been widely employed to make these measurements. The statistical analysis of a large number of molecular junctions with different contact geometries reveals peaks in the conductance histograms, which are used to determine the most probable conductance of a single molecule junction.\(^{(3)}\) This approach allows for meaningful comparisons between experimental data obtained by different groups and between experiments and theories.\(^{(47, 97, 102, 170, 171)}\)

Despite the success, the combined break junction measurement and conductance histogram approach at room temperature is primarily limited to
determining the conductance at a fixed bias. This is because the lifetime of a single molecule bridged across two electrodes is relatively short\(^{(18, 98, 172-177)}\) in a typical STM break junction experiment, making it difficult to perform more detailed measurements, such as current-voltage (I-V), and conductance-voltage (G-V) characteristics. Compared to a fixed low-bias conductance, I-V curves contain significantly more information, and are a basic requirement for device characterization. A capability to rapidly measure the I-V characteristics of a large number of single molecule junctions is thus of great importance for developing a better understanding of the charge transport mechanisms in single molecule junctions, and characterizing the junctions’ device functions.

In the present work, we report on an approach to rapidly acquire thousands of I-V and G-V curves of single molecule junctions at room temperature and carry out a statistical analysis of these curves, thus adding a new dimension (voltage) to the conductance histogram analysis. More importantly, this method allows us to obtain transition voltage spectra (TVS) of the individual molecular junctions.\(^{(139-142, 178-181)}\) Statistical analysis of the TVS of many single molecule junctions provides detailed information about the tunneling barrier height, or more precisely, the alignment between molecular orbital level and the electrode Fermi level, as well as the dependence of the energy level alignment on the detailed contact geometry. We have studied n-alkanedithiols (n=6, 8 and 10) consisting of linear saturated C-C bonds, and biphenyldithiol, containing conjugate aromatic structures.
3.2 Sample Preparation and Experimental Details

Before the measurements, the STM tip was prepared by cutting a 0.25 mm gold wire (99.998%). A Teflon STM cell was used to hold solvent in which the measurement was performed. The cell was cleaned with piranha solution and then sonicated in 18 MΩ water three times before each experiment. (Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care.) The gold substrate was prepared by thermally evaporating 130 nm of gold on mica in a UHV chamber. Prior to each experiment, the substrate was briefly annealed in a hydrogen flame. Further details of the procedures for preparing clean gold substrates and STM tips were given elsewhere.\textsuperscript{(14)}

Note that sample molecules in an STM break junction experiment can be introduced in several different ways.\textsuperscript{(8, 14)} In the present work, we used two methods. In the first method, each experiment started in a pure solvent (e.g., mesitylene in the present work) containing no sample molecules, and the current traces exhibited simple exponential decay curves due to electron tunneling through the solvent. Such a measurement served as a control experiment to ensure cleanness of the gold substrate and solvent, which is critical for a successful measurement. Then a sample solution (1 mM sample molecules dissolved in the same type of solvent) was injected into the solvent to expose the molecules to the substrate, and the measurement on the molecules was carried out using the procedure defined above. The second method was to expose the substrate to a solution containing sample molecules to pre-form a self-assembled monolayer layer of the molecules on the substrate first.\textsuperscript{(8)} The substrate was then mounted
into the setup for STM break junction measurement. For alkanedithiols, we used the first method because of good solubility of the sample molecules in mesitylene. However, due to poor solubility of biphenyldithiol in nonpolar solvents, we used the second method by exposing gold substrate in tetrahydrofuran (THF) containing 0.5 mM biphenyldithiol overnight.

After the sample preparation, we started each measurement by bringing an STM tip into contact with a gold substrate with a small bias voltage applied between the tip and substrate. The tip was then pulled away from the substrate, during which the current between the tip and substrate was monitored. Such a current vs. pulling distance curve is referred to as a current or conductance trace. As we have reported previously, (3) steps appear in the current traces when sample molecules bridge between the tip and substrate electrodes via linker groups, such as thiols. The lowest current steps are assigned to single molecule junctions, which is supported by simultaneously obtained conductance and breakdown force measurement. (124, 172) In a typical STM break junction experiment, a large number of conductance traces are recorded, and analyzed in the form of conductance histograms, from which the single molecule conductance is determined. In contrast, in the present work, once a step was detected, the tip was held still while the bias voltage was automatically swept for one cycle to produce an I-V curve. After the voltage sweep, the tip was pulled further away from the substrate by a given distance while the current level was checked to determine if the molecular junction was still intact. If so, another I-V curve was recorded, and the process continued until the step collapsed as the molecular junction broke,
which was indicated by the sudden drop of current. At that point, the whole procedure started over, and this process was repeated thousands of times. We provide further experimental details in the next section.

3.3 **Software and control system**

The entire I-V-recording process consists of iterations of three steps, tapping, conductance step detection and I-V recording, which is in contrast to the single-step tapping procedure used in the previous STM break junction measurements. In the tapping step, the tip is moved towards the substrate until the current reaches a preset threshold, and then is retracted until it reaches a lower preset current. In the previous STM break junction method, the tapping step is repeated to record a large number conductance traces. However, in the present method, the conductance step detection is applied during each retraction cycle to identify conductance steps. In order to effectively identify a conductance step, we found that a good practice is to avoid the formation of gold quantum point contact between the tip and substrate during the tip approaching process. This is because the abrupt breakdown of the quantum point contact tends to increase instability thus making harder to detect the conductance steps. Another good practice is to identify a conductance step by analyzing the conductance histogram of each trace in logarithmic scale. Peaks in the conductance histogram determine conductance steps, and the logarithmic-scale plot helps to minimize impacts from tunneling current through solvent. (167) Once a conductance step is detected, the I-V recording step is activated, which involves the following sub-steps: 1) The tip is immediately held still, 2) bias voltage is swept by one complete cycle quickly (0.1
second) to acquire an I-V curve, 3) upon completion of the I-V curve, the tip is pulled further by a given distance, and 4) the current is checked for 1 millisecond to determine if the molecular junction is still intact, 5) If yes, another IV curve is recorded and sub-steps 3-5 are repeated, and if no, then the entire process is started over again. The entire algorithm was realized by LabView programming.

During data processing, I-V curves that are incomplete (molecular junction broke in the middle of bias sweep) and contain large switching noises are detected and removed from statistical analysis. An Example of the incomplete and noisy curves is shown in Figs. 2.1c-d. Several selection criteria were used to automatically identify these incomplete or noisy I-V curves. First, we look for sudden drops in the current after an I-V sweep to detect signs of breakdown of the molecular junction. Second, we check the completeness of the I-V curves by examining the current reproducibility of forward and backward sweeps. This procedure is effective to identify molecular junctions that either break completely or switch to a different contact geometry in the middle of I-V curve recording. Finally, we further identify curves with excessive noise by checking the standard deviations. These procedures allowed us to obtain complete I-V curves for statistical analysis.

3.4 Results and discussions

Fig. 3.1a shows a typical current trace in logarithmic scale with stepwise features for octanedithiol (C8), where the colored spots along the step mark the positions where the individual I-V curves were measured. Fig. 3.1b shows the I-V characteristics obtained at those positions in corresponding colors. The process
was then repeated thousands of times, such that a large number (> 2000) of I-V curves from different molecular junctions with varying contact geometries were obtained.

Fig. 3.1 Typical current traces and I-V curves for octanedithiol (C8). (a) A current trace in logarithmic scale showing stepwise features, where colored spots along the step mark the positions where the individual I-V curves were measured. (b) The corresponding I-V curves, in which the colors of I-V curves match the color of spots. (c) Another current trace with a blue dot marking where an incomplete I-V curve was recorded. (d) The corresponding incomplete I-V curve with significant amount of switching and noise. Such curves are rejected from the statistics.
I-V histograms

Fig. 3.2a plots over 2000 such I-V curves for C8, where the color scale represents the occurrence or count number of a current value. The count numbers in the high bias regimes are lower than those in the low bias regimes, which is due to the divergence of the I-V curves at high bias voltages, rather than incomplete I-V curves.Incomplete I-V curves due to the breakdown of the molecular junctions at high bias voltages (e.g., Figs. 3.1c-d)(17, 82, 182) were rejected from the I-V histogram shown in Fig. 3.2a. We also occasionally encounter large telegraphic switching in the I-V curves(168), which were also excluded from the statistical analysis. These incomplete and switching I-V curves constituted~30% of all the curves for a bias range of ±0.5 V, which were automatically detected using the algorithm described in the Supporting Information. The percentage of incomplete I-V curves increased with the bias sweep range due to the instability of the single molecule junctions at high bias voltages.(82) For example, for a bias range of ±2 V (e.g., Fig. 3.2a) the percentage of incomplete I-V curves increased to 50-70% for C8. The breakdown voltage varies from molecule to molecule, and also junction to junction, and has been attributed to current-induced heating in literature.(17, 82, 182, 183)
Fig. 3.2  I-V and G-V histograms for C8. (a) I-V histogram for H-junctions consisting of 2151 curves. (b) G-V histogram for H-junctions. (c) 1-D conductance histogram at different bias voltages for H-junctions. (d) I-V histogram for M- and L-junctions consisting of 1661 curves. (e) G-V histogram for M- and L-junctions. (f) 1-D conductance histogram at different bias voltages for M- and L-junctions.

G-V histograms
From the individual I-V curves, we constructed G-V curves, where \( G = I/V \) is the conductance. Note that this conductance should be distinguished from differential conductance, which is defined as \( g = dI/dV \). These G-V curves are plotted together in logarithmic scale to form a 2-dimensional (2-D) conductance histogram (Fig. 3.2b), where the color scale represents counts at a fixed conductance value and bias voltage. The 2-D conductance histogram shows a clear bowl-shaped red band, corresponding to the distribution of G-V curves within a certain conductance range, from which most the probable G-V curve can be determined. The bowl-shape is present because the current increase is nonlinear with bias in the I-V characteristics, as is discussed in detail below. Such a 2-D conductance histogram contains richer information than the 1-D conductance histogram analysis used in the previous STM break junction experiments. For example, we can directly obtain the “standard” 1-D conductance histogram at various different bias voltages by simply taking vertical profiles from the 2-D histograms. Fig. 3.2c shows several 1-D conductance histograms where each pronounced peak indicates the most probable conductance value at the corresponding bias. The peak shifts towards higher conductance values with bias voltage due to the nonlinearity of the I-V curves.

Previous works observed multiple conductance peaks at low bias voltages in the alkanedithiols.\((14, 19, 47, 48, 97-100)\) This is clearly confirmed in the I-V curve histogram and the 2-D conductance histogram. Fig. 3.2d shows an I-V curve histogram of C8 recorded with a higher gain setting in the current amplifier than that used to record the I-V curves shown in Fig. 3.2a. This gain setting
allowed us to measure lower conductance values of the C8 junctions. The
distribution of the I-V curves falls into two distinct bands, which are marked with
two dashed lines. The corresponding 2-D conductance histogram (G-V histogram)
is shown in Fig. 3.2e, and the 1-D conductance histograms at several bias voltages
are presented in Fig. 3.2f, showing two peaks more clearly. We denote the
molecular junctions in Figs. 3.2a and 3.2b as H-junctions, and the two distinct sets
of junctions in Figs. 3.2d and 3.2e as M- and L-junctions, based on their
conductance values (H- for high, M- for medium and L- for low conductance
values). These different conductance values have been attributed to different
contact geometries(47) and molecular conformations.(14, 99) At low bias
voltages (e.g., 200 mV), the conductance values of H-, M- and L-junctions agree
with the results reported by Li et al.(47) to within 10%, and also with other
independent studies,(14, 99) as is shown in Table 3.1.
<table>
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<th>Molecular Junctions</th>
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<th>(\beta_N)</th>
<th>Literature</th>
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<td>(G(G_0))</td>
<td>(\beta_N)</td>
<td>Ref. (47)</td>
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<td>(1.00\pm0.20)</td>
<td>(1.2\times10^{-3})</td>
<td>(0.96\pm0.15)</td>
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<td>(4.5\times10^{-4})</td>
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<td>(2.6\times10^{-4})</td>
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</tr>
<tr>
<td>(4.8\times10^{-5})</td>
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<td>(3.2\times10^{-5})</td>
<td>(0.45\pm0.09)</td>
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<tr>
<td>(2.8\times10^{-4})</td>
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<td>(2.7\times10^{-4})</td>
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<tr>
<td>(5.9\times10^{-5})</td>
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<td>(5.7\times10^{-5})</td>
<td>(0.94\pm0.05)</td>
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<tr>
<td>(1.1\times10^{-5})</td>
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<td>(2.7\times10^{-5})</td>
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<td>(1.0\times10^{-6})</td>
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</tr>
<tr>
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<td>(1.9\times10^{-4})</td>
<td>NA</td>
<td>(1.8\times10^{-4}) (ref. (184))</td>
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</tbody>
</table>

*Extrapolated from a series including longer chains.

**Table 3.1** Comparison of low bias conductance and decay constants between the present work and literature.

**Summary for alkanedithiols**

We performed similar measurements and analysis for decanedithiol (C10) and hexanedithiol (C6) in order to study the length dependence of the transport properties (Fig. 3.3). The length dependence allowed us to determine the tunneling decay constants, values (Fig. 3.4). The results are summarized and compared with literature results in Table 3.1. For C10 and C8, bowl-shaped G-V curves were clearly observed. However, for C6 the junction became unstable at
high bias voltages, due to the large current density in the shorter molecule, which prevented us from obtaining a large number of complete I-V curves over wide voltage ranges. Therefore, we limited our bias sweep range for C6 to ±0.5 V for both H- and M- junctions (Figs. 3.3c and 3.3g), but we were able to sweep over a large bias range for the L-junction, which shows once again the bowl shape G-V curves that are similar to C8 and C10 (Figs. 3.3d and 3.3h). Note that the G-V curves for the L-junctions show an anomaly near zero bias. This anomaly is due to a small current offset from the current amplifier divided by a small bias voltage in the calculation of $G (=I/V)$, which becomes pronounced for low conductance G-V curves. As a comparison to conventional STM break junction method, we have listed conductance histograms of C8, C10 and C6 acquired from the same samples using conventional method (Fig. 3.5). Furthermore, a small discrepancy is found for the L-junctions conductance of C10 between the present work and that by Li et al. (47), which is probably due to the relatively low level of current and the broad peak. Except for this discrepancy, the overall agreement between different groups is remarkable, especially considering the history of single molecule conductance measurements, which indicates good reproducibility of the STM-break junction and statistical analysis for single molecule conductance measurements.
**Fig. 3.3** G-V histograms (a-d) and 1-D conductance histograms at different bias voltages (e-h) for C8, C10, C6 low bias and C6 high bias junctions, respectively. Note that due to current-induced instability at high bias voltages, the bias sweep range is limited to ±0.5 V for C6 in (d). White dash lines in (a-d) show the bias voltages where the 1-D conductance histograms are extracted.

![Graph showing G-V histograms and 1-D conductance histograms.](image)

**Fig. 3.4** Low bias conductance in logarithmic scale (extracted from Fig. 3.3) vs. molecular length and comparison with Li et al (47) for C6, C8 and C10.

![Graph showing logarithmic scale conductance histograms.](image)

**Fig. 3.5** Logarithmic scale conductance histograms obtained by performing conventional STM-BJ measurement with C8, C10 and C6 respectively.

Biphenyldithiol
In addition to the alkanedithiols, which consist of saturated carbon chains, we studied single-molecule biphenyldithiol junctions. Fig. 3.6a plots an I-V curve histogram of biphenyldithiol created with over 2000 curves, and Fig. 3.6b shows the G-V histogram. Similar to the G-V histograms for alkanedithiols, the G-V histogram of biphenyldithiol shows a clear band. However, an important difference between the two molecular systems is that the G-V band of biphenyldithiol has a much larger curvature near zero bias and looks more like a V-shape, compared to the bowl-shape band found in the alkanedithiols. This difference, as we will discuss later, is due to the increased contribution of frontier molecular orbitals in biphenyldithiol. 1-D conductance histograms at different bias voltages are plotted in Fig. 3.6c. Each histogram shows a pronounced peak, which is in contrast to the multiple peaks in alkanedithiols. The origin for this difference between the two systems is not understood. The peak shifts towards higher conductance values with the bias voltage, indicating strongly nonlinear I-V characteristics for biphenyldithiol. At low biases (e.g., 100 mV), the conductance value is in good agreement with the value reported by Mishchenko et al. However, at higher biases, there is a small but reproducible asymmetry in the I-V curves (Fig. 3.6a). The asymmetry is shown more clearly in the G-V histogram (Fig. 3.6b) and 1-D conductance histograms at positive and negative bias voltages (Figs. 3.6c and 3.6d). We will return to this asymmetry later.
Fig. 3.6 Measurement of biphenyl-dithiol. I-V (a) and G-V (b) histograms for biphenyl-dithiol consisting of 1258 curves. (c) 1-D conductance histogram at different positive (c) and negative (d) bias voltages.

Transition Voltage Spectroscopy

So far we have shown that the new STM break junction method allows us to obtain large numbers of I-V and G-V curves, and to perform a statistical analysis on the charge transport characteristics. At low bias voltages, the G-V histograms recover the results of the previous STM break junction works that measured conductance histogram at a fixed bias, but the I-V characteristic curve
and G-V histograms provide much more information. We show below that this method also makes it possible to perform single molecule Transition Voltage Spectroscopy (TVS), and more importantly, to perform a statistical analysis on thousands of TVS curves. TVS has been introduced recently(139-141, 178, 179) to address one of the most important issues in molecular electronics, tunneling barrier height or the relative alignment of the molecular energy levels with the electrode Fermi energy levels. Energy level alignment determines the charge transport efficiency and mechanism through a molecular junction.

As discussed in Chapter 1, TVS refers to the $\ln(I/V^2)$ vs. $1/V$ plot, or the so-called Fowler-Nordheim plot used to study the tunneling to field emission transition in solid state junctions.(185) Such a transition is indicated by a minimum in the Fowler-Nordheim plot, and the position of the minimum is called the transition voltage, $V_{tran}$. Beebe et al.(139) have shown that the TVS of thin film molecular junctions also develops a minimum, and that the corresponding $V_{tran}$ is proportional to the relative difference between the HOMO (Highest Occupied Molecular Orbital) energy level and the Fermi energy ($E_{homo}-E_F$), where $E_{homo}$ and $E_F$ are the HOMO(24, 142, 186) of the molecule, and the Fermi energy of the electrode, respectively. TVS does not depend on a detailed microscopic model, and has thus become a convenient and quantitative tool to compare the I-V characteristics of the different molecular systems and to extract important information, such as the energy level alignment.(140-142)

To obtain TVS, we started with individual G-V curves (Fig. 3.7). As an example, Fig. 3.7a shows a typical current trace showing a conductance step for
an H-junction of C8, and Fig. 3.7b shows two I-V curves (overlaid) recorded at the position marked by a blue spot in Fig. 3.7a. The corresponding G-V curves are presented in Fig. 3.7c, which show high frequency noise that would be amplified in the TVS plots. Since transition voltage in TVS is determined by nonlinearity of I-V characteristics (low frequency data), each G-V curve was fit (singular value decomposition) with a smooth second order polynomial as shown by the solid lines in Fig. 3.7c (the mean squared error normalized by average current is less than 0.2), from this fitting the TVS curves, or \( \ln(G/V) \) vs. \( I/V \) plots, were determined and are presented in Fig. 3.7d. Minima in the positive bias region are clearly visible (but not in the negative bias region due to the asymmetry of this particular molecular junction). We developed an algorithm to automatically extract the TVS, and determine the minimum position, transition voltage, from thousands of G-V curves. This approach allowed us to perform a statistical analysis of transition voltages for molecular junctions with different contact geometries. Fig. 3.7e shows the histogram of the transition voltage distribution vs. low bias conductance (conductance at 200mV) for the H-conductance value of C8.
Fig. 3.7 Transition voltage spectroscopy (TVS) and histograms. (a) A typical conductance trace for a H-junction of C8. (b) An I-V curve recorded at the position marked by a blue spot in (a). (c) G-V curves and fittings (smooth curves with lighter colors). (d) Corresponding TVS with colors matching the G-V curves in (c). (e) A 2-D histogram showing the distribution of transition voltage vs. low bias conductance. (f) Correlation between contact conductance vs. low bias conductance.
Discussion on Transition Voltage Histogram

Several important conclusions can be drawn from such a statistical presentation of the transition voltage. First, the distribution has a maximum count at a transition voltage (Fig. 3.7e), which will be referred to as the most probable, or peak transition voltage. For the H-conductance of C8, the peak transition voltage is 1.4 V, which is consistent with the value found for thin film alkane monothiols. (178) The value is smaller than the transition voltage for a vacuum tunneling junction, (180) indicating a lower tunneling barrier via the molecule than that via vacuum. Second, there is a distribution with a half width at half maximum (HWHM) of ~0.25 V in the transition voltage obtained from thousands of molecular junctions with different molecule-electrode contact geometries. This fact indicates that the alignment of the molecular energy level relative to the electrode Fermi level varies from junction to junction, and depends on the contact geometry. In other words, the molecule-electrode contact geometry affects the conductance of a molecular junction not only because of the contact resistance change (electronic coupling efficiency) but also through the energy level alignment (barrier height). Note that the bias voltage profile across the molecular junction may also vary from junction to junction, and thus affecting the distribution of the transition voltage (187). However, most of the voltage drop is expected to take place at the molecule-electrode contacts as indicated by the lack of molecular length dependence of the transition voltage found here and in Ref. (178). Also associated with the bias voltage drop at each of the two contacts is an
electric dipole, which affects the barrier height, and is already taken into account in the analysis.

We further studied the correlation between the transition voltage and the low bias conductance. As a measure of dependence between two sets of data $X$ and $Y$, the Pearson's correlation coefficient is defined as

$$r_{xy} = \frac{\sum_{i=1}^{n} (x_i - \bar{x})(y_i - \bar{y})}{(n-1)s_x s_y},$$  \hspace{1cm} (3.1)

where $x_i$ and $y_i$ are individual data points in $X$ and $Y$ ($i = 1, 2, ..., n$), $\bar{x}$ and $\bar{y}$ are the sample means of $X$ and $Y$, and $s_x$ and $s_y$ are the sample standard deviation of $X$ and $Y$. $r_{xy}$ varies between -1 and 1, indicating the degree of linear dependence between $X$ and $Y$. If $X$ and $Y$ are uncorrelated, $r_{xy}$ will be zero. And $r_{xy}$ is 1 in the case of a perfect positive linear correlation and -1 in the case of a perfect negative linear correlation.

If assuming tunneling model, the low bias conductance of a single molecular junction can be represented by

$$G = Ae^{-\beta L},$$  \hspace{1cm} (3.2)

where $A$ is the contact resistance, $\beta$ is the decay constant and $L$ is the molecular length. $\beta$ is proportional to the square root of the barrier height $\Phi, (138)$ which is proportional to the transition voltage $V_{\text{tran}}. (139)$ If one assumes a constant molecular length $L$, the low bias conductance can be simplified as

$$G = A e^{-k\sqrt{V_{\text{tran}}}},$$  \hspace{1cm} (3.3)

where $k$ is a prefactor that includes any proportionality factors between $\beta$ and $\sqrt{V_{\text{tran}}}$ and molecular length. Thus one can find that the contact resistance, $A$, is
proportional to $G/e^{\sqrt{\text{V}_{\text{tran}}}}$, by which one can find the distribution of contact resistance $A$ vs. $G$.

Performing the above correlation analysis, we found that even though there is a significant junction-to-junction variation in the transition voltage, the low-bias conductance value within a given conductance peak (H-, M- or L-) is not strongly correlated with the transition voltage. For example, in the case of C8 shown in Fig. 3.7e, we found a correlation coefficient of 0.02, which means there is almost no correlation between low bias conductance and the energy level alignment. Similarly, the correlation coefficients for other molecular junctions are also small (Table 2). This conclusion may seem counterintuitive at first glance. If assuming a model where the molecule acts as a tunneling barrier, then the conductance can be defined as $G=Ae^{-\beta L}$, where $A$ is the contact conductance, $\beta$ is the tunneling decay constant and $L$ is the length, and $\beta^2$ is proportional to $V_{\text{tran}}$ (138, 139). As such, one would expect that any changes in $V_{\text{tran}}$ would correlate strongly with the conductance. The absence of correlation between $G$ and $V_{\text{tran}}$ in the experimental data means that the large conductance variation is primarily due to variation in $A$, the contact resistance, rather than due to $\beta$ or $V_{\text{tran}}$. In fact, the HWHM of $V_{\text{tran}}$ distribution is rather narrow; e.g., it is ~0.25 V or ~18% for C8 H- and M-junctions. Since $\beta \sim V_{\text{tran}}^{1/2}$ according to the above model, the corresponding variation in $\beta$ is ~10%, which could contribute only ~10% to the conductance variation. The actual observed low bias conductance variation is at least an order of magnitude greater than 10%, so most of it must be due to the contact resistance variation, rather than variation in $V_{\text{tran}}$. 

98
To further confirm above conclusion, we have also calculated the correlation coefficient between the conductance and the contact conductance by plotting the \( \log(G/e^{V_{tran}}) \), which is \((\sim \log(A))\text{vs. } \log(G)\), as is shown in Fig. 3.7f, and found a value of 0.98, thus indicating that the low-bias conductance is strongly correlated with the contact resistance. This indicates that the distribution of contact resistance varies over a much larger range than the tunneling barrier height, and as such any correlation with the transition voltage is obfuscated by the large distribution of contact resistance. This result illustrates the capability of the current approach to determine contributions from both the contact resistance and the energy level alignment, which is in contrast to the previous single-bias measurement that cannot separate the two contributions.

Fig. 3.8 summarizes the statistical analysis of the transition voltages for H-, M- and L-molecular junctions of C8 and C10. For C6, only the transition voltages for L-junctions could be measured due to the instability of H- and M- junctions of C6 at high bias voltages. The transition voltages for H- and M-junctions are similar \((\sim 1.4)\) despite their large conductance difference, which indicates that H- and M-junctions are due to difference in contact resistance rather than energy level alignment. This observation is consistent with the above conclusion that the contact resistance is the primary cause of the large conductance variation in single molecules. In contrast to H- and M-junctions, the transition voltage for L-junctions is \(~1.1\) V, which is significantly smaller. The smaller transition voltage is also reflected by the larger curvature in the G-V curves for the L-junctions, compared to the H- and M-junctions as shown in Fig. 3.3. It is also consistent
with the smaller $\beta$ value for the L-junctions. If assuming tunneling through a barrier model, then $\beta$ should be proportional to the square root of the barrier height and one should compare $\beta^2$ with the transition voltages. The ratio for $\beta^2$ between the M- and L-junctions is $\sim 1.2$, which agrees with the corresponding ratio for the transition voltages ($\sim 1.27$). We caution that given the error bars in the $\beta$ values, this analysis mainly serves the purpose of consistency check between the transition voltages and $\beta$ values.
Fig. 3.8 Transition Voltage histograms for C8, C10 and C6. (a-c) 2-D Transition Voltage histograms for C8 H, M and L, C10 H, M and L and C6 L junctions. (d-f) 1-D histograms summing up the counts between white dash lines in (a-c).
Summary for alkanedithiols

Similar results were also obtained for C10, which are summarized together with the data for C6 and C8 in Table 3.2. The difference in the transition voltage values for C6 (L-junctions), C8 and C10 are small, indicating that they are insensitive to the molecular length, which agrees with the finding by Beebe et al. (178) for self-assembled alkanemonothiol layers, as we mentioned earlier. The transition voltages for C6, C8 and C10 for L-junctions show consistently smaller values than those for H- and M-junctions, which indicates the difference between the HOMO and the electrode Fermi energy (142) for L-junctions are smaller than those of H- and M-junctions, despite their lower conductance values. Although this observation seems to be surprising because one would expect a lower conductance to yield a higher $V_{\text{tran}}$, it is consistent with previous first-principles calculations (47). The L-junctions have been attributed to a gauche conformation by Li et al. (47), and the ab initio calculation showed a smaller HOMO-Fermi gap for the L-junctions. This result further indicates that HOMO-Fermi energy alignment is not the only parameter that determines the conductance of a molecular junction.
Table 3.2  Summary of transition voltage, correlation coefficients and asymmetry ratio of alkanedithiols and biphenyldithiol.

Biphenyldithiol

To further demonstrate the value of single molecule TVS, we measured the TVS of biphenyldithiol. The molecule consists of two aromatic rings linked together with a torsion angle of 36.5°. (175) Previous studies of phenyl systems with different numbers of phenyl rings indicate a smaller tunneling decay constant than in alkane chains. (175) Fig. 3.9 shows the transition voltage distribution of over 2000 biphenyldithiol junctions vs. voltage and conductance. The most probable transition voltage is about 0.7 V, which is significantly smaller than the value for the alkanedithiols. The smaller transition voltage is expected if one
considers the lower energy $\pi$-electrons of the aromatic rings in biphenyldithiol in contrast to the $\sigma$-electrons dominating the alkanedithiols. The smaller $V_{\text{tran}}$ is also consistent with the observation of smaller tunneling decay constants in phenyl systems.\(^{(175)}\)

**Fig. 3.9** Transition Voltage Spectroscopy of biphenyldithiol. (a) G-V curves and fittings. (b) TVS curves determined from the G-V curves in (a). (c) 2-D Transition Voltage histogram. (d) 1-D histograms summing up the counts between white dash lines in (a-c).

**Discussion on Asymmetry**

All of the molecules studied here are symmetric, but many of the individual I-V and G-V curves display asymmetry, as we noted earlier. The
asymmetry is also clearly seen in the transition voltage histograms (e.g., Fig. 3.9c). To examine the statistical significance of the asymmetry, we determined the distribution of the asymmetry factor vs. the conductance, where the asymmetry factor is defined as the ratio of current at a large forward bias to that at a large reverse bias. For alkanedithiols, the most probable asymmetry factors are close to 1. However, for biphenyldithiol the asymmetry factor is 0.45, indicating a large asymmetry. We have analyzed this asymmetry quantitatively and presented the findings in Table 3.2 and in Fig. 3.10. For a given molecule, the asymmetry has always the same polarity, which leads us to believe that it is originated from the asymmetry of the electrodes, namely the relatively flat substrate electrode vs. the sharp tip electrode. The relatively large asymmetry in biphenyldithiol may be attributed to the stronger coupling of the $\pi$-electrons of the aromatic rings to the flat substrate than to the atomically sharp tip, as we have recently reported in other molecular systems.(20) Further studies are clearly needed in order to fully understand the nature of the observed asymmetry, but the ability to measure and perform a statistical analysis on a large number of molecular junctions with different contact geometries over a wide bias range makes the asymmetry studies possible and statistical analysis meaningful.
**Fig. 3.10** Asymmetry histograms for recorded IV curves. X axis is asymmetry ratio in log scale (base of 2). Y-axis is low bias conductance in log scale (base of 10). The asymmetry ratio is defined as the current when substrate is positively biased at a certain voltage divided by the current when substrate is negatively biased at the same voltage. (a) C8-H. (b) C8-M and L. (c) C10-H. (d) C10-M and L. (e) C6-L large bias. (f) Biphenyl. (g) C6-H low bias. (h) C6-M and L low bias.

### 3.5 Measurement of high conductance junctions by using hybrid SAM

Previous 1,6-hexanedithiol high bias range (±2V) I-V characteristics measurement in was limited mostly to L-junctions. M- and H-junctions become unstable at high bias due to large possibility of forming Au point contact. This was also found in the rectification behavior study of a molecular diode using large bias I-V characteristics.\(^{(82)}\) Using C6-dithiol/C6-monothiol hybrid SAM, however, largely reduces such possibility. Fig. 3.11a shows the high bias range (±2V) G-V histogram of 1,6-hexanedithiol/hexanethiol hybrid SAM. M-junctions can be easily measured. The low bias conductance value is similar to the previous measurement. And the transition voltage histogram (Fig. 3.11d) shows a transition voltage of ~1.6 V. The method of using hybrid SAM’s is also used in measuring the 1,4-butanedithiol (Fig. 3.11b and e) and BDT molecules low conductance regimes (Fig. 3.11c and f), which are otherwise difficult by using target molecules only. The yield of I-V curves for these two particular molecules are lower than that for C6. A faster bias sweep rate of 50 Hz was used as oppose to typical 10 Hz
in order to improve the success rate. This also causes the low counts in the
histograms.

**Fig. 3.11** Transition voltage measurement of hybrid SAMs. (a-c) G-V
histograms for 1,6-hexanedithiol/hexanethiol, 1,4-butanedithiol/butanethiol and
1,4-benzenedithiol/hexanethiol, respectively. (d-f) Corresponding transition
voltage histograms.
3.6 Conclusions

In conclusion, a new STM break junction method was developed for the rapid measurement of thousands of I-V and G-V curves of repeatedly created single molecule junctions, thus allowing the construction and analysis of I-V and G-V histograms. The low-bias conductance values reproduced those obtained by measuring the conductance at small fixed biases as reported in literature. However, the present method provides complete I-V and G-V curves, revealing non-linear regimes and asymmetry, and allowing for statistical analyses of the results. More importantly, transition voltage spectroscopy of single molecule junctions was carried out to determine transition voltage, an important parameter that quantifies the alignment of molecular energy levels relative to electrode Fermi levels. The transition voltages of alkanedithiols peak at 1.4 V for the H- and M-junctions, and 1.1 V for the L-junctions, respectively, and these values are independent of the molecular length (n=6, 8 and 10). For biphenyldithiol, the transition voltage is 0.7 V, much lower than for the alkanedithiols. There is a significant distribution in the transition voltage for the repeatedly created individual molecular junctions, which indicates the dependence of the molecular energy level alignment on the molecule-electrode contact geometry. However, the variation in single molecule conductance values is mainly due to contact resistance rather than energy level alignment variations. This work adds a new dimension (voltage) to the widely used conductance histogram analysis approach for single molecule transport studies, and allows for a better understanding of the charge transport
characteristics. This method is anticipated to significantly benefit the study of single molecule charge transport in other molecular systems.
4 SIMULTANEOUS MEASUREMENT OF SINGLE MOLECULE
CONDUCTANCE, THERMOPOWER AND TRANSITION VOLTAGE
SPECTROSCOPY

4.1 Introduction

Understanding charge transport through single molecule junctions is the most basic but important goal in molecular electronics research. (22-25) To achieve this goal, a variety of methods have been developed and proven useful in the recent years, such as single molecule conductance measurement using STM break junction technique (3), current-voltage characteristics and transition voltage spectroscopy (188). In addition, the thermopower measurements reported by several groups recently provided an alternative way of charge transport measurement. A direct thermoelectric voltage measurement on molecular junctions was first reported by Reddy et al in 2007 on molecular monolayers sandwiched between a room-temperature STM tip and a heated substrate in air. (150) Based on STM break junction technique, Vendataraman and colleagues measured single molecule conductance and thermopower simultaneously by measuring the current induced by thermal gradient at zero bias when single molecule bridges the tip and the substrate. (152) In a theoretical model derived from Landauer formula described by Paulsson et al (149), as is discussed in Chapter 1, the thermopower (or the Seebeck coefficient) of a metal-molecule-metal junction provides information on the first derivative of the molecule’s transmission function at the Fermi level of the metal electrodes. In the simplified scenario where the HOMO and LUMO transmission peaks are fitted by
Lorentzian distributions, the thermopower is therefore a measure of the gap between the electrode Fermi level and the nearest molecular orbital (HOMO or LUMO). The current-voltage statistics technique we developed in the last chapter allows one to measure conductance and tunnel barrier height of a single molecule junction at the same time. In this report, we will show that such technique also allows us to simultaneously obtain conductance and thermopower information. Furthermore, we will also present a correlation study of transmission voltage spectroscopy and thermopower of single molecule junctions.

4.2 Sample Preparation

Gold substrates were prepared by thermally evaporating 130 nm of gold on mica under UHV before the experiments. All measurements were performed using STM tips freshly cut from 0.25 mm gold wire (99.998%). Teflon cells were cleaned with piranha solution and sonicated in 18 MΩ water three times prior to the experiment. Self assembled monolayers (SAM) were prepared for the measurements. The substrate was briefly annealed using a hydrogen flame and immersed into solutions with target molecule dissolved for a proper period of time depending on the type of molecules. For example, for long chain alkanedithiols (e.g. 1,6-hexanedithiol and 1,8-octanedithiol) and some conjugated molecules (e.g. 4,7-dithiophenyl-2,1,3-benzothiadiazole-3',3''-dithiol), ~50 µM samples solutions were used, and the reaction time was typically 2-3 hours. For short chain alkanedithiols (e.g. 1,4-butanedithiol) and other conjugated molecules (e.g. 1,4-benzenedithiol), a 1:3 mixture of the target molecule and an alkane monothiol molecule with similar length (total concentration of ~50 µM) was empirically
used in order to enhance the molecular step quality in the STM break junction measurement. The substrate was exposed to such solution overnight to form a compact SAM so that the target molecules stand up among the matrix of monothiol molecules.

4.3 Experimental Setup and Calibration

After the sample preparation, the substrate was mounted onto a STM sample holder that has a resistive heating plate with an integrated thermocouple. The temperature can thus be monitored and controlled by a LakeShore 331 temperature controller. Similarly to the literature\textsuperscript{(150, 152)}, the STM tip is in direct contact with bulk metal so its temperature is always kept at room temperature. A clean Teflon cell was used to hold clean toluene in order to protect the SAM surface during setting up the STM break junction. The toluene was then removed from the sample using a clean glass pipette before the STM head was placed into a glovebox filled with nitrogen.

We performed the same STM break junction measurement described in Chapter 3\textsuperscript{(188)} to acquire a large number of current-voltage (I-V) curves at a set of different substrate temperatures. When a fixed low bias (5 or 10 mV) is applied, the tip approaches to the substrate until close enough to form molecular junctions but without making contact with the surface, and then retracts away from the surface. During retraction process, a step detection algorithm is activated and as soon as a molecular step (the signature of molecular junction formation\textsuperscript{(3)}) is detected, the tip stops retracting and an I-V curve is recorded. The tip is then pulled back by an additional distance during which the current is continuously
monitored to determine if the junction collapses. Another I-V curve is recorded if the step sustains, or the break junction cycle starts over if the step breaks down.

Ideally, when the substrate is heated up, the thermoelectric effect of the single molecule junction induces an offset current to its I-V characteristics, which is basically the current at zero bias. In order to enhance the current resolution at zero bias, a small bias range (5 or 10mV) is used in the I-V measurement.

Practically, however, there is another possible source of the current at zero bias in a recorded I-V curve: the intrinsic offset in the instrument. The circuit offset calibration is thus critical in this experiment and a thorough analysis is provided below. Fig. 4.1a shows the schematics of the current preamplifier used in our setup, in which a resistor $R_M$ represents the molecular junction and a current source $I_{TE}$ represents the thermoelectric current. $U_{os}$ and $I_{os}$ are the input offset voltage and input offset current of the operational amplifier (OP-AMP) model OPA129U used in the preamplifier. Kirchhoff’s current law at the circled node gives rise to

$$ U_{out} = \frac{R_F}{R_M} (U_{os} - U_{bias}) + U_{os} - I_{os}R_F - I_{TE}R_F. \tag{4.3.1} $$

The measured current offset in the I-V curve at zero applied bias, $I_{TE,m}$, is then given by

$$ I_{TE,m} = \frac{U_{out} |_{U_{bias}=0}}{-R_F} = I_{TE} + I_{os} - U_{os} \left( \frac{1}{R_M} + \frac{1}{R_F} \right) = I_{TE} + I_0. \tag{4.3.2} $$

when $I_0 = I_{os} - U_{os} \left( \frac{1}{R_M} + \frac{1}{R_F} \right)$ is the total offset current inherent in the circuit.

In fact, it is more convenient to express in terms of voltage because of the definition of the Seebeck coefficient. And to increase current sensitivity, large $R_F$
is usually used. One can thus find the measured total offset voltage, $U_{TE,m}$, given by

$$U_{TE,m} = U_{TE} + I_{os}R_M - U_{os}R_M \left( \frac{1}{R_M} + \frac{1}{R_F} \right) \approx U_{TE} + I_{os}R_M - U_{os} = U_{TE} + U_0,$$

(4.3.3)

where $U_0 = I_{os}R_M - U_{os}$ is the total offset voltage and should remain constant if $U_{os}$ and $I_{os}$ keep constant over time.

Fig. 4.1 Experimental setup and calibration. (a) The equivalent circuit of experiment. (b) Offset calibration at different time. (c) Setup for measuring the thermopower of connection wire. (d) Thermopower measurement of the connection wire with respect to gold.
A control experiment is carried out using a 10 MΩ dummy resistor to model the molecular resistance. As is shown in Fig. 4.1b, $U_0$ remains constant over very long time. Therefore, $U_{TE,m}$ is a valid measure of $U_{TE}$ at different substrate temperatures.

The temperature gradient in the entire system falls onto two parts: the molecule that bridges the tip and substrate, and the metal wire (55Cu45Ni) that connects the heated substrate to the bias. We measured the Seebeck coefficient of the metal wire with respect to gold using a 1nA/V current amplifier and a 1 kΩ dummy resistor (Fig. 4.1c). By measuring the voltage change at different temperature gradients (Fig. 4.1d), we obtain $\sim 2.5 \mu$V/K for the Seebeck coefficient of the metal wire (we used the Seebeck coefficient of bulk gold, 1.94 $\mu$V/K). The Seebeck coefficient of the single molecule junction can thus given by

$$S_{junction} = S_{wire} - \frac{\Delta U_{TE,m}}{\Delta T_{sub}}. \quad (4.3.4)$$

4.4 Results and Discussions

Small bias range I-V characteristics measurement

Fig. 4.2a shows a typical current-distance trace of 4,7-dithiophenyl-2,1,3-benzothiadiazole-3’,3”-dithiol (DTBTDT, Fig. 4.2a inset) at 40°C substrate temperature, with three I-V curves recorded at points marked with color dots. The corresponding I-V curves are shown in Fig. 4.2b with colors matching that of the dots in Fig. 4.2a. Because of the much smaller bias range ($\pm 5$ mV) applied, the I-V curves are linear. Similarly to Chapter 3, 2-D I-V and G-V histograms can be constructed using hundreds of I-V curves for each substrate temperature (Fig. 4.2c-d). Note that due to the low bias range ($\pm 5$ mV in this case), straight bands
are observed in the I-V histogram instead of curved bands compared to large bias cases. The G-V histogram showing a flat band also indicates the linearity of the I-V curves in low bias range. Also there’s a clear offset current at zero bias in the I-V histogram, which causes the large zero bias anomaly in the G-V histogram within ±1mV bias range. This offset current is the $I_{TE,m}$ discussed above, which is a combined contribution of inherent circuit offset and thermoelectric current.

![Graphs and diagrams](image)

**Fig. 4.2** Small bias range I-V characteristics of 4,7-dithiophenyl-2,1,3-benzo thiadiazole-3’,3’’-dithiol (DTBTDT). (a) A typical current-distance trace. (b) Two I-V curves recorded at marks with corresponding colors in a. (c) I-V histogram. (d) G-V histogram.
Thermoelectric current measurement

As is studied in Chapter 3, the contact geometry variation of single molecule junctions often leads to large variation in the contact resistance, and thus wide distribution of the junction conductance statistics. Such variation also results in larger divergence at higher bias in the raw I-V curves as seen in Fig. 4.2c, which makes it difficult to extract statistics of either current at zero bias or bias at zero current. To correct such divergence, we divide \( I_{TE,m} \) of every I-V curve by the corresponding conductance \( G \) extracted from the current-distance trace to get the offset voltage (or thermoelectric voltage) \( U_{TE,m} \), as discussed above. To simplify the procedure, we smoothed the I-V curves using Savitzky-Golay filter to get rid of the excessive noise as well as the features caused by the resolution of the digital data acquisition (NI card), and then we divided the entire I-V curve by corresponding \( G \) and constructed a normalized I-V histogram (Fig. 4.3a). Note that a straight band with slope of \( \sim 1 \) is observed in all such histograms, which is also an indication of good linearity of I-V curves in low bias range. \( U_{TE,m} \) can thus be extracted from the statistics at zero bias voltage (white dash line in Fig. 4.3a). Furthermore, we can construct the conductance-thermoelectric voltage histogram shown in Fig. 4.3b. As discussed in Chapter 3, the distribution in Fig. 4.3b indicates weak correlation between the conductance variation and thermoelectric voltage.
Fig. 4.3  Thermopower measurement of DTBTDT molecule. (a) Normalized I-V histogram. (b) 2-D conductance-thermoelectric voltage histogram. (c) Thermoelectric voltage measured at different substrate temperatures (tip kept at room temperature). (d) Plot of measured thermoelectric voltage as a function of substrate temperature for Seebeck coefficient extraction.

**Seebeck Coefficient Determination**

By analyzing normalized I-V histograms acquired at different substrate temperatures (26°C, 40°C, 50°C, and 60°C), we obtain a set of $U_{TE,m}$ values (Fig. 4.3c), which allows us to study the dependence of $U_{TE,m}$ on temperature (Fig. 4.3d). The Seebeck coefficient of the junction $S_{\text{junction}}$ can be obtained using
Equation 4.3.4, where \( \frac{-\Delta U_{TE,m}}{\Delta T_{sub}} \) is extracted by linearly fitting the data points. For DTBTDT, we get a Seebeck coefficient of 8.4 ± 6.6 µV/K. Note that the standard deviation is usually large. We have thus carried out several experiments for each molecule and the difference of the measured Seebeck coefficients is typically within 2 µV/K. Such large standard deviation is also in agreement with the single molecule thermoelectric current measurement done by Venkataraman and coworkers. (152) This large deviation can be attributed to several factors. Extrinsically, the noise smoothing procedure may introduce larger error compared to Venkataraman’s work. Intrinsically, the variation of tunnel barrier height is expected to have an influence according to the simplified direct tunneling model provided by Paulsson et al (149). Meanwhile, the large variation of contact geometry between the molecule and electrodes is known to have induced large uncertainty in conductance measurements. However, the weak correlation between the conductance and offset voltage shown in Fig. 4.3b indicates that the variation of the Seebeck coefficient is not primarily determined by that of the conductance. However, such large deviation was not seen in the thermoelectric voltage measurement for molecular monolayer done by Reddy et al (150), in which collective effects could have played a role. Further discussion will be provided in the next section.

**Thermopower measurements for other molecules**

We have performed the same measurements to 1,4-butanedithiol (C4), 1,6-hexanedithiol (C6), 1,8-octanedithiol (C8), 1,4-benzenedithiol (BDT) and 1,4’-biphenyldithiol (BPDT). A summary of the dependence of \( U_{TE,m} \) on \( T_{sub} \) and
corresponding Seebeck coefficients are given in Fig. 4.4. Note that short length molecules are typically more difficult to form good monolayers on gold surface possibly due to its strong interaction with the surface. In order to improve the break junction measurement quality, and also for the concern of large bias range I-V characteristics in the next section, C4 and BDT molecules are mixed with butanethiol and hexanethiol, respectively, during the sample preparation to form a hybrid SAM. Control experiments with SAM’s consisting just butanethiol and hexanethiol are completely featureless. Further discussion on the effects of hybrid SAM will be provided in the next section.
Fig. 4.4  Experimental data and Seebeck coefficients for (a) 1,4-butanedithiol (C4), (b) 1,6-hexanedithiol (C6) (c) 1,8-octanedithiol (C8), (d) 1,4-benzenedithiol (BDT), (e) 1,4’-biphenyldithiol (BPDT), and (f) 4,7-dithiophenyl-2,1,3-benzothiadiazole-3’,3’’-dithiol (DTBTDT).

Discussion on single molecule TVS and thermopower
Derived from Landauer Formula, the Seebeck coefficient of a single molecule junction can be given by (149),

\[ S_{\text{function}} = -\frac{\pi^2 k_B T}{3|e|} \left. \frac{\partial \ln(\tau(E))}{\partial E} \right|_{E=E_F}, \quad (4.4.1) \]

where \( \tau(E) \) is the transmission function of the junction.

In a simplified direct tunneling model, the HOMO and LUMO peaks in \( \tau(E) \) can be fitted by two Lorentzian distributions. \( S_{\text{function}} \) therefore becomes a measure of tunnel barrier height, or the alignment between the electrode Fermi level and the nearest molecular orbital. Segalman and coworkers studied the Seebeck coefficients of benzenedithiol derivatives and proposed a systematic energy level shift with respect to electrodes’ Fermi levels induced by side group substitution. (151) However, no direct measurement of the tunnel barrier height is given in this work. The rapid I-V technique developed in Chapter 3 allows one to acquire single molecule transition voltage, which is a measure of tunnel barrier height. To further study the relationship between Seebeck coefficient and tunnel barrier height, we performed single molecule transition voltage spectroscopy to each molecule by recording and analyzing large amount of I-V characteristics with large bias sweeps similarly to Chapter 3.

Fig. 4.5 shows the 2-D G-V histograms and transition voltage histograms of DTBTDT (Fig. 4.5a-b) and BDT (Fig. 4.5c-d). Bowl shaped bands observed indicate the nonlinearity of I-V curves in high bias regimes (Fig. 4.5a and c). Note that BDT/C6-monothiol hybrid SAM was used and that Fig. 4.5c only includes the low conductance regime of BDT because the possible current-induced heating
effects at high bias makes it difficult to acquire I-V curves for high conductance regime. (17, 82, 182, 183) The transition voltages for DTBTDT and BDT are determined to be $0.71 \pm 0.26$ V and $0.79 \pm 0.30$ V, respectively, from Fig. 4.5b and d. A summary of all measured Seebeck coefficients and transition voltages is given in Table 4.1.

**Fig. 4.5** Single molecule transition voltage statistics for DTBTDT and BDT molecules. (a-b) G-V histograms for DTBTDT and BDT low conductance regime, respectively. (c-d) Corresponding transition voltage histograms.
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Seebeck coefficient (µV/K)</th>
<th>Transition voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4</td>
<td>2.8 ± 5.9</td>
<td>1.8 ± 0.30</td>
</tr>
<tr>
<td>C6</td>
<td>2.8 ± 6.7</td>
<td>1.2 ± 0.16</td>
</tr>
<tr>
<td>C8</td>
<td>1.4 ± 5.9</td>
<td>1.4 ± 0.30</td>
</tr>
<tr>
<td>DTBTDT</td>
<td>8.4 ± 6.6</td>
<td>0.71 ± 0.26</td>
</tr>
<tr>
<td>BDT</td>
<td>6.2 ± 5.4</td>
<td>0.79 ± 0.30</td>
</tr>
<tr>
<td>BPDT</td>
<td>6.8 ± 5.2</td>
<td>0.69 ± 0.20</td>
</tr>
</tbody>
</table>

¹ Hybrid SAM’s are used for improved TVS measurement.
² Only low conductance regime is measured due to high current instability.

Table 4.1 Measured Seebeck coefficients and transition voltages.

Fig. 4.6 plots the Seebeck coefficients versus transition voltages for all six molecules. Due to the large errors in both the Seebeck coefficients and the transition voltages, subtle correlation cannot be determined. A general difference between saturated alkanedithiols and conjugated molecules, however, can be observed. Compared to saturated alkanedithiols, conjugated molecules typically have smaller transition voltages and larger Seebeck coefficients. This observation is consistent with the facts that conjugated molecules have lower tunnel barrier height, or smaller gap between the frontier molecular orbital and the electrodes’ Fermi energy.
Fig. 4.6 The Seebeck coefficients versus transition voltages for all six molecules measured.

4.5 Conclusions

The STM-BJ base rapid I-V technique has been used to study the thermoelectric properties of single molecule junctions. Large amount of I-V characteristic curves are recorded using small bias range when temperature gradients are applied between the tip and the substrate. This method allows for simultaneous measurement and correlation study of low bias molecular conductance and thermoelectric current. The thermoelectric voltage can then be determined by dividing the zero bias current by the corresponding low bias conductance. The Seebeck coefficient can be extracted by linearly fitting the thermoelectric voltage vs. temperature. Single molecule transition voltage is also measured using large amount of I-V characteristic curves recording with large
bias range. By studying the correlation between the Seebeck coefficient and transition voltage, we found that the Seebeck coefficient can also provide a measure of tunnel barrier height for simple direct tunneling molecules.
5 CONCLUSIONS AND PERSPECTIVE

5.1 Conclusions

This dissertation has provided two novice methods and their various applications in attempt to drive the advancement of molecular electronics.

First of all, an AC circuit system operating in radio frequency range has been developed and implemented to conventional break junction system previously using DC current preamplifiers. Such system has been demonstrated useful in studying the breakdown process of atomic-sized metal contacts such as gold quantum point contact. The breakdown time was determined to be faster than 0.1 ns. And multiple events during the breakdown process on the time scale of nanoseconds were observed. The study bridges the wide gap in the time scale between the molecular dynamics simulations and previous experimental work.

Furthermore, a new STM break junction method has been developed to acquire large amount of I-V characteristics. This method allows for meaningful statistical analysis of thousands of I-V and G-V curves of alkanedithiol and biphenyldithiol molecules. Non-linear regimes and asymmetry are clearly observed on the I-V and G-V histograms. Furthermore, single molecule transition voltage spectroscopy was carried out, which measures the alignments of molecular energy levels relative to electrode Fermi levels. By analyzing its correlation to the low bias conductance, we found that the variation of low bias conductance is mainly determined by contact geometry rather than the variation in the energy level alignment.
In addition, the STM-BJ based rapid I-V technique can also be used to study thermoelectric properties of single molecule junctions. Temperature gradients are applied by heating up the substrate while maintaining room temperature of the STM tip. By performing statistical analysis to the zero bias offset current of single molecule I-V characteristics, thermoelectric current can be measured and translated to thermoelectric voltage at different temperatures. The Seebeck coefficient can thus be obtained by finding the linear relation between the thermoelectric voltage and temperature. Combining with single molecule TVS measurement, the Seebeck coefficient is also found to be a measure of tunnel barrier height for a variety of simple molecules.

5.2 Perspective

Although the methods used in single molecule electronics study nowadays are far from real-world application, they have however provided useful quantitative ways of characterizing single molecule charge transport properties. And we expect the field can be benefitted from more applications of the two techniques demonstrated in this dissertation.

The goal for the RF circuit is to eventually use it in the molecular junction studies. However, further development is needed before this can be done. A major difficulty is that most molecular systems are much less conductive than gold quantum point contact, mostly of hundreds of MΩ or even GΩ. Matching such high impedance to the standard 50 Ω RF impedance requires more amplification stages which normally induce higher noise. Also a very common issue for RF circuits is that when the input impedance changes due to change of
experimental environment (e.g. from air to liquid), the reflection coefficient becomes larger than 1, the circuit will be driven into resonance. This is commonly referred as the stability problem. Both noise and stability require very careful design.

More potential applications can also be expected for the STM-BJ based rapid I-V curve technique. For example, the transition from coherent tunneling to incoherent hopping has been a heated topic. Such transitions have been observed using families of molecules of the same repeating unit but different length and the same molecule in a wide range of temperature. The statistical analysis of I-V characteristics will provide unparalleled insight into this transition process. Moreover, the difference in the thermoelectric effect between tunneling and hopping system is of particular interest. On the other hand, the measurements of large bias range I-V characteristics and zero bias offset current have to be carried out in separate experiments due to the resolution limit of linear current amplifier. A logarithmic amplifier will provide such capability and thus can correlate thermoelectricity measurement directly to the TVS.
REFERENCES


