Electromechanical Properties of Single Molecule Devices

by

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ABSTRACT

Understanding the interplay between the electrical and mechanical properties of single molecules is of fundamental importance for molecular electronics. The sensitivity of charge transport to mechanical fluctuations is a key problem in developing long lasting molecular devices. Furthermore, harnessing this response to mechanical perturbation, molecular devices which can be mechanically gated can be developed. This thesis demonstrates three examples of the unique electromechanical properties of single molecules.

First, the electromechanical properties of 1,4-benzenedithiol molecular junctions are investigated. Counterintuitively, the conductance of this molecule is found to increase by more than an order of magnitude when stretched. This conductance increase is found to be reversible when the molecular junction is compressed. The current-voltage, conductance-voltage and inelastic electron tunneling spectroscopy characteristics are used to attribute the conductance increase to a strain-induced shift in the frontier molecular orbital relative to the electrode Fermi level, leading to resonant enhancement in the conductance.

Next, the effect of stretching-induced structural changes on charge transport in DNA molecules is studied. The conductance of single DNA molecules with lengths varying from 6 to 26 base pairs is measured and found to follow a hopping transport mechanism. The conductance of DNA molecules is highly sensitive to mechanical stretching, showing an abrupt decrease in conductance at surprisingly short stretching distances, with weak dependence on DNA length. This abrupt conductance decrease is
attributed to force-induced breaking of hydrogen bonds in the base pairs at the end of the DNA sequence.

Finally, the effect of small mechanical modulation of the base separation on DNA conductance is investigated. The sensitivity of conductance to mechanical modulation is studied for molecules of different sequence and length. Sequences with purine-purine stacking are found to be more responsive to modulation than purine-pyrimidine sequences. This sensitivity is attributed to the perturbation of π-π stacking interactions and resulting effects on the activation energy and electronic coupling for the end base pairs.
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CHAPTER 1
INTRODUCTION TO MOLECULAR ELECTRONICS

1.1 Introduction

Combining concepts from solid state physics, chemistry and molecular biology, the field of molecular electronics seeks to understand charge transport on molecular length scales and develop useful devices from molecular building blocks. Originally dating back to the 1950’s [1,2], molecular electronics was greatly helped by the seminal work of Aviram and Ratner in 1974 [3] in which they propose a single molecule rectifier-like device based on a donor-bridge-acceptor system. The field has grown rapidly with the invention of experimental techniques to electrically contact single molecules with macroscopic electrodes to investigate transport properties and build single molecule devices. These include the scanning tunneling microscope (STM) [4–7], mechanically controlled break junction (MCBJ) [8–11], electro-migration [12,13] and various other experimental designs [14–17]. Using these experimental methods, the transport properties of a variety of molecules and the dependence of charge transport on molecular properties like molecular length [18–24] and chemical structure and substitutions [25–33]. Driven by the miniaturizing of silicon based electronics, much of the recent research into molecular electronics has been focused developing molecular scale devices which mimic conventional CMOS device functionality. For example, asymmetric molecules have been shown to have rectifying behavior by measuring the current-voltage characteristics in single molecule junctions, demonstrating diode functionality suggested by Aviram and Ratner [34–39]. In addition, various schemes have been devised to implement a third
electrode into molecular junctions, either using electrochemical techniques in electrolytic solution [25,27,31,40-43] or a back gate added to a molecular junction in vacuum in a MCBJ or electro-migrated junction [44-48], in order to develop single molecule devices analogous to the transistor.

In addition to developing devices analogous to those of conventional silicone electronics, i.e. diodes and transistors, molecules can be designed to respond electrically to external influences in ways that aren’t seen in conventional electronics. One such characteristic is the interplay between the electronic and mechanical properties that can be seen by mechanically stretching molecular junctions while monitoring the transport properties. Thus, on the molecular scale, electronic properties can be mechanically gated and lead to novel device functionalities. Furthermore, mechanical manipulation can be a powerful tool for analyzing charge transport in molecular devices. By determining the electrical response to controlled mechanical manipulation and correlating this electromechanical response to changes within the molecule, a deeper understanding of charge transport in molecular scale systems can be achieved.

This thesis will develop the concept of electromechanical response in single molecule devices and demonstrate several molecular systems with unique electromechanical properties. First, the important concepts of molecular electronics will be introduced. Next, an investigation into the unique electromechanical properties of 1,4-benzenedithiol will be described, in which a counterintuitive increase in conductance with increased electrode separation is reported. The final two sections will deal with the electromechanical properties of single DNA molecules. The first will deal with the electrical response of DNA molecules when stretched to rupture and what this electrical
response can tell about the structural response within the molecule. The next will look into the response of DNA molecules to small scale mechanical modulation of the $\pi-\pi$ stacking between neighboring bases. Finally, concluding remarks will be made about the work presented in this thesis and further experiments to bolster the results presented will be suggested.

1.2 Measuring single molecules

As mentioned previously, the concept of using single molecules as functional devices was introduced by Aviram and Ratner in 1974 with their idea of a molecular rectifier. Since these early proposals, the driving force for the field has been to understand charge transport in single molecule devices and ultimately build functional single molecule devices. However, in order to build such devices a technique to mechanically manipulate target specimens on subnanometer length scales and read out electrical information is needed. To this end, the advent of the scanning tunneling microscope [4] [49] and mechanically controlled break junction [11] has greatly advanced the study of single molecule transport. Using both techniques conducting electrodes can be brought together with atomic scale precision and single molecule electronic devices can be generated through a break junction method. Here we will discuss the STM-break junction (STM-BJ) technique.

1.2.1 STM break junction technique

Owing to the quantum nature of charge transport in molecular systems, a method to measure single molecules should be able to produce robust contacts between metal electrodes and a target molecule and should ideally be able to do this reproducibly and quickly in order to statistically analyze the most likely molecular conductance. To
accomplish this, Xu et al. [6] developed the STM-break junction technique to measure single molecule conductance. In a conventional STM a conducting, atomically sharp tip is approached to a conducting substrate. If a bias is applied between the two conducting electrodes, a current can be measured when the tip is brought into close enough proximity to the substrate for electrons to tunnel through the intermediate, either vacuum or solvent. This way the topography of the surface can be imaged by tracing the tip across the substrate and monitoring the tunneling current, or conversely maintaining the tunneling current and monitoring the tip displacement. It had been shown that by driving a metal tip into a metal substrate atomic chains could be formed which have a conductance of multiples of the conductance quantum, \( G_0 = 2e^2/h \) [50,51]. In the STM-BJ technique, a similar scheme is performed in solution in the presence of molecules which have terminal groups that strongly interact with the metal electrodes. These terminal groups can include thiol [18,52–58], amine [18] [29,59–61], and carboxylic groups [18], in addition several groups have developed ways to make a direct contact between the carbon and gold [28] [62]. Typically during the STM-BJ technique a gold STM tip is brought into contact, or near contact, with a metal substrate. Monitoring the tip-substrate current during retraction of the tip, in the absence of molecules, produces an exponentially decreasing current vs. tip displacement trace, as expected for charge tunneling through solvent (or vacuum). In the presence of molecules there is a chance that, during the retraction of the tip, molecules will bind between the tip and substrate, producing a plateau in the current vs. tip displacement. The final plateau before the current drops to zero is representative of a single molecule bridging the tip-substrate gap, a single molecule junction. Repeating this process thousands of times, a histogram of the most
probable molecular conductance can be built in order to deal with variation in the molecule-electrode binding geometry and quantum nature of these devices.

Figure 1.1: STM-break junction technique. (a-d) A schematic representation of the formation and breakdown of a single molecule junction. The gold electrode of an STM is approached (a) to a gold substrate on which the target molecule is functionalized. The tip and substrate are contacted (b) and the tip is retracted (c) until the molecular junction is broken (d). (e) During this process plateaus are detected in traces of the tip-substrate current vs. tip displacement representing molecules bridging the tip-substrate gap. (f) Combining thousands of these traces, a conductance histogram can be generated and the most probable molecular conductance can be determined.

The STM-BJ technique has been successfully implemented by several groups around the world and has proven to be a valuable tool for measuring single molecule
conductance reproducibly. In addition, the STM-BJ technique can be easily adapted to gain additional information about transport properties in single molecule junctions. For example, the current-voltage (I-V) characteristics of single molecule devices are valuable for understanding transport properties like tunneling barrier height [21,63–67], differential conductance [68–70], and inelastic tunneling spectroscopy [71] [72–81]. Furthermore, performing STM-BJ experiments in electrolytic environment allows for application of an electrochemical voltage that adjusts the molecular barrier relative to the metal Fermi level, giving additional information about transport phenomena and essentially building a single molecule transistor [25,26,40]. To this end, several groups have implemented schemes to detect single molecule junctions and investigate transport phenomena [82] [34]. One important advance in this area was made by Guo et al., who implemented an algorithm that detects the signature plateau of a molecular junction and halts tip retraction [19]. Once the tip is stopped the bias can be swept while measuring the current and this process can be repeated at relatively fast speeds until the molecular junction breaks down. Added to the STM-BJ technique, this method for characterizing transport in single molecules can rapidly generate large volumes of information that is not limited to the I-V characteristics but can include any adjustable parameter of the single molecule junction, making this a very powerful tool [83].

1.3 Charge transport theory in molecular systems

A predictive model for charge transport in single molecule devices is of equal importance to experimental techniques for single molecule electronics. Such a theory is extremely difficult to develop because of the large computing time needed to calculate fundamental properties form first principles of even the smallest molecular systems.
Fortunately, several theories have been developed which use approximations to make predictions and explain the experimentally measured molecular transport properties [84-93]. These theories have attained varying degrees of success reproducing and predicting experimental measurements, although there are typically differences between experimentally measured and calculated values.

The following section will introduce the basic models for charge transport in molecular and atomic scale systems. First, the idea of coherent charge transport on mesoscopic scales will be introduced, along with the Landauer formula which describes charge transport in mesoscopic scale systems like atoms and molecules as a scattering problem. Next, the relationship of tunneling current and applied voltage will be discussed in relation to the Simmons model and the concept of transition voltage will be introduced. Then inelastic tunneling effects are discussed in reference to the opening of vibrationally coupled transmission pathways. Finally, charge transport in larger molecules will be discussed in terms of a simple thermally activated hopping model.

1.3.1 Landauer formula

When discussing the electrical properties of materials the characteristic length scale of the system under investigation is important. For example, in macroscopic materials the conductance relates the current to an applied bias through Ohm’s law. The conductance is then related to the conductivity, a material specific property, by the ratio of the surface area and the material length. However, for materials on much smaller length scales, when the Ohmic conductance would blow up due to the inverse length relation, there are certain scattering processes to consider. For instance, the electronic mean free path (l), or the distance an electron can travel while maintaining constant
momentum, is an important length scale for electronic properties of small materials. For materials with lengths much larger than $l$, in the diffusive regime, the motion of electrons is like a random walk between elastic collisions with impurities. Alternatively, for materials with lengths smaller than $l$, the ballistic regime, electronic momentum is constant and electrons only scatter off the boundaries of the system.

Another important length for charge transport in small materials is the phase-coherence length ($L_\phi$), or the distance over which information about the phase of the electronic wave can be preserved. Phase information, or coherency, can only be destroyed by inelastic scattering processes, like the electron-electron and electron-phonon interactions, in which the phase of the electronic wave is altered. Materials with lengths which are smaller than $L_\phi$ have coherent charge transport and are said to be mesoscopic scale materials.

The theory for charge transport in mesoscopic scale conductors developed out of quantum theory for scatterers [94,95]. To see how such a system behaves consider a simple molecular junction, like the one shown in figure 1.2, as a one dimensional conductor contacted to two metal electrodes. The metal electrodes can be treated like electron reservoirs connected to the molecule through perfect leads. In such a system, electrons, or holes for that matter, in the electrodes act as free electrons propagating in plane waves through the electrodes. When these waves encounter a barrier to motion, like the molecular junction, there is a certain probability that the electrons will be scattered backward and a certain probability that the electrons will tunnel through the barrier. Approximating the junction as a square barrier, electrons incident from the left will have a reflection probability amplitude $r$ and a transmission probability amplitude $t$. From
scattering theory, the transmission probability can be calculated as $T = |t|^2$. The current going from the left electrode to the right electrode through the scattering center is then given by the group velocity of electrons in the leads $v_g$, the density of states $n(k)dk$ and the transmission probability for electrons through the barrier

$$I_{L\rightarrow R} = e \int dk v_g(k) T(k) f(E(k), \mu_L)n(k) (1.1)$$

where $e$ is the electron charge, and $f_L$ is the Fermi-Dirac distribution for electrode L with chemical potential, $\mu_L$. The density of states for a one dimensional conductor can be expressed in terms of the length of the junction, L, as

$$n(k)dk = \frac{2}{L} \frac{L}{2\pi} dk (1.2)$$

where the factor of 2 is added for degeneracy between up and down spin. In addition, the group velocity can be written in terms of the energy and momentum as

$$v_g = \frac{2\pi}{\hbar} \frac{dE}{dk} (1.3)$$

Combining these terms, the current from left electrode to right electrode can be written

$$I_{L\rightarrow R} = \frac{2e}{\hbar} \int T(E) f_L(E) dE .(1.4)$$

Similarly, the current from right electrode to left electrode can be written as

$$I_{R\rightarrow L} = \frac{2e}{\hbar} \int T(E) f_R(E) dE .(1.5)$$

Taking into account conservation of charge, the total current through the molecular system can be expressed as the difference between the current from left and from right.

$$I_{tot} = I_{L\rightarrow R} - I_{R\rightarrow L} (1.6)$$

$$I_{tot} = \frac{2e}{\hbar} \int T(E)[f_L(E) - f_R(E)] dE .(1.7)$$

Assuming temperatures where the thermal energy is well below the Fermi energy of the metal, for most metals this works at room temperature where $k_B T$ is $\sim 0.025eV$ and $E_F$ is
on the order of eV’s, the Fermi-Dirac distribution can be approximated as a step function with 1 below $E_F$ and 0 above. Additionally assuming that the voltage applied across the junction is relatively small and the transmission is weakly energy dependent, the current can be expressed as

$$I = \frac{2e^2}{h}VT(E). \quad (1.8)$$

Finally, dividing by the voltage gives the familiar Landauer expression for conductance of a one dimensional transport pathway

$$G = \frac{2e^2}{h}T(E) = G_0T(E). \quad (1.9)$$

Here the quantity $G_0 = \frac{2e^2}{h}$ is the conductance quantum, with a value of 77.4nS or inversely 12.9kΩ. This value represents a perfectly open transmission pathway and is approximately the conductance of a single gold atom suspended between gold electrodes.
More generally, due to the small transverse size of the leads, this system with have quantized transverse modes, each of which can be the source or drain of electrons for the scattering center. Electrons can thus scatter from any of these modes to any other mode with a finite probability. To deal with this, the transmission probability is the sum.
of all possible transmission pathways through the junction, from mode i to mode j, \( \sum_{ij} T_{ij}(E) \). Thus the general Landauer formula is

\[
G = \frac{2e^2}{h} \sum_{ij} T_{ij}(E). \quad (1.10)
\]

The Landauer formula is a powerful tool for calculating the conductance of many mesoscopic systems because it creates a convenient framework for describing the system in question, the transmission function \( T(E) \). In the simplest systems, quantum scattering theory can be applied to the system with appropriate approximations to calculate the transmission function and conductance. However, in larger systems, and most molecular systems, calculating the transmission function is not as straightforward and more complicated methods are needed. For this the Green’s function formalism is typically used [96]. In this method the Hamiltonian of the molecule-electrode system is considered as the sum of the isolated Hamiltonians of the molecule and electrode, \( H_0 \), and the coupling between the molecule and electrodes, \( V \), such that

\[
H = H_0 + V. \quad (1.11)
\]

The transfer operator is given by

\[
T = V + VGV. \quad (1.12)
\]

Where \( G \) is the Green’s function of the system

\[
G = \frac{1}{E-H+i\Gamma}. \quad (1.13)
\]

To see how this is useful for calculating the conductance of molecular systems consider a molecule which consists of N bridge sites, figure 1.3, which couple to their nearest neighbor with coupling \( V_{N,N-1} \) and couple to a left electrode, L, and right
electrode, R. This is the so-called coherent tunneling superexchange model. The transfer operator for this model can be written

$$T_{LR} = \langle L|VG(E)V|R \rangle = \langle L|V|1\rangle\langle 1|G|N\rangle\langle N|V|R \rangle = V_{L1}G_{1N}V_{NR}. \quad (1.14)$$

This transfer matrix has its origins from the coupling between two states in the transfer rate equation, Fermi’s golden rule, and is different than the transmission function.

Fortunately, these two functions are related by

$$\sum_{ij} T_{ij}(E) = 4\pi^2 \sum_{LR}|T_{LR}(E)|^2 \delta(E - E_L)\delta(E - E_R). \quad (1.15)$$

Using this relation the transmission function can be expressed in terms of the reduced Green’s function of the molecular Hamiltonian and the coupling terms to the left and right electrodes, $\Gamma_L$ and $\Gamma_R$ respectively, as

$$\sum_{ij} T_{ij}(E) = \Gamma_L\Gamma_R|G_{1N}|^2 \quad (1.16)$$

$$G_{1N} = \frac{1}{E - H_M + \Sigma_M}. \quad (1.17)$$

where $H_M$ is the molecular Hamiltonian and $\Sigma_M$ is the self-energy of the molecule which takes into account the shift of the molecular energy levels due to coupling to the electrodes or other parts of the environment. Additionally the coupling terms $\Gamma$ represent the broadening of the molecular energy level that occurs due to coupling with the electrodes. In the tight binding limit, the linear chain of $N$ bridge sites has a Green’s function of

$$G_{1N} = \frac{1}{(E - E_1 + \Sigma_1)(E - E_N + \Sigma_N)} \prod_{j=2}^{N-1} \frac{V_{j,j+1}}{E - E_j} \quad (1.18)$$

If the bridge sites are identical, as is the case for many molecular systems, the couplings and site energies, $V_{j,j+1}$ and $E_j$ respectively, are constant and the Green’s function for this superexchange model can be expressed as
\[ G_{1N} \propto \left( \frac{V_B}{E-E_B} \right)^2. \quad (1.19) \]

So that the transmission function, which is proportional to the square of the Green’s function, can be rearranged so that

\[ G = \frac{2e^2}{h} \sum_{ij} T_{ij}(E) \propto \left( \frac{E-E_B}{V_B} \right)^{-2N} \propto \exp \left[ -\frac{2}{a} \ln \left( \frac{E-E_B}{V_B} \right) Na \right] \propto \exp(-\beta d) \quad (1.20) \]

where \( d=Na \) is the length of the molecular bridge and \( \beta = \frac{2}{a} \ln \left( \frac{E-E_B}{V_B} \right) \) is the decay constant. Note that for the superexchange model the conductance is exponentially dependent on the length of the molecular bridge as one would expect for tunneling through a square barrier. This is a consequence of the coherent nature of transport considered in this system and the fact that we assume that the phase-relaxation length is longer than the molecular distance.
1.3.2 Current vs. bias voltage characteristics

For simple molecular systems, consisting of alkane or short conjugated molecules, the easiest way to describe charge transport is by approximating the junction as a rectangular tunneling barrier. In this way, the tunneling barrier width is the molecular length \((d)\) and the barrier height can be approximated as the difference in energy between the Fermi energy of the electrodes at zero bias and the energy of the frontier molecular orbital \((\varphi)\), either the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO).
molecular orbital (LUMO). With the application of a bias between the electrodes, a tunneling current can flow through the junction. An expression for the dependence of this tunneling current on bias was derived by Simmons [63,97]. Using the WKB approximation, the current can be written as

\[
I = \frac{eA}{2\pi\hbar d^2} \left[ \left( \phi - \frac{eV}{2} \right) e^{\left( -\frac{4\pi \sqrt{2m_e \phi}}{\hbar} \sqrt{\phi - \frac{eV}{2}} \right)} - \left( \phi + \frac{eV}{2} \right) e^{\left( -\frac{4\pi \sqrt{2m_e \phi}}{\hbar} \sqrt{\phi + \frac{eV}{2}} \right)} \right]
\] (1.21)

where \( e \) is the electron charge, \( A \) the junction area, and \( m_e \) the effective electronic mass.

Note that the applied bias, \( V \), is applied evenly to the donor and acceptor electrodes by \( \pm \frac{eV}{2} \), respectively.

This expression for the tunneling current can be usefully simplified in the two extremes of bias, in the low bias limit and when the applied bias is larger than the barrier. In the low bias limit, when the applied bias is well below the barrier height \( (eV < \phi) \) the barrier is trapezoidal and the tunneling current vs. bias relationship can be approximated as

\[
I \propto V e^{-\left( \frac{4\pi \sqrt{2m_e \phi}}{\hbar} \frac{eV}{2} \right)}. \] (1.22)

While in the other limit, when the energy difference between the two electrodes is larger than the barrier height \( (eV > \phi) \), the barrier changes from a trapezoidal to triangular shape, as incident electrons have more energy than the barrier. In this regime, the current vs. bias relationship can be approximated by

\[
I \propto V^2 e^{-\left( \frac{8\sqrt{2m_e \phi^3}}{3\hbar eV} \right)}. \] (1.23)
This expression can be recast, through the lens of Fowler-Nordheim tunneling [98], to be linearized into

\[ \ln \left( \frac{I}{V^2} \right) \propto -\frac{8\pi d}{3\hbar e} \left( \frac{1}{V} \right) . \] (1.24)

Similarly, the low bias expression (1.22) can be recast to be expressed in terms of \( \ln(I/V^2) \) and \( (1/V) \) as

\[ \ln \left( \frac{I}{V^2} \right) \propto \ln \left( \frac{1}{V} \right) - \frac{4\pi d}{\hbar \sqrt{2m_e\phi \hbar}} . \] (1.25)

Plotting the current and voltage in this way, called a Fowler-Nordheim plot, we can see that at low bias (large \( 1/V \)) the \( \ln(I/V^2) \) term will grow logarithmically. But, at high bias (small \( 1/V \)) the \( \ln(I/V^2) \) term will be linearly dependent on \( 1/V \) with a negative slope. Thus, when the barrier shape goes from trapezoidal to triangular, there is a transition in the slope of \( \ln(I/V^2) \) vs. \( (1/V) \), accompanied by a minimum in the Fowler-Nordheim plot. The voltage associated with the minimum is referred to at the transition voltage and is proportional to the barrier height, see Figure 1.4. It should be noted that in real molecular systems, high enough biases cannot typically be reached to achieve field emission. However, it has been shown by Huisman et al. [66] that using the Landauer formula, with a simple Lorentzian expression for the transmission function, the transition voltage obtained from a Fowler-Nordheim plot is still proportional to the difference in energy between the electrode Fermi level and the frontier molecular orbital. Thus, using the Fowler-Nordheim plot the transition voltage, and effective energy barrier, can be tracked under different experimental conditions, a technique called transition voltage spectroscopy.
1.3.3 IETS – Phonon assisted tunneling

The transport phenomena discussed above dealt exclusively with coherent transport in which the molecule acts as a bridge that reduces the effective barrier height for tunneling electrons but otherwise it was assumed that the lifetime of the electrons was much shorter than the period of molecular vibration and therefore the molecule doesn’t respond to the moving charges. However, in real molecular systems tunneling electrons can exchange energy with molecular vibrational degrees of freedom. One example of this is phonon assisted tunneling, which is probed with inelastic electron tunneling spectroscopy (IETS). This process is seen at low temperature when the vibrational
degrees of freedom are not excited thermally. Under these conditions tunneling electrons can excite a molecular vibration, i.e. a phonon, as they transport through the system. In exciting a phonon the electrons loose energy to the molecule equal to $\hbar \omega$, where $\hbar$ is Plank’s constant and $\omega$ is the frequency of the vibration, before reaching the other electrode. This inelastic tunneling process opens an additional transport pathway through the molecule, which is seen as adding another term to the transmission function so that $T(E) = T_{elastic} + T_{inelastic}$. For junctions far from resonance, i.e. $T(E) << 0.5$, this can be seen as an anti-symmetric increase in the slope of current vs. bias at bias voltages larger than the vibrational energy, $eV = \pm \hbar \omega$. The scattering cross section of this electron-phonon interaction is small and only a small fraction of the electrons tunnel through this inelastic process, typically ~2% for every vibration. As such, the additional current is difficult to observe and is more easily seen as a broadened stepwise increase in the first derivative of current with respect to voltage, the conductance, and a peak in the second derivative of current with respect to bias, known as the IET spectra, as is illustrated in figure 1.4. Although this spectroscopic technique is measured at low temperature, there is still an inherent broadening of the peak width. This broadening has three sources, which are the intrinsic broadening, the thermal broadening and broadening due to the lock-in technique used to measure the spectra. The intrinsic broadening adds ~3mV to the peak signal and has its origin in the electron-phonon coupling. The thermal broadening adds $5.4k_BT$ to the peak width and is from the broadening of the Fermi-Dirac distribution. Lastly, the lock-in broadening add either $2.45V_{RMS}$ or $1.72V_{RMS}$ depending on if the lock-
in is used to measure the first or second derivative signal, respectively. Put together, the total broadened peak width can be calculated as \( W_{tot} = \sqrt{W_{int}^2 + W_{Therm}^2 + W_{Lock-in}^2} \).

IETS is a powerful technique for measuring spectroscopic signatures in tunneling junctions. Originally it was developed by Lambe and Jaklevic [72] in the 1960’s as a technique to identify impurities in metal-oxide-metal junctions. Later, several groups applied this technique to investigating the electron-phonon coupling of thousands of organic molecules in tunnel junctions [99,100]. Additionally, Stipes et al. [75,76] implemented this technique into the STM to investigate the vibrational spectra of molecules on a surface and how this vibrational spectra is effected by the spatial distribution of the molecule. This method was further implemented into the STM-BJ technique by Hihath et al. [101] to measure electron-phonon interactions in single molecule junctions.
Thermally activated hopping

In some molecular systems, especially very long systems, the probability of coherently tunneling through the molecule becomes too small for measurable currents. However, if there are sites on the molecular bridge that can be thermally populated, charge transport can be mediated by a series of superexchange events in which the electron loses all phase information between events [102–105]. This type of transport is called thermally activated hopping and it is important in many biological and redox type molecules. To see how this works, consider the energy diagram shown in figure 1.3b. In this picture the molecule is represented as a series of N sites that can populate charge.

Figure 1.5: Inelastic Electron Tunneling Spectroscopy. (a) Energy diagram representing a molecular junction with phonon assisted tunneling. When the bias, V, is such that the energy of incident electrons matches the energy of a phonon mode, eV=\(h\nu\), electrons can transfer momentum to the molecular vibration and continue tunneling through. This increases the slope of current vs. voltage (b) and can be seen as a stepwise increase in the first derivative of current with respect to voltage, conductance, (c) and a peak in the second derivative with respect to voltage (d).

1.3.4 *Thermally activated hopping*

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Charge is transferred from the left electrode to the first site with a transfer rate $k_{0,1}$ and the reverse process has a rate $k_{1,0}$. Similar transfer rates can express the transfer between the last site and the right electrode, $k_{N,N+1}$ and $k_{N+1,N}$, and the transfer rate between molecular sites can be expressed as $k$, assuming the same rate between all sites. The transport of charge can now be calculated by solving a series of kinetic equations for the occupation, $P_i$, of the different sites, which have the form

$$\frac{dP_i}{dt} = -kP_i + kP_{i+1} - kP_{i+1} + kP_{i-1}. \quad (1.26)$$

Also, the total transfer rate through the junction from left to right electrode, $k_{L \rightarrow R}$, can be expressed in terms of the steady state flux, $J$, at the $N$th position as

$$k_{L \rightarrow R} = \frac{J_{L \rightarrow R}}{p_0} = \frac{k_{N,N+1}P_N}{p_0}. \quad (1.27)$$

Assuming steady state transport, we can express these kinetic equations as

$$\frac{dP_i}{dt} = 0 = -(k_{0,1} + k)P_1 + k_{1,0}P_0 + kP_2 \quad (1.28)$$

$$0 = -2kP_2 + k(P_1 + P_3) \ldots$$

$$0 = -2kP_{N-1} + k(P_{N-2} + P_N)$$

$$0 = -(k + k_{N+1,N})P_N + kP_{N-1}.$$

Combining terms of these equations leaves two steady state equations

$$0 = -k_{0,1}P_1 + k_{1,0}P_0 - k_{N+1,N}P_N \quad (1.29)$$

$$0 = kP_1 - kP_N - (N-1)k_{N+1,N}P_N. \quad (1.30)$$

Setting these equations equal to each other, and after some algebra, it can be shown that the total transfer rate is expressed as

$$k_{L \rightarrow R} = \frac{\frac{k_{1,0}}{k_{0,1}}}{\frac{1}{k_{N,N+1}} + \frac{1}{k_{0,1}} + \frac{N-1}{k}}. \quad (1.31)$$
Assuming an Arrhenius relationship between the left electrode and the first bridge site we can approximate the numerator as \( \exp(-\frac{E_{BF}}{k_BT}) \), where \( E_{BF} \) is the difference between the left Fermi energy and the bridge site energy, \( k_B \) is the Boltzmann constant and \( T \) is the temperature. This results in an expression for the left to right transfer rate

\[
k_{L\rightarrow R} = \frac{\exp(-\frac{E_{BF}}{k_BT})}{k_{N,N+1}^\dagger k_{0,1}^\dagger N^{-1}}. (1.32)
\]

A similar expression can be derived for the right to left transfer rate.

The transfer rate can be related to the current through the junction by multiplying by the electron charge, \( e \), and subtracting the left to right from the right to left. It should be noted that when a bias is applied between the left and right electrodes, the energy difference terms will be offset by a factor of \( \pm \frac{eV}{2} \), depending on the bias orientation.

Thus the current from left to right is

\[
I_{L\rightarrow R} = e \frac{\exp(-\frac{E_{BF}}{k_BT})}{k_{N,N+1}^\dagger k_{0,1}^\dagger N^{-1}} = e k_{et} \exp\left(\frac{eV}{2k_BT}\right). (1.33)
\]

With a similar expression for the right to left current, only the sign of the voltage is reversed. Therefore the total current is

\[
I = 2e \frac{e^{-\frac{E_{BF}}{k_BT}}}{k_{N,N+1}^\dagger k_{0,1}^\dagger N^{-1}} \sinh \left(\frac{eV}{2k_BT}\right) \approx \frac{e^2V}{k_BT} \frac{e^{-\frac{E_{BF}}{k_BT}}}{k_{N,N+1}^\dagger k_{0,1}^\dagger N^{-1}}. (1.34)
\]

Thus the conductance for thermally activated hopping transport is given by

\[
G = \frac{e^2}{k_BT} \frac{e^{-\frac{E_{BF}}{k_BT}}}{k_{N,N+1}^\dagger k_{0,1}^\dagger N^{-1}}. (1.35)
\]
Here, for simplicity, the transfer rate between the left (right) electrode and the molecule is represented as $k_{L(R)}$. Note that this expression is inversely proportional to the number of hopping sites on the molecule. This is a trademark of the thermally activated hopping transport. Also note that the conductance is temperature dependent, something not seen in coherent tunneling transport. These characteristics, length and temperature dependence, are often used to distinguish between different transport mechanisms in molecular electronics.

In addition to the inverse dependence of thermally activated conductance on the number of hopping sites, the conductance term is also dependent on the distance between hopping sites in a complicated manner. First, the transfer rate terms, $k, k_L, \text{ and } k_R$, depend on the separation between the initial and final state through the square of the coupling term between these states, $|\langle i | H_{i,f} | f \rangle|^2$. At small displacements, this term can be approximated to have an exponential dependence on the length between the two states. In addition, the Fermi energy-bridge energy difference, $E_{BF}$, can be dependent on the separation between the hopping sites of the bridge and the bridge and electrodes. This is possible because the energy of the bridge sites is strongly dependent on the coupling term shown above. The bridge energy is also dependent on the coupling between the bridge and the electrodes, due to charge transfer between the electrode and bridge sites upon binding which can realign the bridge sites with respect to the Fermi energy. This complicated dependence on couplings and hopping site separations means that the electromechanical properties of molecules with thermally activated hopping transport mechanism is an interesting and very poorly understood topic.
1.4 Single molecule electromechanical measurements

As mentioned in previous sections, molecular devices possess unique characteristics, due to the interplay between the electrical and mechanical properties. The coupling of the mechanical and electrical properties results in an electromechanical response of the conductance of single molecular junctions to mechanical manipulation.

To this end, the STM break junction technique is a powerful tool to probe the electromechanical properties of single molecules. Indeed, by simply creating a single molecule junction with the break junction technique, one is applying mechanical stress to a single molecule while simultaneously measuring the conductance. Furthermore, through straightforward modification of the break junction technique, additional transport and mechanical parameters can be extracted from single molecule junctions. In this section the recent literature on the electromechanical properties of single molecules will be reviewed. First, the force and length characteristics measurements of simple molecular systems will be discussed to understand the breakdown mechanisms of molecular junctions. Then, several experiments which investigate the tunneling barrier profile with application of a mechanical modulation of the electrode separation will be discussed. Finally, some interesting molecular systems in which the conductance can be mechanically gated are presented.

In single molecule break junction measurements the junction breakdown, the point where the conductance suddenly drops to zero, is the signature of the single molecule junction. However, the conductance vs. electrode separation curve gives little information about the nature of what causes this breakdown. To understand this in a quantitative way, Xu et al. [54] implemented the break junction technique in a conducting
AFM setup, using the gold coated AFM cantilever as the movable electrode, to simultaneously measure the conductance and force of single molecular junctions (Figure 1.6). The molecules studied in this work were octanedithiol, which binds covalently to gold though a Au-S bond, and bipyridine, which binds via the Au-N bond. Correlating the force and conductance traces during stretching of molecular junctions, the researchers were able to measure the maximum force measured during the conductance plateau, i.e. the force measured just before the conductance drops to zero. This value is the breakdown force, or the force required to break a single molecule junction. For the octanedithiol molecule, and for most all dithiol molecules measured subsequently, the breakdown force was found to be 1.5 ± 0.2 nN. Simple analysis of the chemical makeup of this system reveals that the breakdown must be the result of the breaking of the Au-Au, Au-S, S-C or C-C bonds. By comparing the measured breakdown force to that measured previously for atomic gold wires, ~1.5nN [106], the breakdown culprit can be identified as the breaking of the Au-Au bonds nearest to the molecular junction. This result makes sense from a bond elasticity of view, as the Au-Au bond has the smallest spring constant and is easiest to break. Interestingly, the breakdown force for the bipyridine molecule, which binds through the Au-N bond, was found to have a smaller breakdown force of 0.8 ± 0.2 nN. This result suggests that, instead of the Au-Au bond being the weakest point in this junction, the Au-N bond is the first to breakdown. Indeed, considering the binding energetics, the Au-N bond is the weakest link in this type of molecular junction [107]. This work has been confirmed and expanded upon by many groups using conducting AFM to measure the breakdown force of single molecules with a variety of linkers [108–110]. These findings have shown that the largest breakdown
force possible for molecular junctions involving gold electrodes is \(~1.5\text{nN}\), the breakdown force for gold atomic chain. This is not surprising, since the Au-Au bond is relatively weak compared to the covalent bonds inside organic molecules, although most molecule-electrode linker groups have breakdown forces below this value suggesting that the Au-S bond is an especially robust linker for molecular electronics.

Figure 1.6: Single molecule breakdown force. (a) Schematic drawing of the conducting AFM measurement technique. (b-d) Concurrent conductance and force vs. stretching distance measurements for 1,8-octanedithiol (1 molecule in b and 2 molecules in c) and 4,4’-bipyridine (d). Image obtained from [54].

Without simultaneous measurement of the force and conductance, clever analysis of the length of the conductance plateaus, or step length, for single molecule break junction experiments can reveal information about junction breakdown mechanisms. In an insightful early work, Huang et al. [111] used the STM break junction technique
demonstrated this by analyzing the step length of alkanedithiol molecules, with 6, 8 and 10 carbons, under different stretching rates. Comparing step length with the stretching rate they were able to show that these molecular junctions underwent a thermally activated breakdown mechanism. Also, performing similar measurements on gold atomic chains revealed a similar trend and further demonstrated that for dithiol terminated molecules the breakdown mechanism is at the Au-Au bonds near to the junction. In similar experiments, Kamenetska et al. [20] Arroyo et al. [112] used the STM break junction method to measure the step length of molecules with different linker groups, including amine, methyl sulfide, and dimethyl phosphine. The measurements by Arroyo et al. compare thiol and amine terminated alkane molecules of different length and found that the thiol terminated molecules have longer step length than the amine molecules across the board. This is in agreement with the idea of the Au-S bond being more robust than Au-N. Similarly, Kamenetska et al. found that molecules which bind stronger to gold, dimethyl phosphine and methyl sulfide, have longer step lengths than amine terminated molecules which bind more weakly to gold.

In addition to measuring the breakdown properties of molecular junctions, the response of molecular conductance to mechanical stretching can reveal information about the height and profile of the tunneling barrier associated with a molecule. This was first demonstrated by Xia et al. using a modification of the STM break junction technique, in which a sinusoidal modulation is added to the tip position during the break junction experiment [113]. To see how this can lead to greater insight into transport, consider the Taylor expansion of the current in a such a junction

\[ I = I_{DC} + \frac{dI_{DC}}{dz} A\cos(\omega t) \] (1.36)
Where $I_{DC}$ is the DC component of the current, $\omega$ is the frequency of the modulation, and $A$ is the amplitude of the modulation. The first term in this current expression is the current without modulation and the second term is the AC portion of the current due to the modulation. For a purely tunneling junction, the current decays exponentially with distance and can be expressed $\sim e^{-\beta z}$. To gather information about the decay constant, $\beta$, Xia et al. introduced the parameter they called the electromechanical response, $\alpha = -\frac{dI_{DC}}{dz} \frac{1}{I_{DC}}$. For a simple tunneling barrier this value is equal to the decay constant, $\beta$, which, as was shown earlier, is proportional to the tunneling barrier. Analyzing molecular junctions with this technique, Xia et al. were able to distinguish between tunneling through the solvent, which has a large decay constant of $\sim10\text{nm}^{-1}$, and alkanedithiol molecules, which have a smaller decay constant of $<2\text{nm}^{-1}$ due to the reduced tunneling barrier of the molecule.

Implementing a similar tip modulation technique, Zhou et al. have performed a series of experiments on single molecule junctions and developed a model for the barrier height profile which is illustrative of the stretching mechanisms of molecules with different linker groups [114–116]. In this model, conductance through the molecular junction is separated into the terms contributed by the molecule and the left and right molecule-electrode contacts. The tunneling barrier is then split into sections, one for each contributing section with different barrier heights and related decay constants. The conductance can then be expressed as

$$G = Ae^{-\beta\Lambda}e^{-\beta M} (1.37)$$
Where A is a constant, $\beta_C$ and $d_C$ are the barrier and distance associated with the contact and $\beta_M$ and $l$ are the barrier and length associated with the molecule. Assuming that the contact is the weakest portion of the molecular junction, which is supported by the previously discussed breakdown force and length dependence experiments, the molecular portion of the junction length will not change during stretching, all the stretching will happen on the contacts. Using this model to analyze tip modulation measurements performed on alkanedithiol molecules returns a contact decay constant of $0.115 \pm 0.035 \text{ Å}^{-1}$, similar to the value previously mentioned. Importantly, the decay constant measured for alkanediamine molecule is larger, $0.374 \pm 0.105 \text{ Å}^{-1}$. This indicates that, for amine terminated molecules, it is the barrier between the molecule and electrodes which is being modulated while for thiol terminated molecules the Au-Au bonds, which are have less conductance change with stretching, are being modulated. This is further confirmation that the thiol linker is a more robust bond than the amine linker.

Beyond measuring the effect of the molecule-electrode linker group, which the previous measurements predominately focused on, the response of molecular conductance to mechanical manipulation can be interesting from a device point of view. There are several situations in which molecular junctions have been shown to have controllable conductance response when stretched, a kind of mechanical gated molecular transport. One of the first observations of this came from Xu et al. in 2005 [24]. Using STM break junction this paper shows that the change in conductance of oligothiophene molecular junctions with stretching distance is larger than that seen for molecules with similar linker groups. This is attributed to the conjugated nature of the oligothiophene molecule and the way that changes in this conjugation, caused by stretching, can affect
transmission in the molecular junction. A slightly different mechanical gating effect involves modulation of the pi-orbital overlap of a strongly conjugated molecule with the metal electrode [26,117,118]. In these studies, molecular junctions are formed between conjugated molecules and metal electrodes in an STM, either through break junction or by imaging. When the tip is withdrawn from the substrate, the molecule is brought perpendicular to the metal surfaces and the molecular pi-orbitals, which project from the face of the molecular plane, are decoupled from the metallic states. This decoupling reduces the transmission probability associated with the pi-orbitals, reducing the conductance in the process. This conductance change with mechanical manipulation has been shown to be reversible and reproducible in different molecular systems.

Another way interesting example of mechanical gating molecular junctions involves modulating the molecular orbital alignment with respect to the electrode Fermi energy. One example of this was shown by Perrin et al. in 2013 [119], in which the MCBJ method was used to measure zinc-porphyrin molecular junctions. In this experiment it was found that opening and closing the molecular junction caused a change in the energy levels associated with the zinc center, the orbital responsible for transport, due to changing of the image charge in the molecule-metal contact. This effect was shown to be reproducible and reversible. The idea of using mechanical modulation to alter transport properties is an interesting property which molecules can relatively easily manifest over conventional electronic materials and is an interesting field of research, with the possibility of developing a mechanically gated transistor device.
1.5 Stretching DNA and the overstretched transition

At the same time that the break junction technique was being developed to measure single molecule charge transport properties, different techniques were being developed to measure the mechanical properties of single molecules. One type of molecule, of particular importance here, which has been the target of much research in the past few decades, is double strand deoxyribonucleic acid (dsDNA). It has long been known that under biological conditions dsDNA takes on a double helix structure in which the nucleic acid bases are stacked, due to strong pi-pi overlap, in the center, linked by hydrogen bonds between bases on different strands, and the phosphate-sugar backbone is on the outside [120]. This structure is known as B-DNA. Starting in the early 1990’s, researchers began experimenting with different techniques to stretch DNA out of this form and measure the force vs. extension curve during the process. This section will review the recent literature in this, still, hotly debated field. The early experimental work and results, in which the mechanical properties of DNA molecules of different lengths were measured in different environments, will be discussed first. Then the prominent models to explain the measured elastic properties will be presented. The most recent work in this field, which has done a lot to clarify the mechanism of stretching dsDNA, will then be discussed. Finally, the relation between STM break junction and mechanical stretching will be presented.

The early experiments which measured the mechanical properties of stretched DNA were carried out by Cluzel et al. [121] and Smith et al. [122] in 1996 using pipette micromanipulation and optical tweezers, respectively, to stretch λ-DNA, >40,000 base pairs (bp) long. These measurements found that when the DNA molecule was stretched
beyond its contour length, about 0.34nm times the number of bases, the force required to stretch the molecule increased in a linear manner for a small distance. This fit well with the worm-like chain model used to describe extensible molecules of this nature. However, at a tensile force of ~65-70 pN the length of the molecule extended by ~1.7 times within a narrow force window. Once this extension has taken place the force again increased, but with a curvature similar to that of stretched single strand DNA. Remarkably, this overstretching transition was also shown to be reversible, although with varying degrees of hysteresis between stretching and relaxing cycles. Similar results were then found by Noy et al. [123] using an AFM probe to measure the force vs. extension characteristics of shorter, 14bp, DNA stands, although the measured transition occurred at a larger force of ~120pN.
Figure 1.7: DNA overstretching transition. (a) Force vs. Extension curve measured using optical tweezers to stretch λ-DNA. Shows the transition at ~65pN, from [122]. (b) Simulated structure of biological (B-form) and stretched (S-form) DNA, left and right respectively, from [121].

Following these initial experiments, the dependence of the mechanical properties of dsDNA molecules on length, ionic concentration and stretching parameters were measured in order to ascertain the molecular nature of this overstretching transition. Of these, several studied were done to measure the dependence of the overstretch transition force on the concentration of different ions in solution. [124–127] These studies found that increasing the concentration of sodium in solution, which increases the melting temperature and the stability of the hydrogen bonds between bases, increased the force required to cause the overstretch transition. Similarly, Fu et al. [126] found similar results with increasing the concentration of magnesium in solution, which has similar effects on the stability of the hydrogen bonds. Additionally, the dependence of the overstretching transition on the length of the dsDNA molecule was investigated. Several groups have shown that short molecules, less than 30bp, do not undergo the characteristic overstretch
transition plateau, instead the force decreases at a certain stretching distance signifying
the breakdown of the molecule [128–131]. To understand this further, the dependence of
the breakdown force on the loading rate was investigated and it was found by many
groups that the breakdown force increases with the logarithm of the loading rate. This
was shown as evidence that DNA, at least short sequences under certain ionic
environment, melted during stretching. Finally, the dependence of the overstretching
transition on the pulling orientation, either 3`-3`, 5`-5` or 3`5`, was investigated and
found similar results, independent on which end of which strand was pulled. [132]

To explain these experimental results, that there is a reversible overstretching
transition which is dependent on ionic concentration and molecular length, two prominent
models were proposed. In the first, Lebrun et al. [133] and Konrad et al. [134] performed
early molecular dynamics simulations on short dsDNA molecules under tensile
stretching. These simulations found that these molecules undergo a structural change
when stretched to go from a double helix B-DNA form to a ladder like stretched form (S-DNA) which kept the hydrogen bonding between strands intact but distorted the base-
base stacking. The second model, proposed by Rouzina et al. [135,136], uses
thermodynamic calculations of free energy during stretching to show that force-induced
melting is more favorable than distorting the pi-pi stacking between bases. This model of
force induced melting was also supported by simulations by Piana et al. [137] which
showed that after only 25% stretching the DNA is structurally distorted and hydrogen
bonds at the ends and in the center of the sequence are broken.

Recent experiments from several groups have tended to support a model
involving two distinct overstretching processes. [138–142] One of these, Fu et al. [138],
showed that dsDNA undergoes a “fast” reversible overstretch transition, which was attributed to a structural change in the molecule, and a “slow” nonreversible transition which was attributed to melting in the λ-DNA under investigation. Similarly, Bosaeus et al. [140] found that when stretching 60 to 64 bp long dsDNA molecules, the sequence had an effect on the reversibility of the transition. More A-T base pairs in the sequence, they found, would result in a nonreversible stretching transition with an associated extension of 70%. Whereas more G-C base pair content resulted in a reversible transition with a length extension of only 51%. The observed difference for different sequence was attributed to the strength of hydrogen bonding between A-T base pairs and G-C bases pairs, with G-C having more hydrogen bonds to break. For more evidence of a combined melting/structural distortion transition mechanism, Graeme et al. [141] used fluorescent proteins to visually identify the melted portions of the dsDNA while stretching. They found that the melting occurred at the ends and in the middle of the dsDNA molecule but not over the entire strand, suggesting the combined mechanism.

To describe the mechanical properties of short dsDNA molecules under stretching force and to describe how stretching is distributed across the base pairs, de Gennes developed an analytical model of DNA molecules under tension [143]. In this model the DNA double strand is idealized to a ladder, with the sides representing the backbone and the rungs representing the hydrogen bonds. It is assumed that the backbone has a larger spring constant than the hydrogen bonds, because of the π-stacking interaction between bases on a single strand. A picture of this model is shown in Figure 1.8. Stretching this spring network from the 3` ends of opposite strands results in stretching of the distance between the neighboring bases in an uneven manner, with base pairs at the end being
distorted more than sequences in the middle. It characterize the nature if the distortion, de Gennes introduces an “adjustment length”, the number of base pairs at the end of the strand which are stretched, which is given by $\chi^{-1} = \sqrt{Q/2R}$ where Q is the spring constant of the backbone and R is the spring constant of the hydrogen bonds. When the DNA strand being stretched is smaller than or equal to this length the displacement from the force is distributed evenly across all base pairs and the force to break the dsDNA molecule is proportional to the length of the molecule and the force to break the hydrogen bonds of a single base pair $f_0$. When the dsDNA molecule becomes longer than this length, $\chi^{-1}$ base pairs at the ends of the molecule are distorted and the force to break the molecule becomes independent of length. This model has been supported by force spectroscopy measurements of relatively DNA molecules and the adjustment length has been found to be on the order of 6.8 base pairs [132]. Additionally, simulations of the evolution of DNA base pair structure fit the breakdown force characteristics of this analytical model and estimate the adjustment length to be between 8 and 10 base pairs [144,145].
Additionally, more recent molecular dynamics simulations have suggested a combined transition mechanism. [146,147] For example, Roe et al. [147] simulated the structure of 30bp dsDNA sequence during stretching from either the 3’3` or 5`5` ends. In these simulations it was found that stretching from the 3’3` ends of dsDNA molecules resulted in an overstretch transition, 1.7x increase in length, which was accompanied by lose of ~20% of the hydrogen bonds in the sequence and a ladder like structural distortion of the base-base stacking. Interestingly, these simulations also found that stretching from the 5`5` ends resulted in a transition also, but with 60% of the hydrogen bonds broken and a structural distortion with the phosphate-sugar backbone closer together.

The response of dsDNA molecules to mechanical stretching is of importance to STM break junction measurements on dsDNA molecules because during the break junction measurement process the target molecule is inherently under mechanical stress. This means that break junction is an excellent way to study the interplay between the mechanical properties and charge transport properties of dsDNA. Additionally, the response of charge transport in dsDNA to mechanical stretching is another way to
determine the stretching mechanism of DNA. Xu et al. first measured the single molecule conductance of dsDNA molecules in aqueous solution and found that the conductance depends on the inverse of the number of guanine bases in a sequence, suggesting a thermally activated hopping transport mechanism. Following this early work, several groups investigating the charge transport properties of dsDNA have commented on the effect of stretching on dsDNA transport properties. In 2005 Cohen et al. measured the charge transport properties of dsDNA molecules using an unusual method in which a multi-molecular junction was formed between self-assembled molecules on a surface and a gold nanoparticle. [148] The electrical readout was then performed with a conducting AFM probe contacting the nanoparticle. In this study the current though the metal-DNA-nanoparticle-AFM probe junction was measured as the AFM probe was retracted from the surface. This resulted in an overall decrease in conductance as the nanoparticle was pulled from the surface, although specific detail of the impact on DNA structure are not apparent. Also, this experiment was performed in dry environment, due to the nature of conducting AFM, which has poorly understood effects on the structural and mechanical properties of DNA. In additional studies of the charge properties of dsDNA molecules using the break junction technique Kang et al. [149] and Dulic et al. [150] measure single dsDNA molecular junctions using the MCBJ technique. Both studies comment on the charge transport dependence on electrode separation, showing decreases in conductance with increasing separation. However, the experiments are performed in dry or vacuum conditions during these experiments and thus suffer from the same poorly defined structure as the previous study. Therefore, there is a need to investigate the relationship between charge transport and mechanical stress in single dsDNA molecular junctions in
aqueous conditions where the DNA is more stabilized and the mechanical properties are better known.

1.6 Summary

Over the past few decades, the understanding of charge transport in molecular systems has benefited greatly from the development of break junction methods to measure single molecule conductance. The transport properties of certain simple molecules are well understood and molecular systems with semiconductor device functionalities, i.e. rectification and transistor-like behavior, have been demonstrated. However, molecular systems have unique characteristics which are not seen on longer length scales. Of these characteristics, the interplay between the mechanical and electrical properties of single molecular systems is the most natural to probe using the break junction technique. In the following chapters this interplay will be investigated in a number of molecular systems.
CHAPTER 2

LOW TEMPERATURE SCANNING TUNNELING MICROSCOPE

2.1 Introduction

Due to the enhanced stability of molecular junctions at low temperature, it is desirable to implement the STM break junction technique in a STM system which can be cooled to cryogenic temperatures. This enhanced stability is caused by the loss of thermally excited vibrations of the constituent atoms in the molecule at extremely low temperatures. Working at these low temperatures, with the thermal vibrations damped out, it is possible to measure the vibrations caused by electronic current in molecular systems and study the electron-phonon coupling on molecular length scales. [72,73,75,76,151–154] Ultimately, studying the vibrations excited through charge transport will lead to better understanding of current induced heating in molecular scale electronics, a large problem in the miniaturization of electronics. However, in order to perform the STM break junction technique at these low temperatures the microscope system must be carefully design so that it can function at temperatures ranging from room temperature (~300K) to liquid helium temperature (~4.2K). In addition to this extreme temperature window, the STM system must have extremely low mechanical and acoustic noise, not an easy task when dealing with cryogens which are constantly boiling and causing noise. Furthermore, the associated electronics of this system must have appropriate bandwidth and control parameters to measure small signals associated with vibrational signals. In this chapter, a low temperature STM (LT-STM) is described which achieves these requirements and has been used to study several different aspects of electron-vibration coupling in different molecular systems.
The design of the LT-STM discussed here is based on a previous LT-STM system built in the Tao lab at ASU, with several key improvements. [101,153,155] First, whereas the old LT-STM used a continuous flow probe station cryostat to cool the LT-STM, the LT-STM described here uses a liquid helium Dewar cryostat. The Dewar cryostat has significantly less acoustic noise associated with the boiling of the cryogen than the probe station cryostat, for reasons which will be discussed later. Next, the ability to manipulate the STM in three dimensions (2 substrate and 1 tip) is implemented in the new LT-STM design, whereas the older design was limited to two dimensional motions (1 substrate and 1 tip). Finally, the control and measurement electronics are improved upon by increasing the measurement electronics bandwidth and sampling rate. The following sections will address these improvements while discussing the design and working principles of the LT-STM system which was used to perform measurements discussed in the subsequent chapter.

2.2 Dewar cryostat

In order to cool the LT-STM system to temperatures low enough to sufficiently damp thermal vibrations, liquid cryogens are used. These include liquid nitrogen which has a boiling temperature of ~77K and liquid helium which has a boiling temperature of ~4.2K. There are several different ways to introduce these liquid cryogens to the STM system in order to cool it to the desired temperature. However, considerations must be made to the sensitivity of STM to mechanical vibrations, of which liquid cryogen boiling and flowing noise are important offenders. The previous LT-STM system used a Desert Cryogenics TT-Prober manipulated probe system (Desert Cryogenics) to cool the STM within a temperature range from 6K-400K. This probe station system utilized the
continuous-transfer refrigeration design to cool the sample stage on which the STM was in thermal contact. In the continuous-transfer method, as the name implies, the liquid cryogen is transferred through a tube which is in thermal contact with the sample stage during the entire cooling process. As a product of this continuous transfer of liquid cryogen, there are large amounts of mechanical vibrations generated on the sample stage and within the STM. These mechanical vibrations generated a large amount of mechanical noise, defined as vibration of the STM tip relative to the substrate generating a measurable change in the current, while the LT-STM was at low temperatures. For this reason, a different approach was desired for cooling the new LT-STM.
To solve the problem of excess mechanical noise due to liquid cryogen flow and boiling, the new LT-STM system presented here uses a Janis “SuperVaritemp” system (Janis Research Company) built inside a dewar, a schematic of which is seen in Figure 2.1.

Figure 2.1: Schematic of Dewar cryostat system. 1) Stainless steel vacuum-insulated dewar. 2) 55L Liquid cryogen reservoir. 3) Sample canister chamber housing the LT-STM system. 4) Superconducting magnet solenoid system capable of reaching 9 tesla magnetic field. 5) Liquid helium monitoring system. 6) Vacuum port and electronics feed through pipe. 7) Liquid cryogen transfer port.

To solve the problem of excess mechanical noise due to liquid cryogen flow and boiling, the new LT-STM system presented here uses a Janis “SuperVaritemp” system (Janis Research Company) built inside a dewar, a schematic of which is seen in Figure
2.1. This dewar system consists of a 55L liquid helium reservoir insulated from the room temperature by a welded stainless steel vacuum jacket, this constitutes the “dewar” part. When in use, the STM sits inside a sealed sample canister, under high vacuum \( \sim 10^{-7} \) Torr, which is lowered into the dewar reservoir. The reservoir is then filled with liquid cryogen, either liquid nitrogen or liquid helium. Inside the sample canister, there is a sample stage, with which the STM is in thermal contact, which can be cooled to the desired temperature by opening of a needle valve which allows the cryogenic liquid to fill a capillary tube running through the sample holder. The capillary tube and sample canister are in thermal contact but the tube vents outside the reservoir in order to maintain the sample canister vacuum. This way the capillary tube fills with liquid cryogen which cools the sample stage to the desired temperature and once the sample stage reaches the temperature of the cryogen the liquid cryogen in the tube stops boiling, since it is still well insulated from room temperature. In addition, the amount of liquid cryogen needed to maintain the temperature of the sample is small, \( \sim 0.005 \) L/min to maintain 4.2K, insuring that there is not a continuous flow of liquid through the capillary, as in the continuous-transfer system, which can add to mechanical noise.

2.3 LT-STM body

There are many different designs for the variable temperature STM capable of reaching temperatures of 4.2K or below. The most important considerations in designing an STM capable of reaching such low temperature are the movement of the tip and substrate over such a wide range of temperatures, decreasing of mechanical vibration, maintaining thermal contact between the STM and coolant, and monitoring the
temperature at the sample. In this section the designs used to overcome these considerations for the LT-STM presented here are discussed.

![LT-STM body design](image)

Figure 2.2: LT-STM body design. (a) Schematic design of LT-STM body components. (b) Picture of actual LT-STM indicating the location of thermal sensor and tie down points to reduce transfer of mechanical vibration.

The body of the LT-STM system presented here consists of four components milled from titanium, the upper body, the lower body, the substrate holder and the tip holder. The Upper and lower STM body parts are bolted together using aluminum threaded rod and aluminum nuts, 6-32 thread size, forming a rigid platform to contain the moving parts of the STM. Titanium is used because of its low superconducting temperature, 0.4K. The upper body has a groove milled out of it in the vertical direction, z-axis, with walls which are at 120° angles with respect the bottom of the groove. This groove accepts the tip holder, which is triangular with 60° surfaces. The lower body similarly has a rectangular groove milled into it which holds the square substrate holder.
The tip and substrate holder are manipulated using handmade piezo stacks. The tip holder piezo stacks consist of five layers, three copper sheets and two shear piezoelectric ceramics (Noliac), going copper-piezo-copper-piezo-copper such that the piezo layers shear directions are opposite. For the tip holder motion, four piezo stacks are positioned on the 120° surfaces of the upper body, two on each side, with their shear motion directions aligned on the z-axis. Polished alumina (Goodfellow) sheets are glued to the top of the stacks and the sides of the tip holder in order to reduce friction between the moving parts. The tip holder is held against the piezo stacks with a spring which is connected to the back of the upper body. The motion system for the substrate holder is complicated by the desire to move the substrate in two directions, x-axis and y-axis. To accomplish this two piezo stacks are glued together with their shear directions at 90° from one another, allowing for motion in one direction from the bottom stack and the other from the top stack. Four such stacks are glued to the lower STM body and a similar polished alumina friction reduction method is used to insure motion of the substrate holder. Course motion of the tip and substrate holder is achieved by applying high voltage a saw-tooth wave to the copper sheets across the piezo ceramics. Motion of the tip and substrate holder relies on the “slip-stick” style of motion in which the different piezo stacks move independently, several moving forward while one moves back, to ensure that the momentum of the moving part is always in the desired direction. [156,160] This is accomplished by utilizing the piezo ceramics inherent capacitance and designing a RC circuit to delay the saw-tooth wave reaching the different piezo stacks. To accomplish this resistors are mounted in parallel with the piezo stacks to delay the wave through the piezo network. It should be noted that the range of motion of
these piezo stacks is severely decreased at low temperatures. In order to maintain motion of the tip and substrate holder graphite was used to lubricate the touching alumina surfaces and much care had to be taken to ensure frictionless motion of parts before cooling to ensure the proper motion at low temperature.

Thermal contact between the STM body and sample holder in the dewar cryostat system is made by copper braid used to suspend the STM body from the sample holder. This braid is also designed to absorb mechanical vibrations from the sample holder and cryostat and damp the motion of the STM. To ensure the proper temperature of the STM a thermal couple (Lake Shore cryogenics) is added at the bottom of the STM, as far from the sample holder and cryogen as possible. This way the temperature of the STM body is monitored and it is ensured that the substrate and tip are at the desired temperature.

The STM tip is mounted in the tip holder by using a platinum capillary glued into the tip holder and electrically contacted to the outside using conducting silver epoxy which connects to an electrical feedthrough wire. The wire which connects the tip to the feedthrough is secured to the sample holder at a tie down point using unwaxed dental floss. The substrate is mounted to the substrate holder using four brass screws, one of which is electrically connected to the outside by through a feedthrough wire for application of the sample bias.

2.4 Vibration Isolation

As was indicated above, acoustic vibrations are a major problem in low temperature STM design. Typically, STM facilities are designed to minimize the effect of acoustic and building vibrations, the low frequency vibrations which can be seen in the tunneling current, by placing the cryostat and STM in a specially designed environment
which is isolated from the building and environment. To accomplish this isolation for the LT-STM system described here, an acoustic isolation system was built to shield the dewar from room noise. This insulation system consists of a wood framed box, roughly the dimensions of the dewar, which was lined with several layers of foam insulation of differing density, to better insulate from ambient acoustics. In addition, a Faraday cage, consisting of wire screening, was installed between the layers of insulation to shield electronic noise. The dewar cryostat was then placed inside this box during experiments to prevent acoustic noise from the environment from effecting the LT-STM. In addition, because the facility housing the LT-STM was shared with other researchers, low temperature experiments were performed during hours when the facility was vacant, typically at night and on weekends.

In addition to acoustic noise the building housing the LT-STM system has a characteristic frequency, typically around 20Hz. This vibration, while small in amplitude, can be seen in the tunneling current signal and cause problems during sensitive single molecule experiments. To isolate the LT-STM system from this building vibration the LT-STM was placed on top of a piezo driven active vibration isolation system (Halcyonics, Inc.). This active vibration isolation system works by sensing the oscillation of the LT-STM system and driving piezoelectric actuators to dampen the oscillation. This system damps vibrations from ~1Hz to 200Hz, ideal to deal with building vibrations.

2.5 Control and measurement electronics

In order to function, the LT-STM system needs to be able to apply voltages for bias and piezo control and read tunneling current. The components and a schematic layout of the LT-STM system is shown in Figure 2.3. The main components of this
system are the piezo controller, bias adder, breakout box, current amplifier, lock-in amplifier, temperature controller, and liquid helium monitor. In addition, the input signals (piezo and bias) and the output signals (current, lock-in, temperature, and liquid helium level) are controlled and read using a control computer running custom written Labview (National Instruments) programs. These are connected to the LT-STM electronics using a PCI-6289 card (National Instruments) which has 18 bit resolution and 500kS/s sampling rate. This sampling rate and resolution is preferable for more precise measurements of current and wider bias application ranges. The components which will be discussed in this section, the piezo controller and current amplifier, have had improved designs for this generation of LT-STM.

Figure 2.3: Schematic of the LT-STM control and measurement electronics.

The piezo controller consists of three high voltage amplifiers, one for each direction of motion on the LT-STM. These high voltage amplifiers have to have a wide voltage range in order to be able to generate a wide range of motion from the piezoelectric actuators. In addition these amplifiers need to have a high enough
bandwidth to be able to perform the break junction technique without distorting the applied signal. The circuit diagram and board layout for these amplifiers are shown in Figure 2.4. These circuits consist of three portions, a buffer for input from the control computer and potentiometer signal, an adder for adding the input and potentiometer signals, and a high voltage amplification portion where a second input signal is added. The buffer for the computer input and potentiometer signals use LT1169 dual low noise, JFET operational amplifiers (Linear Technology). These operation amplifiers are chosen because of their low noise and high bandwidth. The LT1169 is also used for the addition circuit to combine the input and potentiometer signals. After the addition circuit there is a voltage spike protection circuit to prevent high voltage signals from destroying the low voltage electronics of the LT1169 or the control computer. This consists of two 12V breakdown Zener diodes arranged with their polarity opposite each other in series with ground. This will create a pathway for high voltage signals to go to ground without letting the unamplified signal through. The signal form the adder circuit is then input to the inverting terminal for the PA240 (Apex microtechnology) high voltage amplifier. In addition, a second input signal is added here for the application of modulation to the piezo signal. The PA240 has an output voltage range of ±150V. The feedback and input resistors for the high voltage amplifier portion are chosen so that the amplifier has a gain of ~15V/V. Measurement of the gain and bandwidth of the three high voltage amplifiers shows that the gain of this circuit is ~15.8V/V and the bandwidth is ~10 kHz.
As discussed previously, the LT-STM system has been built to measure electron-phonon interaction and current induced heating in single molecule junctions. In order to measure these effects the rate of change of current through the junction with bias voltage, or the derivative of current with respect to bias, needs to be measured. The method we use to measure this derivative is the lock-in method. Briefly, to do this a sinusoidal modulation is applied to the bias signal at a specific frequency, $\omega$. As the bias is swept, the lock-in amplifier multiplies the output current by a reference signal, another sine-wave of the same frequency, and applies a low pass filter to the product. The result is a

Figure 2.4: High voltage amplifier for piezo controller. (a) Circuit diagram for high voltage amplifier. (b) Layout of the circuit board for high voltage amplifier.
DC signal proportional to the amplitude of the current portion at $\omega$. Considering the Taylor expansion of the current signal with a sinusoidal modulation

$$I(V + V_0 \sin(\omega t)) \approx I(V) + \frac{dI}{dV} V_0 \sin(\omega t) + \frac{1}{2} \frac{d^2I}{dV^2} V_0 \sin(2\omega t) \ldots \quad (2.1)$$

Thus the output of the lock-in amplifier is proportional to the derivative of current with respect to bias.

![Circuit Diagram](image)

**Figure 2.5**: High input impedance current amplifier circuit diagram.

In order to utilize this technique for single molecule measurements, without performing very long bias sweeps, the frequency response of the current amplifier needs to be greater than 10 kHz. Therefore, the current amplifier used to measure the current from the molecular junction was redesigned from a simple single feedback resistor transconductance amplifier, which has a bandwidth of $\sim10$ kHz, to a high input impedance amplifier. The circuit diagram of the high input impedance amplifier is shown in Figure 2.5. The gain of this amplifier is given by the relation of the three resistors in the feedback network as

$$\frac{V_{out}}{I_{in}} = \frac{R_1 R_3 + R_1 R_2 + R_2 R_3}{R_2} \quad (2.2)$$
The operational amplifier used for this design was the OPA606 (Texas Instruments), a low noise op amp with an adjustable offset. The bandwidth of this amplifier is larger than that of the simple transconductance amplifier, with a 3db point at ~33 kHz. This allows for faster bias sweeps, as with higher frequency reference signals the same amount of cycles can be accumulated in shorter times.

2.6 Summary

Altering the apparatus used to cool the LT-STM system reduced the noise associated with cooling the system enough to allow the STM break junction experiments on single molecule systems. Additionally, the reduction of acoustic noise from addition of the acoustic isolation system and active dampening table have allowed for sustained measurement of a single molecular junction for >24 hours. Further, the addition of a third axis of manipulation increases the mobility of the STM tip on the surface and will allow for imaging of surface structure. The improvements of the piezo driver circuit allow for larger voltage range, meaning larger piezo displacement at low temperatures, and include an additional high voltage input for application of a tip modulation. Finally, the improvement of the bandwidth of the current amplifier, used to read the current through a molecular junction, increased the bias sweep frequency and has allowed for more full molecular junctions measured with the lock-in amplifier. These improvements have allowed this LT-STM to be used for measurement of several different facets of the electron-phonon interaction, some of which will be discussed in the following chapters.
CHAPTER 3

MECHANICAL CONTROLLED FRONTIER ORBITAL ALIGNMENT IN 1,4-BENZENEDITHIOL MOLECULAR JUNCTIONS

3.1 Introduction

Much of the research in molecular electronics has focused on building single molecule devices which are analogous to those in conventional electronics, such as transistor and diodes [3]. However, single molecules possess characteristics which are not seen in conventional electronics. One such characteristic is the interplay between the mechanical properties and the electronic properties of single molecule devices [24,117,169–172]. Utilizing the interplay between these properties an applied mechanical force can control charge transport through single molecule junctions. As was discussed earlier, the interplay between mechanical and electronic properties has been investigated for several different molecular systems by exploring the coupling between molecule and electrode. These studies have seen that, as would be expected, the conductance of a single molecule decreases when the molecule-electrode coupling is decreased, either by stretching the contact or decreasing the π-π overlap between molecule and contact.

One of the most widely studied molecules in molecular electronics is 1,4-benzenedithiol (BDT). The transport properties of this simple molecule have been measured experimentally through different methods [8,13,173–177] and calculated using many levels of theory [68,178–187]. However, the single molecule conductance of BDT remains highly disputed. In addition, there is consistently a much larger discrepancy between the measured conductance values and the calculated values than for other
molecular systems studied, with theoretically predicted values being several orders of magnitude larger than the measured conductance values [188].

In this chapter, the electromechanical properties of BDT molecular junctions are investigated as single molecule junctions are compressed and stretched. Counterintuitively, we find that the conductance increases by more than an order of magnitude during stretching, and then decreases reversibly under compression. Simultaneously recorded current-voltage and conductance-voltage spectroscopy, and inelastic electron tunneling spectroscopy are used to attribute this finding to a strain-induced shift of the highest occupied molecular orbital towards the Fermi energy of the metal electrodes, leading to a resonant enhancement of conductance. These results, which are in agreement with theoretically predicted transport, also clarify the origins of the long standing discrepancy between the calculated and measured conductance of BDT.

3.2 Experimental methods

The gold substrates used for these experiments were prepared by thermally evaporating 1300Å of gold (Alfa Aesar 99.9999% purity) on freshly cleaved mica surface (Ted Pella) and annealed at ~360°C in 5x10⁻⁸Torr to attain Au(111) surface structure. Prior to use, the substrate was annealed with a hydrogen flame for ~1min. BDT samples were prepared by dissolving ~1mM 1,4-benzenedithiol (Alfa Aesar 97% purity) in methanol (Sigma Aldrich HPLC grade >99.9%) and submerging a freshly flame annealed substrate for ~12 hours, to form a self-assembled monolayer. The substrate was then rinsed with methanol and dried with nitrogen gas (99%) and placed in the homebuilt LT-STM system described in the previous chapter. A freshly cut gold tip (Alfa Aesar, 99.998% purity) was also placed in the LT-STM and the assembly was placed in the
liquid-helium dewar cryostat and placed under vacuum of $2 \times 10^{-6}$ Torr. Liquid helium was then introduced to the cryostat to cool the LT-STM to ~4.2K. When the temperature of the LT-STM system stabilized the STM tip was brought into contact with the substrate and break junction, current-voltage, and IETS experiments were performed. Break junction experiments at higher temperatures were performed in the absence of liquid helium, once the LT-STM had reached a stable room temperature.

Measurements of the current during break junction and spectroscopic experiments were performed using the double-stage transconductance amplifiers, discussed in the previous chapter, with gains of 100nA/V or 1μA/V. For current-voltage (I-V), conductance-voltage (G-V) and inelastic electron tunneling spectroscopy (IETS) measurements the tip motion was suspended once a plateau was detected and the bias voltage was swept at a rate of 0.005Hz. The electrode separation was then either increased or decreased by moving the STM tip in increments of ~0.01 nm, and the bias was swept again. This process was repeated until the molecular junction broke down, distinguished by a sudden drop in the current to the amplifier background. The G-V curves were obtained using the aforementioned lock-in technique by applying a bias modulation of 1mV at a reference frequency of 23kHz in addition to the bias sweep. The IET spectrum was obtained through the numerical derivative of the G-V curve using a homebuilt Matlab and LabView script [189]. Finally, transition voltage spectroscopy (TVS) plots were obtained by fitting the I-V curves, obtained through high-bias sweeps, with a seventh-order polynomial. This fitted curve was used, instead of the raw current, to generate TVS plots to minimize the effect of noise in the current signal.
3.3 1,4 – Benzendithiol conductance behavior

The charge transport properties of BDT were studied using the STM break junction technique at 300K and at 4.2K. The conductance histograms measured for these two temperatures (Figure 3.1b) show broad peaks in the conductance range $0.01G_0$, which agrees with previous measurements by various groups. [13,173,175] Comparing the conductance histograms at different temperatures, we see that at high temperature the conductance peak is more pronounced at $0.01G_0$ while at 4.2K the peak is a broad feature ranging from $1 \times 10^{-3}G_0$ to $0.05G_0$. This is an interesting result; one would expect a more pronounced peak for molecules at low temperature due to the enhanced stability.
The difference in conductance histogram at room temperature and low temperature, and the broad nature of the histograms, is understood by examination of the individual conductance vs. electrode displacement curves. Here displacement is defined as the relative movement of the two electrodes and zero displacement as the point where the conductance drops from $G_0$ to the tunneling regime. At low temperature, the conductance vs. displacement plots often show an increase in molecular conductance.
with increased electrode displacement. Some of the junctions even show more than an order of magnitude increase in conductance upon stretching, yielding conductance of a few tenths of \(1 G_0\) before breakdown, Figure 3.1c,d. Additionally, many of the conductance vs. displacement curves show a small decrease in conductance before increasing, resulting in a ‘bowl’ shape conductance trace. In total, at 4.2K, roughly 70% of the conductance vs. displacement curves has an increasing conductance region in the molecular plateau. Similar conductance behavior is seen at 300K; however, at higher temperature the probability of having a large increase in conductance is much smaller. This is attributed to the decreased junction stability at room temperature; since the breakdown of a molecular junction is a thermally activated process the likelihood of the junction breaking before the conductance increases is greater at higher temperatures.

Thus, since the less stable configurations are more likely to breakdown at 300K, only the most stable configurations contribute to the conductance histogram. It is also interesting to note that the measured conductance at the last stage of stretching is close to the value of conductance for BDT calculated using theoretical models and that analyzing the initial conductance at low temperature results in a peak conductance around \(3 \times 10^{-3} G_0\), similar to the calculated conductance for relaxed junctions[188].

The increase in conductance upon stretching BDT molecular junctions is counterintuitive, as increasing the distance between the two electrodes is expected to weaken the molecule-electrode coupling and increase tunneling distance, which one would expect to lead to a decrease in conductance. Indeed, for many molecular systems, like alkanedithiols, the conductance has been seen to decrease with stretching. [116,171,190] However, for BDT the increase in conductance is a result of
force induced resonant tunneling, which occurs when weakening of the molecule-electrode coupling causes a shift of the frontier molecular orbital towards the Fermi level of the electrodes [68,176,178,179]. Theoretical calculations predict that changing either of the molecule-electrode contacts in a molecular junction can significantly alter the alignment of the molecular energy levels relative to the electrode Fermi energy, resulting in a change in conductance. In the case of BDT, calculations show that the highest occupied molecular orbital (HOMO)-related states are located far below the Fermi level when the molecular junction is in a relaxed state. However, on stretching the molecular junction, the electronic coupling between the BDT molecule and the gold electrode decreases. This results in the HOMO-related states moving towards the Fermi level, leading to resonant tunneling, Figure 3.1a. Therefore, despite the increased electrode separation during stretching, the shift in the HOMO energy results in a substantial enough decrease in the tunneling barrier to cause an increase in conductance. This increasing conductance with junction stretching behavior has been reported for BDT using many different levels of NEGF-DFT theory to calculate the transport properties. Specifically, although the calculated values for conductance vary between theories, the increasing trend in conductance has been reported for BDT molecular junctions using the LDA [182,191], GGA [68,176,178,179], and ASIC [186] approximations for the exchange-correlation functional.

3.4 Monitoring molecule-electrode coupling and frontier orbital alignment

To better understand the evolution of the BDT molecular junction under stretching and the mechanism behind the associated conductance increase we created many molecular junctions at low temperature. The benefit of working at 4.2K is that the
molecular junctions are stable enough to measure the I-V, G-V, IETS and TVS characteristics under stretching and compressing.

3.4.1 Conductance-voltage and IETS characteristics

One example of a junction in which the I-V, G-V, and IETS curves were recorded while the electrode displacement was changed in ~0.01nm increments is shown in Figure 3.2a. Once this junction was formed (region I in Figure 3.2a), an initial increase in the conductance was noticed as the electrodes were separated by a small distance (region II in Figure 3.2a). To avoid breaking the junction and to explore the reversibility of this feature the direction of the tip movement was reversed, and the electrode displacement was decreased to position 4 (region III, blue portion, in Figure 3.2a). The electrodes were then separated again (region IV, black portion, in Figure 3.2a) to ensure the reproducibility of the conductance behavior. The ‘bowl’ shaped conductance behavior shown in Figure 3.2a is characteristic of the force-induced resonance predicted by theory [182,186]. This shape suggests that when the junction is compressed the BDT molecule is tilted between the electrodes, which causes an increase in conductance due to lateral coupling between the π-electrons of the molecule and the electrodes [171,190]. At the opposite extreme, when the molecule is stretched the electronic coupling between the molecule and electrodes is reduced, causing a shift in the HOMO level towards the Fermi energy of the electrodes, and a corresponding increase in the conductance. The ‘bowl’ shape conductance behavior is fully reversible, and the force-induced increase in conductance is apparent in the initial stretching (region II in Figure 3.2a) and after the retrace is complete (region IV in Figure 3.2a).
In addition to the conductance, the differential conductance and IET spectra as a function of bias voltage was also measured at several different displacements during the compression and extension cycles. The G-V traces reveal significant, continuous and fully reversible changes during the compression and extension cycles. When the junction is extended, as in positions 1 and 8, the G-V curve is highly asymmetric, and this asymmetry decreases as the separation between the two electrodes decreases (Figure 3.3a). Since the molecule is symmetric, the asymmetry in the G-V
curves must be due to asymmetric contacts formed between the molecule and the two gold electrodes. The two contacts are in series, so one expects that the weaker of the two get stretched more, which leads to even more asymmetry in the contacts, and explains the increase in asymmetry with electrode separation.

From the IET spectra, Figure 3.2c, it is possible to discern exactly what is changing in the molecular junction when the conductance increases and the G-V curves become more asymmetric. The most obvious change in the IET spectra during the stretching and compressing cycle is the change in the vibration mode at ±14 mV. Figure 3.3b plots the amplitudes of this low energy vibration mode, which changes continuously with the electrode displacement, and becomes asymmetric as the junction is extended and more symmetric as the junction is compressed. The 14mV mode is due to either a collective motion of the BDT molecule with respect to the gold electrodes [192,193], or vibration of the Au-Au bonds in the contact [155]. In addition, the peak energy of the 50mV mode shifts during stretching of the BDT molecular junction toward smaller voltage, Figure 3.3c and d. This mode is associated with vibration of the Au-S bonds between the molecule and electrode. Changes in the low frequency modes demonstrate that a strain is being applied to the molecular junction [172,194], and that compression/stretching takes place primarily at the molecule-electrode contact. As the theory predicts, this change in the contacts decreases the coupling between the molecule and electrodes, shifting the HOMO level towards the Fermi level and causing an increase in molecular conductance. Additional changes in peak frequency of modes associated with the molecule-electrode contacts have been observed in other junctions (for example, the ~40mV mode in Figure 3.4).
The conductance, the symmetry of the $G-V$ curves, and the low frequency vibration mode in the IET spectrum all change continuously and reversibly upon repeated stretching and compressing of the molecular junction. These observations indicate that the increase in conductance at the end of the stretching cycle is not due to abrupt changes in the molecule–electrode contact geometry, as is seen in amines [195], but is instead due to a gradual, reversible stretching of the bond at the contacts. Abrupt atomic rearrangement at the contacts can also be observed, which is, however, much different from the continuous changes discussed above. One such junction is shown in Figure 3.4.

Figure 3.3: Evolution of G-V and IETS under stretching and compression. (a) Rectification ratio at $V=0.2V$ vs. electrode displacement. (b) Peak height for the $\pm14mV$ mode vs. electrode separation. Red curves are fits to guide the eye. (c–d) Peak position for the $\pm50mV$ mode vs. electrode displacement, with electrode displacement in nm. All measurements performed at 4.2K.
This junction showed a clear plateau, and the stretching process was stopped at position 1 to begin recording the I-V, G-V, and IETS characteristics. Upon further stretching a clear and gradual increase in the conductance is observed along with an increase in the asymmetry of the G-V curve, shown in Figure 3.4b. Then, when the junction is stretched to a distance of ~2.3 Å, close to the size of a gold atom, the conductance drops abruptly to a value below the initial conductance at position 1. This sudden change in conductance is also accompanied by a sudden change in the symmetry of the G-V curves. The G-V curve from position 3, shown in Figure 3.4b, is clearly more symmetric than at position 2, taken near the peak of the conductance increase. Upon further stretching the conductance and the asymmetry increase again for a similar distance of ~2.3 Å before the junction finally breaks down.
The IET spectra for this junction show a large increase in peak amplitude and a change in line shape as the junction is elongated and the conductance increases, Figure 3.4c and d. The modes which are affected are between 0.1 and 0.2 V and are associated with benzene ring vibrations. Although the change in IETS peaks could be caused by other factors, such as dipole coupling [196], it is consistent with IETS peaks near resonance, in which an increase in amplitude and the development of a derivative-like feature are predicted [13,197,198].
Another example of a junction with a switch in the conductance is shown in Figure 3.5. In this junction there is a sudden switch in conductance at a displacement of 0.14nm. The conductance increases upon further stretching until the junction breaks down at an elongation of ~0.27nm. The G-V curves before and after the switch, Figure 3.5b, show a large, abrupt change in symmetry associated with the switch. This further confirms that the continuous changes in conductance, G-V and IETS seen in Figure 3.2 are due to continuous stretching in the molecule-electrode contacts rather than sudden changes in the geometry, which are illustrated in Figures 3.3, 3.4, and 3.5.

Figure 3.5: Conductance switching behavior in BDT junction revisited. (a) Plot of conductance vs. electrode displacement showing switch in conductance. (b) G-V curves collected at positions 1 and 2 marked in (a). All measurements performed at 4.2K.
An additional BDT junction which exhibits an increase in conductance with junction elongation is shown in Figure 3.6. The conductance of this junction increases by roughly 6x as the electrodes are separated by ~0.125nm. During this separation process...
the bias was swept, at a rate of 0.01 Hz, at three positions and the G-V and IET spectra were measured at higher conductance values. A noticeable change in peak shape and amplitude is seen during the stretching of this junction, with the final spectra having larger amplitudes and more “derivative” like shapes. It should be noted that at the high conductance and strain attained by this junction mechanical instability causes switching events during elongation of the junction, as seen in the conductance in Figure 3.6a. However, this switching is unlikely the reason for the amplitude increase in IETS peaks because the increase is systematic and there is no visible switching in the G-V spectra, from which the IETS is obtained. The most likely cause of the observed change in line shape and peak amplitude is the molecular junction transmission getting closer to resonant conditions, which are known to cause “derivative” like features in IETS [13,197,198].

The averaged IET spectra for the junctions shown in Figures 3.2, 3.4, and 3.5 are shown in Figure 3.7. These spectra are made by averaging all the IET spectra collected while the junction was stretched and/or compressed. The peaks highlighted in blue are anti-symmetric with respect to bias, the signature of phonon-mediated inelastic tunneling, and are assigned to molecular vibrations in Table 3.1 by comparing the mode energy with that of previously published experimental and theoretical work [13,79,155,172,175,192,193].
Figure 3.7: Averaged IETS spectra. (a) Averaged IET spectra from 20 IETS curves collected from junction in Figure 3.2. (b) Averaged IET spectra from 10 IETS curves collected from junction in Figure 3.4. (c) Averaged IET spectra from 5 IETS curves collected from junction in Figure 3.5.
Thus far we demonstrated that the conductance of BDT molecular junctions can increase with stretching. Also that this conductance increase is accompanied by a continuous increase in asymmetry of the G-V curves, a change in amplitude of the low-frequency vibrational modes associated with the molecule-electrode contact, and a change in IETS peak amplitude and line shape. These observations demonstrate that the increase in conductance is due to the continuous stretching of the molecule-electrode contact, and support the force-induced shift in the frontier molecular orbital model. However, to fully demonstrate the emergence of resonant tunneling transport during stretching it is necessary to show that the frontier energy levels of the molecular system change during stretching. To explore this possibility we performed similar stretching/bias sweep measurements as were described above, but rather than sweeping the bias slowly to obtain a high-resolution G-V and IET spectra, the bias was

<table>
<thead>
<tr>
<th>Mode #</th>
<th>Mode Energy (mV)</th>
<th>Description</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10-20</td>
<td>Au-Au or BDT-Au</td>
<td>[155,193]</td>
</tr>
<tr>
<td>2</td>
<td>36-51</td>
<td>ν(S-Au)</td>
<td>[13,79,177,192]</td>
</tr>
<tr>
<td>3</td>
<td>80-84</td>
<td>δ(C-C-C)</td>
<td>[79,175,177,192]</td>
</tr>
<tr>
<td>4</td>
<td>135-141</td>
<td>ν(18a)</td>
<td>[175,177,189,192]</td>
</tr>
<tr>
<td>5</td>
<td>186-193</td>
<td>ν(C=C)</td>
<td>[111,175,177,189,192]</td>
</tr>
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Table 3.1: IETS mode assignments. Approximate vibrational mode energy assignment for the averaged IET spectra. Modes assigned are anti-symmetric and reproducible between different junctions.

3.4.2 Transition voltage spectroscopy

Thus far we demonstrated that the conductance of BDT molecular junctions can increase with stretching. Also that this conductance increase is accompanied by a continuous increase in asymmetry of the G-V curves, a change in amplitude of the low-frequency vibrational modes associated with the molecule-electrode contact, and a change in IETS peak amplitude and line shape. These observations demonstrate that the increase in conductance is due to the continuous stretching of the molecule-electrode contact, and support the force-induced shift in the frontier molecular orbital model. However, to fully demonstrate the emergence of resonant tunneling transport during stretching it is necessary to show that the frontier energy levels of the molecular system change during stretching. To explore this possibility we performed similar stretching/bias sweep measurements as were described above, but rather than sweeping the bias slowly to obtain a high-resolution G-V and IET spectra, the bias was
swept quickly and the tip was moved quickly, allowing the junction to reach much higher conductance values before breakdown. I-V characteristics for such a junction are plotted in Figure 3.8. Upon stretching, the current in the I-V curve increases nonlinearly in the higher bias range (Figure 3.8b), and as the junction is stretched the increase becomes even more prevalent, indicating a change in the proximity of the HOMO level to the electrode energy levels.

![Figure 3.8: Exploring the frontier orbital energy level for BDT. (a) Plot of conductance vs. electrode displacement. (b) Current vs. bias voltage curves recorded at positions indicated in (a). (c) Fowler-Nordheim plot (ln(I/V^2) vs. (1/V)) made by fitting the I-V curves in (b) to seventh-order polynomials. All measurements performed at 4.2K.](image)

Another way of plotting the I-V curve to better demonstrate the change in orbital position is by using a technique referred to as Transition Voltage Spectroscopy (TVS), where ln(I/V^2) is plotted vs. 1/V. TVS has recently emerged as a robust method for probing the energy levels of a molecular device [13,21,65,66]. The TVS plots are expected to have a negative slope for biases above |\(\varphi/e|\), and a positive slope below this value, as such there is a minimum at V=\(\varphi/e\), where \(\varphi\) is the barrier height and \(e\) is the electron charge. Therefore, if the energy level of the HOMO is moving closer to the
electrode Fermi level during the stretching process this minimum point should shift to lower biases (higher $1/V$). The TVS plots for the junction shown in Figure 3.8b are plotted in 3.8c and demonstrate that there is a clear shift in the TVS minimum with stretching. This decrease in the minimum voltage with stretching indicates that the energy difference between the Fermi Energy of the electrodes and the HOMO level of the molecule are decreasing, thus moving the system closer to a resonant condition. At point 3 in Figure 3.8a, where the conductance is $\sim 0.09G_0$, the minimum in the TVS yields a barrier height of $\sim 0.14\text{eV}$, indicating that the barrier has decreased to a near resonance condition.

Additional examples of the shift of the TVS minimum with electrode separation are shown in Figure 3.9. The conductance of these molecular junctions does not reach the high levels seen in Figure 3.8a before the molecular junction breaks down, but in the conductance vs. electrode displacement curves in Figure 3.9a and d a clear increase in conductance occurs. As a result of the lower conductance the bias sweeps are of larger amplitude, 1V for Figure 3.8b and 0.8V for Figure 3.8e. Correspondingly, the barrier height estimated from the TVS is larger for these molecular junctions, presumably because the molecule-electrode contact is less distorted. It is interesting to note that the asymmetry in the I-V curves in Figure 3.8e increases with junction stretching, with more asymmetry for the I-V measurement performed with the largest electrode displacement. This can be explained by asymmetric distortion of the molecule-electrode contacts, presumably by distorting the weakest contact, and this asymmetric distortion showing up in the current.
The conductance, I-V, G-V, IETS, and TVS characteristics of individual BDT molecules bridged between two gold electrodes were measured under stretching and compressing the molecular junction. The conductance of the molecule can increase by more than one order of magnitude upon stretching before it breaks down. This counterintuitive observation is attributed to force-induced resonant enhancement, which occurs because the HOMO-related states move towards the Fermi level of the gold electrodes when the molecule-electrode coupling decreases upon stretching. Repeated

Figure 3.9: Approaching resonant transport with elongation. (a) and (d) Plots of conductance vs. electrode displacement. (b) and (e) I-V curves recorded at the positions in (a) and (d). (c) and (f) TVS plots from fitting the I-V curves in (b) and (e) with seventh order polynomial functions to smooth noise in current. All measurements performed at 4.2K.

3.5 Summary

The conductance, I-V, G-V, IETS, and TVS characteristics of individual BDT molecules bridged between two gold electrodes were measured under stretching and compressing the molecular junction. The conductance of the molecule can increase by more than one order of magnitude upon stretching before it breaks down. This counterintuitive observation is attributed to force-induced resonant enhancement, which occurs because the HOMO-related states move towards the Fermi level of the gold electrodes when the molecule-electrode coupling decreases upon stretching. Repeated
stretching and compressing can reproduce the increase and decrease of the conductance with no hysteresis, indicating a continuous stretching and relaxation in the bond at the molecule-electrode contact, rather than an abrupt rearrangement in the contact geometry. This conclusion is further supported by continuous changes in the G-V symmetry and low energy IETS modes (associated with the contact) upon stretching and compression. Furthermore, by examining the transition voltage of TVS during stretching it is possible to demonstrate that the energy barrier is decreasing as the junction is stretched. These results are in excellent agreement with theoretical calculations, and shed new light on our understanding of the conductance of BDT, the most studied molecule in molecular electronics to date. It also demonstrates an electromechanical device based on mechanically tuning electron tunneling into and out of resonance. Such a device function does not occur in conventional semiconductor materials.
CHAPTER 4

EFFECT OF MECHANICAL STRETCHING ON SINGLE DNA MOLECULAR CONDUCTANCE

4.1 Introduction

Studying charge transport in DNA (dsDNA) is fundamental for understanding relevant biological processes and developing electronic devices with DNA molecules [199–201]. Experiments have shown that charge transport in dsDNA molecules is mediated by the $\pi-\pi$ stacking interactions between neighboring base pairs [149,202–206]. These $\pi-\pi$ stacking interactions are sensitive to structural changes within dsDNA molecules, which can be induced by stretching the molecules mechanically [207–209]. As was discussed in section 1.5, it has been shown that DNA undergoes a structural transition when mechanically stretched, [121,124,133,135,210] which has been attributed to either a reversible configuration change from native form (B-DNA) to stretched form (S-DNA) or irreversible force induced melting. [132,141-144,146,147] Both processes are expected to seriously disrupt the $\pi-\pi$ stacking interactions, leading to a large change in the charge transport of DNA. Despite the intensive study of mechanical properties of DNA, the effect of mechanical stretching on charge transport in dsDNA molecules has not been experimentally investigated.

In the following chapter, we describe a study of mechanical stretching effect on charge transport in dsDNA molecules using a scanning tunneling microscope (STM) break junction technique [6] in the native aqueous environment of DNA. The dsDNA molecules are terminated with linkers such that they can bridge between the STM tip
(gold) and substrate (gold) electrodes. Separating the tip and substrate electrodes, the
dsDNA molecule is stretched while the conductance is continuously measured. By
analyzing the evolution of single molecule conductance during electrode separation, the
effect of the stretching transition on dsDNA conductance is studied for dsDNA molecules
with lengths varying from 6 base pairs (~2 nm) to 26 base pairs (~9 nm). The dsDNA
resistance is found to increase linearly with the length, consistent with thermally
activated hopping transport [211], in which holes hop sequentially along the molecule via
the stacked base pairs. However, the charge transport in DNA is highly sensitive to
mechanical stretching, showing an abrupt decrease in conductance at surprisingly short
stretching distances which is weakly dependent on the molecular length. These surprising
observations are attributed to a force induced melting mechanism [212], and are
consistent with simulations [144] and deGennes’ DNA ladder model [143] for dsDNA
mechanics.

4.2 Experimental Methods

DNA sequences

The dsDNA molecules studied here are all self-complimentary strands denoted as
5’-A(CG)_N-T-3’ (N=2 to 12). The thymine and adenine bases at the 3’ and 5’ ends
(respectively) are used to prevent mismatch. The dsDNA molecules are linked to the gold
electrodes (STM tip and substrate) through an alkanethiol linker, which attaches to the
deoxyribose ring at the 3’ end, see Figure 4.1a. As a control experiment, dsDNA
molecules with an amine linker are also studied, Figure 4.1b.
DNA Sample preparation

The HPLC purified oligonucleotide molecules used in this study were purchased from Integrated DNA Technologies. The oligonucleotide samples under investigation here ranged in length from 6 bases to 26 bases. The nucleic acid sequence for the molecules studied is 5’-A-(CG)₈-T-3’, where N ranged from 2 to 12, and were purchased with a thiol linker (3’-thiol modifier C3 S-S). This thiol linker was protected with a mercaptopropanol disulfide group during shipment and storage. Upon receipt of the samples, the oligonucleotides were suspended in 18MΩ DI water for a concentration of 100μM. This sample was then stored at -20°C. Prior to conductance experiments, phosphate buffer solution (pH=7.0) was prepared with 100mM Na⁺ and 10mM tris(2-carboxyethyl)phosphine (TCEP) concentration. The target molecular sample was added to this solution to reach an oligo concentration of 20 μM and allowed to react for ~3
hours at room temperature. The sample was then transferred to a spin column (Roche Applied Science quick spin column sephadex G-25) and centrifuged to remove the TCEP and mercaptopropanol. Phosphate buffer (pH=7.0) containing 10 mM Mg$^{2+}$ was then added to the deprotected sample to get a final oligo concentration of 10 μM. Mg$^{2+}$ can help prevent the formation of hairpin structures for long DNA sequences, as was seen using 10% native polyacrylamide gel electrophoresis (Figure 4.1). As a result, it was not possible to measure conductance in samples longer than 14 bases without adding magnesium before annealing. The samples were then annealed in a thermal cycler by heating to 95 C and cooling gradually to 4 C over 4 hours. The samples were kept at 4 C until break junction measurements were performed. All break junction experiments were performed in phosphate buffer containing 10mM Mg$^{2+}$ and 10μM dsDNA target molecule at room temperature.
STM break junction sample preparation and measurement

The STM substrates used here were prepared in house by thermally evaporating 1300 Å of gold (99.9999% purity, Alfa Aesar) onto freshly cleaved mica slides and

Figure 4.2: Native Polyacrylamide gel electrophoresis. (a) dsDNA annealed in phosphate buffer without Mg\(^{2+}\). From 1 to 4 the sequence is 5’-A(CG)\(_6\)T-3’, 5’-A(CG)\(_9\)T-3’, 5’-A(CG)\(_{12}\)T-3’, and 5’-A(CG)\(_{17}\)T-3’. We see that molecules longer than 14bp are more likely to form a hairpin structure than double strand in only phosphate buffer. (b) dsDNA annealed in phosphate buffer with Mg\(^{2+}\) (columns 2 and 5) and without Mg\(^{2+}\) (the rest). Column 1 is 5’-A(CG)\(_6\)T-3’ in phosphate buffer annealed for 3 hrs, 2 is 5’-A(CG)\(_9\)T-3’ in phosphate buffer with Mg\(^{2+}\) annealed for 3 hrs, 3 is 5’-A(CG)\(_9\)T-3’ in phosphate buffer annealed for 13 hrs, 4 is 5’-A(CG)\(_{17}\)T-3’ in phosphate buffer annealed for 3 hrs 5 is 5’-A(CG)\(_{17}\)T-3’ in phosphate buffer with Mg\(^{2+}\) annealed for 3 hrs, 6 is 5’-A(CG)\(_{17}\)T-3’ in phosphate buffer annealed for 13 hrs. We see that without Mg\(^{2+}\) the hairpin structure is most likely, while with Mg\(^{2+}\) the double strand is most likely structure.
annealed in vacuum to produce Au (111) surfaces. These substrates were under
transferred into individual vials and stored under vacuum until prior to measurement.
Prior to adding the sample the substrates were flame annealed to clean and anneal the
surface with a hydrogen flame. The STM tips used were produced by mechanically
cutting gold wire and coating with Apiezon wax to reduce the leakage current during
measurements in aqueous environment.

The break junction experiments were performed using a Digital Instruments
Nanoscope IIIA controller. A Molecular Imaging STM head and scanner were used to
collect current and control tip motion. For all experiments described here, the current
preamplifier used had a gain of 10 nA/V and the piezo sensitivity in the z-axis was 3.9
nm/V. A custom designed Labview (National Instruments) program, installed on an
external computer, was used to perform the break junction experiments and collect the
data discussed in this report. During all break junction and stretching-compression cycle
experiments the tip was moved at a ramp rate of 5 V/s, resulting in a stretching rate of
~20 nm/s. The stretching-compression cycle experiments were carried out using an
algorithm to detect molecular junctions in real time, which is described elsewhere [19].
The stretching length is measured by processing the break junction data (conductance vs.
tip displacement decay curves) in a home built Labview (National Instruments) program
which measures the length of the molecular conductance plateau within a preset range.
The conductance range for the plateau was set according to the conductance histogram,
roughly the full width at half max of the molecular peak, to ensure the plateau was from a
single molecule. The resulting stretching lengths for thousands of molecular junctions
were then added into a histogram. Gaussian fittings for all histograms were performed in Origin 8.0 (OriginLab).

4.3 dsDNA molecular junctions stretching length

The experimental setup is illustrated in Figure 4.3a. Briefly, a gold STM tip, coated with an insulation layer, is brought into contact with a gold substrate in the presence of the dsDNA molecule. A small bias voltage applied between the tip and substrate causes a current between the two electrodes when the separation between them is small. The tip is then retracted while the current is monitored. In the absence of a molecule bridging the tip and substrate, the current decays exponentially with tip retraction as expected for a tunnel junction. However, when a molecule bridges the tip-substrate gap a plateau is seen in the current vs. tip displacement as shown in Figure 4.3b, which represents a single molecule bridging the tip-substrate gap. Measuring the dependence of the plateau current on stretching allows us to study the effect of mechanical stretching on charge transport in dsDNA. This process can be repeated thousands of times and statistical analysis of these current vs. displacement curves results in a conductance histogram, from which the average conductance for a single molecule is determined (Figure 4.3c).
Figure 4.3: dsDNA molecular conductance. (a) Cartoon illustrating the STM break junction experimental technique. The top electrode is an STM tip and the bottom electrode is an STM substrate. The tip contacts molecules bound to the substrate. The current is measured while the tip is retracted. (b) Examples of conductance vs. tip displacement curves for the 14 base pair dsDNA molecule. Curves are offset on the x-axis for clarity. (c) Conductance histograms with Gaussian fittings for 5’-A(CG)₂T-3’, 5’-A(CG)₅T-3’, and 5’-A(CG)₁₂T-3’ base pair (bottom to top respectively). Red dotted line intended to guide the eye. (d) Average resistance vs. molecular length for all molecules studied. Red line is linear fitting intended to guide the eye. Inset shows structure of molecules.

Figure 4.3d shows the dependence of the measured dsDNA resistance (inverse of
conductance) on molecular length ranging from 6 to 26 base pairs. Over this wide range of molecular length, the resistance is linearly proportional to molecular length, indicating a thermally activated hopping process [213]. As opposed to transport through the tunneling mechanism, which has an exponential dependence on molecular length, this hopping process is characterized by weak length dependence, given by [102]

\[
R \propto \frac{1}{k_L} + \frac{1}{k_R} + \frac{N-1}{k}
\]  

(1)

where \(k_{L(R)}\) is the charge transfer rate between the left (right) electrode and the nearest molecular hopping site, \(k\) the charge transfer rate between hopping sites on the molecular bridge. The ratio between the intercept and slope in Eq. 1, \((k_L^{-1}+k_R^{-1})/k^{-1}\), measures the relative importance of the contact, i.e., hopping between the electrodes and the nearest molecular hopping sites. Eq. 1 fits the experimental data well, and the ratio between the intercept and slope is \(\sim 40\). This large value suggests that the resistance of dsDNA, or the rate limiting step, is determined by the contact transfer rates, \(k_{L(R)}\) and the base to base transfer rate, \(k\), is roughly 40 times more efficient. This observation supports long-range charge transport in DNA [105,214].

The spring constants of dsDNA molecules studied here range from \(\sim 0.5 - 0.1\) N/m (for 6 base pairs to 26 base pairs respectively) [123], soft when compared to the Au-Au bond (~8 N/m) which is known to be the softest part of the thiol-gold linker [106]. Thus, we expect the dsDNA molecules, rather than the contacts, to be substantially stretched when separating the two electrodes apart. Considering the transport model above, one would expect the conductance to decrease as the dsDNA molecule is stretched because of the increase in the distance between neighboring bases. Indeed, as can be seen in Figure 85.
4.3b, a decrease in conductance with tip displacement is observed upon initial stretching in many dsDNA molecular junctions. However, following the initial slow conductance decrease there is an abrupt decrease in conductance, indicating a structural transition in the electrode-dsDNA-electrode junction.

Figure 4.4: Molecular junction stretching length. (a) Example decay curve illustrating the stretching length measurement technique. (b) Stretching length histogram with Gaussian fit for octanedithiol. Arrow indicates peak position. (c-f) Stretching length histograms with Gaussian fit for 5'-A(CG)\textsubscript{2}T-3', 5'-A(CG)\textsubscript{6}T-3', 5'-A(CG)\textsubscript{10}T-3', and 5'-A(CG)\textsubscript{12}T-3' molecules respectively. Drawings of the respective molecular structures are inset to the histograms. Red dotted line are intended as guide to the eye.

An important parameter that characterizes the structural transition is the distance over which the junction can be stretched before the abrupt decrease in conductance, or
simply stretching length as illustrated in Figure 4.4a. As a control experiment, we first examine the stretching length for octanethiol molecules, consisting of a saturated carbon chain terminated with two thiol linkers that bind to the tip and substrate electrodes. Figure 4.4b shows that the stretching length for octanethiol follows a Gaussian distribution with an average value of ~0.23 nm, close the distance required to break a gold atomic contact [106]. Previous studies have indeed shown that the Au-Au bond at the contacts breaks first when stretching a octanethiol junction [111]. This is because Au-Au bond is the softest and weakest link in the octanethiol molecular junction. However, analysis of the stretching length for dsDNA molecules yields several surprising observations. First, as shown in Figure 4.4c, the average stretching length is about 0.14 nm for a 6 base pair dsDNA, much smaller than the length required for breaking the Au-Au bond. This short stretching length shows that, in the case of dsDNA, the thiol-gold linker is not responsible for the abrupt decrease in conductance. Instead, the unique mechanical properties of dsDNA must be responsible for the surprising observation of short stretching length. To confirm this we perform a control experiment by measuring the stretching length of amine-terminated dsDNA molecules. The amine-gold bond is much weaker than the thiol-gold bond and for alkanedithiol molecules has been shown to have much smaller step lengths [112]. However, the measured stretching length of amine terminated dsDNA is similar to that of thiol terminated dsDNA (Figure 4.5), confirming that the surprisingly short step length is due to stretching the dsDNA molecule. The second surprising observation is that the stretching length of dsDNA depends on molecular length weakly (see Figures 4.4c – 4.4f). While dependence on the molecular length is consistent with mechanical stretching of the dsDNA, rather than the
contacts, the stretching length increases by only ~0.03 nm from 6 to 26 base pairs, which is surprising based on the following consideration. According to Eq. 1 the mechanical stretching induced resistance change is proportional to molecular length (N) given by,

\[ \Delta R \propto (N - 1) \Delta \frac{k}{k}, \]

indicating that the stretching length scales with molecular length. This is in contradiction with the experimental data, which reveals very little dependence of the stretching length on molecular length.

Figure 4.5: Conductance and stretching length characteristics of amine linked dsDNA molecules: (a) Conductance and (b) stretching length histograms for 5’-A(CG)₃T-3’ (8 base pair) amine linked dsDNA molecule. (c) Conductance and (d) stretching length for 5’-A(CG)₆T-3’ (14 base pair) amine linked dsDNA molecule. Note that the amine linker group has fewer saturated bonds between the linker and dsDNA hopping sites, resulting in lowered contact resistance and larger overall conductance.

The above model assumes that the mechanical stretching is evenly distributed along the dsDNA chain, which we believe is the reason for its discrepancy with the experimental observations. Alternatively, de Gennes [143] developed a DNA ladder
model to show that the shear force in dsDNA molecules is distributed over only a few base pairs at the end of the sequence (Figure 4.6a). This way, if we assume that most of the stretching takes place at the base pairs near the two ends of the dsDNA molecule, Eq. 2 can be rewritten as

$$\Delta R \propto 2\Delta'_{k_{\text{end}}} + (N - 3)\Delta^1_k,$$

(3)

where the first term represents change in the resistance due to the stretching of the end base pairs, and the second term is the change in the middle section of the dsDNA. When the stretching is large enough, one of the end base pair ruptures first (the first term of Eq. 3), causing the abrupt conductance decrease observed here. This model explains naturally the experimental observations, and is also supported by experiments, simulations and theories of mechanical properties of dsDNA. For example, Hatch et al. [132] used force spectroscopy to show that the shear force is distributed mostly at the end of dsDNA sequences. In addition, simulations by Nath et al. [144] recently showed that ~50% of the stretching was localized at the last base pairs at the ends.
Based on the above analysis we use a spring-in-series model, in which the end springs, representing the end base pairs, have a smaller spring constant than the middle. From this model the stretching length can be expressed as

\[ \Delta z = \left[ \frac{2}{\alpha_{\text{end}}} + \frac{N-3}{\alpha} \right] F \quad (4) \]
where $\alpha_{\text{end}}$ is the end base pair spring constant, $\alpha$ is the spring constant associated with the middle base pairs, and $F$ is the force applied to the molecule. Figure 4.6b shows the measured stretching length of dsDNA vs. molecular length, and fitting of the experimental data to Eq. 4. The fitted ratio of the spring constants between the different sections, $\alpha/\alpha_{\text{end}}$, is found to be 70, agreeing with the assumption that the end base pairs are much softer. Assuming the spring constant for middle base pairs measured by Noy et al. [123] (~2.8N/m per base pair), we find that the force applied to the molecule when the conductance decreases of ~3 pN. This is in good agreement with the force required to break the hydrogen bonds in a base pair found by Hatch et al. [132] through force spectroscopy measurements of DNA molecules of similar length.

According to the above model, the breaking of the hydrogen bonds of the base pairs near the ends by the external shear force will abruptly decrease the charge transfer rate between the electrodes and the dsDNA bridge ($k_{L(R)}$ in Eq.1), resulting in a sudden decrease in conductance. Thus the stretching length is a measure of the distance required to break the end base pairs of the dsDNA molecule. The small tip displacement required to achieve the abrupt decrease in conductance and the weak dependence of stretching length on molecular length are a result of the uneven distribution of the displacement across the dsDNA molecule and the relatively weak hydrogen bonds in the end base pairs.

4.4 dsDNA rupture reversibility

To further ensure that the abrupt decrease in conductance of dsDNA is caused by the rupture of the end hydrogen bonds and not a structural transition in the dsDNA molecule like the B-S transition, we developed a method to stretch and compress single
dsDNA molecules repeatedly while monitoring conductance (Figure 4.7). First the STM break junction method is used to create a molecular junction, and then stretch the DNA molecule over a relative short distance, stopping at a position marked by red circle in Figure 4.7a. [19] After the tip is pushed back towards the substrate (grey line) to compress the molecule, it retracts again to stretch the molecule (black line), by a distance greater than 0.15 nm, until it breaks down as marked by a red arrow. The tip is then pushed (grey line, Figure 4.7b) and retracted (black line, Figure 4.7b) again. The experiment shows that the conductance is reversible if stretching the dsDNA over a short distance. However, the process is irreversible if the molecule is stretched over a large distance such that the abrupt conductance decrease takes place.
The observation above is supported by statistical analysis of ~50 measurements, plotted as a two-dimensional histogram in Figure 4.7c, showing three distinct sections. In the first section (“I”), the conductance changes exponentially with the tip-substrate separation, signaling that the transport is dominated by tunneling through the solvent when the tip is extremely close to the substrate. Similar characteristics for region I are found for other dsDNA molecules and octanedithiol, Figure 4.8. The second section (“II”) is the plateau region, corresponding to the formation and stretching of the...
molecular junction. This plateau-behavior is consistent with the slowly decreasing conductance associated with the initial elongation of the dsDNA molecules discussed above, before the abrupt decrease in conductance. Upon sufficient stretching however, it enters the third region (“III”), in which the conductance decreases abruptly, irreversibly. For a conformational B-S transition, we would expect the conductance changes to be reversible during the second compression/stretching cycle. [138,140–142] The lack of reversibility further indicates that the process responsible for the abrupt decrease in conductance is force induced melting of the hydrogen bonds in the end base pairs.
In summary we have investigated the effect of mechanical stretching on charge transport in dsDNA in aqueous environment. The resistance of dsDNA is found to be

**4.5 Summary**

In summary we have investigated the effect of mechanical stretching on charge transport in dsDNA in aqueous environment. The resistance of dsDNA is found to be
linearly proportional molecular length over a wide range, which supports the thermally activated hopping model, and the relatively small slope indicates long-range charge transport in DNA. The distance over which a dsDNA can be stretched before an abrupt decrease in the conductance is short and its dependence on molecular length is weak. Furthermore, by repeatedly stretching and compressing the molecule, we have found that this process is irreversible. These observations indicate that mechanical stretching in dsDNA is localized near the ends of the molecule, and breaking of the hydrogen bonds in the end base pairs is responsible for the force-induced abrupt conductance decrease. Our results are in good agreement with experiments, theories and simulations of mechanical properties of dsDNA. Based on this model, we found that the shear force to break the hydrogen bonds in the end base pairs is ~3 pN, the spring constant of the end base pairs are ~70 times softer than the those in the middle of the dsDNA.
CHAPTER 5
ELECTROMECANICAL RESPONSE OF CONDUCTANCE IN SINGLE DNA MOLECULES

5.1 Introduction

Charge transport in double strand DNA (dsDNA) plays a crucial role in many biological processes [199,200] and can also allow for future technological advances using dsDNA as functional devices [201,215,216]. Experiments have shown that charge is transported in dsDNA molecules through a thermally activated hopping process mediated by the π-π stacking interaction between neighboring nucleic acid bases [103,148,203,205,214,217-221]. The strength of this π-π stacking is dependent on the spacing between neighboring bases, resulting in strong sensitivity of charge transport in dsDNA to perturbation of the base pair spacing. For example, theory predicts that the π-π stacking between neighboring bases contributes to the electronic coupling between hopping sites, leading to more charge transport for stronger stacked sequences [208,222,223]. Experiments have also shown that stronger π-π stacking in DNA sequences leads to a reduction of the ionization potential of guanine stacked bases, which will decrease the activation energy associated with charge transport [213,224]. However, despite this supporting evidence, there have been no direct investigations into the role π-π stacking and the base to base distance play in charge transport in dsDNA.

Here we present a study of the effect of mechanically modulating the base pair stacking distance on the conductance of single dsDNA molecules using a modified scanning tunneling microscope (STM) break junction technique. Single dsDNA molecules are suspended between the gold STM tip and substrate electrodes by a tholated
linker group. The molecular conductance was then monitored while a mechanical modulation was applied to perturb the \( \pi-\pi \) stacking between neighboring bases. As a result, we obtain information about the molecular conductance and the sensitivity of the molecular conductance to mechanical perturbation, called the electromechanical response. We find that the conductance of sequences with purine bases (guanine and adenine, denoted \( G \) and \( A \)) stacked is more sensitive to mechanical modulation than sequences with purine and pyrimidine base (cytosine and thymine, denoted \( C \) and \( T \)) stacked, owing to stronger \( \pi-\pi \) stacking. In addition, we find that both the molecular conductance and electromechanical response are weakly dependent on molecular length. These results fit well with the thermally activated hopping model and allow us to determine the effect \( \pi-\pi \) stacking has on charge transport in dsDNA molecules.

5.2 Experimental methods

Tip-modulated STM Break Junction

The electromechanical response of single dsDNA molecules is measured using a modified STM break junction technique in which a mechanical modulation is applied to the target molecule while measuring the molecular conductance. The basic idea of the technique is described in Figure 5.1. In the STM break junction technique an STM tip is brought into contact with the target molecule, which is functionalized to a conducting surface. [6] The molecular conductance is then monitored while the tip is retracted until the molecular junction breaks down and the conductance drops to zero. In the present technique a sinusoidal modulation is applied to the tip position along the axis of the tip during the break junction experiment, at a frequency (1kHz) much smaller than any vibrational frequencies within the molecule [113]. When a molecule is detected, an
algorithm [19] detects the plateau in the conductance (Figure 5.1b) and the tip retraction is stopped. The conductance is then measured for 100ms while the tip position is modulated by 0.02nm. After 100ms the conductance is checked to the conductance before the measurement, to determine if a molecule still bridges the electrodes. If the molecular junction is still present the conductance is measured for another 100ms, otherwise the break junction cycle is restarted. Several hundred such molecular junctions were collected for each dsDNA sequence studied here.
Figure 5.1: Experimental setup and principle. (a) Schematic diagram of STM break junction with AC tip modulation applied. (b) Example conductance vs. distance decay curve for single G-C (5'-A(CG)₄T-3') molecule. Blue dot represents the point at which the bulk tip movement is stopped and the low and high frequency portions of the current are collected. (c) Low freq. portion of the current collected from the single dsDNA junction shown in (b), while applying tip modulation. (d) High freq. portion of conductance normalized with conductance collected from single molecule dsDNA junction shown in (b). Red line is the envelope of normalized conductance (α). (e) Sinusoidal modulation applied to the STM tip along the z-axis. (f) Enlarged view of α to show the response of the conductance to the tip modulation.
The conductance measured using this technique can be expressed with respect to the sinusoidal modulation \( A_0 \cos(\omega t) \) as [113]

\[
G \approx G_{DC} + \frac{dG_{DC}}{dz} A_0 \cos(\omega t). \tag{1}
\]

Here \( G_{DC} \) is the low frequency portion of the conductance unaffected by modulation, \( A_0 \) is the tip modulation amplitude, and \( \omega \) is the tip modulation frequency. The conductance thus has two components, a low frequency component which is the molecular conductance (first term in Eq. 1 and Figure 5.1c) and a higher frequency component which contains information about the electromechanical properties of the molecule being studied (second term in Eq. 1 and Figure 5.1d). A useful way of arranging the components of the conductance is to normalize the high frequency conductance amplitude by the low frequency conductance to get the parameter

\[
\alpha = \left| \frac{1}{G_{DC}} \frac{dG_{DC}}{dz} \right| \tag{red curves in Figures 5.1d and 5.1f}
\]

This parameter contains information about how sensitive the conductance is to mechanical modulation and is referred to as the electromechanical response of the junction.

The information collected from the conductance and \( \alpha \) for each molecule studied was compiled into 2-dimensional histograms of \( \alpha \) vs. conductance, each histogram containing the conductance information of several hundred individual molecular junctions. The 2-D \( \alpha \) vs. conductance histograms for each molecule studied are shown in Figure 5.2. These histograms show that there is a correlation between the conductance and \( \alpha \), with higher conductance molecular junctions giving higher \( \alpha \) values. A more convenient way of comparing the conductance and \( \alpha \) values between the different dsDNA sequences is to compile the values for all junctions by projecting the values of
the 2-D histogram onto the conductance and $\alpha$ axes respectively, then the most probable

![Figure 5.2: Constructing molecular conductance and $\alpha$ histograms. (a) Example DC current measured during tip modulation experiment. (b) Example electromechanical response (red line) measured during tip modulation experiment. (c) 2-dimensional histogram compiled from hundreds of DC current and $\alpha$ curves. The projection on the conductance axis (c1) and on the $\alpha$ axis (c2) are fit with Gaussian curves to extract the molecular conductance and electromechanical response.](image)

value of conductance and $\alpha$ can be compared between sequences.

**DNA sample preparation**

The oligonucleotide molecules studied here were HPLC purified and purchased from Integrated DNA Technologies. To facilitate functionalization with the Au STM electrodes, the samples were purchased with a propanethiol linker group attached to the 3’ sugar-phosphate backbone. To prevent polymerization in transit, the thiol linker is
protected with a mercaptopropanol disulfide group. Upon receipt, the oligo samples were suspended in 18MΩ DI water at a concentration of 100μM. The samples were then stored at -20°C. Prior to STM break junction measurements, phosphate buffer solution was prepared with 100mM Na⁺ and 10mM tris(2-carboxyethyl)phosphate (TCEP) concentration. TCEP, a well-known reducing agent, is used here to reduce the disulfide bond and deprotect the thiol linker group by making 20μM target molecule solution in TCEP+phosphate buffer and allowing reacting for 3 hours. The sample was then centrifuged in a sephadex G-25 spin column (Roche Applied Science) to remove the TCEP and mercaptopropanol. The resulting DNA solution was then annealed in a thermal cycler by heating to 95°C and cooling gradually to 4°C over 4 hours. The samples were kept at 4°C until just prior to electromechanical response measurements.

**DNA sequences**

In order to understand the nature of the π-stacking interaction between neighboring base pairs and understand the effect π-π stacking has on charge transport in DNA we studied the molecular conductance and electromechanical response of dsDNA molecules with different sequence and lengths. These molecules are all terminated by a thymine and adenine base on the 3’ and 5’ ends, respectively, in order to prevent mismatches once annealed. To investigate the effect of sequence on electromechanical response the remaining base pairs were chosen to have either purine-purine stacking or purine-pyrimidine stacking between neighboring bases. In the purine-purine stacked sequences a guanine is stacked on top of either another guanine or an adenine (G-G and G-A respectively), while in the purine-pyrimidine stacked sequences a guanine is stacked with a cytosine or thymine base (G-C and G-T respectively). The structures for these
molecules are illustrated in Figure 5.3. The length dependence of molecular conductance and electromechanical response was measured for molecules ranging in lengths from 8bp to 14bp. The two molecular families studied were also purine-purine stacked and purine-pyrimidine stacked, but the sequences were chosen to be self-complimentary. In this way the purine-pyrimidine sequence was the \( G \cdot C \) sequence mentioned above and the purine-purine stacked sequence was a self-complementary version of the \( G \cdot G \) sequence, called \( (G \cdot C)_N \) and \( (G_N \cdot C_N) \) respectively, shown in Figures 5.3e and 5.3f.
5.3 Results and discussion

The conductance and $\alpha$ histograms for these different sequences of molecules are shown in Figure 5.4. We find the most probable conductance values for the purine-purine stacked molecules are higher than those for the purine-pyrimidine stacked molecules, shown in Figures 5.4a and 5.4b respectively. Specifically, the $\text{G-G}$ molecule has a conductance that is $\sim1.27x$ larger than that of the $\text{G-C}$ molecule and the $\text{G-A}$ molecular
conductance is ~1.4x larger than the conductance of the G-T molecule. This is an intriguing result considering the fact that the constituent bases do not change between the G-G and G-C molecules, likewise with the G-A and G-T molecules.

Figure 5.4: Conductance and $\alpha$ behavior with sequence. (a) Conductance histograms comparing G-C (black) with G-G (red). (b) Conductance histograms comparing G-T (black) with G-A (red). Arrows are intended to indicate the Gaussian fitted peak position. (c) $\alpha$ histograms comparing G-C (black) with G-G (red). (d) $\alpha$ histograms comparing G-T (black) with G-A (red). The peak position for purine-purine sequences (G-G and G-A) are larger than for purine-pyrimidine sequences (G-C and G-T). Red conductance histograms are offset along y-axis for clarity.

Similar trends are seen in the electromechanical response, $\alpha$, for the different sequences studied. As can be seen in Figures 5.4c and 5.4d, the electromechanical response of purine-purine stacked sequences is ~1.5x larger than the response of purine-
pyrimidine. This shows that the conductance of the purine-purine stacked sequence is more sensitive to mechanical modulation than the conductance of the purine-pyrimidine sequences. The observation of higher conductance and electromechanical response for purine-purine sequences suggests that the π-π stacking interaction between stacked purine bases is stronger and more sensitive to mechanical perturbation. Intuitively, one would expect stronger overlap between purine stacked sequences, based simply on geometric terms. Another way to understand the contribution of electronic coupling and energy level alignment is to study the effect of molecular length on conductance and electromechanical response.

Figure 5.5 shows the dependence of molecular conductance and $\alpha$ on molecular length. Figures 5.5a and 5.5b show that the resistance (inverse of conductance) is proportional to length, in agreement with the thermally activated hopping transport mechanism [205]. The conductance difference is less pronounced between the different sequences, probably due to the break in stacking for $(G_N-C_N)$ and the differing coupling to the contact for the purine-purine stacked sequences. However, as seen for the other sequences, the values of $\alpha$ are consistently higher for purine-purine stacked sequences over the purine-pyrimidine stacked sequence, Figure 5.5c and 5.5d. In addition, we see that the electromechanical response of these sequences is only weakly dependent on length, decreasing for the purine-purine stacked sequence and remaining relatively constant for the purine-pyrimidine sequence.
In order to understand these experimental results we must consider the dependence of dsDNA charge transport on the distance between neighboring bases. For dsDNA systems, the transport mechanism between the STM tip and substrate has been found to be thermally activated hopping process, where the charge hops between neighboring bases, typically purine derivative bases. [102,103] Considering the model of

Figure 5.5: Length dependence of resistance and $\alpha$. (a-b) Resistance vs. molecular length for $(G-C)_N$ and $(G_N-C_N)$ sequences respectively. Red lines are fittings of resistance vs. molecular length dependence as expected with the thermally activated hopping model, intended to be a guide for the eye. (c-d) $\alpha$ vs. molecular length for $(G-C)_N$ and $(G_N-C_N)$ sequences respectively. Red lines are fitted using the thermally activated hopping model, intended to be a guide to the eye.
a sequential hopping network proposed by Nitzan [102], we find that the conductance for a bridge of $N$ hopping sites can be expressed as

$$G = \frac{e^2}{k_B T} \frac{k e^{-\left(\frac{E_{BF}}{k_B T}\right)}}{\left(\frac{k}{k_L} + \frac{k}{k_R}\right)^{N-1}}$$

(2)

where $k_B$ is Boltzmann’s constant, $e$ is the electron charge, $T$ is the temperature. The terms which are dependent on the details of the molecular system are $E_{BF}$ the bridge site-Fermi level energy difference, $k_{L,R}$ the transfer rate between the left and right electrodes and the molecule respectively, and $k$ the transfer rate between hopping sites along the dsDNA sequence.

The spring constant for the bonds that link the dsDNA to the electrodes are 8N/m for Au-Au, [106,225] 120N/m for Au-S, [226] 249N/m for C-S bonds, [226] 520N/m for C-C bonds. [227] In comparison, the spring constant for dsDNA molecules has been measured by different groups to be in a range of 0.1N/m to 1N/m per base pair [123,228]. This suggests that the dsDNA is the softest portion of the molecular junction and the majority of the tip modulation will be distributed across the dsDNA molecule. Indeed, experimental studies into the mechanical properties of DNA molecules show that the molecule can be mechanically stretched easily [121,210]. The mechanical properties of short dsDNA molecules have been described by the analytical model proposed by de Gennes [143]. In this model, the DNA assumes a ‘ladder’ structure in which the backbone is much stiffer than the hydrogen bonds between base pairs, see Figure 5.6a. Stretching DNA molecules is then unevenly distributed along the sequence, with bases at the end being strongly distorted while bases in the middle are unaffected. This model is supported by experimental and simulation evidence. For example, force spectroscopy
measurements by Hatch et al. [132] showed that shear force is distributed to only a few base pairs at the end of the dsDNA molecule. In addition, simulating dsDNA Nath et al. [144] showed that roughly half of the displacement was localized to the end base pair when stretching dsDNA. Based on these observations, in order to interpret how the conductance in Eq. 2 is affected by modulation, we assume that the mechanical modulation applied is localized to the end base pairs.

![Figure 5.6: dsDNA modulation model. (a) Schematic showing how displacement is distributed in the ladder model. (b) Energy diagram showing modulation effect on dsDNA energy and transfer rate.](image)

As stated above, the electromechanical response is the normalized change in conductance with respect to tip modulation, $\alpha = |(1/G_{DC})(dG_{DC}/dz)|$. The conductance for the thermally activated hopping model, Eq. 2, has two terms which are dependent on hopping site distance modulation. The first is the transfer rate between neighboring hopping sites, $k$, which depends on the electronic coupling between hopping sites. The other distance dependent term is the bridge site-Fermi level energy difference,
$E_{BF}$, which is related to the molecular orbital energy, see Figure 5.6b. Assuming the modulation is distributed over only then end base pairs, the electromechanical response can be expressed as

$$\alpha = \left| \frac{(N-1)d k}{k \, dz} - \frac{1}{k_B T} \frac{dE_{BF}}{dz} \right|. \quad (3)$$

The first term in Eq. 3 depends on the change if transfer rate, $k$, with modulation between the end base pairs and the second term is the change in bridge site energy, $E_{BF}$, with modulation. Eq. 3 can be further simplified by assuming the transfer rate is exponentially dependent on the distance between neighboring hopping sites, $k \approx k_0 \exp(-\beta z)$, resulting in an electromechanical response given by

$$\alpha = \left| \frac{-(N-1)\beta}{\left(\frac{2k_0}{k_L} + (N-1)\right)} - \frac{1}{k_B T} \frac{dE_{BF}}{dz} \right|. \quad (4)$$

The first term in Eq. 4 shows that the electromechanical response is proportional to the decay constant of the transfer rate with respect to distance, inversely proportional to the ratio of the B-form transfer rate and contact transfer rate, and has a rather complicated dependence on the length of the molecule. Eqn. 4 also shows that the electromechanical response is directly proportional to the change in bridge site energy with respect to modulation. Figures 5.5c and 5.5d show the measured electromechanical response fitted using this model, utilizing the base to base transfer rate measured by Lewis et al. ($k \approx 1 \times 10^9 \text{s}^{-1}$) and assuming that the contact transfer rate is much smaller ($k_L \approx 1 \times 10^8 \text{s}^{-1}$) [203,214]. For purine-purine stacked sequences, we find $\beta = 3.8 \pm 1.2 \text{nm}^{-1}$ and $dE_{BF}/dz = 0.06 \pm 0.01 \text{eV/nm}$, while for purine-pyrimidine stacked
sequences we find $\beta = 1.3 \pm 1.2$ nm$^{-1}$ and $dE_{BF}/dz = 0.03 \pm 0.003$ eV/nm. These decay constants are similar in magnitude to the decay between $\pi$-orbitals and gold electrodes measured by Diez-Perez et al. [171] and Meisner et al. [117], 0.8 nm$^{-1}$ and 2 nm$^{-1}$ respectively. This is reasonable considering the interaction between hopping sites is facilitated by $\pi-\pi$ stacking between bases. The change in bridge site energy measured here is smaller than that calculated by Sugiyama et al. [224] for distance modulation of stacked guanines. However, in the real dsDNA molecule mechanical stretching does not result in a simple translation, but more likely rotation and twisting is involved [223].

We find that both the transfer rate decay constant and the change in bridge site energy are larger for purine-purine stacked sequences than purine-pyrimidine sequences, in agreement with the observation of larger electromechanical response for G-G (G-A) than G-C (G-T). The difference in $\beta$ suggests charge transfer between hopping sites is more sensitive to mechanical modulation in sequences with purines stacked on one strand (G$_N$-C$_N$) than sequences with purines alternating between stands (GC)$_N$. In other words, this means the $\pi-\pi$ stacking of intra-strand guanines will be more sensitive to mechanical modulation because the guanines are spatially more overlapped when on the same strand than when on opposing strands. The sensitivity of the bridges site energy to modulation is related to the change in orbital energy of the end base pairs due to mechanical perturbation. Larger $dE_{BF}/dz$ for purine-purine sequences than for purine-pyrimidine sequences suggests that sequences with intra-strand guanines experience a larger change in orbital energy when stretched or compressed relative to neighboring bases, with an increase in energy for compression and a decrease in energy for stretching expected. Similar sensitivity of charge transport to fluctuations in the molecular energy levels has
also been reported in single molecule transport measurements using smaller molecules, changing the molecular energy levels either electrically [13,40] or mechanically. [67,119]

5.4 Summary

In summary, we measured the conductance and electromechanical response of dsDNA molecular junctions while applying a mechanical modulation along the tip axis. The electromechanical response was found to be larger for sequences with purine-purine bases stacked than for sequences with purine-pyrimidine stacked. By investigating the length dependence of the electromechanical response, we found that the electromechanical response fits the thermally activated hopping model for charge transport in dsDNA molecules and suggests that both the bridge site energy and the electronic coupling between neighboring bases are sensitive to mechanical modulation. This sheds light on the impact modification of the \(\pi\)-stacking interaction between neighboring bases can have on charge transport in dsDNA molecules.
CHAPTER 6
CONCLUSIONS AND PERSPECTIVES

Single molecule devices with new and interesting functionalities have been demonstrated for more than a decade but are still far from being applicable for real-world problems. More important, the understanding of charge transport and the unique phenomena that emerge on molecular scales is the ultimate goal of molecular electronics. To this extent, probing the interplay between the electrical and mechanical properties of molecular scale devices is a profound tool for understanding charge transport and demonstrating novel device functionalities. This thesis has presented several examples of understanding gained from and devices demonstrated by probing the electromechanical properties of single molecule devices.

First, the counterintuitive response of 1,4-benzenedithiol to mechanical stretching was reported. It was found that, upon stretching, the conductance of BDT molecular junctions increased, as opposed to the expected decrease seen for most molecular systems. G-V and IETS was used to identify the coupling between molecule and electrode as the portion which was reversibly changed during stretching and compressing cycles. Using transition voltage spectroscopy, it was shown that weakening of the molecule-electrode coupling induced a shift in the frontier orbital of BDT towards the Fermi energy, resulting in the increased conductance upon stretching. This unique conductance behavior has been predicted by many different types of theoretical calculations for BDT, and the experimental demonstration shown here helps to explain inconsistencies between theory and experimental measurements in the past.
Next, the effect of mechanical stretching and base pair rupture on charge transport in DNA molecules was demonstrated. Surprisingly, the distance a single DNA molecule can be stretched before the conductance abruptly decreases is smaller than alkanedithiol molecules many times shorter than DNA. These short stretching lengths were found to be independent of the contact linker group and only weakly dependent on the length of the DNA molecule. The nature of short stretching length for DNA was attributed to breaking of hydrogen bonds at the end base pairs, in matching with the uneven distribution of stretching proposed by the ladder model for DNA. Measuring the reversibility, or lack thereof, of the abrupt decrease in conductance to repeated stretch and compressing cycles further supported a force induced melting mechanism for the conductance decrease. In the future, further evidence to support this model could be provided by conducting atomic force microscopy measurements during stretching of DNA molecular junctions. Obtaining simultaneous information on the conductance and force would allow for a complete characterization of the evolution of DNA molecular junctions during stretching.

Finally, the response of the π-π stacking interaction between nucleic acid bases in DNA molecules was probed. Applying a small scale modulation to DNA molecules suspended between two metal electrodes, the effect of modulating the distance between the bases on charge transport was measured. Double stranded DNA sequences with purine bases stacked on a single strand were found to be more sensitive to mechanical modulation than sequences which alternated between purine and pyrimidine bases on a single strand. This effect is caused by the altering of the activation energy of charge onto the molecule, by mechanically modulating the orbital energy of the end base pairs. In addition, these measurements have allowed for better insight into the role distance
between base pairs plays on the $\pi-\pi$ interactions which facilitate charge transport in DNA. Understanding charge transport in DNA systems, and its dependence on sequence and structure, will allow for better understanding of numerous biological processes which depend on charge transport and allow for the exploitation of these properties for developing unique molecular scale devices.
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BIOGRAPHICAL SKETCH

Born on May 5, 1986 to Brent and Barbara Bruot, Chris was raised with his older brother Nathan in Kent, Ohio. At an early age, he developed an interest in building, destroying, and understanding how things work, encouraged by, among others, his grandfather, a mechanic and master craftsman. An early interest in astronomy led to an awareness of physics as a possible academic path, however his interests in primary and secondary school were decidedly non-academic, leading to what some would characterize as “underachieving results.” Studying physics at Kent State University, Chris’s focus turned to a more academic passion when introduced to the concepts and weirdness of quantum mechanics. Working in the lab of Dr. Qui- ho Wei, Chris found a passion for and enjoyment of experimentation and discovery that only scientific endeavor can provide. Graduating with honors and a degree in physics, Chris attended graduate school at Arizona State University to study physics some more. After completing a rotation in the lab of Dr. Nongjian Tao, Chris was lucky enough to receive a research position to study charge transport in single molecule devices and joined the low temperature STM team with Dr. Joshua Hihath. Though laboratory work has consumed most of his time over the last few years, Chris has found time to expand his interests in blues and folk guitar, the music of Bob Dylan, exploring nature, and enjoying the fine Arizona scenery.