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Electron Transport in Single Molecules Measured by a Distance-Modulation Assisted Break Junction Method

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ABSTRACT

We describe a method to determine whether a measured current in a break junction is due to electron tunneling via space or conduction through a molecule bridged between two electrodes. By modulating the electrode separation, we monitor both the DC and the AC components of the current. The AC component indicates if a molecule is connected to the electrodes while the DC component is the transport current through the molecule. This method allows us to remove the tunneling background from conductance histograms and unambiguously measure the $I-V$ characteristic of single molecules. Furthermore, it provides valuable information about the electromechanical properties of single molecules.

Understanding electron transport in a single molecule is a basic task in molecular electronics.[1] Because of sensitive dependence of the transport current on how the molecule is brought into contact with external electrodes, conductance of a molecule measured by different methods can vary by orders of magnitude. It is, thus, important to form a well-defined molecule−electrode contact. One strategy is to provide the molecule with two linker groups that can bind to the electrodes covalently. This strategy dramatically reduces the variability in the measured molecular conductance; but, identical contact geometries are still difficult to create, and conductance variability cannot be eliminated.[2] To overcome this difficulty, a STM break junction approach was introduced to quickly form thousands of molecular junctions with different contact geometries.[3] By performing statistical analysis on the individual curves, it determines the conductance of a single molecule with the most probable contact geometry. This approach has been used and further developed by many groups to provide reproducible measurement of single molecule conductance. For example, recent reports on the conductance of alkanedithiols by eight different groups are in excellent agreement.[4–12]

However, the method has limitations. It works by repeatedly bringing the STM tip close to and pulling the tip away from a substrate. If no molecule is bridged between the tip and the substrate electrodes, the current transient is a smooth exponential decay due to electron tunneling via space or solvent. On the other hand, if a molecule bridges between the tip and the substrate electrodes, a step appears in the current transient. Including all of the data in the conductance histogram analysis is preferred,[13] but it may wash out peaks due to molecules, especially when the probability of forming a molecular junction is low or data are noisy. Removing the tunneling contribution from the analysis not only is time-consuming but also introduces a subjective component. This especially is the case when a curve contains both tunneling and molecular conduction contributions. Several data analysis procedures have been introduced to automatically select curves or suppress the tunneling background in the conductance histogram.[5–11] Instead of improving data analysis, we describe here an experimental method to remove the background tunneling current from the statistical analysis. More generally, it provides a way to determine whether a measured current is due to conduction via a molecule or tunneling via the medium. In addition, it allows us to extract electromechanical information of single molecule junctions.

The basic principle of the method is sketched in Figure 1. An STM tip is moved toward a substrate electrode until the tunneling current reaches a preset value. Then the tip is pulled back until the current drops to zero. The process is controlled and automatically repeated to generate a large number of transient current traces during the individual pulling stages. In order to determine if there is a molecule bridged between the tip and the substrate, we modulate the tip−substrate distance rapidly and measure the DC and AC components of the current. The DC component gives the usual current transient traces, but the AC component measures the current response induced by the tip−substrate distance modulation. For the reasons discussed below, the AC response in the case of tunneling via space is distinctively different from the case of conduction via a molecule.

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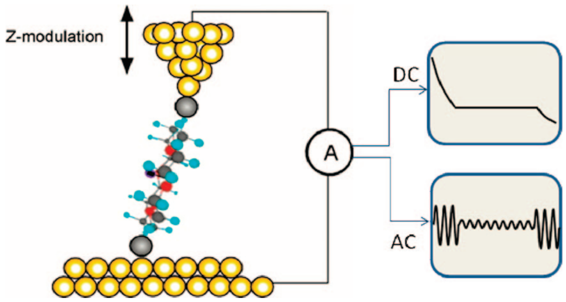

Figure 1. Schematics of the AC modulated STM break junction measurement. An AC voltage is applied to the *z*-piezoelectric transducer of the STM to modulate the tip−substrate distance, and the current is separated into an AC and a DC component. The AC component of the current provides an indicator for one to determine if a molecule is bridged between the tip and the substrate, and the DC component measures the transport current through the molecule.

The tip-substrate distance modulation is described by $A_0 \cos(\omega t)$, where A_0 and ω are the modulation amplitude and angular frequency, respectively. Current, I, in the limit of small A_0 is given by

$$I \cong I_{DC} + \frac{dI_{DC}}{dz} A_0 \cos \omega t \tag{1}$$

If no molecules are between the tip and the substrate, I decays exponentially with the tip−substrate distance, z, and the DC component, I_{DC}, is $\sim\exp(-\beta z)$, where β is the tunneling decay constant. The AC component (second term in eq 1) is the current response to the modulation in the distance. An important parameter that describes the amplitude of the AC current is $\alpha = -(1/I_{DC})(dI_{DC}/dz)$, which is equal to β in the absence of molecules. In contrast, if a molecule is bridged between the two electrodes, the DC component is the conduction current through the molecule, and α measures the electromechanical property of the molecular junction rather than tunneling decay constant. We note that, for a molecule whose conduction mechanism is tunneling or superexchange via the bonds, the conductance decays exponentially with the molecular length. This decay constant has been determined by measuring the conductance versus molecular length. For molecules with saturated C−C bonds, for example, alkanes, the decay constant is between 6 and 8 nm^{-1}, smaller than tunneling decay via an organic solvent, such as mesitylene, or vacuum. It is also important to distinguish α from the decay constant of molecular conduction.

Since electron tunneling decays rapidly over distance in vacuum and in solution, β is large (e.g., $\sim 20\ \text{nm}^{-1}$ in vacuum and $\sim 10\ \text{nm}^{-1}$ in solutions) which results in a large modulation in the measured current. For example, a modulation with amplitude of ~0.05 nm will lead to 50% variation in the tunneling current. In sharp contrast, if a molecule is covalently bound to two electrodes, the tip−substrate separation modulation causes a much smaller current modulation. This is because the Au−Au bond is the weakest link of the molecular junction so most of the distance modulation falls at Au−Au near the molecule−electrode contacts, rather than in the molecule.[14] Based on the previous measurements of the dependence of molecular conductance on pulling forces, a modulation of ~0.05 nm will result in only a 5−10% variation in the transport current.[15] The residual current modulation is due to force-induced change in the molecular conductance, which reflects electromechanical properties of the molecular junction. We describe here several ways to use the AC modulation for studying electron transport properties in single molecules.

Before discussing experimental results, we describe some of the key experimental details. It has been reported that large variation in the tip−substrate separation can lead to different molecule−electrode contact geometries.[16] To minimize possible effects of the distance modulation on the measurement, we keep the modulation amplitude small (<0.05 nm), which is less than the typical stretching distance of the Au−Au bond. We also keep the modulation frequency high (a few kilohertz) so that many modulation cycles occur during one measurement. This is necessary for accurate determination of the amplitude of the current modulation. Cleanness of the tip, substrate, and the sample cell is critically important for the success of the measurement. It has been reported that the tunneling decay constant is extremely sensitive to surface contamination and solution impurities.[17] We use Au-coated mica substrates prepared using a UHV thermal evaporator and Au wire STM tip freshly cut using a pair of scissors. Before each experiment, the substrate is annealed in a hydrogen flame and then immediately mounted in a solution cell filled with mesitylene (p.a. standard GC purity grade). The solution cell, made of Teflon, is cleaned before each measurement. The cleaning procedure involves boiling the cell in piranha and rinsing it in deionized water three times. The measurement is performed in a glass chamber to minimize contamination from impurities in air.

Figure 2 shows several examples of the DC and AC components of the current transient curves measured in pure mesitylene and in mesitylene containing 0.2 mM octanedithiol. Note that the AC component plotted in the figure is normalized by the DC component and by the *z* modulation amplitude (A_0), so its amplitude measures α. In pure mesitylene, the DC component is a smooth exponential decay curve. The amplitude of the AC component is large, and the corresponding $\alpha \sim 10\ \text{nm}^{-1}$, which is in agreement with the tunneling decay constant reported in literature.[17,18] A contaminated surface would have a considerably smaller β value. In the presence of sample molecules, for example, 1,8′-octanedithiol, the DC component often shows stepwise decreases due to the breakdown of molecular junctions. The current modulation is small, and α in the region corresponding to the last conductance step is typically $<2\ \text{nm}^{-1}$. Following the breakdown of the last molecule, the current modulation becomes large again as the conduction through the molecule is replaced by tunneling via the solvent.

The simultaneously recorded DC and AC currents provide interesting details about the formation and breakdown of individual molecular junctions. Figure 2c shows a case involving two molecules bridged between the tip and the substrate electrodes in parallel. Pulling the tip away causes breakdown of the two molecular junctions one by one. Immediately after the breakdown of the first molecule, there is a sudden increase in the amplitude of the current

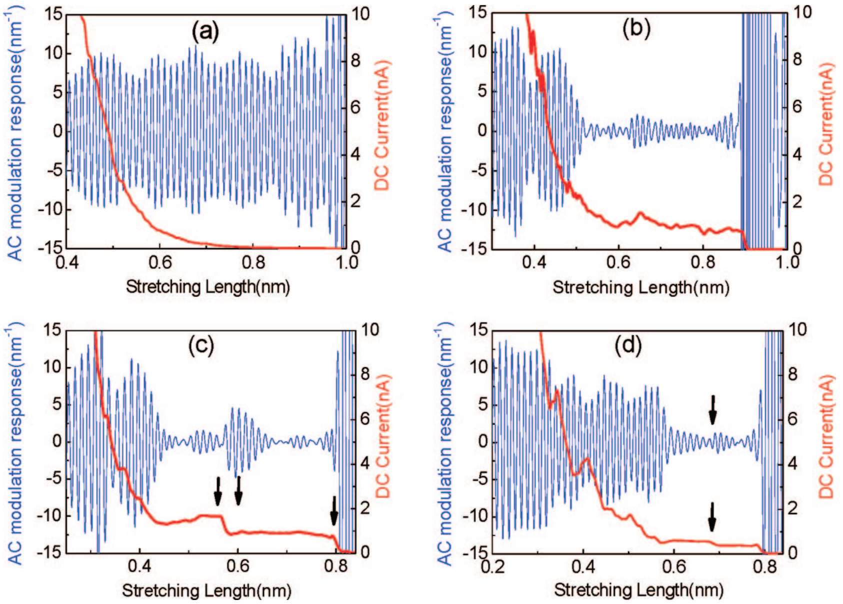

Figure 2. DC and AC components of current traces recorded during the pulling away stage in (a) pure mesitylene and in (b−d) mesitylene containing 0.2 mM 1,8′-octanedithiol. The AC component is normalized by the DC component and by the distance modulation amplitude, so its amplitude measures α. The applied bias is 100 mV; the pulling speed is 27 nm/s, and the modulation frequency and amplitude are 2 kHz and 0.05 nm, respectively.

modulation as the conduction through one molecular junction is replaced by electron tunneling through the solvent. Since the second molecular junction is still intact, it creates a situation where molecular conduction and tunneling coexist. Since the current is expected to decrease with stretching, $\alpha = -1/I_{DC}dI_{DC}/dz$ should be positive, which is reflected in the phase of the AC component of the current. Shifts in the phase are rarely observed, which is consistent with the expectation. However, the current occasionally appears to rise with stretching and the rise does not accompany with 180° phase shift. We believe that the rise in the current is either due to noise or spontaneous rearrangement in the molecule−electrode contact or molecular conformation.

Although the current modulation in the molecular junction is small, its amplitude (α) is not zero. The small α value measures the dependence of the molecular conductance on the applied force, which reflects the electromechanical properties of single molecule junctions. The α varies from junction to junction and can even change for the same junction during the pulling process (see arrows of Figure 2d). Each variation is accompanied by a kink or a small stepwise change in the DC current. We have found in a previous force and conductance study that such relatively small variations in the current are due to the small rearrangement of Au atoms near the molecule−electrode contact.[14] We attribute the sudden changes in the current modulation of a molecular junction during pulling to changes in the molecule−electrode contact.

The large difference in the current modulation (α value) between electron tunneling through the solvent and conduction through the molecules allows us to remove the tunneling background from the conductance histograms. From each current transient curve, we obtain both the DC component, $I = I(t)$, and the AC component that determines $\alpha = \alpha(t)$. So each data point in the current transient curve is associated with an α value. When constructing a conductance histogram, we can thus use the α value as a weighting factor to describe the relative importance of each data point. This makes it possible to remove not only the entire exponential decay curves from the histogram but also portions of curves originated from tunneling. A simple approach is to set up a cutoff value for α and count only the data points that have α smaller than the cutoff value. An alternative approach is to define a weighting factor inversely proportional to α, but we found little difference in the final conductance histograms constructed with the two approaches.

Figure 3a shows conductance histograms of 1,6′-hexandithiol constructed with different cutoff values. The histogram including all of the curves but that without using the AC modulation is also shown for comparison. Although a peak located at $3.9 \times 10^{-4}G_0$, where $G_0 = 2e^2/h \sim 77$ uS, is visible without the AC modulation, it is dwarfed by a large background caused by the electron tunneling through the solvent. The tunneling gives rise to exponential decay that leads to large counts at low conductance values. Gonzales et al. have developed a logarithmic analysis to remove the tunneling background at low conductance.[7] Figure 3 shows the tunneling background can be significantly reduced by cutting off data points with $\alpha > 5$ nm^{-1}, and the peak at $3.9 \times 10^{-4}G_0$ becomes more pronounced. Decreasing the cutoff threshold below 5 nm^{-1} does not result in additional improvement in the conductance peak. This is because most of the tunneling decay contributions are already effectively removed. The AC-modulation measurement and statistical analysis have also been performed on 1,8′-octanedithiol and 1,10′-decanedithiol, both of which also demonstrate substantial improvement in the conductance histograms (Figure 3b,c). The measured conductance values for all of the

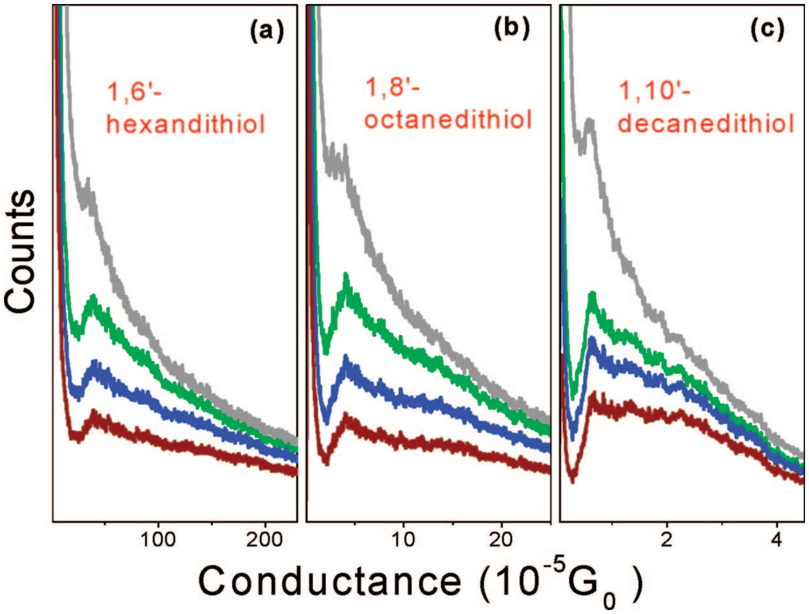

Figure 3. Conductance histograms of (a) 1,6′-hexandithiol; (b) 1,8′-octanedithiol; (c) 1,10′-decanedithiol in mesitylene obtained with different cutoff α values (gray, no cutoff; green, 5/nm; blue, 3/nm; wine, 2/nm). The applied bias is 100 mV; the pulling speed is 27 nm/s, and the modulation frequency and amplitude are 2 kHz and 0.05 nm, respectively.

molecules using the AC-assisted conductance histogram analysis are in good agreement with those obtained using different statistical analysis methods.[4–12] We note that the AC-modulation method can be used to remove tunneling background from the histograms, but it does eliminate conductance variations due to other factors, such as contact effects.

The AC modulation also allows us to ambiguously measure $I-V$ characteristics of single molecules. We start the $I-V$ measurement by bringing the STM tip close to a substrate until the tunneling current reaches a preset value (set-point current). The substrate is covered with molecules terminated with dithiols (or other linkers) and the set-point current is chosen such that the tip−substrate distance is smaller than the molecular length to allow the molecules to bridge between the tip and the substrate. We then turn off the proportional and differential gains but maintain a small integral gain. The small integral gain corrects slow drift due to thermal or mechanical sources, but it does not affect the high frequency current modulation and abrupt DC current change associated with the formation and breakdown of molecular junctions. In order to determine if a molecule is bridged between the tip−substrate electrodes, the tip−substrate distance is modulated and the induced current modulation is monitored during the entire experiment. Again, the distance modulation is kept small (e.g., 0.05 nm) to avoid its impact on the measurement.

If the tip is placed over a clean Au area in pure mesitylene, a large modulation is always observed in the current (Figure 4a). From the amplitude of the current modulation, we determine the decay constant to be ~8 nm^{-1}, which is expected for electron tunneling through the solvent. In contrast, if the substrate is covered with molecules, the decay constant is somewhat smaller because of the reduction in the tunneling barrier by the adsorbed molecules (Figure 4b). The dependence of work function of metal surface by molecular adsorbates has been well-studied.[19] If we hold the tip in position, the amplitude of the current modulation frequently drops abruptly to a very small value (<~2 nm^{-1}), and then returns abruptly to the original value. We have followed the current modulation over time and found that the amplitude "blinking" is stochastic at a fixed tip position, but it depends on the tip−substrate distance. When the distance is greater than the length of the molecule, no blinking is observed. Haiss et al.[20] have reported random switching in the STM current of dithiol molecules and attributed the switching events to the bridging of the molecules between the tip and the substrate. We believe that the blinking in the amplitude of the current modulation is also due to the formation/breakdown of single molecule junctions. When a sudden decrease in the amplitude occurs, it signals that a molecule is bridged between the two electrodes, and we then perform the $I-V$ measurement. Figure 4c shows a typical $I-V$ curve for 1,8′-octanedithiol. The $I-V$ curve is linear for $V < 0.5$ V and becomes increasingly nonlinear for $V > 0.5$ V. The conductance under small bias is about $\sim 5 \times 10^{-5} G_0$, which corresponds to the conductance of single 1,8′-octanedithiol junction. We have also measured the current modulation amplitude (α) as a function of bias voltage. While α does not depend on bias in a systematic manner, we frequently observed abrupt switching in α (Figure 4b). The abrupt switching is random, and it is attributed to the rearrangement in the molecule−electrode contact during the $I-V$ curve measurement.

In summary, we have introduced an AC-modulated STM-break junction approach to study electron transport in single molecules. By applying a small AC modulation to the

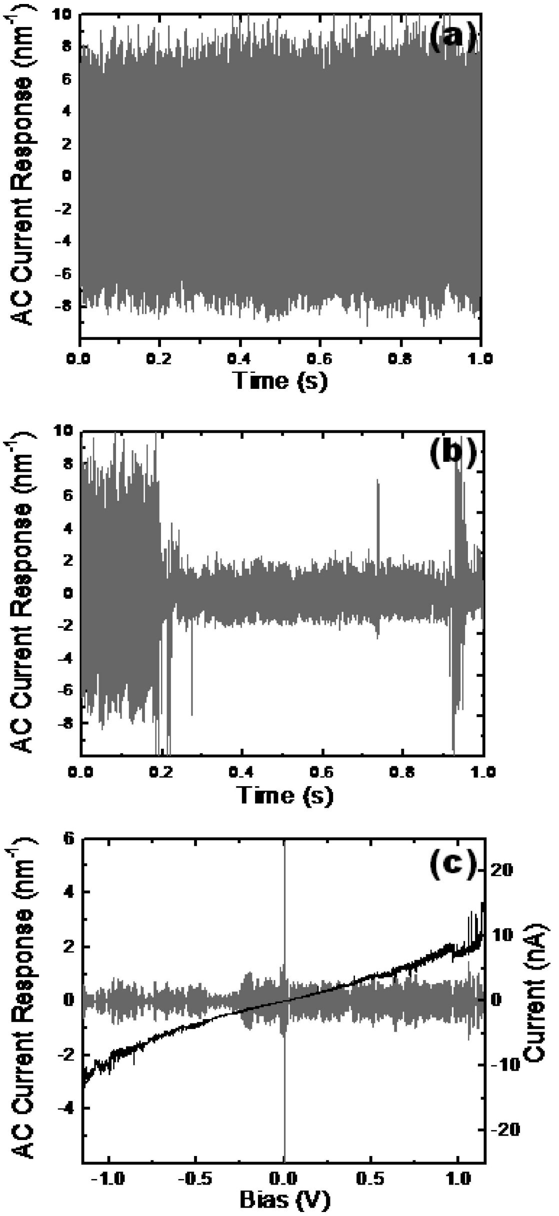

Figure 4. (a) Current modulation for a bare Au surface in mesitylene. (b) Current modulation for a 1,8′-octanedithiol-covered Au substrate in mesitylene. The abrupt decrease in the current amplitude corresponds to the formation of the molecular junction. The bias was fixed at -50 mV and the initial current set point was set at 0.8 nA. (c) $I-V$ curve (black line) of a molecular junction recorded when the current modulation drops to ~ 1 nm^{-1}. The AC modulation during the $I-V$ measurement is also shown (gray). The modulation frequency and amplitude are 2 kHz and 0.05 nm, respectively.

tip−substrate distance, we monitor the induced modulation in the measured current. In the absence of molecules, the modulation current is large, because of the sensitive dependence of tunneling current on the tip−substrate. When a molecule bridges across the tip and substrate gap, the current modulation drops dramatically. We demonstrated that the amplitude of the current modulation serves as a good indicator for us to distinguish current due to tunneling via solvent from conduction through a molecule. Using the modulation amplitude as a weighting factor, we can remove background counts due to tunneling from the conductance histograms of alkanedithiols. We also show that the AC modulation approach allows us to measure unambiguously the $I-V$ curves of single molecules bound between two electrodes. Furthermore, the amplitude of the current modulation provides valuable information about the electromechanical properties of single molecules.

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Supporting Information Available: Additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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