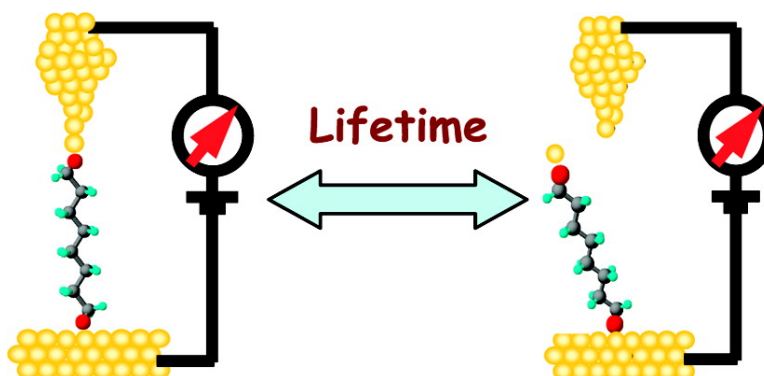


## Single Molecule Junctions Formed via Au–Thiol Contact: Stability and Breakdown Mechanism

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## Single Molecule Junctions Formed via Au–Thiol Contact: Stability and Breakdown Mechanism

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**Abstract:** The stability and breakdown mechanism of a single molecule covalently bound to two Au electrodes via Au–S bonds were studied at room temperature. The distance over which a molecular junction can be stretched before breakdown was measured using a scanning tunneling microscopy break junction approach as a function of stretching rate. At low stretching rates, the stretching distance is small and independent of stretching rate. Above a certain stretching rate, it increases linearly with the logarithm of stretching rate. At very high stretching rates, the stretching distance reaches another plateau and becomes insensitive to the stretching rate again. The three regimes are well described by a thermodynamic bond-breaking model. A comparative study of Au–Au atomic point contacts indicates that the breakdown of the molecular junctions takes place at Au–Au bonds near the molecule–electrode contact. By fitting the experimental data with the model, the lifetime and binding energy were extracted. Both quantities are found to have broad distributions, owing to large variations in the molecule–electrode contact geometry. Although the molecular junctions are short-lived on average, certain contact geometries are considerably more stable. Several types of stochastic fluctuations were observed in the conductance of the molecule junctions, which are attributed to the atomic level rearrangement of the contact geometry, and bond breakdown and reformation processes. The possibility of bond reformation increases the apparent lifetime of the molecular junctions.

### Introduction

Building an electronic device using molecules has motivated many researchers to search for a reliable way to connect a molecule to two electrodes and form a molecular junction. A widely used approach is to attach the molecule with two linkers that can bind to the electrodes. Thiol is the most studied linker because of its well-known capability to bind strongly to metal electrodes, such as Au, although several other linkers, such as isocyanide,<sup>1,2</sup> amine,<sup>3</sup> pyridine,<sup>4</sup> carbon–carbon,<sup>5</sup> and carboxylic acid,<sup>6</sup> have also been used to establish a molecule–electrode contact. It has been concluded that the linkers can play an important or even dominant role in the conductance and other electron transport properties of molecular junctions.<sup>7,8</sup> Since the

molecule–electrode contact is often the weakest link in a molecular junction, an important question that has not yet been well studied is: *How stable is a molecular junction due to the finite lifetime of the linker–electrode bond?*<sup>9</sup> In the present work, we investigate the stability and breakdown mechanism of a single molecule covalently attached to two gold electrodes via Au–S bonds at room temperature.

The technique we used in this work is based on an STM break junction approach which creates and breaks single molecule junctions repeatedly. The method and related mechanically controlled break junction (MCBJ) have been used to determine the conductance of single molecules.<sup>10–19</sup> We show here that

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in addition to the electron transport properties the method can provide important information about the stability and bonding nature of molecule–electrode contacts. We find that the breakdown of the molecular junctions takes place most likely at a Au–Au bond near the molecule–electrode contacts. The breakdown process is thermally activated and can be described by a thermodynamic bond-breaking model. We have determined important thermodynamic parameters, the average natural lifetime, and binding strength, as well as their distributions. We have also studied the correlation between the conductance of a molecular junction and the breakdown process, conductance fluctuations associated with microscopic bond breakdown and reformation, and rearrangement of metal atoms near the molecule–electrode contact.

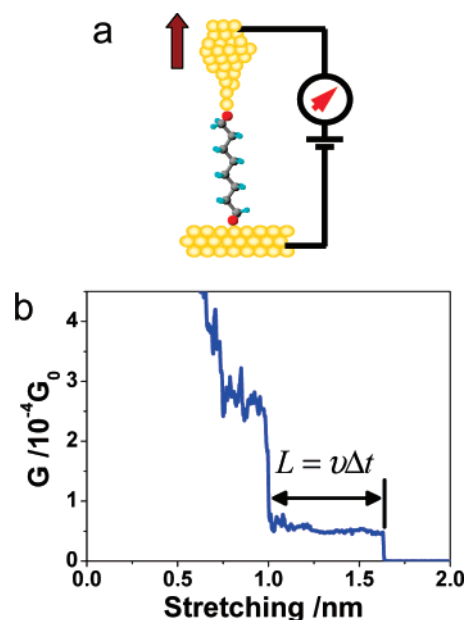
### Experimental Details

STM tips were freshly prepared by cutting gold wires (99.998%) with a diameter of 0.25 mm. A Teflon sample cell was cleaned in boiling Piranha (98%  $\text{H}_2\text{SO}_4$ /30%  $\text{H}_2\text{O}_2 = 3:1$ , v/v) for  $\sim 0.5$  h and then was thoroughly rinsed in boiling water (18 M $\Omega$ , Nanopure system fed with campus distilled water) three times, followed by drying with  $\text{N}_2$ . (Caution: Piranha reacts violently with most organic materials, so extreme care should be taken while handling it.) Gold substrates were prepared by thermally evaporating 100–130 nm gold (99.999%) on freshly cleaved mica surfaces in a UHV chamber. Before each experiment, a gold substrate was annealed with a  $\text{H}_2$  flame for  $\sim 1$  min and then immediately immersed in toluene with/without 1 mM  $n$ -alkanedithiol ( $\text{HS}-(\text{CH}_2)_n-\text{SH}$ , or  $C_n$ ;  $n = 6, 8$ , or 10) in the sample cell, followed by the break junction measurement in toluene. The voltage bias was 20 mV for Au monatomic wires, 50 mV for C6, and 100 mV for C8 and C10.

The STM break junction measurement was carried out using a modified Pico-SPM (Molecular Imaging) with the Nanoscope IIIa controller (Digital Instruments).<sup>10,20</sup> The first step was to image the surface with the regular STM imaging mode. After clear images of Au (111) surfaces were obtained, the STM tip was brought to gentle contact with the molecular monolayer during which one or several molecules might bind to the tip via Au–S bonds. Then the tip was pulled away from the substrate, and the molecules bridged between the substrate and tip electrode broke individually. After breaking the last molecule, the above process was automatically repeated to create and break a large amount of molecule junctions (Figure 1a), during which individual conductance traces were recorded (Figure 1b). In order to study the thermodynamic nature of the bond breakdown process, the rate of the pulling process (called stretching rate) was varied from a few tenths to hundreds of nanometers per second. The experiment was performed in an environmental chamber using toluene as solvent to minimize possible contaminations from impurity molecules in ambient air.

### Statistical Analysis

Of the conductance traces recorded during the breakdown of individual molecular junctions 30–40% show well-defined steps and the rest are either smooth exponential decays or noisy. The last step in each conductance trace has been assigned to the formation and breakdown of a single molecule bridged between the tip and substrate, with the conductance position corresponding to the single molecule conductance.<sup>10</sup> The width of the step measures the time duration ( $\Delta t$ ) over which a molecular junction is stretched before breakdown. The stretching distance ( $L$ ), a quantity that provides important information about the nature of the molecule–electrode contact and breakdown mechanism,



**Figure 1.** (a) Schematic illustration of STM break junction measurement. (b) A conductance trace recorded during pulling C8 away from the electrodes until dissociation. The arrow marks the width of the last conductance step, which corresponds to the distance ( $L$ ) and time duration ( $\Delta t$ ) over which a molecule can be stretched before breakdown. The applied bias voltage and stretching rate were set at 100 mV and 43.3 nm/s, respectively.

can be calculated by  $L = v\Delta t$ , where  $v$  is the stretching rate, defined as the stretching distance per unit time (Figure 1b). This time duration, when extrapolated to zero stretching rate, provides a measure of the natural lifetime of the molecular junctions. Histograms of the step position, time duration, and stretching distance were constructed from the conductance traces that show well-defined steps.

### Thermodynamic Model of Bond Breaking Process

A thermodynamic theory describing the breakdown of a chemical bond under an external stretching force has been developed.<sup>21–23</sup> The theory has provided an excellent description of bond breakdown in single biological molecules measured by atomic force microscopy (AFM). According to the theory, a chemical bond may dissociate spontaneously (in the absence of any external forces) due to thermal fluctuations. The average time that it takes for thermal fluctuation to break or dissociate a bond is called the natural lifetime,  $t_{\text{off}}$ , which is given by

$$t_{\text{off}} = t_{\text{D}} \exp\left(\frac{E_{\text{b}}}{k_{\text{B}}T}\right) \quad (1)$$

where  $t_{\text{D}}$  is the diffusion relaxation time,  $E_{\text{b}}$  is the dissociation energy barrier,  $k_{\text{B}}$  is Boltzmann's constant, and  $T$  is the temperature in kelvin.  $k_{\text{B}}T$  is the average thermal energy at temperature  $T$ . When applying a force to stretch the bond, the chance of bond dissociation increases rapidly due to a decrease in  $E_{\text{b}}$ . The dependence of the dissociation process vs applied force provides a wealth of information about the nature of the chemical bond.

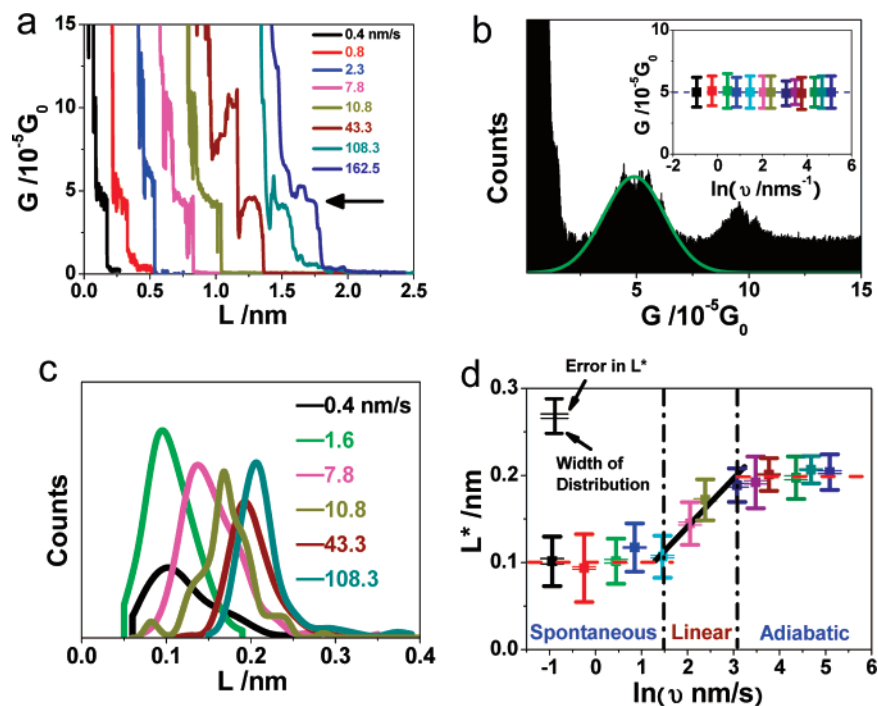
Experimentally, the chemical bond is often stretched by ramping up the force linearly, and the average force at which

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**Figure 2.** (a) Conductance traces of C8 at various stretching rates. The black arrow marks the conductance step corresponding to single C8 junctions. (b) Conductance histogram at 7.8 nm/s. The green line is the Gaussian fit, and the inset plots the conductance of C8 vs logarithm of the stretching rate. (c) Stretching distance histograms at various stretching rates. (d) Most probable stretching distance,  $L^*$ , vs logarithm of the stretching rate. Two kinds of error bars, corresponding to the error in  $L^*$  and the broad distribution of the stretching distance, are separately marked. The black line is the linear fit of  $L^*$  with the logarithm of the stretching rate, according to eq 3. The bias in the measurements was kept at 100 mV.

the dissociation takes place is measured. At slow stretching rates, the breakdown force diminishes because of a high probability that the bond dissociates spontaneously. This regime is called the spontaneous breakdown regime, which, as we will return to later, may include the bond reformation process. At faster stretching rates, the external force increases quickly enough to lower  $E_b$  before a spontaneous breakdown takes place. In this case, the breakdown force is finite and increases linearly with the logarithm of the force loading rate ( $r_F$ ) according to<sup>22,23</sup>

$$F^* = \frac{k_B T}{x_\beta} \ln\left(\frac{t_{\text{off}} x_\beta}{k_B T}\right) + \frac{k_B T}{x_\beta} \ln r_F \quad (2)$$

where  $F^*$  is the most probable breakdown force and  $x_\beta$  is the average thermal bond length along the pulling direction until dissociation. The above relation may be re-expressed in terms of the most probable stretching distance by

$$L^* = \frac{k_B T}{k_s x_\beta} \ln\left(\frac{t_{\text{off}} k_s x_\beta}{k_B T}\right) + \frac{k_B T}{k_s x_\beta} \ln v \quad (3)$$

where  $L^*$  is the most probable stretching distance,  $k_s$  is the effective spring constant of the bond, and  $v$  is the stretching rate defined earlier. To obtain eq 3,  $F^*$  is assumed to be linearly proportional to  $L^*$  by  $F^* = k_s L^*$ , which was found to be approximately correct over the entire breakdown process.<sup>4</sup> Note that  $v$  and  $r_F$  are related but different quantities, given by  $r_F = k_s v$ . This regime is so-called the logarithmically linear loading regime. Finally, at very fast stretching rates, the external force lowers  $E_b$  to zero before thermal fluctuations play any significant role. This is the so-called adiabatic regime, in which  $F^*$  reaches the maximum plateau. The three regimes have all been observed in the breakdown of biological molecules measured by AFM<sup>24–27</sup>

but have not been reported for the STM breakdown junction of single molecule junctions.

## Results and Discussions

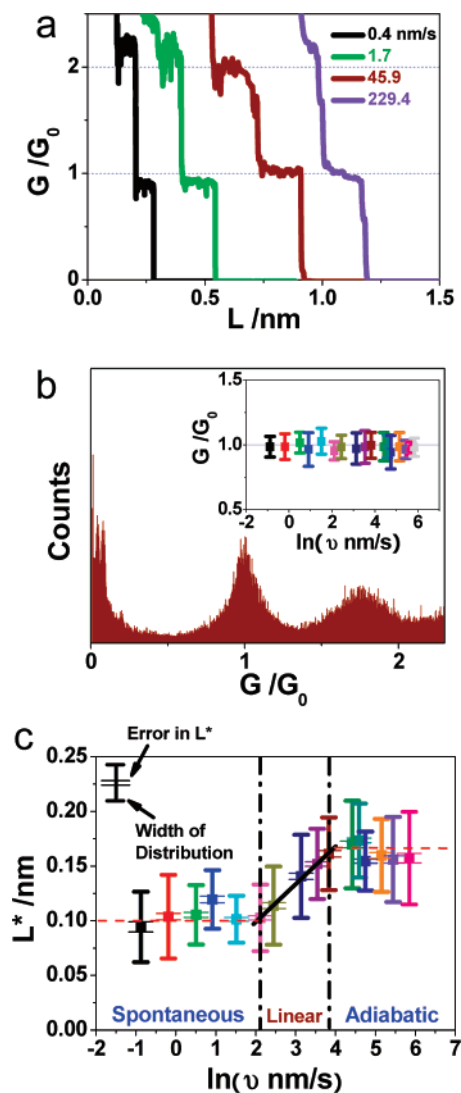
**Conductance and Stretching Distance Histograms.** We performed repeated formations and breakdowns of individual C8 junctions by varying the stretching rate from 0.4 to 160 nm/s. The applied bias voltages in these measurements were kept at 100 mV to ensure that the current-induced local heating of the molecular junctions is negligible.<sup>28</sup> At each stretching rate, at least 2000 individual traces were recorded, among which 30–40% show pronounced steps. Figure 2a shows some typical conductance traces that exhibit steps. A conductance histogram constructed from the individual traces show a peak near  $5 \times 10^{-5} G_0$  ( $G_0 = 2e^2/h$ , where  $e$  is the electron charge and  $h$  is the Planck constant). We have obtained conductance histograms at various stretching rates and found that the conductance value is independent of the stretching rate (inset in Figure 2b). A higher conductance value has been reported previously, which has been attributed to different contact geometries.<sup>29</sup> In this paper, we focus on the low conductance (LC)<sup>13,14,19,29</sup> and discuss some of the results for the higher conductance value in the Supporting Information.

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Another important quantity that can be determined from the STM break junction experiment is the distance over which a molecular junction can be stretched before breakdown. We refer to this distance as the stretching distance which provides detailed information about the stability of single molecule junctions, natural lifetime, and binding strength of the molecule–electrode contact. Due to large variations in the stretching distance from one molecular junction to another, we constructed stretching distance histograms (Figure 2c) by analyzing the last conductance steps in the individual conductance traces recorded at each stretching rate. Similar to the conductance histogram, the stretching distance histogram also shows a peak, which corresponds to the most probable stretching distance ( $L^*$ ). However, unlike conductance,  $L^*$  is sensitive to the stretching rate and the dependence can be divided into three regimes (Figure 2d). At low stretching rates (0.4–4.3 nm/s),  $L^*$  is  $\sim 0.1$  nm which does not change much until the stretching rate is increased to 4.3 nm/s. Above 4.3 nm/s,  $L^*$  increases linearly with the logarithm of the stretching rate. When the rate is increased to 22 nm/s,  $L^*$  reaches another plateau value,  $\sim 0.2$  nm, and maintains the value even when the stretching rate is increased to 163 nm/s. Even at the fastest stretching rate, the hydrodynamic damping is still negligible due to the slow speed and rigid STM tip in the direction of stretching. The observed three regimes agree well with the thermodynamic bond-breaking theory, indicating a thermal activated breakdown process. The transition regime between the two plateaus is sensitive to thermodynamic parameters and described by eq 3. By fitting the data with the equation, we found that  $t_{\text{off}}$  and  $x_{\beta}k_s$  are 95 ms and 74 pN, respectively. We will discuss these parameters later.

**Origin of Molecular Junction Breakdown.** A molecular junction here consists of a molecule covalently bound to two Au electrodes via Au–S bonds. Upon stretching, it may break in the middle of the molecule (C–C), S–C, Au–S, or Au–Au near the molecule–electrode contact. Our previous AFM force measurement strongly indicates that the breakdown takes place at the Au–Au bond.<sup>4,28</sup> To further validate the conclusion, we performed the STM break junction measurement without introducing molecules into the system. In this case, an atomic point contact forms between the Au tip and substrate and the conductance is an integer multiple of  $G_0$  (Figure 3a). This phenomenon is known as conductance quantization, which has been studied extensively using various techniques.<sup>30–38</sup> The conductance of the lowest step, corresponding to the formation and breakdown of a single Au atom or a linear chain of several Au atoms, is independent of the stretching rate (Figure 3b). We note that the conductance of the Au–Au point contacts are  $\sim 4$  orders of magnitude higher than that of single C8 junctions. In contrast to conductance, the stretching distance of the Au–Au point contact depends on the stretching rate in a similar way to



**Figure 3.** (a) Conductance traces of Au–Au point contacts at various stretching rates. (b) Conductance histogram at 45.9 nm/s. The inset plots the conductance of gold point contacts vs stretching rate. (c) Most probable stretching distance,  $L^*$ , vs logarithm of stretching rate. The black line is the linear fit of  $L^*$  with the logarithm of the stretching rate, according to eq 3. The applied bias was 20 mV, under ambient conditions.

that of the molecular junctions (Figure 3c). At low stretching rates (0.4–8.3 nm/s), the stretching distance maintains a constant of  $\sim 0.1$  nm. At high stretching rates (45.9–344 nm/s), it reaches a maximum plateau of  $\sim 0.17$  nm. Between the two plateaus lies a regime in which the stretching distance is linearly proportional to the logarithm of the stretching rate (8.3–45.9 nm/s). The observed stretching rate dependence demonstrates that the breakdown of the Au–Au bond is also thermally activated. By fitting the transition regime with eq 3,  $t_{\text{off}}$  and  $x_{\beta}k_s$  were found to be 81 ms and 120 pN, respectively, which are similar to the corresponding parameters found for C8 junctions. This control experiment shows that the conductance of C8 junctions is  $\sim 4$  orders of magnitude smaller than that of Au point contacts, but both Au–Au and Au–C8–Au junctions share the same thermodynamic breakdown properties, thus showing that the breakdown of C8 junctions most likely involves Au–Au near the contacts.

We have also studied *n*-alkanedithiol (or C<sub>*n*</sub>) with different molecular lengths ( $n = 6, 8,$  and  $10$ ) and observed similar

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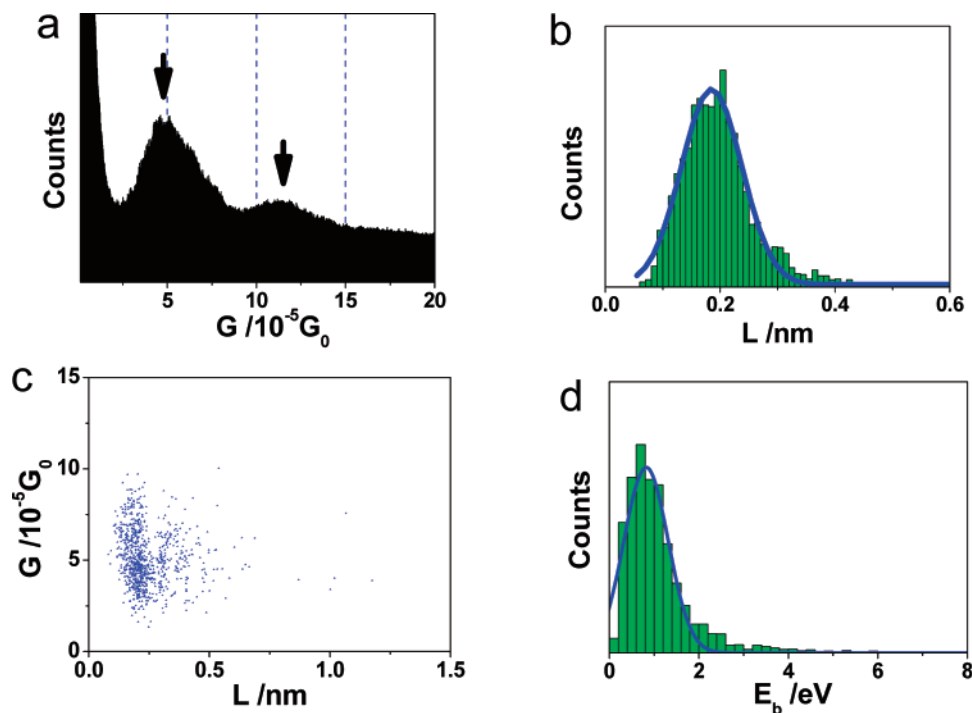
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**Figure 4.** (a) Conductance histogram of C8 constructed from  $\sim 10\,000$  measurements. The black arrows mark conductance peaks corresponding to one and two molecules. (b) Stretching distance histogram of C8. (c) Correlation of conductance vs stretching distance. (d) Binding energy ( $E_b$ ) histogram. The blue lines in both (b) and (d) are Gaussian fittings. The applied bias and stretching rate were set at 100 mV and 98.3 nm/s, respectively.

thermodynamic breakdown behaviors at low biases (Figure S2). The bias was again always kept low to avoid a possible current induced heating effect which is particularly pronounced for the short molecule C6.<sup>39</sup> The study indicates that the most probable breakdown location of molecular junctions involving Au–S is at Au–Au.

**Correlation of Stretching Distance with the Molecule–Electrode Contact Configuration.** The conductance of single molecule junctions created by the STM break junction method exhibits a broad distribution, as shown in Figure 2b. The distribution is due to the variation in the atomic scale details of the molecule–electrode contact and to the sensitive dependence of the molecular conductance on the contact. Muller et al.<sup>40</sup> have recently carried out first-principle calculations on C6 bound to Au electrodes with various contact geometries. To simulate the STM break junction experiments, they have considered S atoms bound directly to the top, bridge, and hollow sites of the Au-(111) lattice, as well as to a single or a chain of several Au atoms pulled out of flat Au electrode surfaces. Their calculations show that the conductance can vary by an order of magnitude depending on the different geometries. To investigate the dependence of the stretching distance on the contact geometry, we studied the correlation between the conductance and stretching distance of the individual molecular junctions.

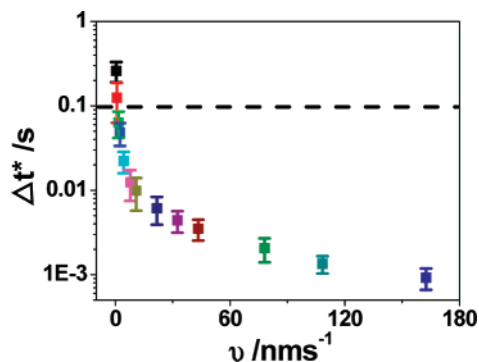
Since the stretching distances of a vast majority of the molecular junctions are short at room temperature, involving, most likely, pulling just a single Au atom out of the electrodes, we repeatedly created and broke over  $\sim 10\,000$  molecular junctions in order to observe rare events that involve pulling multiple atoms into a chain. In addition, we performed the measurement at a fast stretching rate (98.3 nm/s) so that the

bond breaking process is in the adiabatic regime to avoid complications due to thermal fluctuations. The most probable conductance and stretching distance are  $5 \times 10^{-5} G_0$  and 0.2 nm, as shown in Figure 4a and b, respectively. Note that although the most probable stretching distance is only 0.2 nm, a small number of molecular junctions can be stretched over 1 nm, corresponding to the length of  $\sim 4$  Au atoms in a chain. The conductance varies over a wide range ( $(2-9) \times 10^{-5} G_0$ ), but no obvious correlation is found between the conductance and the stretching distance (Figure 4c).

**Lifetime of Single Molecule Junctions.** By fitting the stretching distance vs stretching rate data using the thermodynamic bond-breaking theory, we have extracted the natural lifetime ( $t_{\text{off}}$ ) of a molecular junction formed via Au–S contacts to be about 100 ms. An alternative way to determine  $t_{\text{off}}$  is to directly measure the average lifetime over which a molecule has contact with two gold electrodes until spontaneous breakdown. However, this approach is complicated due to the unavoidable mechanical instability and thermal drift of the instrument, which will lead to an underestimate of the real lifetime of the molecular junctions. To overcome this problem, we measured the average lifetime as a function of the stretching rate, and the lifetime extrapolated to zero stretching rate should provide a measurement of  $t_{\text{off}}$ . Figure 5 plots the average lifetime vs stretching rate, which shows a rapid increase in the lifetime as the stretching rate decreases. For example, the lifetime is  $\sim 0.25$  s at 0.4 nm/s, the slowest stretching rate used in the experiment. This is the lower limit of the actual lifetime of the molecule junctions, which appears to contradict with  $\sim 0.1$  s as extracted by fitting the experimental data with the thermodynamic theory in the linear logarithmic regime. The apparent contradiction is also reflected in the measured stretching distance in the spontaneous breakdown regime, shown in Figure 2d.

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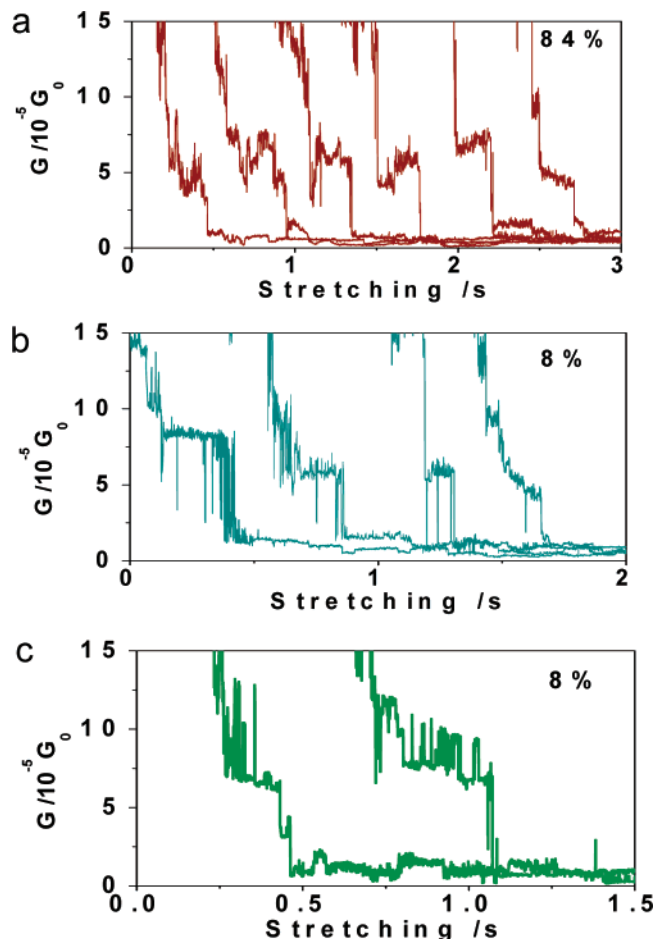


**Figure 5.** Semilogarithmic plot of lifetime  $\Delta t^*$  vs the stretching rate, where the error bars are the width of the distributions.  $\Delta t^*$  was derived by  $\Delta t^* = L^*/\nu$ , where  $L^*$  values were measured in Figure 2d. The black dash line shows the natural lifetime,  $t_{\text{off}}$ , evaluated from the linear fitting in Figure 2d.

According to the thermodynamic model, the stretching distance at slow stretching rates should diminish to zero due to spontaneous breakdown. In contrast, we observed a finite  $L^*$  of  $\sim 0.1$  nm in the slow stretching regime. The lifetime,  $\Delta t^*$ , is given by  $\Delta t^* = L^*/\nu$ , so a constant stretching distance implies a rapid increase in lifetime with decreasing stretching rate (Figure 5).

A nonzero breakdown force at slow stretching rates has been observed in other systems and attributed to bond reformation.<sup>23</sup> At slow stretching rates, both bond breaking and reformation can take place as competing thermodynamic processes. In the present system, since the weakest link is the Au–Au bond near the molecule–electrode contacts, it may also involve a Au atom switching from one binding site to another in addition to the simple bond breaking and reformation processes. For example, the binding site of a Au atom may switch between hollow and top sites, which will result in conductance fluctuations.

We have analyzed conductance fluctuations in thousands of transient curves and observed three types of abrupt switching behaviors in the last conductance step. The most common ( $\sim 84\%$ ) one is relatively small switching events around  $5 \times 10^{-5}G_0$ , the average conductance of the last steps (Figure 6a). The switching amplitude is less than 50% of the average conductance but much greater than the noise level in the measurement. This type of switching could be due to the change in the binding site or rearrangement of atomic configuration near the molecule–electrode contacts, as well as to the conformational change in the alkylene chain from *gauche* to *trans*.<sup>41</sup> Stochastic switching in conductance has been reported in the STM images of  $\pi$ -conjugated molecules attached to a Au substrate via thiol linkers and attributed to the fluctuation of the tilt angle of adsorbed molecules to the electrode surface.<sup>42</sup> The second type of switching is large abrupt conductance fluctuations between  $\sim 5 \times 10^{-5}G_0$  and  $\sim 0$  (Figure 6b). This switching has  $\sim 8\%$  occurrence and may be attributed to the breaking and reformation of the molecular junction associated with Au–Au bonds. Random bond breaking and reformation at the molecule–electrode contacts have been proposed to explain large random conductance fluctuations of alkanedithiols



**Figure 6.** Three types of conductance fluctuations of single C8 junctions at room temperature. The applied bias and stretching rate in these measurements were 100 mV and 0.4 nm/s, respectively.

measured by conducting AFM<sup>43</sup> and the negative differential resistance effect observed in molecular junctions formed by a mercury droplet.<sup>44</sup> Finally, the residual  $\sim 8\%$  of switching is large fluctuations between  $\sim 5 \times 10^{-5}G_0$  and  $\sim 2 \times (5 \times 10^{-5}G_0)$ , which is likely due to the switching between one and two molecules bridged across the two electrodes (Figure 6c).

The switching of the binding site and the processes of both bond breaking and reformation at the molecule–electrode contact prolong the lifetime of molecular junctions and explain the observed nonzero breakdown force or stretching distance in the slow stretching regime. A more sophisticated model shows that the bond reformation leads a nonzero breakdown force at slow stretching rates, and the magnitude of the force depends on the stiffness of the AFM cantilever.<sup>23</sup>

### Binding Energy

An important parameter in the description of a chemical bond is the binding energy or dissociation energy barrier in the thermodynamic model, which can be extracted in the present system from the stretching distance. Our previous C-AFM study shows that the force applied on a molecular junction increases approximately linearly with stretching distance until the breakdown of the junction.<sup>4,28</sup> In the adiabatic regime (fast stretching

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rates), the binding energy,  $E_b$ , is related to the adiabatic stretching distance,  $L_a$ , given by

$$E_b = \frac{1}{2}F_b L_a \quad (4)$$

where  $F_b$  is the force required to break a Au–C $n$ –Au junction. Previous studies of both Au–C8–Au molecular junctions and Au–Au point contacts have found that  $F_b \approx 1.5$  nN.<sup>4,32,45</sup> Using the breakdown force, we extracted  $E_b$  from  $L_a$  (Figure 4b) by eq 4. The distribution of  $E_b$  is rather broad with a peak near 0.82 eV and a half width of  $\sim 0.45$  eV (Figure 4d). The result is in agreement with the C-AFM measurement<sup>28</sup> and also consistent with the theoretical calculation of Au–Au binding strength.<sup>46</sup> The wide distribution reflects the large variation in the molecule–electrode contact configurations of the individual molecular junctions. Since the lifetime is an exponential function of the binding energy (see eq 1) and  $t_D$  was determined as  $\sim 0.1$  ps from the C-AFM measurement at room temperature,<sup>28</sup> the distribution in the binding energy leads to an extremely large distribution in the natural lifetime, from 0.1  $\mu$ s to 3.5 years. So although the average natural lifetime of a molecular junction formed via a Au–S bond is on the order of seconds, some binding geometries can be rather long-lived even at room temperature.

## Conclusions

The stability and breakdown mechanism of single C8 junctions were studied by analyzing thousands of molecular junctions formed and broken at various stretching rates using an STM break-junction approach at room temperature. A comparative study of Au–Au point contacts shows that the breakdown of the molecular junctions takes place most likely at Au–Au bonds. The stretching distance depends on the stretching rate, which follows a sigmoidal shape as predicted by a thermodynamic bond-breaking theory.

At fast stretching rates (adiabatic regime), the stretching distance is independent of stretching rate and the breakdown is primarily caused by the external force that overcomes the binding energy barrier. Statistical analysis of  $\sim 10\,000$  curves shows that the most probable stretching distance is about 0.2

nm, roughly corresponding to pulling a single atom, but a small number of molecular junctions can be stretched over 1 nm, corresponding to 3–4 Au atoms in a chain. The adiabatic stretching distance has no obvious correlation with the molecule–electrode contact geometries. At very slow stretching rates, the stretching distance reaches another plateau with an average value of  $\sim 0.1$  nm. This regime is called a spontaneous breakdown regime in which thermal fluctuations cause the bond to break. Between the fast adiabatic and slow spontaneous breakdown regimes lies a regime in which the stretching distance is linearly proportional to the logarithm of the stretching rates.

The observation shows that the breakdown of the molecular junctions is thermally activated, and thermodynamic parameters, such as binding energy and natural lifetime, were extracted. The binding energy has a broad distribution with a peak near 0.8 eV and width  $\sim 0.45$  eV. The distribution in the binding energy leads to natural lifetime variations from 0.1  $\mu$ s to 3.5 years, although the most probable lifetime of the molecular junctions at room temperature is on the order of seconds or less. The wide distribution results from various molecule–electrode contact configurations, so highly stable molecular junctions at room temperature are possible only for some rare contact configurations.

Three types of stochastic fluctuations are often observed in the conductance at slow stretching rates. The most frequent ones have small amplitudes which are attributed to atomic scale rearrangement at the molecule–electrode contacts and conformational changes in the molecules. Two other types of fluctuations involve large and abrupt switching in the conductance between a stable value and zero and between a stable value and twice the stable value, respectively. These large fluctuations are likely due to the bond breakdown/reformation of a single and two molecules. The rearrangement of metal atoms at the molecule–electrode contacts and bond breakdown/reformation contribute to the further stabilization in the molecular junctions.

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**Supporting Information Available:** Multiple conductance values and the molecular length dependence of lifetime in single C $n$  ( $n = 6, 8,$  and  $10$ ) junctions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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