Electron transport properties of single molecular junctions under mechanical modulations

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Electron transport properties of single molecular junctions under mechanical modulations

Jianfeng Zhou, Cunlan Guo and Bingqian Xu

Molecular Nanoelectronics Laboratory, Faculty of Engineering and Nanoscale Science and Engineering Center, University of Georgia, Athens, GA 30602, USA

E-mail: bxu@engr.uga.edu

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Abstract
Electron transport behaviors of single molecular junctions are very sensitive to the atomic scale molecule–metal electrode contact interfaces, which have been difficult to control. We used a modified scanning probe microscope-break junction technique (SPM-BJT) to control the dynamics of the contacts and simultaneously monitor both the conductance and force. First, by fitting the measured data into a modified multiple tunneling barrier model, the static contact resistances, corresponding to the different contact conformations of single alkanedithiol and alkanediamine molecular junctions, were identified. Second, the changes of contact decay constant were measured under mechanical extensions of the molecular junctions, which helped to classify the different single molecular conductance sets into specific microscopic conformations of the molecule–electrode contacts. Third, by monitoring the changes of force and contact decay constant with the mechanical extensions, the changes of conductance were found to be caused by the changes of contact bond length and by the atomic reorganizations near the contact bond. This study provides a new insight into the understanding of the influences of contact conformations, especially the effect of changes of dynamic contact conformation on electron transport through single molecular junctions.

(Some figures may appear in colour only in the online journal)

1. Introduction
A detailed, quantitative understanding of the electron transport behaviors in a molecular junction, which is a structure of a molecule core contacting to metallic electrodes, has intrigued researchers for decades [1–3]. This is because molecular junctions are believed to possess potential applications in constructing nanoscale multi-functional devices for electronics [4–6], optics [7–9] and chemical/bio-sensors [10–12]. For the electronic transport of single molecular junction, the contributions of molecule cores have been intensively investigated by measuring the conductance of the carefully chosen or designed molecules [13, 14]. However, the measured conductance value still suffers from large variances, even for the simplest single alkane chain molecule core contacting to two metal electrodes [15, 16]. These variances probably resulted from the uncontrolled variations of contact conformations.

As suggested by Lindsay and other researchers [17–19], the contact interface between the molecule core and the metallic electrodes plays a significant role in the electron transport of single molecular junctions. In practical molecular junctions, the structures of molecules and electrodes are usually predetermined, but the contact interface is the least controllable factor [19–21]. Therefore, it becomes critical to determine the influence of contact interface on electron transport in single molecular junctions, which is helpful for an in-depth and thorough understanding of the fundamental transport mechanisms. Recently, several related issues have been studied. One of the findings was that in a single molecular junction, multiple sets of conductance values were measured, which was attributed to the effects of the different
contact conformations [22, 23]. Second, for the molecular junctions that were composed of the same molecule core but different anchoring groups, the conductance was found to be correlated with the nature of couplings between different anchoring groups and electrodes [24]. Finally, the dynamic changes of the contact interface that universally exist in the practical molecular junctions [25, 26], were recently studied through introducing regular modulations of the molecular junctions to manipulate the contact conformation changes by using the SPM break junction technique (SPM-BJT) [27, 28]. These studies demonstrated that the overall measured conductance changes in response to external modulations [27, 28]. However, to quantitatively evaluate the influences of contact changes introduced by the modulations, it is necessary to find a way to precisely control the modulations so that the corresponding changes only due to the contacts can be isolated from the overall results.

To understand the fundamental mechanisms of electron transport properties under the dynamic modulation of the contacts, a feasible model is required to correlate the measurable quantities. At low bias, a widely accepted theoretical regime to describe the electron transport through single molecular junctions is the Landauer–Büttiker formalism. In this regime, the conductance of molecular junctions can be simply written as [29]:

$$G = \frac{2e^2}{h}T_{lc}T_{mol}T_{rc}$$  \hspace{1cm} (1)

where $e$ is the elementary charge and $h$ is Planck’s constant; $T_{mol}$ is the transmission efficiency of the molecule core that depends on the electronic structures of the molecule; $T_{lc}$ and $T_{rc}$ are the contact transmission efficiencies, which reflect the charge transport across the left and right contacts, respectively. In current theoretical discussions, density functional theory (DFT) and the non-equilibrium Green function (NEGF) [30–32] were generally used to analyze these three transmission efficiencies. However, the calculated results often cannot fully provide direct explanations for the experimental data. Thus, more simplified models, such as Simmons tunneling model [33, 34], were used to explain the experimental results. For the simplest alkane molecule core related experiments, the molecular junction can be described as follows: the molecule core is considered as a rectangular barrier, which usually follows non-resonant tunneling transport. The contact transmission efficiencies are assumed as constants. Thus equation (1) can be simplified as:

$$G = A_G \exp(-\beta l) \hspace{1cm} \text{or} \hspace{1cm} \ln(G) = -\beta l + \ln A_G$$  \hspace{1cm} (2)

where $A_G$ is the constant reflecting the contact features and $\beta$ is the molecular decay constant. Therefore, with this model, the influences of the contact and the molecule core on the conductance can be evaluated separately. A molecule core with relatively large HOMO–LUMO gap was used to discuss electron transport mechanisms of stabilized simple single molecular junctions [15, 22, 35]. However, when closely examining the influences of contact features, especially the dynamic contact conformation changes under modulation, $A_G$ was found not to be a constant any more. Instead, another rectangular barrier was used to replace $A_G$ to represent the contacts in the molecular junctions [36, 37]. The changes of contact conformation that are induced by the modulations could therefore be described as the resulting width or height changes of the rectangular contact barrier.

In this paper, we report our detailed studies on the effects of the dynamic changes of the contact interface on the electronic transport in single molecular junctions by monitoring the conductance and force corresponding to the controlled mechanical extensions. We used our recently developed modified SPM-BJT with which the regular modulations were applied to the stabilized molecular junctions [36]. The measured conductance and force changes in response to the modulation were fitted into a modified tunneling model to elucidate the electronic transport mechanism of single molecular junctions under mechanical extensions.

2. Experimental details

1,6-hexanediathiol (C6DT), 1,8-octanediathiol (C8DT), 1,10-decanediathiol (C10DT), 1,6-hexanediamine (C6DA), 1,8-octanediamine (C8DA), and 1,10-decanediamine (C10DA), were purchased from Aldrich. These molecules were either terminated with thiol(–SH) or amine (–NH$_2$) anchoring groups on both ends to chemically contact to the Au electrodes. All the other chemicals were purchased from commercially available sources and used directly as received.

Au(111) substrates were used as one of electrodes in the molecular junctions. The Au(111) substrates were prepared by thermally deposited pure gold (99.999%, Kurt J Lesker) onto freshly cleaved mica sheets (Ted Pella, Inc.) under a vacuum of 10$^{-7}$ Torr using a custom-modified thermal evaporator (Thermionics). Firstly, the cleaved mica sheets were heated to 420°C for 10–12 h under 10$^{-7}$ Torr vacuum in the evaporator and then a 100 nm thick Au layer was deposited at a rate of about 0.5 Å s$^{-1}$. After the deposition, the coated gold substrates were slowly cooled down to room temperature at a rate of 5 °C min$^{-1}$ and taken out to keep in a nitrogen cleaned vacuum desiccator. Before each experiment, hydrogen flame annealing was applied on the gold substrate to produce contaminant-free Au(111) surfaces.

To fabricate the molecular junction devices with different molecules, an AFM nanografting technique [38] was used to insert alkanedithiol and alkanediamine molecular patterns in an alkanethiol self-assembled monolayer (SAM). First, to form an alkanethiol SAM, the Au(111) substrate was immersed in a toluene solution of 1 mM 1-tetradecanethiol (CH$_3$-(CH$_2$)$_{13}$SH) (C14). After 6 h, following rinse with ethanol to remove excess molecules and drying with nitrogen gas, the substrate was immediately covered by 18 M Torr vacuum de-ionized water for protection from contaminations. Second, to fabricate alkanedithiol and alkanediamine molecular patterns on the C14 SAM, a 40 N m$^{-1}$ rectangular AFM tip was used to do nanoshaving for easy locating. Visible markers were made on the surface of the sample under the loading force of 6 μN and shaving speed of 5 μm s$^{-1}$. The
size of the markers was 10 µm × 10 µm and the distance between two closest markers was 30 µm. The relocation of the AFM tip then became much easier in the next steps. Finally, alkanedithiol and alkanediamine molecular patterns were inserted in the C14 SAM using an AFM nanografting technique described as the following: after rinsing with pure water and drying with nitrogen gas, the sample with C14 SAM was put in the 1 mM alkanedithiol (toluene solution). The two 250 nm × 250 nm square patterns were made in an area within the markers with a 0.27 N m⁻¹ triangular AFM tip by nanografting (figures 1(a) and (c) show an example for C8DT). Then the sample was thoroughly cleaned to remove the extra molecules and put into 1 mM alkanediamine (water solution). The AFM tip was relocated to make two circular patterns with diameters of around 200 nm just beside the square patterns (figures 1(a) and (b) show an example for C8DA). The picolith.exe 2.1 in Picoscan 5.3.3 software (Agilent Inc.) was used for the nanoshaving and nanografting.

A modified SPM-BJT based on a PicoPlus SPM system (molecular imaging) (figure 2(a)) [38, 39] was used for all the measurements. Homemade Labview programs were used to control the piezotransducer (PZT) in the SPM system. The conducting SPM tip was driven to contact into and out of sample substrates to form the molecular junctions. Current and force signals were monitored and recorded by a digital oscilloscope (DL750 Yokogawa) during the SPM tip retracting from sample substrates. In this modified SPM-BJT, instead of the usual continuous retracting, the SPM tip retraction process was divided into a series of two types of movement: abrupt stretching and free-holding (figures 2(a) (A) and (b)). The tip was first withdrawn abruptly for 1 nm and then stably held at that position for 50 ms. So the conductance of molecules could be measured without the tip retracting movements until the next abrupt withdrawal. Those two types of movement alternated until the monitored conductance and force vanished, which indicated the complete breaking of the molecular junctions. Finally, to measure the dynamic changes of the contact interface, we applied a regular modulation during the free-holding of the molecular junction between two electrodes (figure 2(a) (B)), which was realized by adding a small amplitude (1.2 Å) triangular AC signal to the PZT. The corresponding conductance and force curves could also be monitored and collected for the offline analysis (figure 2(c)).

The conducting AFM tip was prepared by coating a Si AFM tip (Nanoscience Instruments) with a 15 nm layer of chromium and then a 35 nm layer of gold (99.999%) in an ion beam coater (Gatan model 681) before each measurement. The spring constant of the AFM cantilever was calibrated before the measurements and was found to be around 40 N m⁻¹.

In all the experiments, a clean Teflon SPM liquid cell was used to keep the measurements in the solution to minimize the
Figure 2. (a) Schematic of the modified SPM-BJT. The inset showed the retracting modes of the SPM tip driven by PZT: (A) modified SPM-BJT with abrupt withdrawal and free-holding processes; (B) a regular modulation applied during the free-holding process. The current and force signals were recorded simultaneously. (b) Typical conductance (solid) and force traces (short dash) for C8DA under (A) mode in (a). (c) Typical conductance (solid) and force traces (short dash) for C8DA under PZT modulation (dash) as the (B) mode in (a).

3. Results and discussion

3.1. Multiple-barrier tunneling model

To describe the electron transport through single alkane chain molecular junctions under mechanical extensions, we adopted the multiple-barrier tunneling model. In this model, the left and right contacts were considered as two rectangular potential barriers with different decay constants and geometric parameters from the molecule core (figure 3(a)). However, it was difficult to control the exact contact conformations of the junctions under experimental conditions. As a further simplification, we combine the left and right contacts into one contact barrier (figure 3(b)). Since the junctions had the same chemical structure in both contacts and we can therefore average out the differences by repeating the experiments many times and using statistical analysis, this symmetric contact approximation is reasonable. Therefore, the conductance of molecular junctions can be written as:

\[ G = A \exp(-\beta l) \exp(-\beta_C d_C) \]  

where \( A \) is a constant and \( d_C \) is the width of contact potential. \( \beta_C \) is the contact decay constant. For a rectangular barrier, \( \beta_C \) depends on the height of the contact potential barrier \( \Phi_C \) [34]:

\[ \beta_C = \frac{2 \sqrt{2m}}{\hbar} - \alpha \sqrt{\Phi_C} = 1.03 \alpha \sqrt{\Phi_C} \]  

where \( m \) is electron mass, \( h \) is Planck’s constant, and \( \alpha \) is an adjustable parameter, equal to 1 with a simple rectangular model at lower bias range (<0.5 V). Thus \( \beta_C \) and \( d_C \) are two indices that can be used to describe the properties of contact conformation.

When the molecular junction was held stable during the free-holding process, the contact decay constant \( \beta_{C0} \) and \( d_{C0} \) could be considered as constants (figure 3(b)). Therefore, the multiple-barrier model became the original Simmons tunneling model as described by equation (2). The term \( A \exp(-\beta_{C0}d_{C0}) \) could be replaced by a constant \( A_G \), which could be used to deduce the static contact resistance \( R_C \) for specific contact conformations:

\[ R_C = \frac{1}{A_G} \]  

When a small mechanical extension \( \Delta d \) was introduced to the stable molecular junctions (figure 3(c)), the induced changes should mainly come from contact conformation changes. That was because covalent C–C bonds in the molecule core were much stronger than S–Au, NH₂–Au, and Au–Au bonds in the contacts [36]. So the molecule core (C8DT and C8DA) could be considered as a rigid body and therefore should remain intact under the extension \( \Delta d \). Under this condition, the width of the contact potential barrier became \( d_{C0} + \Delta d \), and the contact decay constant would change to \( \beta_C(d_{C0} + \Delta d) \). According to equation (3), the changes of contact potential barrier would finally alter the electron transport through the molecular junctions.
correlate the model with the measured quantities of $G$ and $d$, the contact decay constant with the mechanical extension can be determined as:

$$\beta_C(d) = -\frac{\partial \ln(G)}{\partial(d)}. \quad (6)$$

### 3.2. Static contact resistance $R_C$

As discussed above, the static contact resistance $R_C$ describes the contact’s potential barrier contribution to the electron transport in the molecular junctions and can be determined by holding the junctions stable. It is an important index reflecting the fundamental features of contact conformations and can be used to identify different contact conformations in stable molecular junctions. Equation (2) was used to obtain the values of $R_C$ by analyzing the changes of the measured single molecular conductance with molecular length (figure 4). In our studies, we tested alkanedithiol and alkanediamine molecules with 6, 8, and 10 carbon atoms by using our modified SPM-BJT. From the measured conductance of stable molecular junctions during the free-holding process, less-populated single molecular conductance sets were identified as reported before [38], and four different single molecular conductance sets were observed for both alkanedithiol and alkanediamine molecular junctions. According to equation (2), the conductance was linearly fitted with molecular length for each conductance set and the line was extrapolated to get the intercept $\ln A_G$ (figure 4).

As was shown, multiple conductance sets had almost the same molecular decay constant (0.8–0.9 Å$^{-1}$) but the static contact resistances had large differences from each other (table 1). Therefore, we can conclude that the multiple single molecular conductance sets do not come from the molecule core but rather result from the different contact conformations. In addition, for each conductance set, alkanediamine had a smaller single molecular conductance value than its counterpart of alkanedithiol. Therefore, it demonstrated that different anchoring groups lead to different contact conformation structures and thus different conductance values in the molecular junctions with the same molecule cores. Note that because $R_C$ values were calculated from data fitting, considering the error bars in determining the conductance value, the results presented here agreed well with our previous report [38].

### 3.3. Contact decay constant $\beta_C(d)$ changing with external mechanical extensions

As was discussed in section 3.1, under mechanical extension, the changes of contact potential barrier width would cause the variation of the height of contact potential, or contact decay constant $\beta_C$. In our previous report, we compared the contact decay constant of CSDT and C8DA with some specific contact conformations under the mechanical extension [37]. The results suggested that different strength of contact bonds between anchoring groups and Au electrodes resulted in different changes of contact conformation under the same extensions. However, direct mechanical evidence is needed to further confirm the conclusion. In addition, to have a complete and detailed understanding of the influence of dynamic contact conformation changes, we also need to compare the effects of contact decay constants on the different original contact conformations evidenced by the four conductance sets.

Therefore, we studied the changes of contact decay constant with extensions for alkanedithiol and alkanediamine molecular junctions with all the contact conformations.

![Schematic descriptions of the multiple-barrier models.](image)

**Figure 3.** Schematic descriptions of the multiple-barrier models.

(a) The molecular junction with molecular core length $l$; in (b) and (c), the molecule core was considered as a rectangular potential barrier with decay constant $\beta$ and potential barrier width $l$ while the contact was treated as another rectangular potential barrier with decay constant $\beta_C$ and width $d_C$. (b) is the schematic potential profile in the free-holding process and (c) is the schematic potential profile with the mechanical extension $\Delta d$.

<table>
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<th>Set</th>
<th>$\beta_L$ (Å$^{-1}$)</th>
<th>$R_C$ (kΩ)</th>
<th>$\beta_L$ (Å$^{-1}$)</th>
<th>$R_C$ (kΩ)</th>
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</thead>
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<td>1</td>
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<td>432.3</td>
<td>0.86 ± 0.06</td>
<td>178.0</td>
</tr>
<tr>
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<td>0.83 ± 0.04</td>
<td>242.6</td>
<td>0.83 ± 0.07</td>
<td>152.0</td>
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</tr>
<tr>
<td>4</td>
<td>0.82 ± 0.01</td>
<td>140.3</td>
<td>0.77 ± 0.01</td>
<td>33.7</td>
</tr>
</tbody>
</table>

Table 1. The obtained molecular decay constant and static resistance for alkanediamine and alkanedithiol molecular junctions with different contact conformations.

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**Table 1.** The obtained molecular decay constant and static resistance for alkanediamine and alkanedithiol molecular junctions with different contact conformations.

### 5
Figure 4. Natural logarithm of conductance versus molecule length and number of carbon atoms (N) for the different single molecular conductance sets of alkanediamine (a) and alkanedithiol (b) single molecular junctions. The static contact resistance can be obtained from different conductance sets by the intercept of the line shown in the figures, which indicated different contact conformations. The detailed values are listed in table 1.

Figure 5. The typical curves of both changes of conductance and force corresponding to the mechanical extensions. (a) The measured conductance (solid) and force (short dash) trace under the regular mechanical modulations. (b) The representative ln\((G/G_0)\) versus extension \(\Delta d\) curves obtained from the labeled part in (a) with rectangles. (c) The \(\beta_C(d_\text{c})\) changes with the extension \(\Delta d\), which were obtained from the curves of (b). (d) The measured relevant force changes with the mechanical extensions.

reported in section 3.2. Typical traces of a C8DA molecular junction in figure 5(a) showed the changes of both conductance and force corresponding to the mechanical modulation (PTZ). Then, four parts of the traces were selected for further analysis (marked by rectangles). First, plots of the logarithmic conductance ln\((G/G_0)\) versus the extension \(\Delta d\) showed nonlinear relations (figure 5(b)). It indicated that the stretching came from the contacts otherwise the curves would be linear if it were the molecule that was elongated. Second, by differentiating ln\((G/G_0)\) with respect to the extension \(\Delta d\), the relationships between contact decay constant values \(\beta_C(d)\) and extension \(\Delta d\) were obtained (figure 5(c)), which showed complicated features. Third, the corresponding changes of force \(\Delta F\) with the extension are shown in figure 5(d); they provided direct mechanical information for the contact conformation changes under the extensions. \(\beta_C(d)\) obtained from four selected parts of the traces (figure 5) showed a complicated relationship with extensions. To obtain a reliable overall realization for the \(\beta_C(d)\) changing by the extensions, statistic analysis was done.
Figure 6. The average changes of $\beta_C(d_C)$ for $G_{S1}$–$G_{S4}$ conductance sets corresponding to the mechanical extensions for (a) C8DT and (b) C8DA molecular junctions.

with over 200 $\beta_C(d_C)\!-\!d$ curves for each single molecular conductance set under different $\Delta d$ following the previous reported procedure [37]. Figure 6 plotted the averaged contact decay constants $\beta_C$ at 13 extensions for each of the four contact conformations of C8DT and C8DA. Several specific phenomena were observed: firstly, the differences of the constant decay constants $\beta_C$ for the stable molecular junctions $G_{S1}$–$G_{S4}$ were larger for C8DT (figure 6(a)) than that for C8DA (figure 6(b)). For example, for C8DT, $\beta_{C0}$ of the $G_{S1}$ set was almost three times the $G_{S4}$ set, but for C8DA, the $\beta_{C0}$ for each of the four conductance sets were close to each other. That explained why the static contact resistances had much smaller differences in C8DA, while in C8DT the static contact resistance of the $G_{S1}$ set was much larger than that of $G_{S4}$. This large difference among $\beta_{C0}$ of C8DT resulted in the large variations of the static contact resistances for the four conductance sets. Second, $\beta_C$ changed with $\Delta d$ in different ways. For the $G_{S4}$ set of C8DT, as shown in figure 6(a), $\beta_C$ increased linearly with mechanical extension at small displacement and saturated at a value of around $0.4$ Å$^{-1}$ where $\Delta d$ was 0.5 Å. The result was consistent with the former report [37]. For $G_{S2}$ and $G_{S3}$ sets, similar results were observed with $\beta_C$ saturating at a value of around $0.4$ Å$^{-1}$ where $\Delta d$ was 0.2 Å. Surprisingly, for the $G_{S1}$ set, $\beta_C$ remained approximately constant at around $0.4$ Å$^{-1}$ for all the 13$\Delta d$ values. It is interesting to notice that at larger $\Delta d$, the $\beta_C$ of all the four sets became close to each other and saturated...
at about 0.4 Å⁻¹, which suggested that the width changes of contact potential mainly helped increase the contact resistance in molecular junctions [36]. For all the four different contact conformations of C8DA, β_C showed no obvious dependence on ∆d.

According to our earlier discussions [37], the width changes of contact potential were attributed to the length changes of the contact bond, while the changes of contact decay constant or the height changes of the contact potential barrier resulted from the reorganizations of atoms in contacts. In C8DT molecular junctions, the Au–thiol bond of the contact was stronger than the Au–Au bond of the electrodes [40], so the applied external mechanical extension ∆d should affect the Au–Au bond first. The extensions of the Au–Au bond could subsequently cause the reorganizations of the gold atoms near the contact bond, which led to the changes of contact potential barrier height or the contact decay constant. However, in C8DA molecular junctions, the Au–amine bond was weaker than the Au–Au bond [40], therefore the extensions could only extend the Au–amine bond but would not cause the reorganizations of Au atoms. Therefore, only the width of the contact potential barrier changed with the extensions but β_C would keep approximately the same (figure 6(b)). Finally, for C8DT, the changes of β_C with extensions ∆d also depended on their original contact conformations. According to the previous theoretical reports [41], the alkanethiol molecule can be absorbed on the Au(111) surface at different adsorption sites and cause different single molecular conductance [22]. Based on our experimental results, we suggest that for a G_S4 set of C8DT, the molecule may originally sit in the hollow sites of Au electrodes so that the mechanical extension could cause the largest extent of atomic reorganization. While for the G_S1 set, the molecule was originally wired on the top sites of electrodes so the extension could only extend the contact bond but would not cause any atomic reorganization. G_S2 and G_S3 with relatively smaller extent of atomic reorganizations might be related to some contact conformations between the G_S1 and G_S4. Since the bond extension and atom reorganization would both cause force changes, β_C and the change of measured force ∆F were correlated with the extensions ∆d to verify the above explanations (figure 7).

Figure 7 shows the plots of the statistical results obtained from over 200 β_C−∆d and ∆F−∆d curves. For the G_S4 set of C8DT (figure 7(a)), the change of force showed two different modes: above 0.4 Å extensions, the force changes ∆F increase almost linearly with a slope k = 3.10 nN nm⁻¹ with extensions ∆d [42], while below 0.4 Å ∆F showed a different curvilinear mode. In contrast, for the G_S1 set of C8DT (figure 7(b)) and all the sets of C8DA (we only show the G_S4 set in figure 7(c)), only one mode of linear force changes was observed. The slope k was 3.98 nN nm⁻¹ for the G_S1 set of C8DT and 2.85 nN nm⁻¹ for the G_S4 set of C8DA, respectively. These results demonstrated that the linear force change could be connected with the change of bond length, which was induced by the small mechanical extensions and could follow the elastic mode. Also, the nonlinear force changes with extension should be about some creep deformation that should relate to the atomic reorganizations. Therefore, for the G_S1 set of C8DT and the G_S4 set of C8DA, ∆d mostly leads to the bond length changes. For the G_S4 set of C8DT, small ∆d would cause atomic reorganizations from the hollow contact until ∆d reached 0.5 Å where the extensions led to the change of bond length. About the change of bond length, we believe that it happens on the contact interface because the C–C bond of the alkane molecule is much stronger. However, according to Lii and Alinger [42], there were low frequency modes called collective C–C–C bending modes that associated with the elongation of alkane molecules. The linear changes of force might also be included in such bending modes. Obviously, further experimental measurements and advanced theoretical studies are needed for the further understanding of the mechanism details.
4. Conclusions

In summary, we studied the electronic transport mechanisms of the molecule–electrode contacts in single molecular junctions by using our modified SPM-BJT and fitting the data into a modified tunneling model. In our modified tunneling model, the molecule–electrode contacts were considered as a rectangular potential barrier where the contact decay constant $\beta c$ (the height of the potential barrier) and the width of the potential barrier $d$ were used as two crucial indices to describe the effects of contact conformation change. With our modified potential barrier model, the molecule–electrode contacts were considered as a modified tunneling model. In our modified tunneling junctions by using our modified SPM-BJT and fitting the data of the molecule–electrode contacts in single molecular junctions, we found that $\beta c$ changed linearly with extensions accompanied by a curvilinear mode force change. At a certain extension, $\beta c$ reached saturation. In contrast, for $G_C$ of the C8DT junction and all the C8DA junctions, $\beta c$ did not show strong dependence on the extensions, while the force changed linearly with extensions. The different changes of contact decay constant under extensions can help us to correlate the different single molecular conductance sets with the specific microscopic conformations of the molecule–electrode contacts. Our discussions bridged the directly observed experimental results to the simple physical model.

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