First-principles Study of the Electron Transport of Single Alkanedithiol Molecule under the Influence of Compression

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The effect of compression on electron transport of a single alkanedithiol molecule has been investigated by the first-principles method that combines the nonequilibrium Green's function technique and density functional theory. The compression effect on the transportation behavior has been discussed in terms of electronic structures and transmission spectra. The results demonstrate that compression of the molecule may affect the conductance dramatically.

As silicon-based microelectronics approaches its technological and physical limit, molecular electronics have received great attention in recent years.[1] The recent developments in nanofabrication, chemical synthesis, and atomic resolution characterization tools make it feasible now to construct molecular electronic devices and study their electron-transport properties.[2] Currently, many potentially useful molecular electronic devices, such as molecular wires, molecular rectifiers, molecular resonant tunneling rectifiers, molecular switches, and molecular storage devices as well as molecular motor have been proposed and studied extensively at real molecular level.[3] It is well recognized that many factors, such as the nature of the molecule itself, the interface configuration, the electrode material, and the electrode shape, may affect the electron-transport properties of a molecule sandwiched between two metal electrodes. Recently, it has been demonstrated experimentally that the compression of the molecule may greatly influence the electron-transport properties in alkanethiol/alkanedithiol molecules.[4] However, because of the high complexity, low observability, and limited controllability of the experiments, little information within the molecular-scale electronic devices can be obtained and accordingly hampers our understanding of the transport properties. It is not clear sometimes whether the measurement results are due to the molecule itself or artifacts.[5] First-principles theoretical studies will be very valuable in this effort by supplementing and guiding the experiments.[6] In this work, we present first-principles calculations on the electron-transport behavior of single alkanedithiol molecular junctions by considering the influence of compression.

The calculations follow two main processes. The initial geometry of the model molecule [–S–$(CH_2)_8$–S–] (referred to as C8) are optimized at the B3LYP/LANL2DZ level with Gaussian 03.[7] We use two small gold clusters for simulating the attachment to the metal leads. In this configuration, each gold cluster consists of three atoms that are placed as an equilateral triangle with sides of 2.88 Å to simulate the gold (111) surface. Sulfur atoms are always confined at the centers of the triangles, that is, the hollow site. The relative positions of gold atoms are frozen in each triangle, but the distance between the two clusters are relaxed during the geometric optimization.

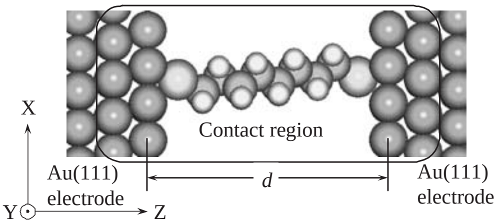

Figure 1. Schematic illustration of a C8 molecule sandwiched between two gold (111) electrodes.

After geometric optimization, the molecule except the two gold clusters [–S–$(CH_2)_8$–S–] (12.42 Å long) is translated into the gold junction with (111) surfaces (Figure 1). The distance between the two gold electrodes (referred to as *d*) is set to 16.92, 16.42, 15.91, and 15.41 Å, to mimic the molecular compression during conductance measurement by an atomic force microscope (AFM).[4] Then the atomic positions of the –S–$(CH_2)_8$–S– segment are relaxed until the residual forces are less than 0.05 eV/Å and follows the *I*–*V* calculations using the first-principles computer code TRANSIESTAC,[8] which is based on the Keldsh nonequilibrium Green's function (NEGF) technique combined with density function theory (DFT) calculations. In the above calculations, double-ζ plus polarization (DZP) basis set is chosen for all atoms except gold, for which single-ζ plus polarization (SZP) is used.

Figure 2a presents the current–voltage (*I*–*V*) curves of C8 junctions (Figure 1) with various *d* values. The current increases linearly when the bias is less than 0.1 V for all the systems. When the bias increases to larger than 0.1 V, a nonlinear feature is observed. With the *d* value decreasing (i.e., compression of the molecule), the molecular current increases evidently when the bias is less than 0.4 V. Further increasing bias tends to decrease the increment of molecular current, and at higher bias the molecular current even yields a negative increment. For example, the molecular current corresponding to a *d* value of 2.25 Å is higher than that corresponding to a *d* value of 2.00 Å when the bias increases to 0.9 V, suggesting that the compression of the molecule may decrease the current under high bias. This behavior is quite different from the AFM experimental results,[4] in which the tunneling current through the molecules always increases with increasing tip loading force. This discrepancy between the results from theoretical calculations and AFM experiments can be attributed to the following reason: Theoretical calculations consider only one molecule, while in AFM experiments several or even more molecules are involved in the molecular junction. Generally, in AFM experiments the contact junction area increases with increasing tip loading force, resulting in more molecules involved in the junction and accordingly increases the

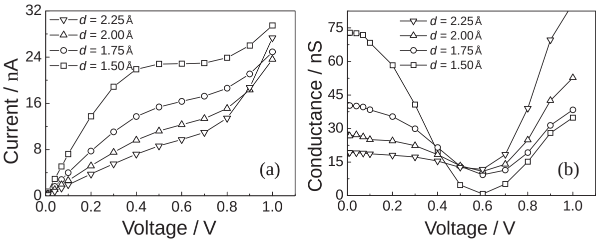

Figure 2. (a) Current–voltage (*I*–*V*) curves and (b) conductance–voltage (*G*–*V*) curves of C_8 junctions with various *d* values.

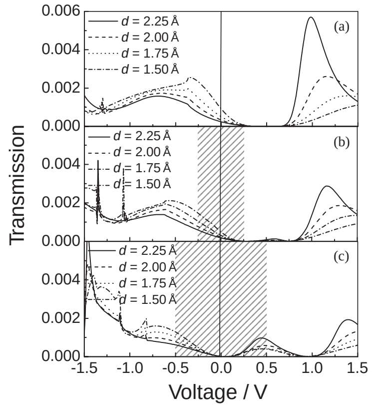

Figure 3. Transmission spectra of C_8 junctions with various *d* values under (a) 0.0, (b) 0.5, and (c) 1.0 V. The Fermi level is set to be 0.0 V, and the filled region represents the *bias window*.

current through the junction. Moreover, the chain-to-chain tunneling at a molecular junction under compression may also enhance the electron transport through molecules and even dominate the overall transport in addition to the already existing through-bond tunneling.[9]

The differential conductance of the C_8 junctions with various *d* values is shown in Figure 2b, from which we can see that the conductance decreases initially and then increases after ca. 0.5 V. The calculated single molecular conductances under *zero* bias are 19.30, 26.68, 40.26, and 72.76 nS for *d* values of 2.25, 2.00, 1.75, and 1.50 Å, respectively. These values are slightly larger than those obtained from experiments (1–20 nS).[10]

To understand the change of the *I*–*V* curves of C_8 junctions with different *d* values (i.e., different magnitude of molecular compression), we give the transmission spectra of the series C_8 junctions under 0.0, 0.5, and 1.0 V as shown in Figure 3. Under 0.0 V, with the *d* value decreases, the broad transmission peak below Fermi level increases gradually while the transmission peak above Fermi level decreases markedly. The transmission coefficients at Fermi level are 2.45×10^{-4}, 3.39×10^{-4}, 5.11×10^{-4}, and 9.25×10^{-4} for systems with *d* values of 2.25, 2.00, 1.75, and 1.50 Å, respectively. This is in good agreement with the order of zero bias conductances as shown in Figure 2b. This change of the transmission coefficient can be further understood from the shift of the HOMO and LUMO eigenvalues of the molecular projected self-consistent Hamiltonian (MPSH).[11] With the decrease of *d* values, the energy gap between MPSH HOMO and LUMO decreases (the HOMO–LUMO gap is 5.7 and 4.8 eV for *d* value of 2.25 and 1.50 Å, respectively). According to Simmons model,[12] the barrier height and width are the most predominant factors for electron transport. Since the barrier height is directly correlated with the HOMO–LUMO gap, the increase of the transmission coefficients under 0.0 V can be attributed to the decrease of the MPSH HOMO–LUMO gap.

When external bias is applied, both the transmission peak height and position change. Since the current is calculated by transmission integral within the range of $\pm|V|/2$ from the Fermi level (defined as *bias window*), the height of the transmission spectra within the *bias window* should be an excellent indicator of the molecular conductance. Under the bias of 0.5 V, the tail of the transmission peak below Fermi level enters the *bias window*, resulting in dramatic increase of the current. Another feature that should be noted is the appearance of a new transmission peak above the Fermi level though it is very low and does not enter the *bias window*. Under a bias of 1.0 V, the transmission peaks below the Fermi level are further decreased and shift away from the Fermi level. The new transmission peak above the Fermi level increases and enters the *bias window*. With the decrease of *d*, this new transmission peak decreases. Therefore, the increment of molecular current tends to decrease and even yields negative increment with the decrease of *d* (i.e., molecular compression).

In summary, we have studied the compression effect on electron transport through a single alkanedithiol molecule by NEGF and DFT methods. The results demonstrate that molecular compression may increase the molecular current under low bias while decreasing the molecular current under high bias.

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