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Theoretical demonstration of symmetric I – V curves in asymmetric molecular junction of monothiolate alkane

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ABSTRACT

A molecular junction of an asymmetric molecule generally demonstrates an asymmetric current–voltage (I – V) curve, due to the unequal voltage drops at the two molecule–electrode contacts. However, for asymmetric $\text{S}(\text{CH}_2)_n\text{CH}_3$ molecules, symmetric I – V curves are always obtained in the experimental measurements. Here, we investigate the electronic transport of the $\text{Au}-\text{S}(\text{CH}_2)_7\text{CH}_3-\text{Au}$ molecular junction in order to reveal the mechanism of the symmetric I – V curve with ATK package, in which the density functional theory is combined with Keldysh nonequilibrium Green's function method to calculate the electronic and transport properties of nanoscale systems. And the symmetric I – V curve can be interpreted by the curved surface model, which reproduces curved surface of the top electrode in the experiment.

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1. Introduction

In molecular electronics, generally, symmetric I – V curves are obtained for symmetric molecular junctions, while asymmetric ones correspond to asymmetric I – V curves. It is due to the asymmetric molecule–electrode contacts [1,2], resulting in the unequal voltage drops at the two molecule–electrode contacts [3,4]. However, for asymmetric monothiolate alkane $\text{S}(\text{CH}_2)_n\text{CH}_3$, symmetric I – V curves are obtained in the experimental measurements [5,6], and the reason is not clear yet [2].

Here, first-principles calculations are performed on the electrical transport properties of the self-assembled monolayer (SAM) junction, asymmetric $\text{Au}-\text{S}(\text{CH}_2)_7\text{CH}_3-\text{Au}$. And we illuminate the reason of symmetric curves observed in the experiments.

2. Theoretical approach

Nanoscale tunnel junctions of thiolalkane SAMs are usually formed by contacting a conductive probe atomic force microscopy (CP-AFM) to SAMs on metal substrates [5]. Considering the size of the contact area in CP-AFM junctions (about 50 nm^2) and a radius of curvature less than 10 nm for the tip [7], then the maximum separation between the molecule and the top electrode is around 9 Å . Thus, it is reasonable to introduce the curved electrode surface model to calculate the transport properties, as displayed in Fig. 1.

Our theoretical calculations were performed with the program ATK [8], in which the density functional theory is combined with Keldysh nonequilibrium Green function (NEGF) method to calculate the electronic and transport properties of nanoscale systems. In the calculation, the Perdew and Zunger exchange–correlation functional and standard norm conserving pseudopotential are used. The valence wave functions are expanded by localized numerical atom orbitals, with the single zeta plus polarization basis set for Au, C, and H atoms, while the double zeta plus polarization for S atom. The k-point sampling is 1, 1, and 99, respectively, in the x -, y -, and z -directions (z -direction is the transport direction).

3. Results and discussions

Fig. 2 illustrates the current–voltage curves of the $\text{S}(\text{CH}_2)_7\text{CH}_3$ molecule with different separations from the right electrode and the weighted summation of two asymmetric parts of currents. For 1.45 and 3.8 Å , asymmetric thioloctane molecule exhibits asymmetric I – V curves as depicted in Fig. 2(a) and (b), but they show a symmetric I – V curve with the ratio of 1.45 and 3.8 separations to be 0.4% and 99.6% , demonstrated in Fig. 2(d). And the ratio is reasonable because the case of separation 3.8 has more space to contact molecules than the case of separation 1.45 , therefore contributes more parts to the symmetric I – V curve. While the separation 2.25 Å directly shows a symmetric I – V curve in Fig. 2(c), which means the separation of the CH_3-Au interface balance the effect of the $\text{Au}-\text{S}$ binding and make equal voltage drops of the two molecule–electrode contacts under bias.

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Obviously, the change of the separation, thus the interaction between molecule and electrode, plays an important role in obtaining symmetrical I – V curves for asymmetric molecule measured in experiments [5].

The current $I(V)$ is determined by the transmission coefficient $T(E, V)$, which is the function of the energy E and bias voltage V , through the Landauer–Büttiker formula [9]

$$I(V) = (2e/h) \int T(E, V) [f_L(E) - f_R(E)] dE \quad (1)$$

where f_L/R is the Fermi distribution function of the left/right electrode. To understand the reason of the curved surface model

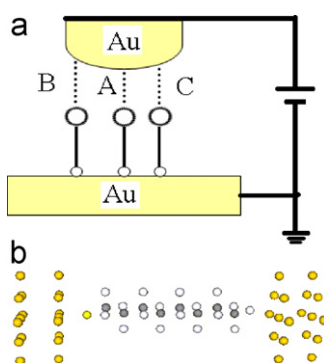


Fig. 1. (Color online) The simulation model of the Au–S(CH₂)₇CH₃–Au monolayer junction: (a) A, B, and C illustrate the separations of the molecule from the top electrode, which, respectively, are 1.45, 3.8, and 2.25 Å, while the separations from the substrate are the same. (b) Calculation model for ATK package: the right electrode is the top electrode in experiments.

resulting in symmetric I – V curves, we analyze the transmission spectra (T) at equilibrium and the evolution of T under bias voltages through the spatially resolved density of states (DOS).

Fig. 3 shows the transmission spectra of the thiolactane junction with these separations and the spatially resolved DOS corresponding to the peaks of the transmission coefficient. For different separations of the molecule from the right electrode, the peaks labeled by “R”, especially near the Fermi level, have different shapes, as depicted by Fig. 3(a), (b), and (c). But the spatially resolved DOS of these peaks all notably appear at both of molecule–electrode interfaces. For CH₃–Au interface, that means remarkable resonance between them (shown by Fig. 3(d)). And it is well known that the transmission coefficient is mainly determined by the two interfaces [1,2], especially by the CH₃–Au interface with weak interaction between them. All of these indicate that the separations, hence the interactions of the CH₃–Au interface, change the shape of the transmission coefficient near the Fermi level by influencing the resonance of the CH₃–Au interface.

And combined with the evolution of the transmission peaks under bias voltage [10,11], different separations of the right interface will generate different types of I – V curves. For example, in the case of 3.8 Å, the move of the transmission peaks labeled by “R” dominate the magnitude of the current since these resonance peaks are close to the Fermi level. Consequently a negative bias voltage applied to the left electrode results in the downshift of the energy points for the higher transmission peak, and then the area under the transmission coefficient near Fermi level will become larger, which means a larger electrical current through the two-probe system. However, a positive bias shifts the lower resonance peak near the Fermi level that result in a smaller one. Hereby, the current is larger for the negative bias than that of the positive

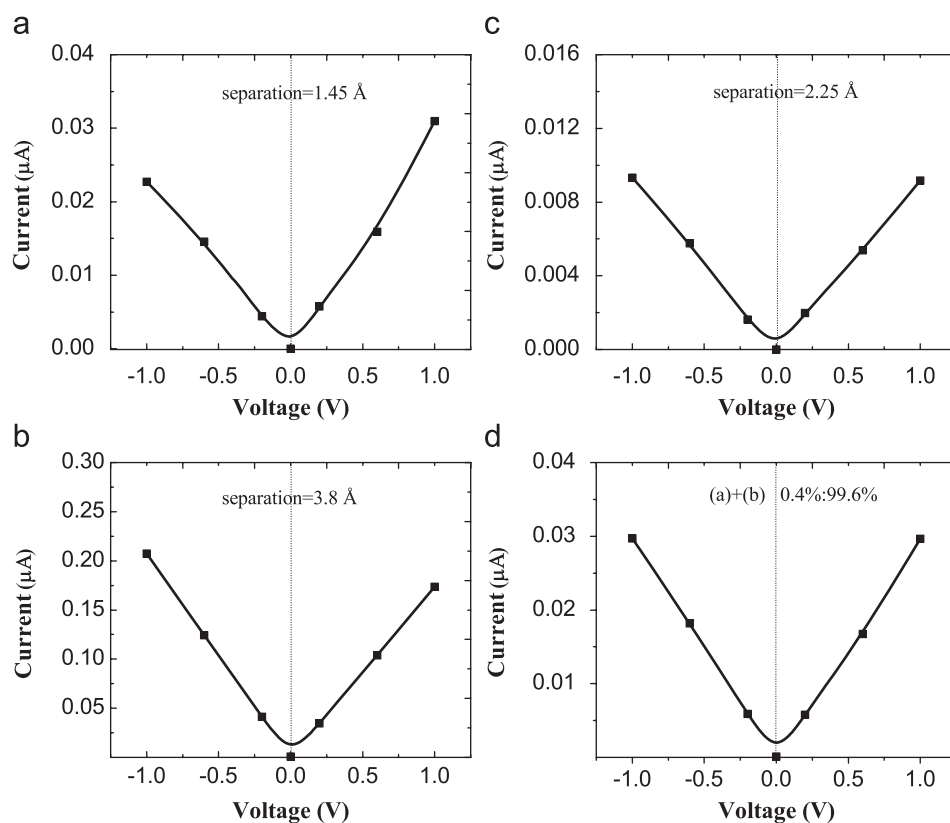


Fig. 2. The current–voltage characteristics of the monolayer junction with different separations between the right electrode and the molecule: (a) and (b) for separations 1.45 and 3.8 Å with asymmetric curves, (c) and (d) for separation 2.25 Å and weighted summations of the currents contributing from the 1.45 and 3.8 separations.

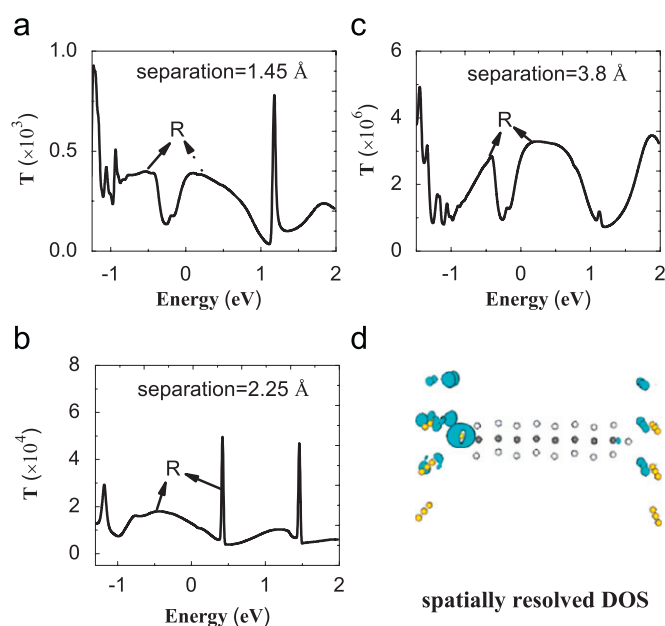


Fig. 3. (Color online) (a), (b), and (c) show the transmission spectra, respectively, with 1.45, 2.25, and 3.8 Å separations between the molecule and the right (top) electrode. (d) The spatially resolved density of states corresponding to the peaks near the Fermi level, labeled by “R”.

one, as presented in Fig. 2(b). The same analysis is also applicable to the other cases. Above all this point of view successfully explains the reason of different types of I – V curves correspond to different separations of the CH_3 –Au interface, and the key point is that the weighted summation of these curves gives a symmetric I – V curve.

4. Conclusion

In conclusion, the electrical transport properties of a typical thiolalkane monolayer junction was investigated by

first-principles based NEGF calculations. The symmetric current measured in the experiments for this kind of asymmetric monolayer junction is explained by the curved surface model, which reproduces the surface of the top electrode in the experimental measurements.

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