Electronic transport properties of phenylacetylene molecular junctions*

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(Received 30 March 2011; revised manuscript received 8 June 2011)

Electronic transport properties of a kind of phenylacetylene compound— (4-mercaptophenyl)-phenylacetylene are calculated by the first-principles method in the framework of density functional theory and the nonequilibrium Green's function formalism. The molecular junction shows an obvious rectifying behaviour at a bias voltage larger than 1.0 V. The rectification effect is attributed to the asymmetry of the interface contacts. Moreover, at a bias voltage larger than 2.0 V, which is not referred to in a relevant experiment [Fang L, Park J Y, Ma H, Jen A K Y and Salmeron M 2007 *Langmuir* **23** 11522], we find a negative differential resistance phenomenon. The negative differential resistance effect may originate from the change of the delocalization degree of the molecular orbitals induced by the bias.

Keywords: phenylacetylene compound, electronic transport, rectification

PACS: 73.63.–b, 85.65.+h, 31.15.ar **DOI:** 10.1088/1674-1056/20/10/107302

1. Introduction

Due to the potential applications offered by plastic electronic devices based on organic materials instead of traditional silicon-based semiconductors,[1] molecular electronics has received considerable attention in recent years. The main goal of molecular electronics is to reach the ultimate in miniaturization in future nanodevices, in which individual molecules play the role of conducting elements,[2,3] switches,[4] diodes,[5] and transistors.[6]

Ever since a concept for a molecular rectifier based on a single organic molecule was proposed by Aviram and Ratner,[7] a large amount of work has been devoted to molecular electronics.[8−19] With only a few exceptions, the most widely used molecular wire junctions have been formed so far by organic molecules that are assembled between gold electrodes via thiol anchoring groups. More recently, these efforts have been extended to the self-assembled monolayers (SAMs) of aromatic thiols[20,21] because of the potential applications in charge transfer control, organic electronics and anometer-scale patterning.[22]

As a candidate for building molecular devices, phenylacetylene compounds are promising because of their stability in air and against ultraviolet light, their rigid framework and the fact that they can be attached to gold via thiol-terminated groups.[23] Rapid advances in experimental techniques have realized the fabrication of SAMs of several kinds of phenylacetylene compounds such as (4-mercaptophenyl) anthrylacetylene (MPAA) and (4-mercaptophenyl)-phenylacetylene (MPPA).[23−25] Atomic force microscopy study of the mechanical and electrical properties of MPPA and MPAA monolayer films has been carried out. The conductivities of these SAMs were measured in the presence of relatively small biases.[23]

In this paper, we present a detailed theoretical study on the transport properties of MPPA molecular junctions with the first-principles method. Moreover, the bias voltage is extended to a relatively wide range compared with the experiments.

2. Model and method

In the present work, by using the first-principles computational method, we investigate the transport properties of the MPPA-based molecular junction as shown in Fig. 1. The MPPA molecule is switched be-

*Project supported by the Special Funds of the National Natural Science Foundation of China (Grant No. 11047148) and the Jining University Research Program, China (Grant No. 2010QNKJ04).

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tween two parallel Au(111) surfaces that correspond to the surfaces of the gold electrodes. The molecular wire junction is divided into three regions: the left electrode, the right electrode and the central scattering region, which actually includes a portion of the semi-infinite electrodes as the screening layers considering the coupling interaction between the MPPA molecule and the gold electrodes. Each layer of the electrodes is represented by a (3×3) supercell with periodic boundary conditions that imitate the bulk metal structure. The semi-infinite electrodes are calculated separately to obtain the bulk self-energy.[26]

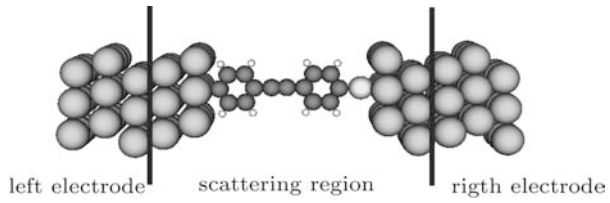


Fig. 1. Structure of molecular wire junction Au-MPPA-Au in our simulation.

The structure of a free thiol capped molecule wire is first optimized. Then the atomic structures of the molecule and the distance between two electrodes are optimized. The free molecular geometrical optimizations and the electronic transport properties of molecular junctions are calculated by a fully self-consistent NEGF formalism combined with the first-principles density function theory (DFT). In our calculations, the exchange–correlation potential is described by the generalized gradient approximation (GGA). Core electrons are modeled with the Troullier–Martins nonlocal pseudopotential[27] and valence electrons are expanded in a SIESTA localized basis set.[28] The single-zeta plus polarization (SZP) basis set for Au atoms and tge double-zeta plus polarization (DZP) basis set for other atoms are adopted. The current through a molecular junction is calculated from the Landauer–Butiker formula:

$$I = \frac{2e}{h}\int T(E, V_{\rm b})[f_{\rm L}(E-\mu_{\rm L}) - f_{\rm R}(E-\mu_{\rm R})]\,{\rm d}E,$$

where $T(E, V)$ is the transmission coefficient for electrons with energy E at bias voltage $V_{\rm b}$, $f_{\rm L/R}$ the Fermi function, and $\mu_{\rm L/R}$ the electrochemical potential of the left/right electrode.

3. Result and discussion

Figure 2 shows the transmission spectrum at zero bias. In order to demonstrate which molecular orbitals contribute to the transmission, we first plot the projected Hamiltonian energy spectrum in the figure with vertical short lines. The energy locations of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are −2.02 eV and −0.97 eV, respectively. The energy origin is set to be at the Fermi level $E_{\rm F}$ of the system. We can expect that electrons only with energy within a range near $E_{\rm F}$ can contribute to the current. LUMO which lies on the left of the energy origin is close to the Fermi level, suggesting that charge transport is dominated by LUMO at low bias voltage.

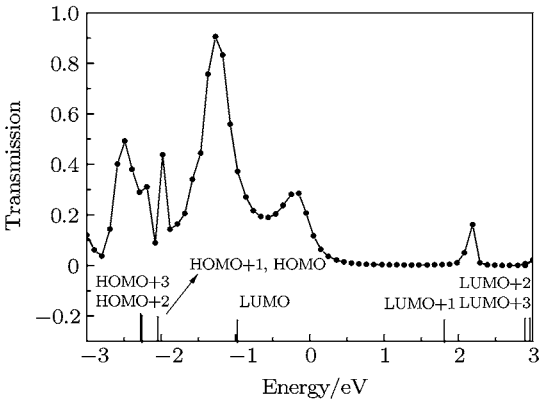


Fig. 2. Transmission spectrum of the system and the projected Hamiltonian energy spectrum (short vertical lines) at zero bias.

If we project the self-consistent Hamiltonian onto the Hilbert space spanned by the basis functions of the extended molecule, we obtain the molecular projected self-consistent Hamiltonian (MPSH). The eigenstates of MPSH can be considered as molecular orbitals renormalized by the molecule–electrode interaction. Figure 3 shows several MPSH orbitals near the Fermi level of the electrodes. From the figure it can be recognized that these orbitals can be divided into two groups. For HOMO, LUMO, and LUMO+1, the charge density distribution spreads over the orbitals. These orbitals are delocalized. For the others, the charge density is localized at the right interface between the molecule and the electrode, at the benzene ring or at the triple C bond. It is known that if the charge density distribution of the molecular orbital is delocalized, it is easy for electrons with energies comparable to the delocalized molecular orbital to tunnel from one electrode to the other. When the energies of the peaks in the transmission spectrum are compared with the eigenvalues of MPSH, it can be found that the transmission peaks near the Fermi level at −1.98 eV, −1.22 eV, 2.19 eV are mainly contributed by HOMO, LUMO, and LUMO+1, respectively. It is worth while

noting that a transmission peak appears at 0.15 eV, however, there is no molecular orbital corresponding to it. This phenomenon will not appear in isolated molecules. The peak is related to the so-called metal-induced gap state, a mixture of the metallic surface state and the extended molecular state.[16,17]

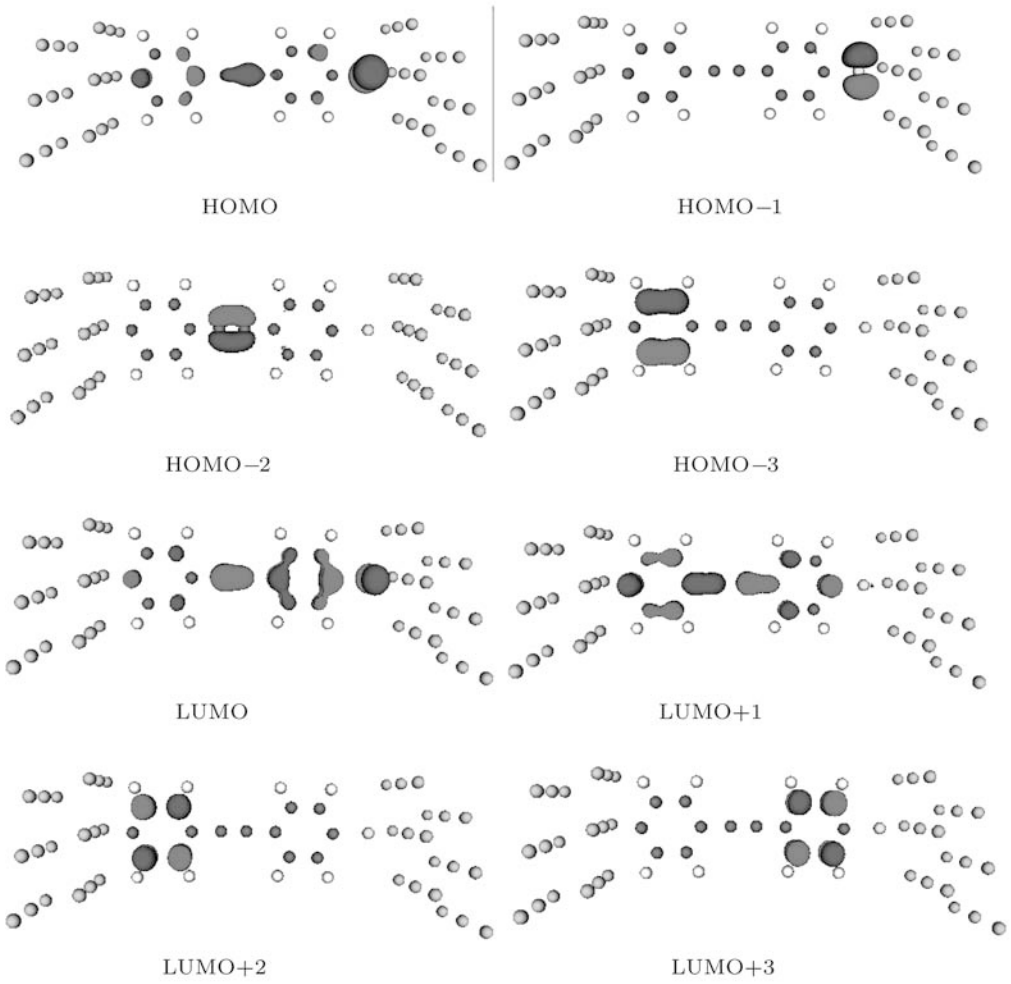


Fig. 3. MPSH orbitals from HOMO-3 to LUMO+3 at zero bias.

We plot in Fig. 4 the I–V characteristic of the system. With the increase of the positive bias voltage the current increases rapidly, which indicates that some transmission channels are opened. However, in the negative bias, the values of the current undergoes a long step until the bias voltage reaches 1.8 V at which the transport channel LUMO+1 is opened. Recent experiments have concentrated on the atomic microscopy study of the mechanical and electrical properties of monolayer films of phenylacetylene compounds, including MPPA, MPAA, and some derivatives of MPAA.[25] Significant rectifying behaviour was not observed in MPPA films in the bias voltage range (−1.0 V, 1.0 V). For our system the rectification ratio ($I(V_\mathrm{b})/I(-V_\mathrm{b})$) is also small, less than 1.8, in the same bias voltage range. When the bias is further increased, an obvious rectification behaviour is found. For example, the rectification ratio reaches 4 at bias voltage 2.0 V. A great deal of effort has been devoted to the design of the molecular rectification and the explanation of the rectification mechanism since a concept for single molecular rectifier was proposed.[29,30] The rectifying behaviour observed here is relatively simple. The molecule structure is symmetric except for the interface contacts. The contacts between the molecule and the electrodes are S–Au and C–Au contacts separately.

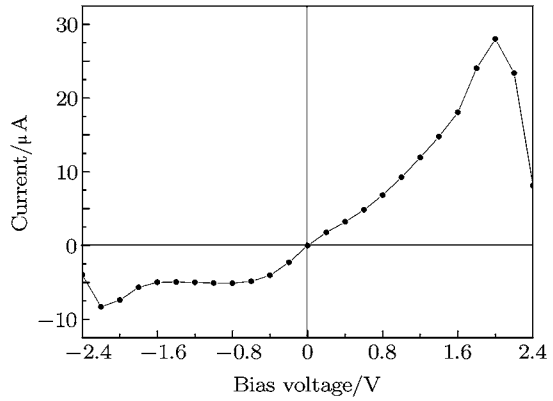


Fig. 4. Current–voltage curve for the system at bias voltage in a range from −2.4 V to 2.4 V.

Moreover, it is interesting to find that when the bias voltage is higher than 2.0 V, the current decreases as the bias voltage increases, which is the negative differential resistance (NDR) effect. In order to understand the origin of the NDR phenomenon, we illustrate in Fig. 5 the energy shift of frontier molecular orbitals with the increase of bias voltage. These orbitals shift towards lower energy except HOMO and HOMO–1. Figure 6 displays these MPSH orbitals at bias voltage V_b = 2.0 V and 2.4 V. These two bias voltages are corresponding to the maximum and minimum of the current in NDR region. At bias voltage V_b = 2.0 V, it is clear that LUMO, LUMO+1, HOMO–1 are delocalized, corresponding to opened transport channels which lead to a large current of about 30 μA. LUMO+3 is partially delocalized because the charge density on the sulfur atom bonding with the right electrode is nearly zero, that is, the S–Au interface coupling is extremely weak. However, when the bias voltage is increased to V_b = 2.4 V, we find that HOMO–1 turns localized and HOMO–2 becomes delocalized. The delocalization degrees of LUMO and LUMO+1 show almost no change with the bias voltage increasing. Therefore, we can infer that the NDR behaviour at higher bias voltage originates from the change of the delocalization degree of the molecular orbitals, which is induced by the bias voltage.

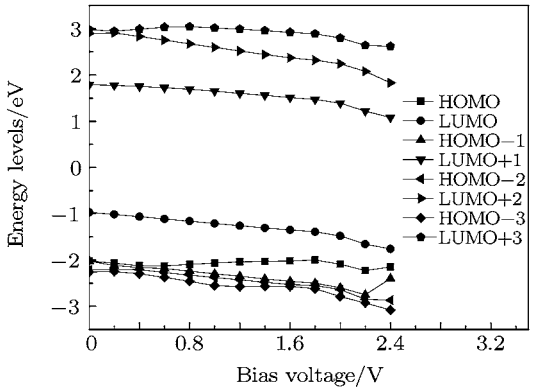
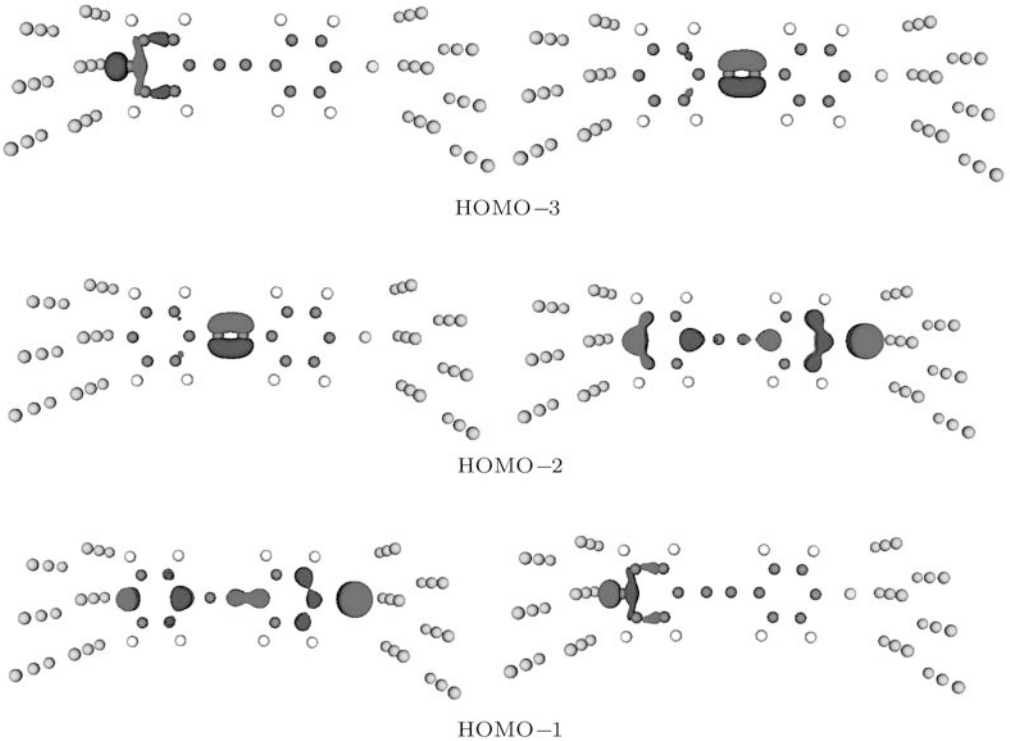


Fig. 5. Energy shifts of frontier molecular orbitals from HOMO–3 to LUMO+3 in a bias voltage range from 0.0 V to 2.4 V.



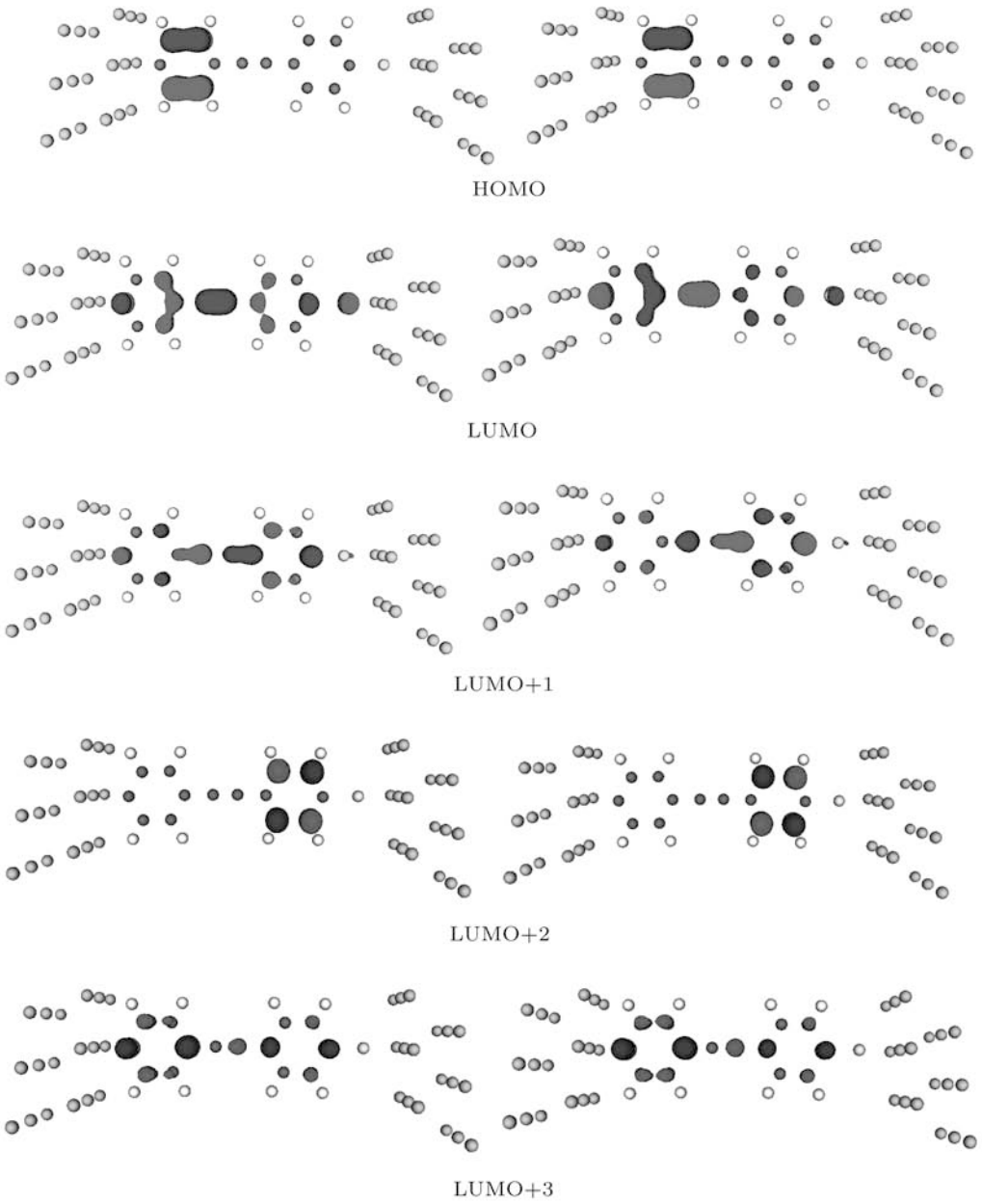


Fig. 6. MPSH orbitals from HOMO–3 to LUMO+3 at bias voltage $V_b = 2.0$ V (left column) and $V_b = 2.4$ V (right column).

4. Conclusion

It is known that phenylacetylene compounds are promising candidates for building molecular devices. In this paper, we investigate the electronic transport properties of a kind of phenylacetylene compound—(4-mercaptophenyl)-phenylacetylene (MPPA) with the first-principles method. The system shows an obvious rectifying behaviour at a bias voltage larger than 1.0 V. The rectification effect is attributed to the asymmetry of the interface contacts. Moreover, at a bias voltage larger than 2.0 V, which is not referred to in a relevant experiment, we find an NDR phenomenon. The NDR behaviour may originate from the change in the delocalization degree of the molecular orbitals, induced by the bias.

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