

Current rectification by asymmetric molecules: An *ab initio* study

Yan-hong Zhou

Department of Physics, Jangxi Normal University, Nanchang 330022, China

Xiao-hong Zheng

Key Laboratory of Material Physics, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, Anhui 230031, China

Ying Xu^{a)} and Zhao Yang Zeng

Department of Physics, Jangxi Normal University, Nanchang 330022, China

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Current rectification effect in an asymmetric molecule $\text{HCOO}-\text{C}_6\text{H}_4-(\text{CH}_2)_n$ sandwiched between two aluminum electrodes has been studied using an *ab initio* nonequilibrium Green's function method. The conductance of the system decreases exponentially with the increasing number n of CH_2 . The phenomenon of current rectification is observed such that a very small current appears at negative bias and a sharp negative differential resistance at a critical positive bias when $n \geq 2$. The rectification effect arises from the asymmetric structure of the molecule and the molecule-electrode couplings. A significant rectification ratio of ~ 38 can be achieved when $n=5$. © 2006 American Institute of Physics. [DOI: 10.1063/1.2409689]

I. INTRODUCTION

Electronic transport properties of single molecule junctions have gained tremendous interest in recent years since they may have wide variety of important applications in future electronic components such as transistors, diodes, and switches.¹⁻⁵ With the advantages of experimental techniques, for example, scanning tunneling microscope and mechanically controllable break junction,⁶⁻⁸ measurement of current through nanoscale systems is now allowed. A lot of interesting behaviors, such as highly nonlinear I - V characteristics, negative differential resistance (NDR), and electric switching behavior, are found in various systems such as organics,⁹ carbon nanotubes,¹⁰ DNA,¹¹ etc. Meanwhile, a considerable amount of theoretical work has been performed to study transport properties of molecular devices.

Rectification, one of the most important functions in a traditional electronic component, has also been suggested and observed in molecular devices. Some mechanisms for rectification phenomena in such devices have been suggested.¹²⁻¹⁵ The first molecular rectifier was proposed by Aviram and Ratner in 1974 using D - σ - A molecules, where D and A are, respectively, an electron donor and an electron acceptor, and σ is a covalent "sigma" bridge (insulator). In this model, the inelastic electron transfer is more favorable from A to D , rather than in the opposite direction, thus rectification happens. However, electrical rectification was observed in experiment only recently, specifically, in Langmuir-Blodgett multilayers or monolayers of the molecule $\text{C}_{16}\text{H}_{33}\text{Q}-3\text{CNQ}$ sandwiched between metallic electrodes.¹⁶⁻¹⁸ The physical mechanism, which was first considered to be a possible implementation of the Aviram-Ratner mechanism, is of somewhat different D - π - A type. Although

the molecule does show rectification, it behaves as an anisotropic insulator rather than a conductor because of the long alkane tail $\text{C}_{16}\text{H}_{33}$. In fact, the current is of the order of 10^{-17} A/molecule for the structure $\text{Al}/\text{C}_{16}\text{H}_{33}\text{Q}-3\text{CNQ}/\text{Al}$ and 10^{-15} A/molecule for the structure $\text{Au}/\text{C}_{16}\text{H}_{33}\text{Q}-3\text{CNQ}/\text{Au}$ in Ref. 9, which is too small for practical application. To achieve good rectification by a molecule with a reasonable conductivity, one should avoid using molecules with long saturated groups, which would make them prohibitively resistive. Then, a suggestion to use relatively short molecules with certain end groups to allow their self-assembly on a metallic electrode's surface seems to be very attractive. In a previous literature, the transport through two phenyl rings connected to electrodes by asymmetric alkane chains (molecule $(\text{CH}_2)_m-\text{C}_{10}\text{H}_6-(\text{CH}_2)_n$) has been studied.¹⁹ It suggests a new mechanism of molecular rectification, where a single electroactive unit is positioned asymmetrically with respect to electrodes and the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are positioned asymmetrically with respect to the Fermi level. With most of the applied voltage dropping on the longer insulating barrier, the conditions for resonant tunneling through the level are achieved at very different voltages for the two opposite polarities. A maximum rectification ratio of about 35 is obtained with longer alkane chains $n=10$ and $m=2$, but the current is small, with the order of 10^{-10} A. Recently, good rectification is demonstrated in diblock oligomer diode molecule¹⁴ and single C_{59}N molecule.²⁰ But the current reported in both the two references (Refs. 14 and 17) is still of the unsatisfactory order of 10^{-10} A. In this work, we perform a systematic study

on the transport properties of a single molecule $\text{HOOC}-\text{C}_6\text{H}_4-(\text{CH}_2)_n$. Some of our findings are interesting. First, a significant rectification ratio of ~ 38 is achieved at a

^{a)}Electronic mail: yingxu@jxnu.edu.cn

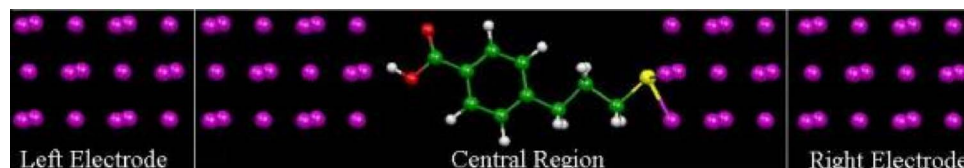


FIG. 1. (Color online) Model structure of a two-probe system with a single molecule $\text{HOOC-C}_6\text{H}_4\text{-(CH}_2\text{)}_n\text{-S}$ coupled to two Al(100) electrodes.

bias of 1.2 V for much shorter alkane tail ($n=5$), and a feasible current of the order of 10^{-8} A is observed, two orders larger than those reported in Refs. 14 and 19. Second, the rectification effect persists in a much wider region than in previous investigations. We even also get rather high rectification ratios in other configurations, such as ~ 24 for $n=3$ and ~ 28 for $n=7$.

The paper is organized in the following way: the computation method and the device model are presented in Sec. II, the results and discussion are given in Sec. III, and a short summary comes in Sec. IV.

II. METHOD AND MODEL

The calculations for transmission and current-voltage (I - V) characteristics have been performed using a recently developed first-principles package TRANSIESTA-C method, which is based on the nonequilibrium Green's function (NEGF) technique. The TRANSIESTA-C, as is implemented in the well tested SIESTA method, is capable of fully self-consistently modeling the electrical properties of nanoscale devices that consist of an atomic scale system coupling with two semi-infinite electrodes as shown in Fig. 1. Such nanoscale devices are divided into three parts: left and right electrodes and a central scattering region. In fact, the central region includes a portion of the semi-infinite electrodes. The external potential bias takes part in the self-consistent calculation directly. Therefore, the effects of the bias voltage on the electronic structure of the system can be fully considered. Details of the method and relevant references can be obtained elsewhere.²¹⁻²⁴ In our calculation, the convergence criterion for the Hamiltonian, charge density, and band structure energy is 10^{-4} and the atomic cores are described by norm conserving pseudopotentials.

The model structure for our theoretical analysis is illustrated in Fig. 1. The single molecule $\text{HOOC-C}_6\text{H}_4\text{-(CH}_2\text{)}_n$ with sulfur end is sandwiched between the two Al(100) electrodes with finite cross section. The electrode is chosen from the perfect Al crystal along the (100) direction, and the number of atoms in each atomic layer is arranged as 5, 4, 5, 4, Four Al atomic layers (5, 4, 5, 4) are selected for the electrode cell. The single molecule $\text{HOOC-C}_6\text{H}_4\text{-(CH}_2\text{)}_n$ with sulfur end together with four surface atomic layers in the left electrode and three surface atomic layers in the right electrode is chosen as the central scattering region, as indicated by two vertical lines. The structure of every molecule $\text{HOOC-C}_6\text{H}_4\text{-(CH}_2\text{)}_n$ with sulfur end is optimized via Hartree-Fock calculations by ARGUSLAB (Refs. 25-28) and the energy convergence of 10^{-10} kcal/mol has been achieved. The molecule-electrode distance is fixed to be a constant for all the systems: the distance between the left

terminal H atom and the Al surface is 1.5 Å and it is 1.0 Å between the right S atom and Al surface. Both the left H atom and the right S atom lie above the surface center of the electrodes.

III. RESULTS AND DISCUSSIONS

Firstly, the equilibrium conductance as a function of the number n of CH_2 has been studied and is presented in Fig. 2. We find that the conductance decreases exponentially as the increase of number n . The conductance is $0.15G_0$ ($G_0=2e^2/h$, conductance quantum) for $n=0$, $0.043G_0$ for $n=1$, $0.0043G_0$ for $n=2$, $0.00026G_0$ for $n=3$, etc. The exponential decrease of conductance with the length increase of carbon chains has been found in other literature.²⁹

The I - V curves are plotted in Fig. 3 (the cases $n=4, 6$ are not shown). When $n=0$ and 1, the current takes a large value both at the negative bias and at the positive bias. When $n \geq 2$, the current through the molecule structure increases rather slowly with the increase in the negative bias, but increases quickly in the positive bias and reaches its maximum at a certain bias. A significant rectification ratio of ~ 38 is found when $n=5$, where the negative bias current is negligible. For every configuration, a strong NDR is shown under positive bias, which indicates a potential application of switches.

From the transport properties indicated by the I - V curves, we are faced with two essential questions. One is why the rectification can be observed only when the number of CH_2 exceeds 1, and the other is the underlying mechanism of rectification and NDR. Two essential conditions for rectification are that the resonance must be very sharp and happens at one vicinity side of the Fermi energy.³⁰ The $T(E)$ spectra are plotted in Fig. 4 for $n=0, 1$, and 2 cases. We can see from Fig. 4 that the resonance is rather wide for $n=0$ case and it has a long tail near the Fermi energy. A direct comparison reveals that the resonance in the case $n=1$ is wider than that in the case $n=0$, but moves toward right. However, the resonance becomes much more narrow and

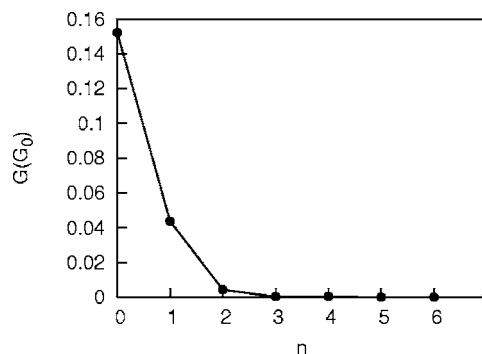


FIG. 2. The equilibrium conductance as a function of the number n .

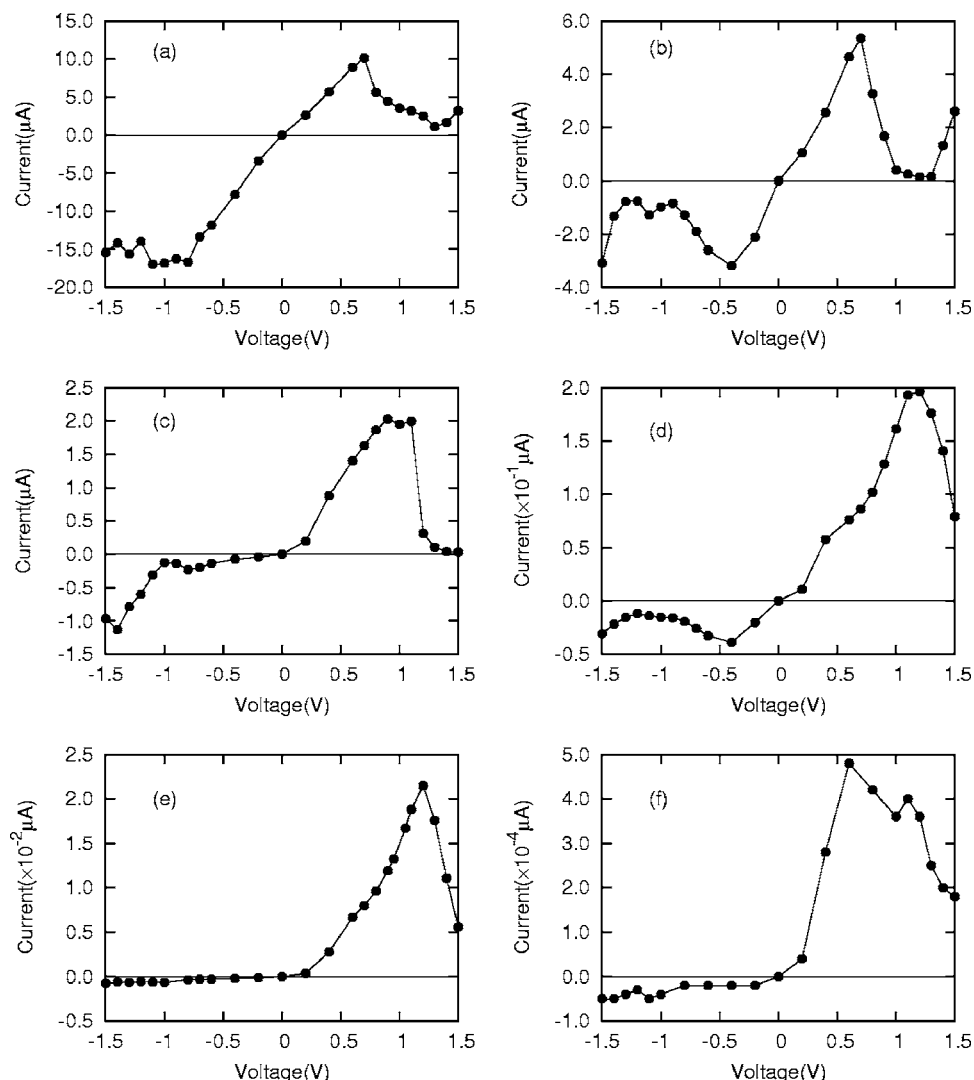


FIG. 3. The current-voltage (I - V) curves for single molecules of $\text{HOOC}-\text{C}_6\text{H}_4-(\text{CH}_2)_n$; (a) $n=0$, (b) $n=1$, (c) $n=2$, (d) $n=3$, (e) $n=5$, and (f) $n=7$.

only has values on the right side of the Fermi energy for the case $n=2$. The reasons are the following: when $n=0$, the sulfur atom is directly attached to the benzene, thus the orbital of the lone electron pair of the sulfur overlaps with that of the π electrons of the ring, resulting in molecular orbitals distributed almost over the ring and the sulfur, which can be verified in Fig. 5(a), where both the LUMO and HOMO distribute almost over the whole molecule. Since the sulfur is

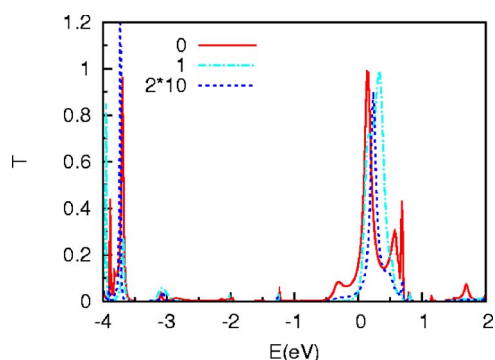


FIG. 4. (Color online) The equilibrium transmission T as a function of energy E for $n=0, 1$, and 2 . For comparison, the transmission for $n=2$ has been magnified by 10.

directly coupled to the electrode, the molecular orbital is broadened. In the $n=1$ case, the sulfur is separated from the ring by a single insulating $-\text{CH}_2-$ group. However, the separation between them is not large enough to prevent elongated p orbitals of sulfur and sp_3 hybridization of carbon from direct overlapping which can be verified in Fig. 5(b), where the LUMO and HOMO still distribute almost over the whole molecule. As a result, the electronic level is still much broadened. The case changes radically for $n=2$. Two insulating groups move the sulfur away from the ring by 4.09 \AA , so that direct overlap between the sulfur and the ring wave function becomes very small and the LUMO and HOMO do not distribute on the left $(\text{CH}_2)_2$ (which is not shown). That is why rectification is obtained only for $n \geq 2$.

To probe clearly the origin of rectification and NDR, we take the molecule $\text{HOOC}-\text{C}_6\text{H}_4-(\text{CH}_2)_5$ as an example. With the LUMO energy of the molecule being 0.394 eV when coupled to two Al electrodes, and the HOMO energy -2.896 eV , we can get the conclusion that the molecule conducts via the LUMO which can also be known from the T - E relation at zero bias voltage (Fig. 6). Two transmission peaks induced by the renormalized HOMO and LUMO are clearly observed at ~ -2.9 and 0.4 eV , while the LUMO-

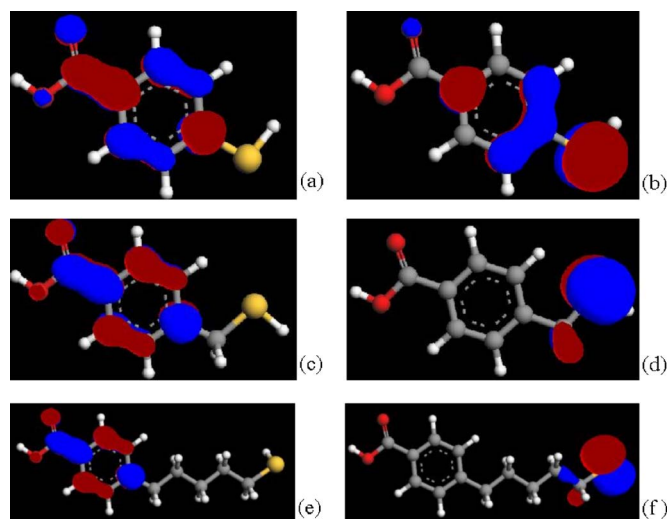


FIG. 5. (Color online) The LUMO and HOMO distributions on the molecule for $n=0, 1,$ and $5,$ respectively: (a) LUMO for $n=0,$ (b) HOMO for $n=0,$ (c) LUMO for $n=1,$ (d) HOMO for $n=1,$ (e) LUMO for $n=5,$ and (f) HOMO for $n=5.$

induced peak is very close to the Fermi level. We can see from Fig. 5(c) that the LUMO distributes over the $-\text{COOH}$ and the carbon atoms in benzene ring and the HOMO mainly on the sulfur atom. The electron has an accessible LUMO near the Fermi energy only on one electrode, in this example the left electrode. This asymmetry leads to significant current in the positive bias direction and negligible current under rather high negative bias. A quantitative explanation will be given in the following.

The calculated transmission spectra $T(E, V_b)$ are presented in Fig. 6 for different applied bias voltages from -1.5 to 1.5 V (each curve is vertically shifted for clarity, representing a difference of 0.2 V for bias range $[-0.6, 0.6]$ and 0.1 V for the remaining bias voltages). The dashed line represents the transmission spectrum at equilibrium. The current is obtained using the Landauer-Büttiker formula: $I = \int_{\mu_L}^{\mu_R} T(E, V_b) dE$. The bias window contributing to the current integral above is indicated by the two dotted lines in

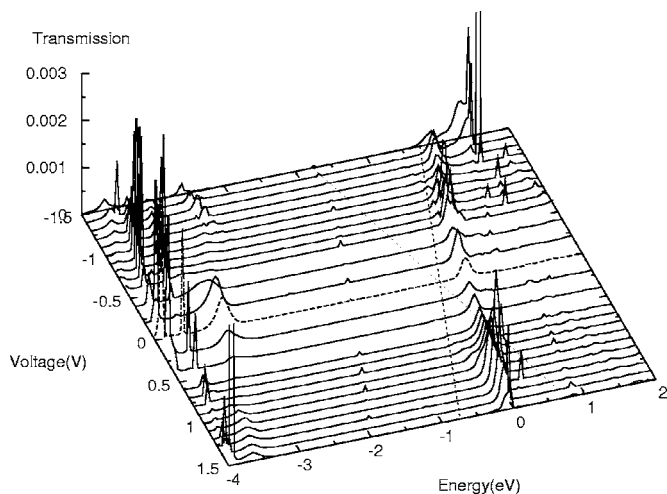


FIG. 6. Transmission spectra, $T(E, V_b),$ for the $n=5$ case. The two crossing dotted lines indicate the bias window.

Fig. 6. The transmission resonance in equilibrium happens on the right side of the Fermi energy, and its width is narrow, about 0.13 eV. With the increase of the positive bias, the resonance moves toward the Fermi level and enters the bias window and makes contributions to the current, so the current increases rapidly and reaches its maximum at the bias of 1.2 V. However, with the increase of the negative bias, the resonance moves far away from the Fermi energy and is pushed out of the bias window, resulting in negligible current. So rectification happens. A notable rectification ratio of ~ 38 is obtained at bias of 1.2 V. When the bias continues to increase, the transmission coefficient within the bias window is degraded in magnitude and width, leading to a NDR phenomenon.

IV. CONCLUSION

A system of $\text{HOOC}-\text{C}_6\text{H}_4-(\text{CH}_2)_n$ is studied systematically using a first-principles method based on NEGF. The equilibrium conductance decreases exponentially with the increase of the number n of CH_2 . Strong rectification effect is obtained when $n \geq 2$ and a significant rectification ratio of ~ 38 is gained from $n=5$ at the bias of ± 1.2 V. Irrespective of the number of CH_2 , a strong NDR is shown under positive bias, which indicates a potential application of switches. A detailed analysis on the origin of rectification is given from the distribution of the HOMO and LUMO and from the transmission spectra at various biases.

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