

Rectifying and conductance switch behaviors of molecular devices modulated by intramolecular hydrogen bonding



Yang Song^a, Zhen Xie^a, Ming-Zhi Wei^{a,b}, Jian-Cai Leng^{a,b}, Zong-Liang Li^a, Chuan-Kui Wang^{a,*}

^a College of Physics and Electronics, Shandong Normal University, Jinan 250014, China

^b College of Science, Qilu University of Technology, Jinan 250353, China

ARTICLE INFO

Article history:

Received 12 January 2015

Received in revised form 5 June 2015

Accepted 6 June 2015

Available online 18 June 2015

Keywords:

Hydrogen bonding

Conductance switch

Rectification

Single-molecule junction

Nonequilibrium Green's function method

ABSTRACT

By applying nonequilibrium Green's function method in combination with density functional theory, we theoretically investigate the effect of intramolecular hydrogen bonding on transport properties of a new synthesized α -hydroxyphenyl pyridine molecular diode (Wang and Yu, 2011). Numerical results show that intramolecular hydrogen bonding presents obvious influence on rectifying behaviors of the diode, as the hydrogen bonding could rotate the adjacent aromatic rings into coplanar structure. Appropriate contact configurations between the molecule and electrodes are shown to be important for obtaining the experimental rectifying characteristics. Furthermore, bistable state configurations related to the intramolecular hydrogen bonding are obtained and conductance switch behavior is presented. Accordingly, a molecular conductance switch with high On–Off ratios is proposed. The analysis of molecular projected self-consistent Hamiltonian and the spatial distribution of frontier molecular orbitals as well as the transmission coefficients reveals the mechanism of these consequences.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

With miniaturizing electronic devices in nanoscale, molecular devices have been paid much attention to both experimentally and theoretically in recent years. Among those molecular devices, nano wires [1,2], rectifiers [3–8] and switches [9–14] are located at the center of concerns. Especially the nano wire, as one basic element in constructing molecular circuit, needs to be studied primarily. Previous researches have shown that conductance of molecular junctions is closely related to their molecular configuration, for instance, dihedral angles between adjacent aromatic rings could manage current values prominently [15,16]. Recently, Wang et al. have experimentally modulated charge transports of molecular junctions by adjusting dihedral angles between adjacent aromatic rings [17]. In this work, intramolecular hydrogen bonding has been used to change molecular configurations. The molecular conductance and rectifying behaviors caused by intramolecular hydrogen bonding have an obvious variation. Nevertheless, to the best of our knowledge, there is no detailed theoretical analysis on the experimental measurement.

Using nonequilibrium Green's function method combined with density functional theory, we calculate the charge transport

properties of molecular junction with α -hydroxyphenyl pyridine motif. The effect of intramolecular hydrogen bonding is analyzed. In order to simulate the experimental circumstance, asymmetric electrode configurations are introduced, which are shown to have obvious influences on rectifying behaviors of molecular diodes [18,19]. Our results are in good agreement with the experimental measurements. Furthermore, bistable state configurations related to the intramolecular hydrogen bonding are observed, which brings a conductance switching behavior. On the basis of this observation, we design a molecular switch with giant On–Off ratio, which may serve as novel molecular switches pursued in molecular circuits.

2. Computational details

In order to investigate the hydrogen bonding effect in molecular conductance, single molecule consisting of α -hydroxyphenyl pyridine motif which is sandwiched between two Au (111) surfaces as illustrated in Fig. 1, is adopted as our computational model. The entire molecular junction contains three regions: a left electrode, an extended molecule and a right electrode. Two semi-infinite gold electrodes are simulated by a $4 \times 4 \times 3$ unit cell and the periodic boundary conditions are applied in the electrode calculation. Three Au surface layers at each molecule end are included into the extended molecule region. Then, the screening effects can be

* Corresponding author. Tel.: +86 531 86180892.

E-mail address: ckwang@sdu.edu.cn (C.-K. Wang).

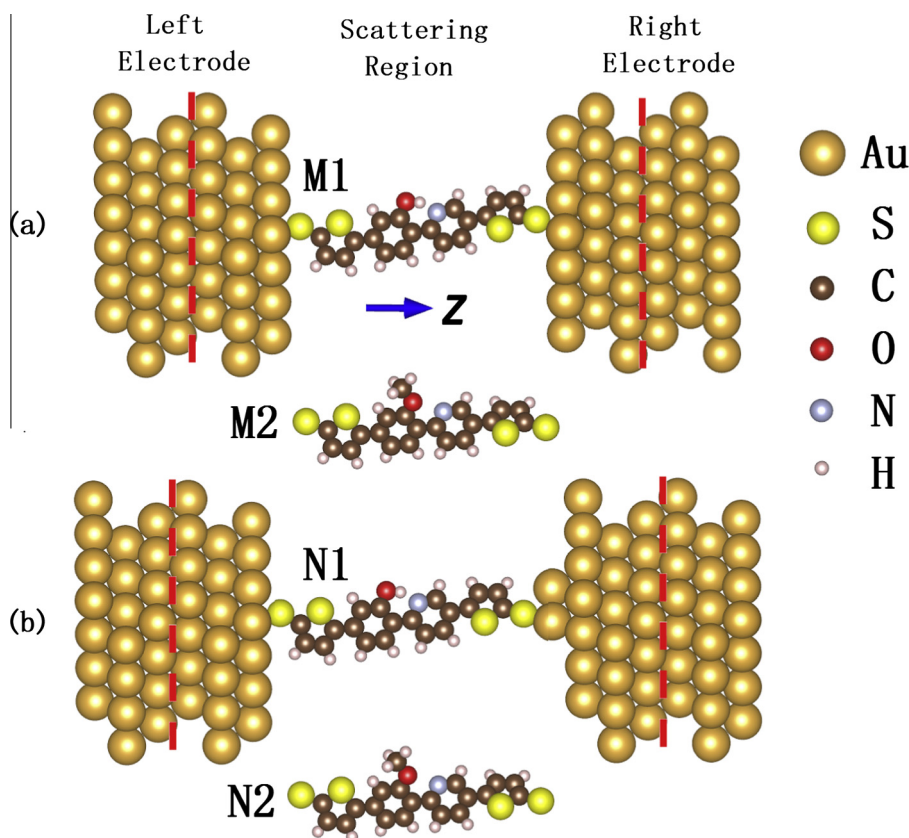


Fig. 1. Schematic structures of molecular junctions. (a) Symmetric contact configuration, (b) asymmetric contact configuration.

taken into account. In Fig. 1, there are four molecular devices considered here, denoted as M1, M2, N1 and N2. Fig. 1(a) shows the symmetric molecule–electrode contact arrangements, where the surfaces of both electrodes are planar, while Fig. 1(b) gives models with asymmetric electrode interfaces to simulate the Au STM tips in experiments. Besides, the hydrogen atom of hydroxyl in device N1 can be moved to the other side of the oxygen atom over an energy barrier around 0.87 eV, presenting a metastable state. And our results show that the energy difference is 0.56 eV between the stable state and the metastable state. Therefore, it can be affirmed that both of these two states can exist stably, being similar with previous research [20]. Then, bi-stable configurations of intramolecular hydrogen bond are investigated to explore their effect on the transport properties of the molecular junction. Switch behaviors caused by structural changes are highlighted. Moreover, two new molecular junctions with four intramolecular hydrogen bonds are designed to enhance the switching effect. The energy difference between them is calculated to be 3.1 eV. The structure of the bare molecule is optimized first in the SIESTA package [21]. When the molecule couples with the electrodes, the extended molecule is optimized, and the maximum force is 0.02 eV/Å. During this optimization, we freeze the relative positions of the Au atoms on each side, but relax the distance between two Au clusters along the z axis (namely the transport direction).

In the SIESTA and TranSIESTA [22] calculations, we use numerical atomic orbitals as the basis set, and apply Troullier–Martin-type norm-conserving pseudopotentials represent the core electrons [23]. An energy shift parameter of 100 meV is chosen for generating the cutoff radii of the pseudoatomic orbitals. The generated gradient approximation (GGA) adopts the Perdew–Burke–Ernzerhof (PBE) exchange–correlation functional [24]. A single- ζ plus single polarization (SZP) basis set is employed in

depicting Au atoms and a double- ζ plus single polarization (DZP) basis set is prepared for the other atoms. Generated by the Monkhorst–Pack method, the Brillouin zones are sampled with a 4×4 grid of k -points. The grid sampling is chosen as 300 Ry mesh cutoff. The convergence criterion for the density matrix is 10^{-4} . The current through the junctions is calculated by the Landauer–Büttiker formula, as shown below:

$$I = \frac{2e}{h} \int T(E, V) [f(E - \mu_L) - f(E - \mu_R)] dE$$

where $T(E, V)$ is the bias-dependent electron transmission coefficient which is defined as $T(E, V) = \text{Tr}[\Gamma_L G_M \Gamma_R G_M^\dagger]$. $\Gamma_{L(R)}$ is the coupling matrix between the scattering region and the left (right) electrode, and G_M is the retarded Green's function of the extended molecule. f in the Landauer–Büttiker formula is the Fermi–Dirac distribution function under different energies and $\mu_{L(R)}$ is the electrochemical potential of the left (right) electrode.

3. Results and discussions

3.1. Effect of intramolecular hydrogen bonding on charge transport

With the optimized structures of M1 and M2, one can see that there are different dihedral angles between adjacent aromatic rings due to the intramolecular hydrogen bonding. The product of $\cos^2\theta$ values for these molecular junctions is calculated, in which the value of M1 is 0.82 that is larger than 0.34 of M2 (Table 1). The previous results have shown that conductance of aromatic molecules is positively correlated with the $\cos^2\theta$ [15,16]. Therefore, a higher current can be expected in device M1, the junction with intramolecular hydrogen bonding. As shown in Fig. 2, the current values of the molecular junctions with symmetric planar

Download English Version:

<https://daneshyari.com/en/article/1560160>

Download Persian Version:

<https://daneshyari.com/article/1560160>

[Daneshyari.com](https://daneshyari.com)