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Ambient Molecule Effects on the Electronic Transport of Pyrene-1,8-dithiol Molecular Junction

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Abstract. Due to the small size, single-molecule device may be sensitive to the ambient molecules. Thus, it is significant for fabricating single-molecule sensors to understand the influence of ambient molecule on molecular device. Based on the *ab initio* calculations combined with non-equilibrium Green's function method, the adsorption effects of H_2O, CO_2 and NO_2 molecule on the pyrene-1,8-dithiol molecular junctions are studied systematically. The numerical results show that, the influence of H_2O or CO_2 molecule on the pyrene-1,8-dithiol molecular junction is very slight when they are adsorbed on the pyrene-1,8-dithiol molecules, which attributes to the closed-shell ground states of these two molecules. Different from H_2O and CO_2 molecule, being a radical, NO_2 molecule shows obvious influence on the electronic transport of pyrene-1,8-dithiol molecular junctions. The system with NO_2 adsorbate is more conductive in the positive and lower negative bias regime than those of the other two molecular systems, which is due to the evident coupling between the states of NO_2 molecule and pyrene-1,8-dithiol molecule.

1. Introduction

Due to the rapid progress of single molecular technologies, great achievements have been obtained for single-molecule-device fabrications in recent years [1-15]. In the meantime, different strategies were developed to control and improve the functional properties of single-molecule device [16-18]. The effects of molecule-electrode interfaces [19-21], electrode distance [16,22], molecular anchor [23-25], side group [26-28], external field [29-31], external ambient [32,33], doping [18,34] and contamination [35-38] have been studied intensively. Attribute to the micro-dimension, the performance of single molecular device is easily affected by the external environment. The extent of the influence is not only related to the structure of the functional molecule, but also related to the surrounding molecule. It is important to understand the effects of surrounding molecule adsorption on the surface of functional molecule for which can provide the environmental information for building molecular devices [39]. According to the information one can know that: 1) which kind of functional molecule is more sensitive to the ambient molecule, and to which ambient molecule; 2) in what condition the performance of molecular devices can be unaffected or affected very slightly. Thus the optimal condition can be provided properly to build molecular device. Additionally, the molecular gas sensors can be also constructed by the corresponding study.

Since graphene is first discovered by Dr. Novoselov and Professor Geim in 2004 [39,40], the two-dimensional crystal have gained significant attention in condensed matter physics, chemistry, nanotechnology, and material science [39,41]. Particularly, graphene is an excellent adsorbent for its large specific surface area, rich pore structure and strong adsorption, which attracted many researchers to investigate the adsorption properties of graphene with gas molecule adsorbates extensively. Studies show that graphene is a potential material for gas sensors [36,37,39]. Pyrene can be seen as 2×2 graphene segment with the edge being saturated by H atoms. Therefore, pyrene may have some properties similar to the graphene, although the small size must result in obvious different characters from large surface graphene. Thus in this paper, the adsorption effects of the single H_2O, CO_2 and NO_2 molecule on pyrene molecule are studied systematically. In order to connect the functional molecule with gold electrodes, the S atoms are used to replace two H atoms at the two end of the pyrene molecule to form pyrene-1,8-dithiol molecule (denoted as PDT). Our studies show that, the H_2O and CO_2 adsorbate have slightly influence on the electronic transport of PDT molecular junction. However, the NO_2 adsorbate changes the current of PDT molecular junction with different extent in different bias regime.

2. Theoretical methods

In order to investigate the adsorption effects of H_2O, CO_2 and NO_2 molecules on the PDT molecular junctions, we sandwiched PDT molecule into the separation of two gold electrodes with H_2O, CO_2 or NO_2 molecule adsorbed on pyrene molecule backbone to form Au—PDT+H_2O/CO_2/NO_2—Au systems (see Figure. 2.1). The geometries of PDT molecular junctions with or without adsorbate molecules were optimized with a maximum force of 0.05 eV/Å in the Atomistix ToolKit (ATK) package. The Troullier–Martin type norm-conserving pseudopotentials are applied to represent the core electrons[42], the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) formulation is applied as the exchange-correlation functional[43,44]. For Au atoms, a single-ζ plus polarization basis set is used, and for other atoms, a double-ζ plus polarization basis set is employed. According to the Landauer– Buttiker formula[45], the current with different bias for the molecular junction is written as

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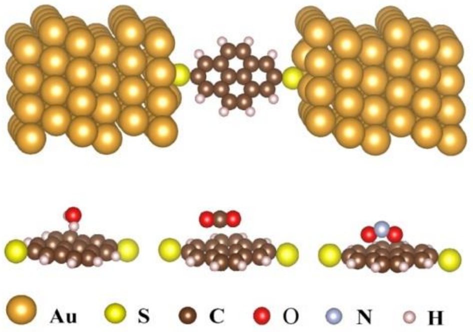

Figure 2.1: Schematic structures of PDT molecular junctions without or with $H_2O/CO_2/NO_2$ molecule adsorbed

$$I = \frac{2e}{h}\int T(E,V)[f(E-\mu_L)-f(E-\mu_R)]dE \qquad (1)$$

where, $T(E, V)$ is the transmission probability. μ_L and μ_R are the electrochemical potentials of the two electrodes. The transmission probability $T(E, V)$ is calculated by non-equilibrium Green's function (NEGF) method employing the ATK package. After current calculations, the differential conductance is obtained by $G = \partial I / \partial V$. A 5×5 k-point grid was used for the Brillouin-zone (BZ) sampling in the transverse directions.

3. Results and discussion

The geometric optimizations show that, the O atom of H_2O, the C atom of CO_2 and the N atom of NO_2 are all approximately sited on the top position of one central C atom of pyrene molecule with the perpendicular distances of about 0.36 nm, 0.31 nm and 0.34 nm, respectively. The geometries of the PDT molecules are changed very slightly with the effects of H_2O, CO_2 or NO_2 molecule adsorbate. The affinities for the three molecules adsorbed on the PDT molecules are 0.23 eV, 0.21 eV and 0.30 eV, respectively. One can see that the affinity of nonpolar CO_2 molecule is relatively weaker than those of the other two. While for the radical molecule NO_2 adsorbed on the PDT molecule, the affinity is obviously stronger than those of H_2O and CO_2 molecules adsorbed on the PDT molecules, which is due to the open-shell ground state of NO_2 molecule.

Figure 3.1 shows the currents and differential conductances of PDT molecular junction and the junctions with H2O, CO2 or NO2 adsorbate as functions of bias voltage. To our surprise, both the dipolar H2O molecule and nonpolar CO2 molecule adsorbed on the PDT molecules have little effects on the electronic transport of PDT molecular junction. Only the NO2 molecule has obvious influence on the electronic transport of the molecular junction. The peak conductance values appear at about ±1.0 V for the PDT molecular junctions with or without adsorbates. Figure 3.1(a) shows that the system with NO2 adsorbate is more conductive in the positive and lower negative bias regime than those of the other molecular systems. However, the differential conductance for the system with NO2 is decreased more rapidly when the positive bias is larger than 1.0 V. For the negative bias, the NO2 molecule only performs small effect on the current and differential conductance of the PDT molecular system.

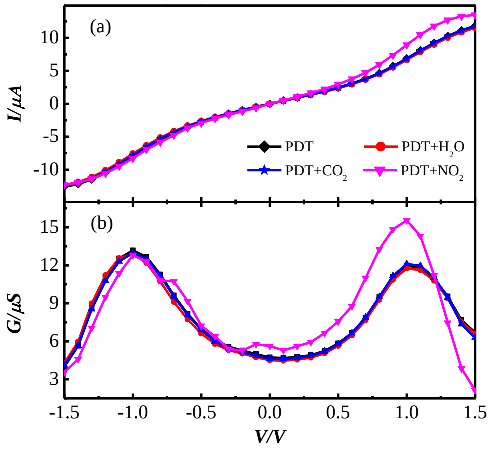

Figure 3.1: Electronic transport properties of PDT molecular junctions with H_2O, CO_2 and NO_2 molecule adsorbate. (a) Current and (b) Differential conductance as functions of applied bias voltage.

In order to understand why only NO_2 adsorbate has obvious effect on the electronic transport of PDT molecular junction, we present electronic transmissions of these four molecular junctions in Figure. 3.2. The figure shows that, for the bias of 0.0 V, the transmission shows a high and wide peak in the negative energy regime with a sharp transmission peak located on it. With the absolute value of the bias increasing, the height of the wide transmission peak decreases and slightly shifts to the high energy regime, however, the sharp transmission peak located at about -0.93 eV is slightly influenced by the change of bias voltage. The transmissions for the systems with H_2O and CO_2 molecules are almost unchanged in the bias windows. The main differences of transmissions for the system with H_2O and CO_2 molecules from the system without adsorbate are presented at about -1.0 eV, which

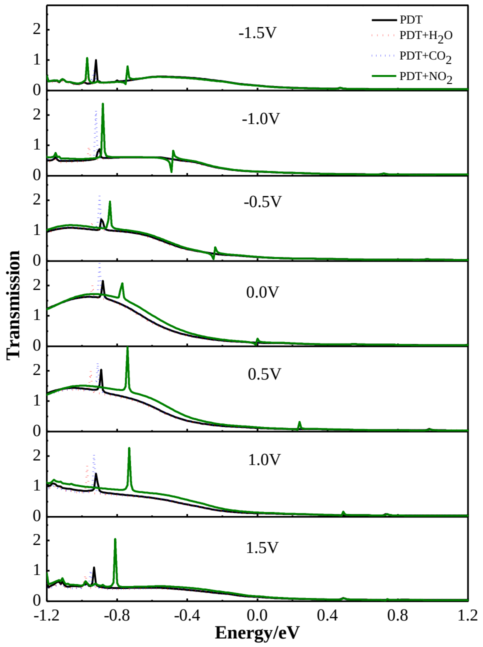

Figure 3.2: Transmission spectra of PDT molecular junctions without or with H_2O, CO_2 or NO_2 adsorbate