



First-principles study of the electronic transport properties of a dihydroazulene-based molecular optical switch



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ABSTRACT

By using non-equilibrium Green's function formalism combined with density functional theory, we investigate the electronic transport properties of a dihydroazulene molecule with the open and closed configurations by photo-excitation sandwiched between two Au electrodes. This study demonstrates the current through the closed configuration is significantly higher than that of the open configuration, indicating that the dihydroazulene molecule can be used as molecular optical switch within a stable switching ratio at finite bias. The mechanisms of the molecular switch are in detail analyzed by transmission spectra, spatial distribution of molecular orbitals and molecular projected self-consistent Hamiltonian (MPSH) states.

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1. Introduction

In recent years, molecular device has intrigued tremendous research interests because of many prominent properties such as negative differential resistance [1–3], molecular rectification [4,5], field-effect characteristics [6], and molecular switch [7–13], which can be widely used in future molecular electronics. Among all kinds of properties, a molecular switch is a critical element of modern design in logic and memory circuits. The realization of the molecular switch is achieved through single molecule with bistable states, high conductance state and low conductance state, which can be reversibly transformed between each other in response to environmental stimuli, such as mechanical control [14], redox reaction [15] and photo-excitation [16]. Among those, optical switch is of quite importance as a stimulus to the feasibility of addressing, quick response time as well as a wide range of condensed phases [17]. There are lots of photochromic molecules such as azobenzene [18,19] and diarylethene [20–22], whose realizations of molecular switch mainly depend on the change of molecular structure under optical stimulation. For instance, the azobenzene molecule has two stable structural states under the stimulus of light: the “trans” and the “cis” states. Two convertible configurations of the diarylethene molecule, one being “open”

form and the other being “closed” form, are caused by the photo-excitation. As a result, the reversible change of molecular structure leads to molecular switch when the molecule is connected to metal electrodes.

Just as the diarylethene [20–22], the dihydroazulene molecule can also reversibly achieve the conformational change from one geometric state to the other state under the irradiation of UV light (365 nm) and thermal relaxation [23]. Both geometric states, which correspond to a closed and an open form of the molecule, are shown in Fig. 1. Thus we investigate the switching properties of the dihydroazulene molecule with the open and closed configurations sandwiched between two Au electrodes. It is shown that the current through the closed form is larger than that of the open form. These attractive properties make the dihydroazulene molecule useful in molecular electronics applications.

2. Computational methods

The schematic structures of the molecular devices are shown in Fig. 1. The dihydroazulene molecule with two configurations is bonded to two gold electrodes linked by sulfur atom, which is called two-probe system. The system is divided into three regions: left electrode, right electrode, and central scattering region. There are three gold layers in each electrode, which means Au (111) – (4 × 4) supercell. The central scattering region includes the dihydroazulene molecule and the two gold layers on each electrode

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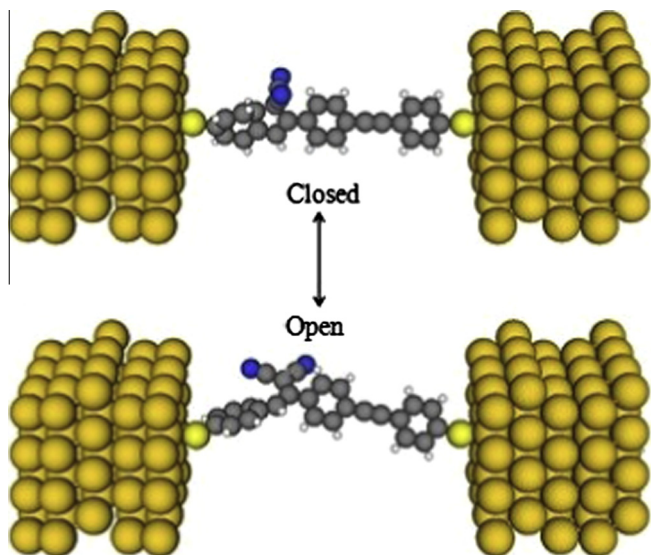


Fig. 1. Schematic structures of two molecular devices. The yellow, gray, white, blue and golden balls represent S, C, H, N, and Au atoms respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

side to screen the perturbation effects of the central region. The sulfur atom is located at the hollow site of the Au surface. The distance between the Au surface and the sulfur atom is 2.0 Å, which conforms to the reasonable distance range (1.90–2.39 Å) used in lots of theoretical studies [24–26]. The geometrical optimization and electronic transport properties are all calculated by non-equilibrium Green's function formalism (NEGF) combined with first-principles density functional theory (DFT) as implemented in the Atomistix Toolkit (ATK) [27,28] package. The core electrons are described by norm-conserving pseudo-potentials and the exchange–correlation potential is represented by the local-density approximation (LDA) [29]. A double-zeta plus polarization (DZP) basis set is used for all atoms of the molecule, and a single-zeta plus polarization (SZP) basis set is used for Au atoms. The convergence criterion is set to 1×10^{-5} for grid integration to obtain accurate results. The k-points sampling is 3, 3, and 500 in x , y , z direction respectively. A mesh cutoff energy of 150 Ry is selected to achieve a balance between the calculation efficiency and the accuracy. Then, the current of whole device is obtained from the Landauer–Büttiker formula [30]:

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

where $\mu_{L/R}$ are the electrochemical potentials of the left and right electrodes. Under external bias, the electrochemical potential $\mu_{L/R} = \mu_{L/R} \pm eV/2$ is used. The energy region of the transmission spectrum that contributes to the current is referred to as the bias window. The transmission coefficient of the device is

$$T(E, V) = \text{Tr} [\Gamma_L(E) G^R(E) \Gamma_R(E) G^A(E)] \quad (2)$$

where $\Gamma_L(E)$ and $\Gamma_R(E)$ denote the broadening functions of the left and right electrodes respectively; $G^R(E)$ and $G^A(E)$ represent the retarded and advanced Green functions of the central region.

3. Results and discussion

The currents through the molecular junction with closed and open configurations in the bias range from 0 to 2.0 V are plotted in Fig. 2(a). One can see that the currents of the closed form increase quickly with the increases of the bias, while the currents

of the open form are tiny in the bias region from 0 V to 1.4 V. Beyond 1.4 V, the current of the open form increases rapidly. From the figure, we can also find that the current of the closed configuration is larger than that of the open one. So the molecular junction of the dihydroazulene molecule can shift controllably upon photo-excitation from the closed configuration (high conductance state) to the open configuration (low conductance state), and vice versa. The current switching ratio, $R(V) = I_{\text{Closed}}/I_{\text{Open}}$ as a function of applied bias is also shown in Fig. 2(b). At the zero bias, we calculate the switching ratio using the zero-bias conductance. As shown in Fig. 2(b), the switching ratio varies from about 32 to 40 in bias region from 0 V to 1.4 V and changes little. However, it falls rapidly beyond 1.4 V. The switching ratio is obviously affected by the applied bias which also appeared in previous studies [18,20]. Therefore, the relatively stable switching ratio in a low bias region suggests that this molecular switch can be used in the application of future molecular electronics. Our calculated I – V characteristics show that the closed system exhibits high conductance which agrees with a recent experimental study of the reversible photo isomerization of dihydroazulene (DHA)/vinylheptafulvene (VHF) system [31]. They found that the conductance of DHA (closed form) is higher than that of the VHF (open form).

According to the Landauer–Büttiker formula, the current is directly dependent on the transmission amplitude. The transmission coefficient at a given energy E corresponds to the transmission probability of an electron incident at this energy through the molecular junction. To understand the switching mechanism of the two isomers, we compute the energy dependence of total zero-bias voltage transmission in Fig. 3(a). The average Fermi level, an average value of the chemical potentials of the left and the right electrodes, is set to zero. The positions of MPSH eigenvalues are marked with squares and circles for the closed and open form respectively. From Eqs. (1) and (2), we can know that only electrons with energies within a range near the Fermi level E_F contribute to the electronic transport. As shown in Fig. 3(a), the two isomers have significantly different transmission spectra around the Fermi level respectively. From the calculation, the equilibrium conductance of open form ($0.0011G_0$, $G_0 = 2e^2/h$) is much lower than that of closed form ($0.0397G_0$). The transmission spectrum of the closed form has two broad and strong transmission peaks locating at HOMO and LUMO below and above the Fermi level E_F , respectively, which means the electrons can easily transport through the scattering region. However, for the open form, though the transmission peak of HOMO of the open structure moves toward to the Fermi level, its transmission coefficient of HOMO drops significantly. The transmission peak of LUMO of the open form is farther from the Fermi level E_F than that of the closed form. What is more important, there are only very weak transmission peaks in the vicinity of the Fermi level, which accounts for the low conductance in the open form. In Fig. 3(b), we also show isosurface plot of transmission eigenstates at E_F with two forms. The transmission eigenstate of eigenchannels of the whole system is seen as a scattering state, which displays the coupling between the molecule and two electrodes. From Fig. 3(b), the transmission eigenstates are both delocalized on the molecule and the left electrode. For the closed form, there are a few more transmission eigenstate in the right electrode, while there is barely any transmission eigenstate of the open form. Therefore, the better coupling between the molecule and the right lead of the closed form results in the favorable transport channel for electron to transport through the whole device, which agrees with the transmission spectra shown in Fig. 3(a). On the whole, the conductance of the open form is smaller than that of the closed form at low bias, which results in an obvious switching behavior.

To make a further analysis on the features of transmission spectra and transport characteristic of two molecular junctions, we

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