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Research paper

Intermolecular interaction effect on the inelastic electron tunneling spectroscopy of bi-octane-monothiol junctions

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ABSTRACT

The inelastic electron tunneling spectroscopy (IETS) of bi-octane-monothiol junctions is theoretically studied based on first-principles calculations. The results reveal that IETS is very sensitive to the vertical and lateral distance of the two molecules in the bimolecular junctions owing to the changes of interaction between the two molecules. It is further demonstrated that the transverse vibrational modes ν(C-H) around 0.38 V will be triggered when the two molecules are close to each other and open a new path for electron tunneling. Our theoretical results provide new insight into understanding the origin of the IETS peaks around 0.38 V.

1. Introduction

Since Aviram and Ratner initially proposed the concept of molecular rectifier in 1974 [1], the application of single molecule or molecular monolayer in electronic devices has attracted much attention in the past few decades [2–9]. Although great progress has been achieved, there are still some challenges in the study of single molecular junctions, such as the uncertainty of the contact configurations between molecules and electrodes, the determination of the molecular geometry and even the numbers of molecules in the junctions. All these factors can significantly influence the charge transport properties of molecular junctions. Thus the accurate determination of molecular junctions has become important and urgent issue. Inelastic electron tunneling spectroscopy (IETS), which can be obtained by performing the second derivative of the current to the bias voltage, has been proven as a powerful tool to determine the geometric details of molecular junctions by combining the theoretical and experimental spectra [10–14]. Through making accurate assignments and interpreting peaks in the IETS, one can confirm the geometrical structure of molecular junctions and actual bonding situations [11–18]. Luo's group has demonstrated that IETS can also be a powerful technique for studying intermolecular interactions inside junctions [19].

Alkane-thiol molecules are classic prototype of molecular junctions for IETS studies, which have attracted wide attentions recently [19–26]. However, the relative intensity of IETS peaks obtained by different research groups for the same type of molecule are different, especially the spectral peak around 0.38 V, which is caused by C-H stretching vibration. The controversy about the origin of the ν(C-H) spectral peaks lasted for a long time until Beebe and Lin confirmed that this mode was attributed to the CH_2 groups closest to the anchoring thiol from both experiments and theoretical simulation [27,28]. At the same time, Okabayashi's group inferred that intermolecular tunneling also played an important role on the intensity of these peaks [29]. Inspired by this, we investigated a series of bi-octane-monothiol junctions to explore the effect of the intermolecular interaction on the IETS, especially the intensity of C-H stretching vibration. The influence of intermolecular interactions on the IETS is also systematically studied by adjusting the vertical and lateral distances between two molecules.

2. Computational details

As shown in Fig. 1, in our simulation models, two face-to-face octane-monothiol molecules are sandwiched between two semi-infinite gold electrodes with each molecule oppositely connected to one electrode through its terminal thiol group. The backbone of octane-monothiol molecules lies in *yoz* plane. To save computational efforts while still obtaining good coupling energies between the electrodes and molecules, we replace the semi-infinite gold

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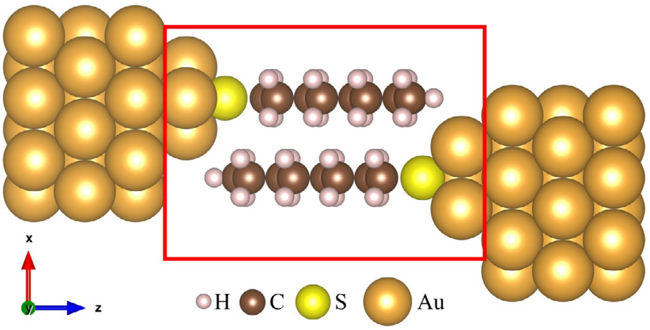

Fig. 1. Schematic of the bi-octane-monothiol junction. The solid red frame highlights the extended molecular system. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

electrodes with two equilateral triangle gold atomic clusters. And the terminal sulfur atoms are located at the hollow sites of gold atomic clusters, where a strong chemical bond is formed between each sulfur atom and gold atoms. The extended molecule investigated in this work consists of the two gold atomic clusters at both sides and bi-octane-monothiol molecules. Therefore, the extended molecule is treated as an isolated system and not periodic in all directions. In all calculations, the S-Au and Au-Au bond length are fixed to be 0.285 nm and 0.288 nm, respectively [11,12,30].

For each of the configurations of extended molecules used in the following, geometry optimizations are conducted at the density functional theory (DFT) level using B3LYP [31] functional and the LanL2DZ [32] basis set in the GAUSSIAN 03 program package [33]. During the optimization, all atoms in the octane-monothiol molecules are relaxed until each component of the force on atom is less than 0.03 nN (0.02 eV/Å). The IETS are calculated by means of the QCME program, which implements a generalized quantum chemical method for the elastic and inelastic transport in molecular junctions developed by Luo's group [34]. The formalisms and more details can be introduced in Refs. [11,30,35].

3. Results and discussion

Firstly, we investigate the effect of vertical distance between the two molecular planes on the profile and intensity of IETS. Here, we denote the vertical distance between two molecular planes by *dx*, which is initially set to be 0.66 nm as shown in the inset of Fig. 2. At this stage, the sulfur atom of each octane-monothiol molecule has been set the same (y, z) coordinates with the carbon atom of the terminal methyl group of the other octane-monothiol molecule. The distance between the two equilateral triangle gold planes is 1.218 nm, and there is a tilt angle of about 40.0° for the octane-monothiol molecules with respect to the normal vector of the gold plane. Then, the upper octane-monothiol molecule is pushed along the negative x axis with a step of 0.1 nm till the distance between the two molecular planes *dx* reaches 0.26 nm. The IETS of the bi-octane-monothiol junctions at each *dx* are correspondingly calculated and shown in Fig. 2(a)–(e). From Fig. 2, one can easily see that the IETS are very sensitive to the vertical distances, and these spectra can be divided into three parts (plotted in red[1], green and blue solid lines, respectively). In the first part (the red lines), the intensities of peaks below 0.05 V are very strong. These peaks come from the vibration of the gold atoms and the group motion of the molecule toward the electrode. The vibration peaks in the second part are located between 0.10 V and 0.20 V, which are plotted in green lines in Fig. 2. These peaks are attributed from the molecular vibrations, and involve the vibrational modes of ν_s(C-C) and $w(CH_2)$. It is interesting that more vibrational modes of the octane-monothiol molecule are manifested in the IETS with the decrease of *dx*. Furthermore, an in-plane rocking vibrational mode β (CH_2) in transverse direction also appears when *dx* is as small as 0.26 nm, which is in evidence that the intermolecular interaction between molecules promotes the inelastic electron tunneling. For the third part plotted in blue lines, there is hardly any obvious IETS peak above 0.20 V when *dx* is larger than 0.36 nm. However, when the vertical distance *dx* is reduced to below 0.36 nm, the ν(C-H) modes around 0.38V become quite obvious, and have significant contributions to the IETS when *dx* is further decreased to 0.26 nm.

It is noted that the IETS peaks around 0.38 V in Fig. 2(e) are mainly contributed by four vibrational modes, namely, $\nu_{as}(CH_3)$, $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$. These four vibrational modes are schematically shown in Fig. 2(f)–(i). Further analysis reveals that the relative higher IETS peak at 0.37 V mainly contributed by $\nu_{as}(CH_3)$ arises from the strong coupling between the terminal CH_3 group of one molecule and the gold electrode where the other molecule is attached, and the coupling decrease between the C atom closest to the S atom and the other molecule. However, the IETS peaks at 0.38 V are contributed by $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ vibrational modes, which are triggered by the strong interactions between the two molecules. This observation directly verified the Okabayashi's deduction theoretically. It should be noted that, easily seen from Fig. 2(h) and (i), these two vibrational modes locate at the C atoms nearest to the terminal S atoms. This will result in a quick decrease in the intensity of IETS peaks around 0.38 V as the two molecules are pulled apart along the molecular backbones, which will be discussed in the following context.

From the above discussions, we can see a strong dependence of the IETS profile as well as the relative intensity of IETS peaks on the vertical distance of the two molecular backbone planes. As is well-known, electron tunneling relies heavily on the length of the tunneling path. The length of such bimolecular junction is closely related to the overlap of the two octane-monothiol molecules. Therefore, it is highly needed to investigate the effect of the overlap between two octane-monothiol molecular backbones on the IETS profile. This would facilitate understanding the inelastic electron tunneling pathway in self-assembled molecular layers. In what followed, we fix the vertical distance between the two molecular backbone planes to be 0.26 nm and pull the lower molecule along the backbone axis of the octane-monothiol molecule. The step Δl is set to be 0.129 nm, which equals to the projected length of C—C bond to the backbone axis (see inset, Fig. 3(b)). At this stage, as shown by the pictogram in Fig. 3, we start with a configuration where the carbon atom of the terminal methyl group of each octane-monothiol molecule has the same (y, z) coordinates as that of the carbon atom next to sulfur atom of the other octane-monothiol molecule. That is to say, each carbon atom has the same (y, z) coordinates with a carbon atom in the other octane-monothiol molecule. We denote this configuration with $l = 0$. Then, four more stretches are sequentially implemented. Due to the periodical structures of alkane backbone, each carbon atom of the upper octane-monothiol molecule is located above the corresponding carbon atom of the lower molecule in the overlap region for cases of $l = 0$, $2\Delta l$, $4\Delta l$, while they are located at the middle of two next-nearest neighboring carbon atoms viewed from the x axis for cases of $l = \Delta l$, $3\Delta l$. We studied the IETS for these five configurations as shown in Fig. 3(a)–(e). It is evident that the IETS peaks around 0.38 V are largely reduced when the two molecules are pulled apart compared with the configuration in Fig. 2(e). This can be attributed to the coupling decrease between the terminal CH_3 group of one molecule and the gold electrode where the other molecule is attached. In addition, we also observe that the IETS

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[1] For interpretation of color in 'Fig. 2', the reader is referred to the web version of this article.