

Theoretical investigation of inelastic electron tunneling spectroscopy of bimolecular junctions

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Abstract. First-principles investigation on the inelastic electron tunneling spectra of bi-oligophenyleneethynylenes (OPEs)- monothiol molecular junctions is performed. It is demonstrated that the inelastic electron tunneling spectra are very sensitive to the deviation, stagger or separation of the two molecules in the bimolecular junctions. To some extent, the spectra of bimolecular junctions can present similar characteristics as a single OPE-monothiol molecular junction, which reflects the neglectable interaction between two molecules. When the overlap between the two molecules is relatively strong, out of plane vibration modes are active in the spectra and provide more inter-molecular tunneling paths for electrons.

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Key words: inelastic electron tunneling spectrum, vibration modes, molecular junction

1 Introduction

Oligo phenylene ethynylenes, consisting of three phenyl rings connected by triplet-bonded carbon atoms, have been widely investigated as prototype molecular junctions both experimentally and theoretically [1]. Long *et al.* studied the electronic transport properties of a molecular device constructed by two cofacial oligo(phenylene ethynylene)-dithiol molecules and gold electrodes, and a negative differential resistance behavior induced by intermolecular interaction was predicted [2]. The conformation of bi-oligo phenylene ethynylenes (OPEs)-monothiol molecular junctions based on $\pi-\pi$ interaction between aromatic molecules was first found by Wu *et al.* using Mechanically Controllable Break Junction method [3]. However, the determination of the configurations of

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the bimolecular junctions formed is still out of reach experimentally. As one of the most favorable tools to detect configuration details in molecular junctions, inelastic electron tunneling spectroscopy (IETS) has attracted much attention and has been widely used in the area of molecular electronics [4–6]. However, less investigation has been focused on the inelastic electron tunneling spectra of bimolecular junctions. Since IETS is very sensitive to the configurations of molecular junctions, it will be very efficacious to detect the conformation of bimolecular junctions. Although there has been no experimental report on the IETS of bimolecular junctions, theoretical investigation will provide direct connection between the conformations of bimolecular junctions and the IET spectra.

Based on the harmonic approximation, we developed our quantum chemistry method to investigate the electron-phonon interaction and have successfully reproduced some experimental results [7–13]. Our method has been proved to be very efficient to predict the conformations of molecular junctions, the contact configurations, the transport mechanism as well as the intermolecular interactions. In this paper, the IET spectra of OPE bimolecular junctions with different configurations have been investigated and some interesting phenomenon has been found.

2 Methods of calculation

Based on our former developed elastic scattering Green's function theory, the inelastic electron tunneling theory has been built, which is also based on the harmonic approximation. In Born-Oppenheimer approximation, the Hamiltonian can be written as two terms

$$H(Q) = H(Q, e) + H^v(Q), \quad (1)$$

where $H(Q, e)$ is the electronic Hamiltonian and $H^v(Q)$ is the vibration Hamiltonian. The wavefunction can also be written as $|\psi^\eta(Q, e)\rangle|\psi^v(Q)\rangle$, where $|\psi^\eta(Q, e)\rangle$ is the electronic wavefunction and $|\psi^v(Q)\rangle$ is the vibration wavefunction. Based on the harmonic approximation, the wavefunction can be expanded as follows

$$|\psi^\eta(Q, e)\rangle|\psi^v(Q)\rangle = \left| \psi_0^\eta + \sum_a \frac{\partial \psi_0^\eta}{\partial Q_a} Q_a \right\rangle |\psi^v(Q)\rangle \quad (2)$$

The transmission function T can be written as

$$T(Q) = \sum_{k'} \sum_k \sum_\eta V_{ks}(Q) V_{Dk'}(Q) \sum_{\nu', \mu, \nu} g_{k, k'}^{\eta, \nu', \mu, \nu}, \quad (3)$$

where $V_{kS}(Q)V_{Dk'}(Q)$ is the coupling energy between the atom $k(k')$ and the source (drain) electrode. The Green's function can be written as

$$g_{k,k'}^{\eta,\nu',\mu,\nu} = \frac{\langle \psi^{\nu'}(Q) | \langle k'(Q,e) | \psi^{\eta}(Q,e) \rangle | \psi^{\mu}(Q) \rangle \langle \psi^{\mu}(Q) | \langle \psi^{\eta}(Q,e) | k(Q,e) \rangle | \psi^{\nu}(Q) \rangle}{Z_{\eta} - H(Q)}$$

$$= \frac{\langle \psi^{\nu'}(Q) | \langle k'(Q,e) | \psi^{\eta}(Q,e) \rangle | \psi^{\mu}(Q) \rangle \langle \psi^{\mu}(Q) | \langle \psi^{\eta}(Q,e) | k(Q,e) \rangle | \psi^{\nu}(Q) \rangle}{E - E_{\eta} - \sum_a n_a \hbar \omega_a + i\Gamma_{\eta}}, \quad (4)$$

where ω_a and n_a is the frequency and quantum number of vibration mode a , Γ_{η} is the broadening factor. The current from the source electrode to the drain electrode can be calculated as follows

$$I^{\alpha(\beta)} = A j^{\alpha(\beta)} = \pi r_{3s}^2 j^{\alpha(\beta)}$$

$$= \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \frac{9ek_B\Theta}{16\hbar E_f^2} \int_{eV}^{\infty} \left\{ \ln \left[1 + \exp \left(\frac{E_f - E_z + eV}{k_B\Theta} \right) \right] \right.$$

$$\left. - \ln \left[1 + \exp \left(\frac{E_f - E_z}{k_B\Theta} \right) \right] \right\} \times |T^{\alpha(\beta)}(E_z)|^2 \frac{dE_z}{E_z}, \quad (5)$$

where Θ is the temperature which is assumed as 4.2 K in this paper, k_B is Boltzmann's constant and E_z is the energy of transport electrons. The IET spectra can be calculated according to the formula: $\frac{\partial^2 I}{\partial V^2}$.

In our calculation, the OPE-monothiol molecule is first optimized, then, connected with two electrodes. The extended bimolecular junction is shown within the dashed frame in Fig. 1, where each molecule is connected with one electrode by the end sulfur atom respectively. The S-Au bond length is assumed as 2.85 Å in accordance with our former report [7–13]. Each electrode is represented by three gold atoms in triangle with the Au-Au bond as 2.88 Å. The two molecular surfaces keep parallel with each other and the sulfur atom of the upper OPE molecule is located at the zero point of the coordinate. The geometry optimization and the electronic structure calculation are performed at the hybrid density-functional theory (DFT) B3LYP level with the Lanl2DZ basis set in the GAUSSIAN 03 package [14], where the effective core potential (ECP) is used for the gold atoms. The IET spectra are obtained from our developed QCME program [15].

3 Results and discussion

In our model, the vertical distance between two molecules is assumed as 3.4 Å at first. The two molecules overlap with each other completely and the horizontal distance between the two sulfur atoms are 20.39 Å. This regular configuration is named as "R" and the calculated IET spectra of configuration "R" is shown in Fig. 2(a). When the upper molecule moves along the X axis with the step of 0.6 Å, the configurations are defined

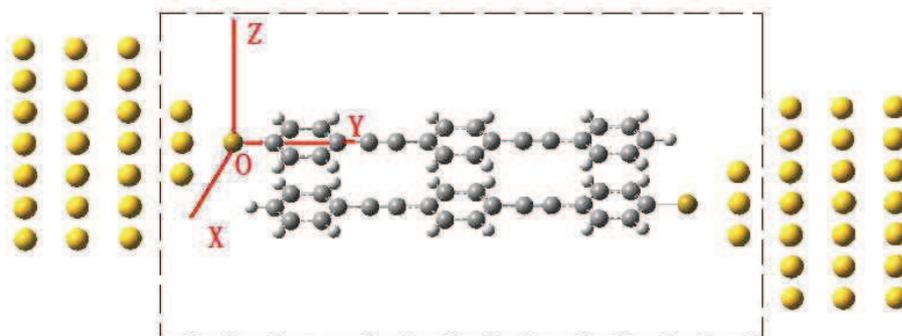


Figure 1: Stacking conformation of the bi-OPE-monothiol junction. The dashed frame outlines the extended molecular system.

as “R-Xd”, where letter “d” represents the distance moved from the initial position in configuration “R”. The IET spectra of the other four different configurations have also been shown in Fig. 2. From Fig. 2(a) to Fig. 2(c), the IET spectra can be divided into three parts as shown by vertical dashed lines. In the first part, the intensity of the peaks is very strong and the peaks in this area come from the vibration of the electrode atoms and the group motion of the molecule towards the electrode. The vibration peaks in the second part involves the out of plane C-H bending modes of the OPE molecules as shown in Fig. 3(a). It is interesting to find that the active vibration modes in the second part become less and less with the increasing deviation of the two molecules. When the deviation is 1.8 Å, there is no out of plane C-H bending modes presented in the IET spectra any more. With the deviation further increasing, the IET spectra become relatively invariable with four peaks below 0.1 V and three peaks between 0.1 V and 0.2 V. Take “R-X2.4” as an example, the seven vibration modes are shown in Fig. 3(b)-(h).

When the upper molecule moves along the Y axis to go far away from the lower molecule, the configurations can be defined as “R-Yd”, where d is the stagger distance of the two molecules. The calculated IET spectra of bimolecular junctions at different stagger configurations can be seen in Fig. 4. It is clear that the out of plane vibration modes become not active in the IET spectra as soon as the stagger configuration forms. The IET spectra become relatively stable when the stagger is larger than 1.2 Å, where only seven in-plane vibration modes are active in the IET spectra. It can be found that the four peaks below 0.1 V keep their dominance in the IET spectra, while the three vibration modes between 0.1 V and 0.2 V becomes relatively weaker with the stagger increasing. The two vibration modes at 0.13 V compete with each other to get stronger. It is interesting to find that the IET spectrum at configuration “R-Y2.4” is very similar to that of configuration “R-X2.4”. It is reasonable to deduce that the IET spectra may present the similar characteristics as in single OPE molecular junction due to the weak interaction induced by the deviation or stagger of the two molecules.

When the upper molecule moves along the Z axis, the vertical distance between the

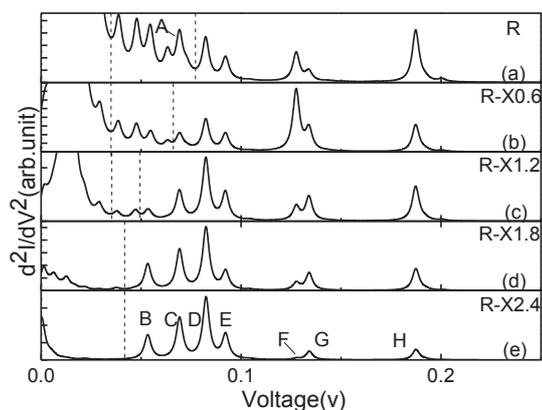


Figure 2: (a)-(e) Calculated IET spectra of the bimolecular junctions with the configuration "R", "R-X0.6", "R-X1.2", "R-X1.8" and "R-X2.4" respectively. The Lorentzian lineshape has been adopted and the broadening factor is 16 cm^{-1} .

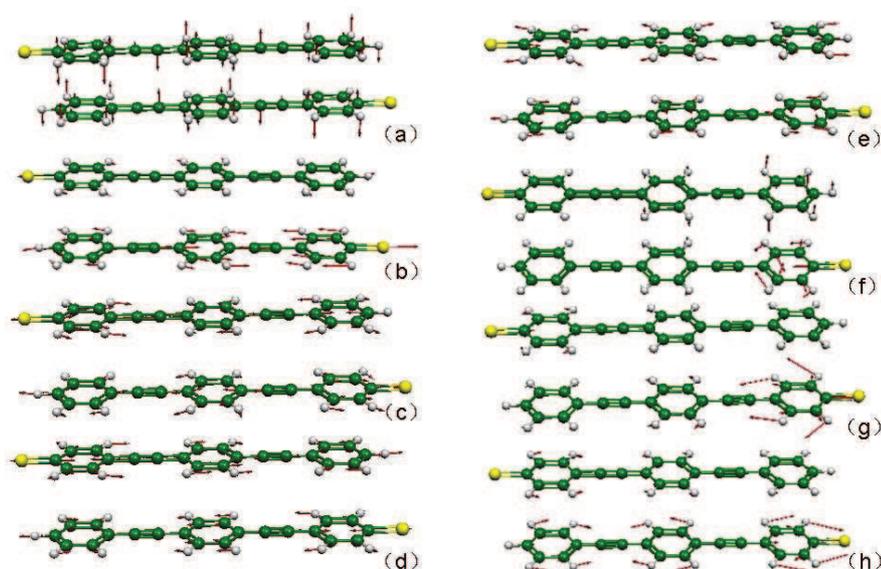


Figure 3: (a) one of out of plane vibration modes of the regular configuration "R", (b)-(h) correspond to the B-H vibration modes respectively labeled in Figure 2 (e).

two molecules become larger. The configurations are defined as "R-Zd", where d represents the vertical distance further moved from the initial configuration "R". The calculated IET spectra of five different configurations are shown in Fig. 5. It can also be seen that the out of plane vibration modes are very sensitive to the vertical distance. At configuration "R-Z1.0", the out of plane vibration mode disappear in the calculated IET spectrum. When d is larger than 1.0, the calculated IET spectra preserve similar charac-

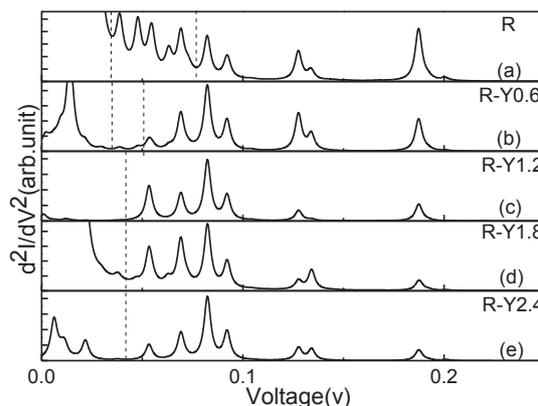


Figure 4: (a)-(e) Calculated IET spectra of the bimolecular junctions with the configuration "R", "R-Y0.6", "R-Y1.2", "R-Y1.8" and "R-Y2.4" respectively. The Lorentzian lineshape has been adopted and the broadening factor is 16 cm^{-1} .

teristics as that of "R-X2.4" and "R-Y2.4". The only difference between them is that the peaks at 0.13 V become very weak here. It is indicated that both the out of plane vibration modes and the in-plane vibration modes are very sensitive to the vertical distance change.

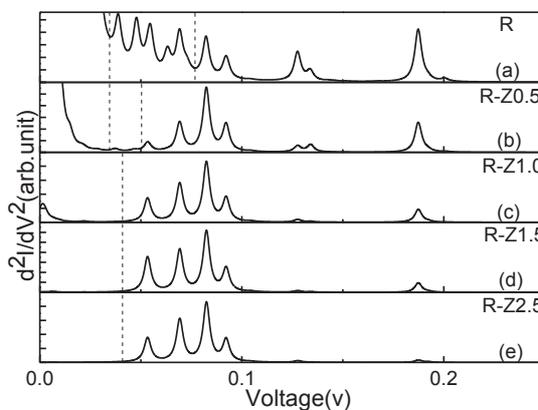


Figure 5: (a)-(e) Calculated IET spectra of the bimolecular junctions with the configuration "R", "R-Z0.5", "R-Z1.0", "R-Z1.5" and "R-Z2.5" respectively. The Lorentzian lineshape has been adopted and the broadening factor is 16 cm^{-1} .

Based on upper investigation, it is found that the out of plane vibration modes are active in the IET spectra only when the two molecules overlap with each other with great degree. When the deviation, stagger or separation between two molecules increases to some extent, the out of plane vibration modes disappear in the IET spectra. Fig. 6 shows

the IET spectra of three bimolecular junctions at configuration "R-X2.4", "R-Y2.4" and "R-Z2.5" respectively compared with the spectra of the single OPE molecular junction. It is found that the IET spectra of the three bimolecular junctions are similar to the spectra of the single OPE molecular junction, which indicates that the intermolecular interaction no longer has significant effect on the IET spectra of the bimolecular junctions when the deviation, stagger or separation between the two molecules are large enough.

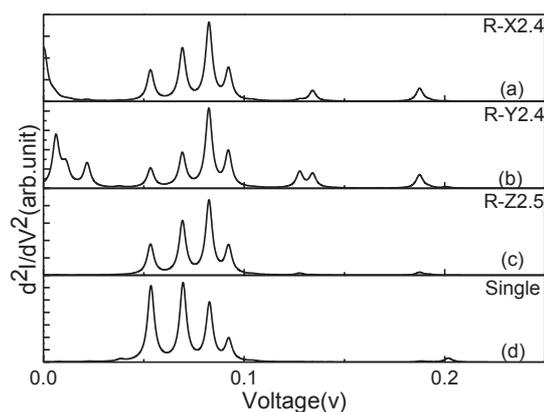


Figure 6: (a)-(c) calculated IET spectra of configuration "R-X2.4", "R-Y2.4" and "R-Z2.5". (d) Calculated IET spectra of single OPE-monothiol molecular junction.

4 Conclusion

Inelastic electron tunneling spectra of bimolecular junctions with different configurations have been intensively investigated. When the two OPE molecules overlap with each other completely, the out of plane vibration modes are active in the IET spectra, which provide new intermolecular tunneling paths for electrons. When the deviation, stagger or separation between the two molecules in the bimolecular junction is large enough, the out of plane vibration modes disappear in the spectra. To some extent, the IET spectra of the bimolecular junctions present the characteristics of single molecular junction. Our theoretical investigation provide the direct configuration-spectra relationship of bimolecular junctions, which will help experimental workers to understand their results better and perform more precise measurement of the molecular junctions.

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