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Theoretical investigation of inelastic electron tunneling spectroscopy of bimolecular junctions

Wei Li[a], Jian-Cai Leng[b], and Chuan-Kui Wang[a,*]

[a] *College of Physics and Electronics, Shandong Normal University, Jinan 250014, China*
[b] *College of Mathematics and Physics, Shandong Institute of Light Industry, Jinan 250353, China*

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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 intermolecular 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

*Corresponding author. *Email address:* ckwang@sdnu.edu.cn (C. K. Wang)

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

$$H(Q)=H(Q,e)+H^{\nu}(Q), \tag{1}$$

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

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

The transmission function T can be written as

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