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Theoretical studies on electronic transport properties of 2,5-dimercapto-pyridazin molecular junctions: influence of CO and H_2O molecules

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Abstract. Based on first-principles calculations, the electrode force acted on 2,5-dimer capto-pyridazin molecular device is studied. The pressing effects of CO and H_2O molecules on the 2,5-dimercapto-pyridazin molecular junctions are also studied at B3LYP level to simulate the effects of little ambient molecules on the functional molecular junctions. The electronic transport properties of 2,5-dimercapto-pyridazin molecular junction with the pressing of CO and H_2O molecules are studied by employing elastic scattering Green's function method. The numerical results show that the 2,5-dimercapto-pyridazin can be squeezed out of the electrode gap when the electrode distance is compressed to 1.02 nm. It is need about 1.5 nN stretching force to break down the 2,5-dimercapto-pyridazin molecular junction, which agrees with the experiment probes very well. The 2,5-dimercapto-pyridazin molecule is bent by the pressing of CO or H_2O molecule, and is pushed to the edge of Au (111) triangles with the terminal S atoms first to the bridge and then to the top positions of Au (111) triangles, until at last one terminal S atom is pushed out of Au (111) triangle. The pressing of CO and H_2O molecules to the molecular junctions will enhance the couplings between molecule and electrodes, which further enhances nonresonant transmission of the molecular junctions.

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Key words: molecular device; 2,5-dimercapto-pyridazin molecule; electronic transport properties; effect of small ambient molecule.

1 Introduction

Due to its high efficiency, low energy consumption and high integration density, the single molecular devices have been paid more and more attention to in the studies in recent

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years. Various kinds of nano-structures like atomic wires [1], short organic molecular wires [2,3,4], long-chain polymers [5], carbon nanotubes [6] and fullerenes [7] have been investigated experimentally, and many valuable properties have been found. Most of the studies in this area are focused on the spatial structure, electrical transport properties, negative differential resistance, rectification or switching properties of the molecular devices, and so on. Both experimental and theoretical works have proved that the electronic transport properties and functional performance of the molecular devices are determined by many factors [5,8-28], for instance, molecular structure [9], contact configuration [19], positions of the terminal atoms on the metal surfaces [11], distance between the electrodes [20], pressure of the electrodes [10,15], ambient [12,13,18], etc..

In experimental measurement, molecular junctions may be probed in different circumstance, such as solution or gas, etc. It is inevitable that the irregular movements of the ambient molecules may push the functional molecule out of the electrode gap. Thus in this article, the effects of small ambient molecules on the geometric structures and electronic transport properties of organic molecular junctions are investigated. Based on the *ab initio* calculation, the presses of small ambient molecules such as CO and H_2O on 2,5-dimercapto-pyridazine molecular junctions are simulated, and the electronic transport properties with different pushing displacements are discussed applying elastic scattering Green's function method. The studies not only reveal that the pushing of the small ambient molecules can break down organic molecular junctions, but also are helpful to understand gas sensitivity or humidity sensitivity of molecular device.

2 Theoretical details

A molecular junction consists of a functional molecule and two gold electrodes. In order to simulate the 2,5-dimercapto-pyridazin molecular junction [29], we sandwiched the molecule between two gold atom clusters to form gold-molecule-gold extended molecule. By this way, the influence of electrodes on the functional molecule can be approximately considered, because the gold atom clusters which consist of the gold atoms nearby the functional molecule can screen the influence of the other gold atoms which are far away from the molecule. The schematic structure of 2,5-dimercapto-pyridazin molecular junction is shown in Fig. 1, where the terminal S atoms on the hollow position of Au (111) surfaces/triangles. In the calculation, we changed the electrode distance and relaxed the functional molecule by performing geometric optimization at B3LYP level with Lanl2DZ basis set in Gaussian03 packages [30]. The distance with the lowest energy corresponds to the equilibrious electrode distance. At equilibrious distance, the pressing of small ambient molecule on the molecular junction was simulated by moving the small ambient molecule close to the functional molecule gradually, which are also simulated at B3LYP level with Lanl2DZ basis set in Gaussian03 packages [30].

The electronic transport properties of molecular junctions are studied applying elastic scattering Green's function method based on the general Green's function formalism of

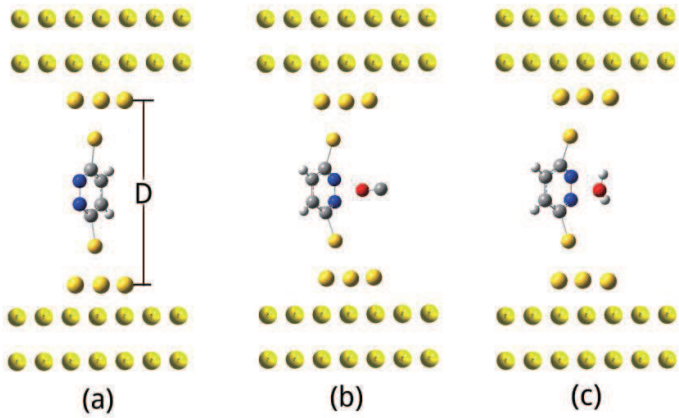

Figure 1: (a) Schematic structure of 2,5-dimercapto-pyridazin molecular junction, and the 2,5-dimercapto-pyridazin molecular junction with pressing of (b) CO or (c) H_2O molecules.

Mujica *et al.* [31], for a three dimensional electrode, the net current density of molecular junction from source (one electrode) through molecules to drain (the other electrode) can be written as [32]

$$i_{SD}=\frac{4em^*k_BT}{\hbar^3}\int_{eV_{SD}}^{\infty}1n\frac{1+\exp[(E_f+eV_{SD}-E_z)/k_BT]}{1+\exp[(E_f-E_z)/k_BT]}|\tau(E_z,V_{SD})|^2n^S(E_z)n^D(E_z)dE_z \quad (1)$$

where V_{SD} is the external bias voltage, m^* is the effective mass of electron, e is the charge of electron, E_f is the Fermi energy, n^S and n^D are the state densities of the source and drain electrodes, $\hbar$ is the reduced Planck constant. And the transmission matrix elements between the source and drain electrodes are:

$$\tau(E_z,V_{SD})=\sum_J\sum_K U_{JS}(V_{SD})U_{KD}(V_{SD})\sum_n\frac{\langle J|n\rangle\langle n|K\rangle}{[E_z-E_n(V_{SD})]+i\Gamma_n} \quad (2)$$

where $|n\rangle$ is the eigenvalues of the Hamiltonian of a finite system, which consists of two clusters of gold atoms and functional molecules. $J(K)$ runs over all atomic sites, which are denoted as 1,2$\cdots$N, sites 1 and N are two end sites of molecular that connect with two electron reservoirs. Γ_n is the energy broadening. $U_{JS}(U_{KD})$ represents the coupling energy between certain atom $J(K)$ and the electrode $S(D)$. It can be written as:

$$\begin{aligned}U_{JS}(V_{SD})&=\langle J|H|S\rangle=\sum_{n,\alpha,i}C^J_{n\alpha}\langle J_\alpha|H|S_i\rangle C^S_{ni}\\ U_{KD}(V_{SD})&=\langle K|H|D\rangle=\sum_{n,\beta,j}C^K_{n\beta}\langle K_\beta|H|D_j\rangle C^D_{nj}\end{aligned} \quad (3)$$

where $C^J_{n\alpha}$ is the expansion coefficient of the orbital $|n\rangle$ on the atom orbital $|\alpha>$ of the atom J of the molecular, and $C^K_{n\beta}$ is on the atomic orbital $|\beta\rangle$ of the gold atom cluster. The calculation about electronic transport properties of molecular devices is completed in QCME-V1.1 package [33].

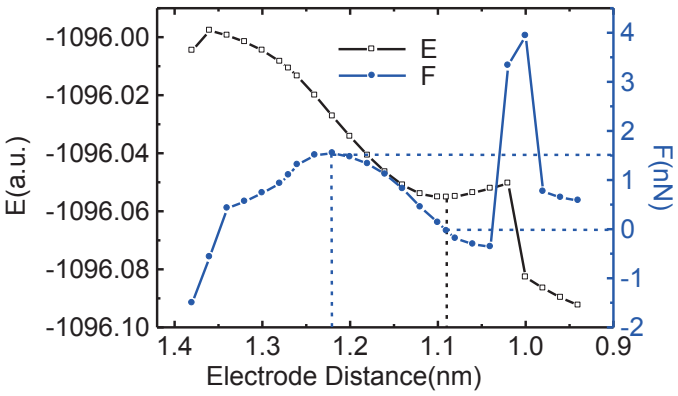

Figure 2: Ground state energy (E) of 2,5-dimercapto-pyridazin molecular junction and the force (F) of electrodes acted on the functional molecule versus electrode distance (D).

3 Results and discussion

Fig. 2 shows the ground state energy (E) of the extended molecule and the force (F) of electrodes on the functional molecule versus electrode distance (D) in the stretching and compressing process of 2,5-dimercapto-pyridazin molecular junction. The figure shows that the lowest ground state energy of the molecular system is occurred at the electrode distance of about 1.09 nm, which corresponds to the equilibrious electrode distance. When compress the electrode distance from 1.09 nm, the energy of the molecular system increases slowly. Then at d=1.02 nm, the energy sharply drop to a lower state, which indicates that the functional molecule is compressed out of the electrode gap. The force of the electrodes act on the functional molecule is also shown in Fig. 2, where the positive values correspond to stretching force, while the negative values are pressure action. It is noticeable that, at 1.22 nm, the compressing force has a local maximum value of about 1.5 nN, which suggest that, if one elongate the 2,5-dimercapto-pyridazin molecular junction, the junction will be broken at about 1.22 nm with a broken force of about 1.5 nN, which is agreed with the experiment probes very well [33-36].

Fig. 3 shows the ground state energy of 2,5-dimercapto-pyridazin molecular junctions with the pressings of CO and H_2O molecules. From the figure one can see that, the energies of the complex molecular junctions show similar variation trends for the junctions with the pressings of the two molecules. When the displacements of CO or H_2O are about 0.212nm and 0.165nm, the energies of the complex molecular junctions show local maximum values. From the geometries of the complex molecular junctions we find that, with the pressing of CO (Fig. 4 C1-C3) or H_2O (Fig. 4 H1-H3) molecule, the 2,5-dimercapto-pyridazin molecule is bent and pushed to the edges of Au (111) triangles with the terminal S atoms are about located on the bridge positions of Au-Au bonds (correspond to C1 and H1 in Fig. 3 and Fig. 4) at first. Further pressing make 2,5-dimercapto-pyridazin molecule moving to the top sites of Au atoms (correspond to C2 and H2 in Fig. 3 and Fig.

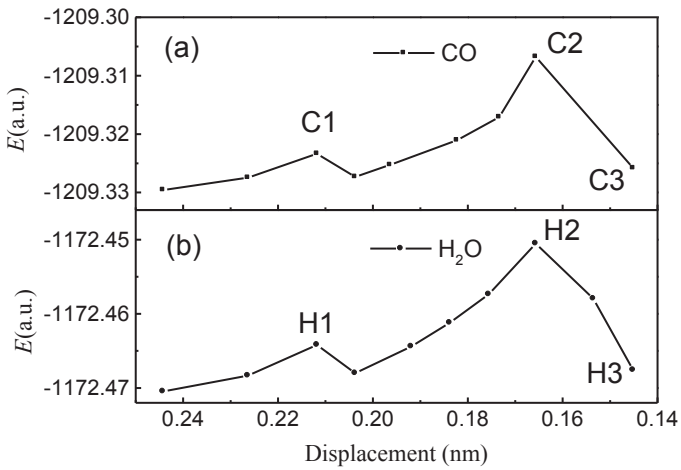

Figure 3: Ground state energy (E) of 2,5-dimercapto-pyridazin molecular junction with the pressing of CO and H_2O molecules.

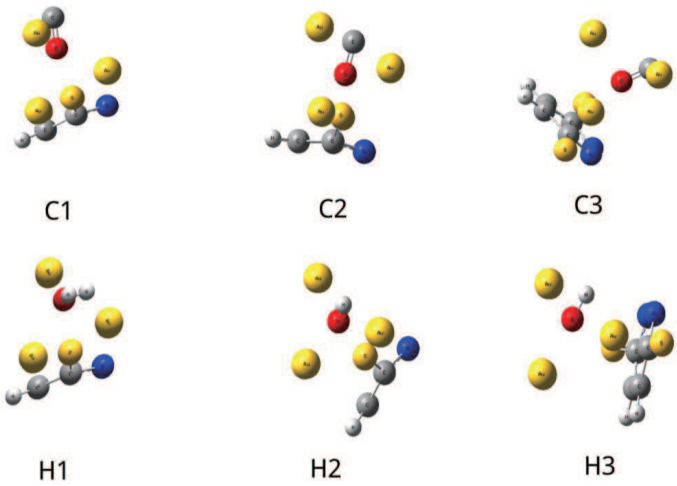

Figure 4: The processes of 2,5-dimercapto-pyridazin molecule being pushed out Au (111) triangles by CO (C1-C3) or H_2O (H1-H3) molecule.

4), and at this position the complex molecular systems have largest ground state energies as Fig. 3 shows. Then, keeping to press CO or H_2O molecule can induces 2,5-dimercapto-pyridazin molecular junction broken with one terminal S atoms out of Au (111) triangles (correspond to C3 and H3 in Fig. 3 and Fig. 4).

Then we studied the electronic transport properties of 2,5-dimercapto-pyridazin molecular junction and the junctions with the pressings of CO and H_2O molecules. Fig. 5 shows the current-voltage ($I-V$) characteristics of 2,5-dimercapto-pyridazin molecular junction and the complex molecular systems with CO and H_2O molecules. In the figure, C0 (or

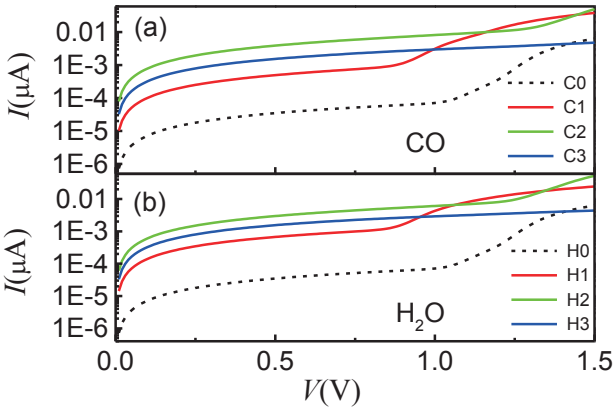

Figure 5: The I-V curve of the 2,5-dimercapto-pyridazin molecular junction and the molecular junction with pressing of CO and H_2O molecules.

H0) is the current of 2,5-dimercapto-pyridazin molecular junction without CO and H_2O molecules. C1, C2 and C3 correspond to the systems being pressed by CO molecule with the displacements and positions as Fig. 3 and Fig. 4 showing, and H1, H2 and H3 correspond to the systems being pressed by H_2O molecule. The figure shows that, with the pressing of CO or H_2O molecule, the molecular junctions show more conductive than the 2,5-dimercapto-pyridazin molecular junction without pressing at lower bias regime, especially for the complex systems at C2 and H2 state which correspond to the systems being pressed to the highest energy states. When the bias voltage is larger than 0.8 V, the current intensity increases rapidly with the increase of the bias for the molecular system with C1 (or H1) state. The current of the molecular junction without the pressing of CO and H_2O molecule also shows increasing quickly when the bias voltage is greater than 1.1V.

The electronic transport properties can be understand by the transmission spectra and the coupling constants between 2,5-dimercapto-pyridazin molecule and electrodes. From Fig. 6 one can see that, the mean transmission value of 2,5-dimercapto-pyridazin molecular junction is obviously less than those of the molecular systems with CO or H_2O. Despite that no evident transmission peak is appeared in the lower energy range, the transmission of C2 and H2 complex molecular systems have the largest mean values compared with the other systems. The transmission in the lower energy range corresponds to nonresonant transmission which has close relationship with the couplings between functional molecule and electrodes, especially the couplings between terminal S atoms and electrodes. From Tab. 1 one can see that the couplings of 2,5-dimercapto-pyridazin molecular junction without CO and H_2O molecules is obviously weaker than those of the other molecular systems. Thus based on the Eq. (2) one can easily understand why the nonresonant transmission of C0/H0 system is obviously weaker than the other systems. Fig. 6 also shows that, for C1 and H1 molecular systems, two high transmission

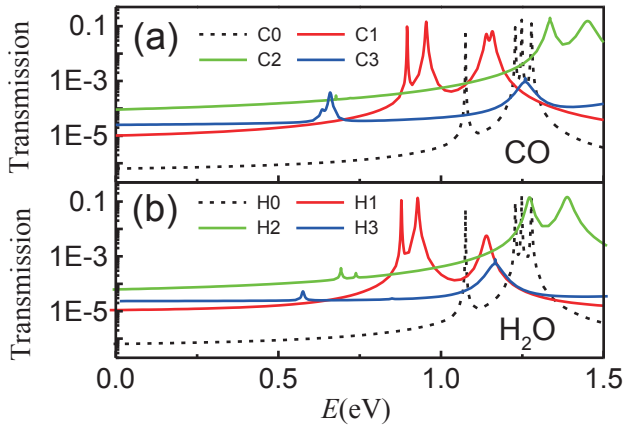

Figure 6: The transport spectra of 2,5-dimercapto-pyridazin molecular junction and the junctions with the pressing of CO and H_2O molecules.

peaks are appeared at 0.7-1.0 eV, so the currents of these two molecular systems begin to increase rapidly at about 0.8 V. Despite the coupling constants between the upper terminal S atom and the upper electrode of C3 and H3 are obviously larger than those of other systems, the C3 and H3 molecular systems are not show more conductive than the others. Because the upper terminal S atom are pushed out of Au (111) triangles by CO or H_2O molecules, which further make the transmission channels more localization and not as conductive as other molecular systems, which can also be seen from the heights of transmission peaks of C3 and H3 molecular systems in Fig. 6. Fig. 5 and Fig. 6 also show that find the CO and H_2O molecules have similar effects on the electronic transport properties of 2,5-dimercapto-pyridazin molecular junctions, only most of the transmission peaks of the system with H_2O are a little red-shift compared with the system with CO.

From Tab. 1 one can see that, for the molecular junctions with the pressing of CO or H_2O molecule, the couplings between 2,5-dimercapto-pyridazin molecule and electrodes are approximately equal to the couplings between the terminal S atoms and electrodes. That is to say, with the pressing of CO or H_2O molecule, the couplings between 2,5-dimercapto-pyridazin molecule and electrodes mainly come from the couplings between the terminal S atoms and electrodes. However, for molecular junctions without CO and H_2O molecules, the other atoms also have obvious contributions to the couplings between 2,5-dimercapto-pyridazin molecule and electrodes. Additionally, the coupling constants show negative values for the molecular systems being pressed by CO or H_2O molecule. Because the 2,5-dimercapto-pyridazin molecule has been bent and pushed to the edge of Au (111) triangles by the pressing of CO or H_2O molecule, which further lengthened the distances between the terminal S atoms and electrodes. Thus attractive interaction has emerged between the terminal S atoms and electrodes, and which further induces negative coupling constants.

Table 1: The coupling constants between 2,5-dimercapto-pyridazin molecule (or terminal S atoms) and two electrodes.

State of molecular system	2,5-dimercapto-pyridazin molecule		Terminal S atom	
	Upper electrode	Lower electrode	Upper electrode	Lower electrode
C0 or H0	0.140	0.148	0.411	0.413
C1	-1.21	-1.17	-1.04	-1.00
C2	-1.81	-1.76	-1.84	-1.81
C3	-2.60	-1.78	-3.05	-1.80
H1	-1.23	-1.21	-1.08	-1.07
H2	-1.64	-1.60	-1.61	-1.60
H3	-2.55	-1.78	-3.04	-1.78

4 Conclusions

Applying hybrid density functional theory and elastic scattering Green's function method, the mechanics properties and the electronic transport properties of 2,5-dimercapto-pyrida -zin molecular junctions with pressings of CO or H_2O molecule are investigated. The numerical results show that the stretching force to break gold-2,5-dimercapto-pyridazin-gold molecular junction is about 1.5nN, which is in a good agreement with the experimental probes [33-36]. When the electrode distance is compressed to 1.02 nm, the 2,5-dimercapto-pyridazin molecule is squeezed out of the electrode gap. With the pressing of CO or H_2O molecule, the 2,5-dimercapto-pyridazin is bent and pushed to the edges of Au (111) triangles with the terminal S atoms of the 2,5-dimercapto-pyridazin first being pushed to the bridge positions of Au-Au bonds, then being pushed to the top positions of Au atoms, until at last, one terminal S atom being pushed out of Au (111) triangles. In the lower bias voltage regime, the currents of 2,5-dimercapto-pyridazin molecular junctions are enhanced by the pressing of CO or H_2O molecule, which attribute to the increase of the couplings between 2,5-dimercapto-pyridazin molecule and electrodes by the effect of CO or H_2O molecule.

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References

[1] Lang N. D.; Avouris P.; Phys. Rev. B .2000, 62, 7325- 7329.
[2] Reed M. A.; Zhou C.; Muller C. J.; Burgin T. P.; Tour J. M.; Science .1997,278, 252-254.
[3] Reichert J.; Ochs R.; Beckmann D.; Weber H. B.; Mayor M.; Löhneysen H. V.; Phys. Rev. Lett. 2002, 88, 254-264.
[4] Xu B. Q.; Tao N. J.; Science.2003, 301, 1221-1223.

[5] Hu W. P.; Nakashima H.; Furukawa K.; Kashimura Y.; Ajito K.; Torimitsu K.; Appl. Phys. Lett. 2004,85, 115-117.
[6] Tans S. J.; Verschueren A. R. M.; Dekker C.; Nature .1998,393, 49-52.
[7] ParK H.K.; Park J.; Lim A. K. L.; Anderson E. H.; Alivisatos A. P.; McEuen P. L.; Nature .2000,407, 57-60.
[8] Cui X. D.; Zarate X.; Tomfohr J.; Sankey O. F.; Primak A.; Moore A. L.; Moore T. A.; Gust D.; Harris G.; Lindsay S. M.; Nanotechnology .2002,13, 5-14.
[9] Ulrich J.; Esrail D.; Pontius W.; Venkataraman L.; Millar D.; Doerrer L. H.; Doerrer Li. H.; J. Phys. Chem. B. 2006,110, 2462-2466.
[10] Wold D. J.; Frisbie C. D.; J. Am. Chem. Soc. 2001,123, 5549-5556.
[11] Venkataraman L.; Klare J. E.; Tam I. W.; Nuckolls C.; Hybertsen M. S.; Steigerwald M. L.; Nano Lett. 2006,6, 458-462.
[12] Chen F.; Li X. L.; Hihath J.; Huang Z. F.; Tao N. J.; J. Am. Chem. Soc. 2006,128, 15874-15881.
[13] Fagas G.; Greer J. C.; Nanotechnology. 2007,18, 424010(1-5).
[14] Park Y. S.; Whalley A. C.; Kamenetska M.; M. L. Steigerwald.; Hybertsen M. S.; Nuckolls C.; Venkataraman L.; J. Am. Chem. Soc. 2007,129, 15768-15769.
[15] Hu W.; Li Z. L.; Ma Y.; Li Y. D; Wang C. K.; Acta Phys. Sin. 2011,60, 017304(1-6).
[16] Li X. L.; He J.; Hihath J.; Xu B.Q; Lindsay M S.; Tao N. J.; J. Am. Chem. Soc. 2006,128, 2135-2141.
[17] Hybertsen M. S.; Venkataraman L.; Klare J. E.; Cwhalley A.; Steigerwald M. L.; Nuckolls C.; J. Phys.: Condens. Matter.2008,20, 374115(1-14).
[18] Song H.; Lee H.; Lee T.; J. Am. Chem. Soc. 2007,129, 3806-3807.
[19] Li Z. L.; Zou B.; Wang C. K.;Luo Y.; Phys. Rev. B. 2006,73, 075326(1-7).
[20] Zou B.; Li Z. L.; Wang C. K.; Xue Q. K.; Acta Phys. Sin. 2006, 54, 1341-1346.
[21] Liu F. T.; Cheng Y.; Yang F.B.; Cheng X. H.; Chen X. R; Acta Phys Sin. 2013,62 ,140504(1-5).
[22] Parameswaran R.;Widawsky J.R.;Vázquez H.; Park Y. S.; Boardman B. M.; Nuckolls C.; Steigerwald M L.; Hybertsen M S.;Venkataraman L.;J. Phys.Chem.Lett. 2010,1,2114-2119.
[23] Ma C. L.; Nghiem. D.; Chen Y. C.; Appl. Phys. Lett. 2008, 93, 222111(1-3).
[24] Guo C.; Zhang Z. H.; Pan J. B.; Zhang J. J.; Acta Phys. Sin. 2011,60 ,117303(1-7).
[25] Fu X. X.; Zhang L. X.; Li Z. L.; Wang C. K.; Chin. Phys. B. 2013, 22, 028504(1-5).
[26] Xia J. L.; Diez-Perez I.; Tao N. J.; Nano Lett. 2008, 8, 1960-1964.
[27] Pan Z.; Li Q. X.; Shi Q. W.; Wang X. P.; Chin. J. Chem. Phys. 2009, 22,7-12.
[28] Wang G.; Kim T. W.; Lee T.; J. Mater. Chem. 2011,21,18117-18136.
[29] Li Z.L.; Fu X. X.; Zhang G. P.; Wang C. K.; Chin. J. Chem. Phys. 2013, 26, 185-190.
[30] Frisch M. J.; Trucks G. W.; Schlegel H .B.; 2004 Gaussian 03, Revision E.01, Caussian, Inc., Wallingford CT.
[31] MujicaV.; Kemp M.; Ratner M. A.; J. Chem. Phys. 1994,101, 6849-6855.
[32] Jiang J.; Kula M.; Luo Y.; J. Chem. Phys. 2006,124, 034708(1-10).
[33] Xu B. Q.; Li X. L.; Xiao X. Y.; Sakaguchi, H.; Tao N. J.; Nano Lett. 2005, 5, 1491-1495.
[34] Chen I-W.P.; Tseng W.H.; Gu M.W.; Su L.C.; Hsu C.H.; Chang W. H.; Chen C.H.; Angew. Chem. Int. Ed. 2013,52, 2449-2453.
[35] Frei M.; Aradhya S. V.; Hybertsen M. S.; Venkataraman L.; J. Am. Chem. Soc. 2012,134, 4003-4006.
[36] Frei M.; Aradhya S. V.; Koentopp M.; Hybertsen M. S.; Venkataraman L.; Nano Lett. 2011,11, 1518-1523.