PHYSICAL REVIEW B **73**, 045403 (2006)

Effect of the atomic configuration of gold electrodes on the electrical conduction of alkanedithiol molecules

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(Received 28 June 2005; published 5 January 2006)

The nonequilibrium Green's function approach in combination with density-functional theory was used to perform *ab initio* quantum-mechanical calculations of the electrical conduction of single alkanedithiol molecules sandwiched between two gold electrodes. The atomic configuration of the gold electrodes was varied in the vicinity where the molecule attaches, using configurations most likely to occur in break-junction experiments. The zero-voltage conductance is shown to depend strongly on the detailed atomic configuration of the electrodes. The transmission coefficients reveal nonresonant tunneling, which is enhanced by localized states. For certain electrode configurations, good agreement with conductance measurements [B. Q. Xu and N. J. Tao, Sci. **301**, 1221 (2003)] is obtained.

DOI: 10.1103/PhysRevB.73.045403 PACS number(s): 85.65.+h, 73.23.−b, 31.15.Ar, 31.15.Ew

I. INTRODUCTION

Understanding the transport of electrons through individual organic molecules currently attracts much interest due to the potential importance to molecular electronics.[1,2] Despite significant efforts, theoretical predictions for the electrical conductance of single organic molecules are often in strong disagreement with experimental findings, with theoretical conductances usually several orders of magnitude larger than the experimentally measured values. Although there are many questions regarding the accuracy of the various theoretical approaches, it is likely that some of the low experimental conductance values are due to contaminants at the electrode-molecule interfaces or are caused by structurally nonideal electrode surfaces.[3] To determine the electrical conductivity of self-assembled molecular layers, sandwiched between two metal electrodes, a number of different experimental techniques have been employed, comprising mechanically controlled break junctions,[4] microfabricated structures,[5–7] crossed wire geometries,[8] atomic force microscopy,[9,10] and contacting self-assembled monolayers with a mercury drop.[11–13] The conductances of single molecules, chemically bonded between two metal electrodes, have recently been measured by Cui *et al.*,[14,15] Xu and Tao,[16] Xu *et al.*,[17] Reichert *et al.*,[18] Weber *et al.*,[19] and Haiss *et al.*[20] Out of the experimental techniques suitable for single molecule conductance measurements, probably the most promising one is the technique where individual molecular junctions are created by repeatedly moving a gold scanning tunnel microscope (STM) tip into and out of contact with a gold substrate in a solution containing the sample molecules.[16,17,20] This technique, which we will call in the following the STM break-junction technique, largely eliminates possible electrode-molecule interface contamination by forming fresh electrode interfaces during junction breakage to which single molecules can attach almost instantly. The disadvantage of this STM break-junction technique is that the molecule is attached to electrode surfaces of unknown atomic configuration. A number of different theoretical approaches have been used to calculate the electrical conduction of single molecules sandwiched between two electrodes.[21–27] State-of-the-art approaches are self-consistent first-principles quantum-mechanical calculations.[24–28] In particular, Brandbyge *et al.*[27] have developed the TRANSIESTA code, which interfaces the SIESTA[29] electronic structure package for molecules in such a way that the density matrix of the system can be calculated self-consistently when the system is in nonequilibrium, i.e., subjected to an external bias voltage. In this *ab initio* approach the charge transfer between the molecule and the electrodes as well as the voltage drop along the molecule and electrode surfaces are calculated in a parameter-free, self-consistent manner.

This paper theoretically investigates the dependence of the electrical conductance of single alkanedithiol molecules on the atomic configuration of the two Au electrodes. Plausible electrode configurations are assumed that are likely to occur in STM break-junction experiments where one repeatedly opens and closes a junction. The theoretical results are compared to the experimental findings of Xu and Tao.[16]

II. THEORY

In the calculation to be reported below, the first-principles computer code TRANSIESTAC[27,28] (a later version of TRANSIESTA), which is based on the Keldysh nonequilibrium Green's function technique combined with density-functional theory is employed. The mathematical method on which the code is based can be summarized as follows.

The electrical current I through a single molecule that bridges two metal electrodes is given by[30]

$$I=\frac{2e}{h}\int dE\,T(E,\Phi_b)[f(E-\mu_L)-f(E-\mu_R)], \qquad (1)$$

where f is the Fermi-Dirac distribution characterizing the left (L) and right (R) metal electrodes, μ_L and μ_R are the chemical potentials of the left and right electrodes, and Φ_b is the applied bias voltage across the electrodes where $\Phi_b=(\mu_L-\mu_R)/e$ and E is the energy of the incident electrons. The transmission coefficient $T(E,\Phi_b)$ in Eq. (1) is given by[27,28,30,31]

$$T(E,\Phi_b) = Tr[\mathrm{Im}\,\Sigma_L(E)G^{+}(E,\Phi_b)\mathrm{Im}\,\Sigma_R(E)G(E,\Phi_b)] \tag{2}$$

where Σ_L and Σ_R are the bulk self-energies used to map the infinite left and right electrodes onto finite electrodes.[30] The Green's function $G(E,\Phi_b)$ of the system is given by

$$G(E,\Phi_b) = [ES - H_c(\Phi_b) - \Sigma_L - \Sigma_R]^{-1}, \tag{3}$$

where

$$\Sigma_{L/R} = V_{L/R}g^{L/R}V_{L/R}. \tag{4}$$

Here S is the overlap matrix. The Hamiltonian H_c describes the contact region, i.e., the "extended molecule." The extended molecule consists of the molecule itself as well as that part of the left and right electrodes where all the screening takes place, i.e., usually the first two atomic layers of each metal electrode. V_L and V_R are the interactions between the extended molecule and the semi-infinite electrodes. The Green's functions $g^{L/R}$ of the isolated left and right semi-infinite leads are determined by the Hamiltonians H_L and H_R. For H_c, H_L, and H_R, single-electron Hamiltonians are chosen where the effective electron interaction potentials are expressed in terms of the density-functional theory, containing both the Hartree and the exchange-correlation potentials. The electron density is obtained by employing the Keldysh nonequilibrium Green's function technique,[30] and the calculation is performed self-consistently without any adjustable parameters. The density matrix ρ to calculate the effective electron-interaction potential is given by[27]

$$\rho = \frac{1}{\pi}\int dE[f(E-\mu_L)G\,\mathrm{Im}\,\Sigma_L G^{+} + f(E-\mu_R)G\,\mathrm{Im}\,\Sigma_R G^{+}]. \tag{5}$$

III. RESULTS AND DISCUSSIONS

Experiments carried out recently, using the STM break-junction technique[16] where molecules attach to freshly cleaved gold contacts, seem to give reliable electrical conductance measurements of single molecules. These measurements, contrary to others, are not affected by possible atomic contamination at the molecule-electrode interfaces. In the STM break-junction experiment by Xu and Tao,[16] a gold-coated STM tip is repeatedly pushed into and pulled out of the surface of a gold film. During pullback, just before the gold contact breaks, a chain of gold atoms forms and molecules are supposed to attach across the breaking gold chain. When the gold chain breaks, the conductance changes from the quantum conductance value, $G_0 = 2e^2/h = 1/(12.9\ \mathrm{k}\Omega)$, of the gold chain to the lower conductance value of the attached molecule. The molecule conductance can be measured for a short time before the thiolated molecule disconnects under increasing strain. As the S atom of the thiol group is thought to bind more strongly to gold than gold to gold, a dithiolated molecule most likely pulls out short chains of gold atoms from both electrodes during the junction separation process, possibly creating chain and/or conelike features. It is important to note that according to break-junction experiments carried out by Untiedt *et al.*,[32] the number of Au atoms forming a gold chain is most likely one or two, while forming gold chains containing more than three Au atoms seems highly unlikely.

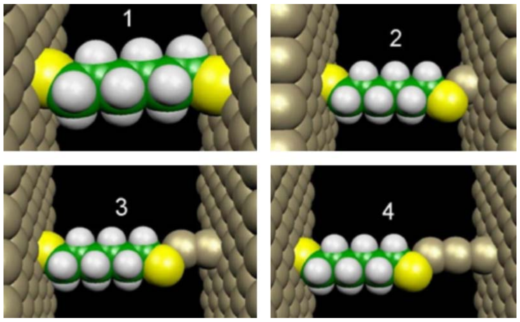

FIG. 1. (Color online) Au electrode configurations 1–4 used to calculate the conductance of a single 1,6-hexanedithiol molecule.

TRANSIESTAC was used to calculate the zero voltage conductances and transmission coefficients $T(E,\Phi_b)$ of alkanedithiol molecules $[\text{-}S\text{-}(\mathrm{CH}_2)_N\text{-}S\text{-}]$ (N=4,6,8,10) placed between two (111) Au electrodes where the cone and/or chain structure of the electrodes was varied. Plausible atomic configurations were chosen that might form when a gold junction breaks and molecules attach to the freshly cleaved break-junction electrodes. Figures 1–4 (produced with MOLEKEL[33]) show the 16 different electrode configurations investigated, separated into four groups where the bridging molecule in this case is a 1,6-hexanedithiol. In the first group in Fig. 1, the left S atom is directly placed above a hollow-site on the (111) Au surface, while the right S atom is either placed above the opposite hollow site on the right (111) Au surface or connected via a chain of one, two, or three Au atoms. In the second group (Fig. 2), for configurations 5–7, the left S atom is bonded to a single Au atom, which is placed above a hollow site of the (111) Au surface, while in configuration 8, the left S atom is connected via a chain of two Au atoms. The number of Au atoms in the chain that connects the right S atom to the opposite hollow-site on the right (111) Au surface varies from one to three. In the third group (Fig. 3), the left S atom is placed above the hollow site formed by a triad of Au atoms sitting on the (111)

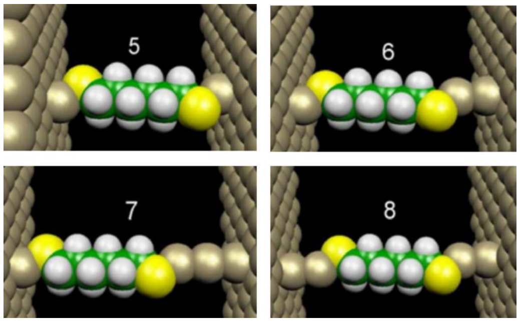

FIG. 2. (Color online) Au electrode configurations 5–8 used to calculate the conductance of a single 1,6-hexanedithiol molecule.

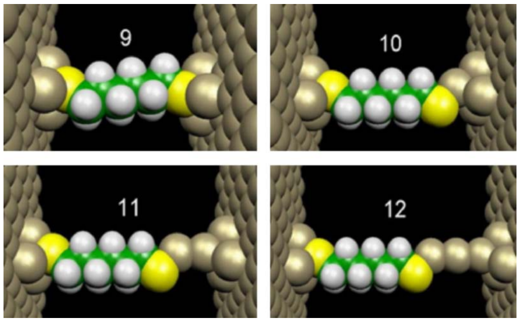

FIG. 3. (Color online) Au electrode configurations 9–12 used to calculate the conductance of a single 1,6-hexanedithiol molecule.

Au surface. The right S atom is connected either directly or via a chain of one, two, or three Au atoms to the opposite hollow site of a triad of Au atoms that sits on the right (111) Au surface. Finally, in the last group (Fig. 4), the left S atom is connected to a gold atom, which is placed above the hollow site of a triad of Au atoms. The right S atom is connected to the right electrode in configuration 13–15 via a chain of one, two, or three Au atoms placed above the hollow site of a triad of Au atoms sitting on the right (111) Au surface. Configuration 16 is similar to 14 but has an additional Au atom placed between the left S atom and the left conelike electrode.

In an experiment by Xu *et al.*,[17] it was shown that the conductance of a 1,8-octanedithiol molecule that is covalently bonded to two Au electrodes does not change noticeably with the tensile stress applied to the molecule during a break-junction experiment. Therefore, electrode-molecule-electrode equilibrium structures were used in the calculations. The equilibrium positions of the atoms were determined as follows using the relaxation mode of the TRANSIESTAC code. First, the geometry of the molecule was optimized as a free molecule with single Au atoms terminating the S atoms. The distance between the S (or Au) atom above a hollow site on the (111) Au surface was calculated by "relaxing" the position of the S (or Au) atom. The conelike structure formed by a triad of Au atoms on the (111) Au surface, with one S (or Au) above its hollow site, was determined by relaxing this four-atom structure. The residual forces in these relaxation calculations were <0.05 eV/Å. The distance between Au atoms in a chain was found by minimizing the total energy of an infinite Au chain. All results shown in this paper are for a double-zeta basis set, whereas a double-ζ plus polarization basis set was used in a few cases to check that the accuracy of the calculation was sufficient.[34] Norm-conserving Troullier-Martins pseudopotentials were applied.[35] For the exchange-correlation potential, the local-density approximation was used, employing the Perdew-Zunger parametrization.[36]

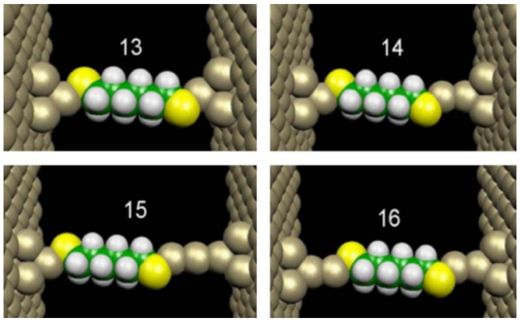

FIG. 4. (Color online) Au electrode configurations 13–16 used to calculate the conductance of a single 1,6-hexanedithiol molecule.

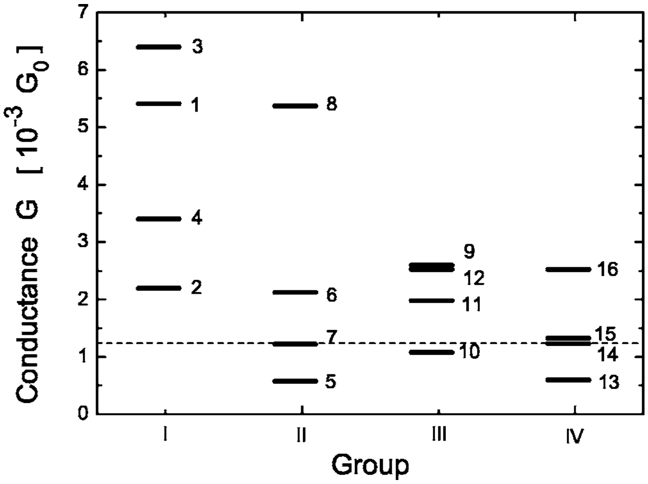

FIG. 5. Calculated electrical conductance values of a single 1,6-hexanedithiol molecule for the different electrode configurations 1–4 of group I (Fig. 1), 5–8 of group II (Fig. 2), 9–12 of group III (Fig. 3), and 13–16 of group IV (Fig. 4). The dashed line indicates the experimental conductance value found by Xu and Tao.[16] G_0 is the quantum conductance.

Figure 5 displays the calculated zero voltage conductance values of a single 1,6-hexanedithiol molecule for the four different groups of electrode configurations shown in Figs. 1–4. Large conductance values are found for the first group of configurations, where the S atom(s) or chains of Au atoms are directly placed above hollow-sites on the (111) Au surfaces. Smaller conductance values are found for the third and fourth groups (Figs. 3 and 4), where the S atom(s) or Au-chains are placed above the hollow site of traids of Au atoms sitting on the (111) Au surfaces. The largest conductance value is obtained for configuration 3 (Fig. 1), where the S atom on the left is directly placed above a hollow site on the left (111) Au electrode surface and where a chain of two Au atoms connects the right S atom to the opposite hollow site on the right (111) Au surface. The smallest conductance value, about 11 times smaller than the largest one, is found for configurations 5 and 13. Here, a one-atom chain connects the S atom on both sides to a hollow site on the (111) Au surface or to a hollow site of a triad of Au atoms that sits on the (111) Au surface. The dashed line in Fig. 5 corresponds to $G=1.2\times10^{-3}G_0$, which is the 1,6-hexanedithiol conductance value measured by Xu and Tao.[16] The experimental conductance of $G=1.2\times10^{-3}G_0$ agrees well with configurations 7, 10, 14, and 15, which seem to be plausible configurations expected to be formed in STM break-junction experiments.

In order to obtain a more quantitative theoretical estimate for the relative probability of each of the configurations of gold atoms in the electrodes, realistic molecular-dynamics

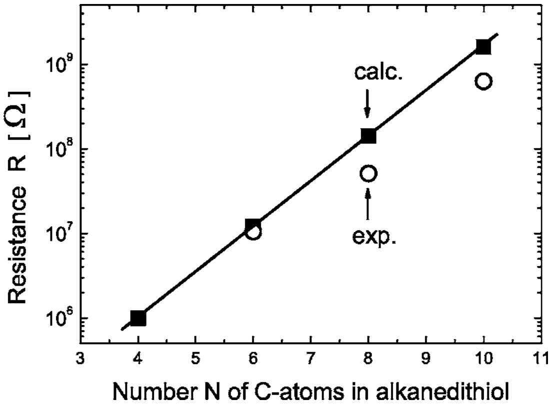

FIG. 6. Measured[16] and calculated resistance of single alkanedithiol molecules vs the number N of carbon atoms in the molecule.

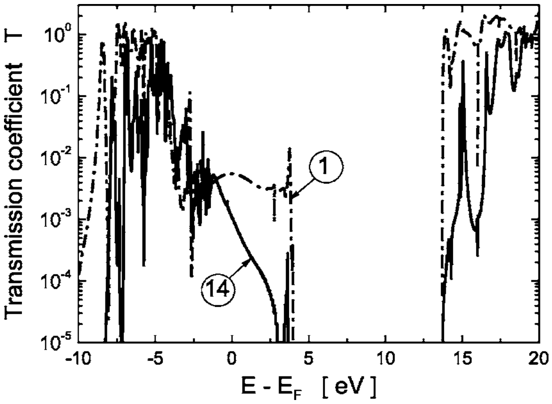

FIG. 7. Transmission coefficient $T(E,\Phi_b=0)$ defined in Eq. (2) versus energy $E-E_F$ of incident electrons for electrode configurations '1' and '14' of Fig. 1 and 4 for a single 1,6-hexanedithiol molecule.

simulations would be required that are computer-time intensive. Simulations closely related to this problem have been performed to study the evolution of the breaking process of metal nanowires without a bridging molecule.[37–39] These studies indicate that just before breakage only certain electrode tip configurations prevail. The experimental data of Xu and Tao,[16] which are obtained by statistical averaging over many contact breaking events, show predominantly a single conductance value for an alkanedithiol molecule with a spread of about ±15%, suggesting a single prevailing electrode configuration when breakage occurs.

Using the electrode configuration 14 displayed in Fig. 4, the zero voltage conductance of 1,4-butanedithiol ($N=4$), 1,8-octanedithiol ($N=8$) and 1,10-decanedithiol ($N=10$) were calculated. The results are shown in Fig. 6 where the resistance (i.e., the inverse of the conductance) is shown as a function of the number N of C atoms in the alkanedithiol molecules. As can be seen, the resistance increases exponentially with the number of C atoms, i.e., $R\sim\exp(\beta N)$, where $\beta=1.24/\mathrm{C}$ atom. Although the calculated and experimentally found resistances agree very well in the case of the 1,6-hexanedithiol molecule, the calculated values are about three times larger than the measured values given by Xu and Tao[16] for the 1,8-octanedithiol and 1,10-decanedithiol molecules. No measured value is given by Xu and Tao[16] for the 1,4-butanedithiol molecule. It is interesting that the above value for β is also close to the value found by Wold and Frisbie[9,10] in self-assembled monolayers of alkanethiols at low AFM loads ($\beta\approx 1/\mathrm{C}$ atom). A theoretical value of $\beta=0.95/\mathrm{C}$ atom for alkanethiols was obtained by Kaun and Guo[40] based on an *ab initio* quantum-mechanical code similar to the one used in this paper. The exponential increase of the resistance with the length of the molecule is not obvious when one uses a density-functional Hamiltonian, but can be understood easily by using a simple tight-binding Hamiltonian.[41,42]

As an example, Fig. 7 displays the transmission coefficient $T(E,\Phi_b=0)$ versus the energy $E-E_F$ of the incident electrons for the configurations 1 and 14 of Figs. 1 and 4, where E_F is the Fermi energy. Figure 7 shows large transmission peaks below −4 eV and above 13 eV. These are due to resonance transmission through HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) molecular energy levels that are broadened due to the interaction of the molecule with the two Au-electrodes. As can be seen, the Fermi level E_F lies in the HOMO-LUMO gap with the HOMO closer to the Fermi level than the LUMO. Additional states, which govern the small conduction values at zero bias voltage, are produced in the HOMO-LUMO gap. The resonance features of these additional states are most pronounced for electrode configuration 1, where the left and right S atoms are directly bonded to the (111) Au surface of the electrodes and are much weaker for configuration 14 where the S atoms connect via cone and/or chain-like structures to the (111) Au-electrodes surfaces.

Figure 8 shows the transmission coefficient $T(E,\Phi_b=0)$ for alkanedithiols with $N=4$, 6, and 8 for electrode configuration 14 versus the incident electron energy $E-E_F$ in the range from −2 to 2 eV. Although the value of the transmission coefficient depends strongly on the number of C atoms in an alkanedithiol molecule, the shape of the transmission coefficients as a function of $E-E_F$ does not vary significantly as seen in Fig. 8. This is in contrast to the strong variations around $E-E_F=0$ for different electrode configurations as il-

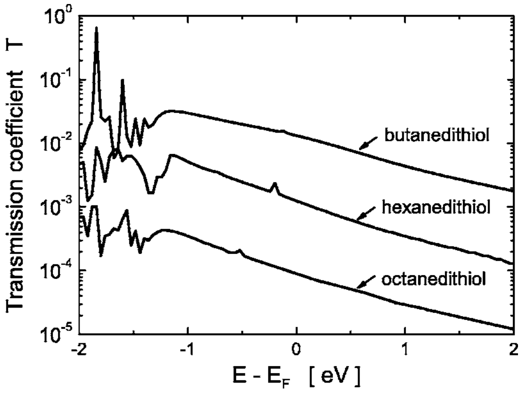

FIG. 8. Transmission coefficient $T(E,\Phi_b=0)$ for 1,4-butanedithiol, 1,6-hexanedithiol, and 1,8-octanedithiol versus $E-E_F$ in the range from −2 to 2 eV for the elctrode configuration 14 of Fig. 4.

lustrated in Fig. 7. Kaun and Guo[40] have shown that, in the case of alkanethiols, the features in the transmission coefficients near $E-E_F=0$ originate from states localized near the S atom site, which leads to nonresonant conductance that causes the exponential increase in resistance with the length of the molecule. The same is true in the case of alkanedithiol molecules for different electrode configurations studied in this paper.

IV. CONCLUSION

In summary, our results indicate that conductance data obtained from STM break-junction experiments, where single molecules can attach to freshly cleaved Au surfaces and where the electrode atomic configuration is most likely cone and/or chainlike, can be modeled using first-principles quantum-mechanical TRANSIESTAC calculations. The calculated results reveal that the zero-voltage conductance is strongly dependent on the details of the atomic configuration of the electrodes. Although the calculated conductance of alkanedithiol molecules agrees well for certain model electrode configurations with the experimental data of Xu and Tao,[16] it is very difficult to establish a direct comparison between experiment and theory since the real geometry of the electrodes is unknown. Furthermore, our results show that the calculated resistance increases exponentially with the length of the molecule in accordance with experimental data. The transmission coefficients of the alkanedithiol molecules indicate a nonresonant tunneling process enhanced by localized states.

ACKNOWLEDGMENT

We acknowledge funding via the CSIRO Emerging Science Area program.

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[1] C. Joachim, J. K. Gimzewski, and A. Aviram, Nature (London) **408**, 541 (2000).

[2] M. A. Ratner, Mater. Today **5**, 20 (2002).

[3] A. Salomon, D. Cahen, S. Lindsay, J. Tomfohr, V. B. Engelkes, and C. D. Frisbie, Adv. Mater. (Weinheim, Ger.) **15**, 1881 (2003).

[4] M. A. Reed, C. Zhou, C. J. Muller, T. P. Burgin, and J. M. Tour, Science **287**, 252 (1997).

[5] J. Chen, M. A. Reed, A. M. Rawlett, and J. M. Tour, Science **286**, 1550 (1999).

[6] W. Y. Wang, T. Lee, and M. A. Reed, Physica E (Amsterdam) **19**, 117 (2003).

[7] C. Zhou, M. R. Deshpande, M. A. Reed, L. Jones, and J. M. Tour, Appl. Phys. Lett. **71**, 611 (1997).

[8] J. G. Kushmerick, D. B. Holt, S. K. Pollack, M. A. Ratner, T. L. Yang, T. L. Schull, J. Naciri, M. H. Moore, and R. J. Shashidhar, J. Am. Chem. Soc. **124**, 10654 (2002).

[9] D. J. Wold and C. D. Frisbie, J. Am. Chem. Soc. **122**, 2970 (2000).

[10] D. J. Wold and C. D. Frisbie, J. Am. Chem. Soc. **123**, 5549 (2001).

[11] K. Slowinski and M. J. Majda, J. Electroanal. Chem. **491**, 139 (2000).

[12] R. E. Holmlin, R. Haag, M. L. Chabinyc, R. F. Ismagilov, A. E. Cohen, A. Terfort, M. A. Rampi, and G. M. Whitesides, J. Am. Chem. Soc. **123**, 5075 (2001).

[13] Y. Selzer, A. Salomon, and D. J. Cahen, J. Phys. B **106**, 10432 (2002).

[14] X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, G. Harris, and S. M. Lindsay, Science **294**, 571 (2001).

[15] X. D. Cui, A. Primak, X. Zarate, J. Tomfohr, O. F. Sankey, A. L. Moore, T. A. Moore, D. Gust, L. A. Nagahara, and S. M. Lindsay, J. Phys. B **106**, 8609 (2002).

[16] B. Q. Xu and N. J. Tao, Science **301**, 1221 (2003).

[17] B. Q. Xu, X. Y. Xiao, and N. J. Tao, J. Am. Chem. Soc. **125**, 16164 (2003).

[18] J. Reichert, R. Ochs, D. Beckmann, H. B. Weber, M. Mayor, and H. von Lohneysen, Phys. Rev. Lett. **88**, 176804 (2002).

[19] H. B. Weber, J. Reichert, F. Weigend, R. Ochs, D. Beckmann, M. Mayor, R. Ahlrichs, and H. von Lohneysen, Chem. Phys. **281**, 113 (2002).

[20] W. Haiss, H. van Zalinge, S. J. Higgins, D. Bethell, H. Hobenreich, D. J. Schiffrin, and R. J. Nichols, J. Am. Chem. Soc. **125**, 15294 (2003).

[21] V. Mujica, M. Kemp, and M. A. Ratner, J. Chem. Phys. **101**, 6849 (1994).

[22] W. Tian, S. Datta, S. Hong, R. Reifenberger, J. I. Henderson, and C. P. Kubiak, J. Chem. Phys. **109**, 2874 (1998).

[23] S. N. Yaliraki and M. A. Ratner, J. Chem. Phys. **109**, 5036 (1998).

[24] M. Di Ventra and N. D. Lang, Phys. Rev. B **65**, 045402 (2001).

[25] Y. Xue, S. Datta, and M. A. Ratner, J. Chem. Phys. **115**, 4292 (2001).

[26] J. Taylor, H. Guo, and J. Wang, Phys. Rev. B **63**, 245407 (2001).

[27] M. Brandbyge, J.-L. Mozos, P. Ordejon, J. Taylor, and K. Stokbro, Phys. Rev. B **65**, 165401 (2002).

[28] K. Stokbro, J. Taylor, M. Brandbyge, J.-L. Mozos, and P. Ordejon, Comput. Mater. Sci. **27**, 151 (2003).

[29] D. Sanchez-Portal, P. Ordejon, E. Artacho, and J. M. Soler, Int. J. Quantum Chem. **65**, 453 (1999).

[30] S. Datta, *Electronic Transport in Mesoscopic Systems* (Cambridge University Press, Cambridge, England, 1995).

[31] T. N. Todorov, G. A. D. Briggs, and A. P. J. Sutton, J. Phys.: Condens. Matter **5**, 2389 (1993).

[32] C. Untiedt, A. I. Yanson, R. Grande, G. Rubio-Bollinger, N. Agrait, S. Vieira, and J. M. van Ruitenbeek, Phys. Rev. B **66**, 085418 (2002).

[33] MOLEKEL 4.0, edited by P. Flükiger, H. P. Lüthi, S. Portmann, and J. Weber, Swiss Center for Scientific Computing, Manno, Switzerland, 2000.

[34] J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanches-Portal, J. Phys.: Condens. Matter **14**,

2745 (2002).
[35] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[36] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[37] E. Z. da Silva, A. J. R. da Silva, and A. Fazzio, Phys. Rev. Lett. **87**, 256102 (2001).
[38] S. R. Bahn and K. W. Jacobsen, Phys. Rev. Lett. **87**, 266101 (2001).
[39] P. Jelinek, R. Perez, J. Ortega, and F. Flores, Nanotechnology **16**, 1023 (2005).
[40] C.-C. Kaun and H. Guo, Nano Lett. **3**, 1521 (2003).
[41] A. Nitzan, Annu. Rev. Phys. Chem. **52**, 681 (2001).
[42] Y. Asai and H. Fukuyama, Phys. Rev. B **72**, 085431 (2005).