Resistive and rectifying effects of pulling gold atoms at thiol-gold nano-contacts

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We investigate, by means of first-principles calculations, structural and transport properties of junctions made of symmetric dithiolated molecules placed between Au electrodes. As the electrodes are pulled apart, we find that it becomes energetically favorable that Au atoms migrate to positions between the electrode surface and thiol terminations, with junction structures alternating between symmetric and asymmetric. As a result, the calculated $IV$ curves alternate between rectifying and non-rectifying behaviors as the electrodes are pulled apart, which is consistent with recent experimental results.

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Stimulated by recent experiments $[1, 2, 3]$, the use of organic molecules as basic components of nanostructured circuits has been envisaged as a way to the further miniaturization of electronic devices. In order to achieve real devices it is required a good understanding of the features affecting the conductance of a single molecule attached to electrodes. The atomic structure of the contact region may strongly affect the conductance and the current-voltage ($IV$) characteristics of a molecular junction. For instance, the choice of different functional groups connecting the molecular core to the electrodes has been shown to lead to very asymmetric $IV$ curves $[4]$. Surprisingly, rectification can also occur in symmetric molecules: in some experiments the careful manipulation of the electrode distances in a symmetric molecule-gold junction can result in asymmetric $IV$ characteristics $[2, 3]$. Since the organic molecule is symmetric, the probable reason for the asymmetric $IV$ curves is the presence of asymmetric contacts. Experimentally, it has been found that the force required to break a molecular junction of a single octanedithiol molecule attached to gold electrodes is similar to the value of the force required to break a Au-Au bond in an atomic gold chain (1.5 - 1.8 nN) $[8]$. This fact strongly suggests that the dithiol molecule can pull Au atoms off the electrodes when a external force is applied. Molecular dynamics simulations also indicate that a thiolate molecule can pull gold atoms off a stepped surface $[10]$. Therefore, asymmetric contacts could be formed by stretching the molecular junctions which in turn could be the source of such asymmetries in the $IV$ curves.

In this paper we have investigated the effect of the strain on the atomic structure and on the electron transport properties of molecular junctions composed by symmetric dithiolated molecules attached to Au(111) electrodes. We find that the conductance is not very sensitive to small applied forces, in agreement with experimental observations made by Reichert et al. $[5]$. However, as the electrodes are pulled apart, we find that it becomes energetically favorable that Au atoms migrate to positions between the electrode surface and thiol terminations, with junction structures alternating between symmetric and asymmetric. As a result, the calculated $IV$ curves alternate between rectifying and non-rectifying behaviors as the electrodes are pulled apart, which is consistent with the results of Reichert et al. $[5]$.

Our methodology is based on density functional theory (DFT) $[11]$ within the generalized gradient approximation (GGA) $[12]$ and norm-conserving Troullier-Martins pseudopotentials $[13]$ as implemented in the SIESTA method $[14, 15]$. The solutions of the Kohn-Sham equations are expanded as a linear combination of atomic pseudo-wavefunctions of finite range. We used a basis set previously used to study methylthiol functionalized gold nanoclusters $[16, 17, 18]$. The conductance and the current are calculated within a nonequilibrium Green’s-function formalism at the same DFT level using the TranSiesta method $[19]$.

We have considered the three organic molecules shown...
in Fig. 1: an insulating alkane chain (octanethiol); a conducting alkane chain (octenedithiol); and the symmetric conjugated polymer [9,10-Bis((2'para-mercaptophenyl-ethinyl)-anthracene)](BPMEA). The molecules are connected to the gold electrodes through the sulphur atoms of the thiol groups, as shown in Fig. 2. The electrodes are described as in Ref. [19], with a (111) gold slab that connects to the bulk of gold leads through their self-energy matrix. The thickness of the slab is 9 layers, out of which one is defined as buffer and the lateral supercell repetitions used are 3x3 and 5x5. We find that the 3x3 cells are large enough for the convergence of the total energy calculations, while the conductance calculations demand 5x5 cells for a convergence of the positions of the transmission peaks within 0.25 eV [20].

In order to address the question of the stability of additional gold atoms between the sulphur atom and the gold surface, we considered the five systems shown in panels (i) through (v) in Fig. 2. In (i) the molecule (alkane in the figure) is directly connected to the gold slabs; in (ii) an extra gold atom is placed in between one sulphur atom and the gold surface; in (iii) extra gold atoms are found at both contacts; in (iv) two atoms are placed between the sulphur and the surface in one of the contacts; in (v) one contact has two extra atoms and the other contact has one. Similar configurations have been also considered for the alkene chain. The Helmholtz free energy $\Omega$ is calculated at the intersections (the force is $F_z = -\delta\Omega/\delta\delta$ as coming from the low $L$ side). These force values can be seen as estimates of the forces required to extract atoms from the gold surface, at least in the adiabatic low-temperature limit. Indeed, the force required to extract the first atom (1.8-2.2 nN) is in good agreement to the value obtained by Krüger et al. [10] using Car-Parrinello molecular dynamics simulations. These extracting forces are not very different for alkane and alkene junctions. This suggests that the forces required to pull off Au atoms from the surface do not depend much on the organic molecular core, and one could expect similar values for other dithiolated molecules. The structures (iii) and (iv) in Fig. 2 have the same number of atoms. Their Helmholtz free energies shown in Fig. 3 indicate that structure (iii) is the most stable one, by 0.7 eV. Therefore, considering energetics aspects only, the results of Fig. 3 would indicate the following sequence of junctions during the pulling of the electrodes: (i) symmetric; (ii) asymmetric; (iii), symmetric; (v), asymmetric. Since an additional gold atom between the sulphur and the electrodes generates

\[ \Omega = E_{\text{total}} - \mu_{\text{Au}} N_{\text{Au}}, \]

where $E_{\text{total}}$ is the calculated total energy, $N_{\text{Au}}$ is the number of extra gold atoms, and $\mu_{\text{Au}}$ is the chemical potential of gold. As a lower bound for $\mu_{\text{Au}}$ we consider $\mu_{\text{Au}} = \mu_{\text{bulk}}$, the total energy per atom for bulk gold. As a plausible upper bound we choose $\mu_{\text{Au}} = \mu_{\text{adatom}}$, the energy of an adatom on the Au(111) surface, i.e., the energy difference between the Au(111) slab with and without an adatom.

Fig. 3 displays the Helmholtz free energy as a function of the length. We also indicates the value of the force at the intersections (the force is $F_z = -\delta\Omega/\delta\delta$ as coming from the low $L$ side). These force values can be seen as estimates of the forces required to extract atoms from the gold surface, at least in the adiabatic low-temperature limit. Indeed, the force required to extract the first atom (1.8-2.2 nN) is in good agreement to the value obtained by Krüger et al. [10] using Car-Parrinello molecular dynamics simulations. These extracting forces are not very different for alkane and alkene junctions. This suggests that the forces required to pull off Au atoms from the surface do not depend much on the organic molecular core, and one could expect similar values for other dithiolated molecules. The structures (iii) and (iv) in Fig. 2 have the same number of atoms. Their Helmholtz free energies shown in Fig. 3 indicate that structure (iii) is the most stable one, by 0.7 eV. Therefore, considering energetics aspects only, the results of Fig. 3 would indicate the following sequence of junctions during the pulling of the electrodes: (i) symmetric; (ii) asymmetric; (iii), symmetric; (v), asymmetric. Since an additional gold atom between the sulphur and the electrodes generates

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asymmetries in the IV characteristics of dithiol junctions, as we shall show below, the sequence of symmetric and asymmetric contacts described above is consistent with the observation of both symmetric and asymmetric IV curves by Reichert et al. for a BPMEA attached to gold slabs. In that experiment, starting with a symmetric IV they increased the inter-electrode distance obtaining an asymmetric IV. After further manipulations they recovered the symmetric IV followed again by asymmetric curves.

Fig. 4 shows the conductance of the octenedithiol as a function of the distance between electrodes for the first and second junctions in Fig. 2(i) junction, for unrelated electrodes. There is no appreciable change in conductance for any of the systems over the quite substantial extensions displayed, which is consistent with what is observed experimentally by Reichert et al. They find essentially unaltered IV characteristics upon extension of up to a few Å, and suggest that the strain is relieved by the soft gold bonds. To test this hypothesis we performed calculations keeping the geometry of the gold electrodes fixed, relaxing only the molecule for each elongation. In this non-relaxed case, the conductance of the alkene chain increases from approximately 0.4 $G_0$ to almost 1 $G_0$ when the electrode distance is increased by only 0.6 Å, as shown Fig. 4. This shows that the weak dependence of the conductance with elongation is due to the relaxation of the electrode geometry near the contact region.

In contrast with the small effect of elongation on the conductance described above, the effect of extra Au atoms in the conduction of the molecular junction is very large, as indicated in Fig. 4. The figure shows that the conductance of the Au/octenedithiol/Au junction is reduced by a factor of three upon the inclusion of an extra Au atom between one of the molecular thiol terminations and the electrode. This effect is further explored in Fig. 5 for BPMEA [(a) and (b)] and for octenedithiol [(c) and (d)]. The upper panels show the effect of the applied bias on the extra-atom junctions in both cases. In lower panels, the energy origin corresponds to the average of the chemical potentials in the left and right electrodes, $\mu = \mu_L + \mu_R$.

In conclusion, we find that the forces normally present in experiments with molecular nanojunctions do not
directly affect the conductance characteristics through these devices due to the softness of the gold leads. They can, however, stabilize extra gold atoms at the electrode-thiol junctions, which do change the conductance and give rise to asymmetry and appreciable rectification effects, which is in qualitative agreement with recent experimental results. Our results concerning the mechanical properties of the junctions are weakly dependent on the actual molecule between the electrodes, being mainly determined by the thiol-gold chemistry.

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