Resistive And Rectifying Effects Of Pulling Gold Atoms At Thiol-Gold Nano-Contacts

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The use of organic molecules as basic components of nanostructured electronic circuits is envisaged as a way to the further miniaturization of electronic devices. This possibility has been stimulated by a large number of experiments, but is still far from becoming a reality in practical applications. Achieving this goal will require important advances in fabrication techniques, but also in the basic understanding of the features that affect the transport properties of devices made of single molecules attached to electrodes. As an example, the atomic structure of the contact region may strongly affect the conductance and the current-voltage (*I/V*) 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 *I/V* curves [1]. 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 *I/V* characteristics [2]. Since the organic molecule is symmetric, the probable reason for the asymmetric *I/V* 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 force required to break a Au-Au bond in an atomic gold chain (1.5 - 1.8 nN) [3]. This 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 [4]. Therefore, asymmetric contacts could be formed by stretching the molecular junctions, which in turn could be the source of such asymmetries in the *I/V* curves.

In this work we use first principles Density Functional Theory simulations [5,6] to investigate the effect of the strain on the atomic structure and on the electronic transport properties of molecular junctions composed by dithiol molecules attached to Au(111) electrodes. We have studied how the changes in the atomic structure of the molecule/electrode contacts can influence the transport properties. We have found that the conductance is not very sensitive to small applied forces, in agreement with experimental observations of Reichert *et al.* [2]. However, if the forces are larger than 1.9 nN, gold atoms can be pulled from the gold surface forming junctions in which additional gold atoms are placed between a sulphur atom and the surface. We show that these additional atoms may strongly affect the conductance of the molecular junction and lead to asymmetries in the *I/V* curves. We find that it is energetically more favorable to pull off one gold atom from each electrode than two gold atoms from the same electrode. Therefore, by stretching the junction it is possible to generate asymmetric contacts followed by symmetric ones, which could be an explanation for the sequence of symmetric and asymmetric *I/V* curves obtained by Reichert *et al*. [2] in experiments in which the distance between electrodes in a symmetric molecule junction is manipulated.

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