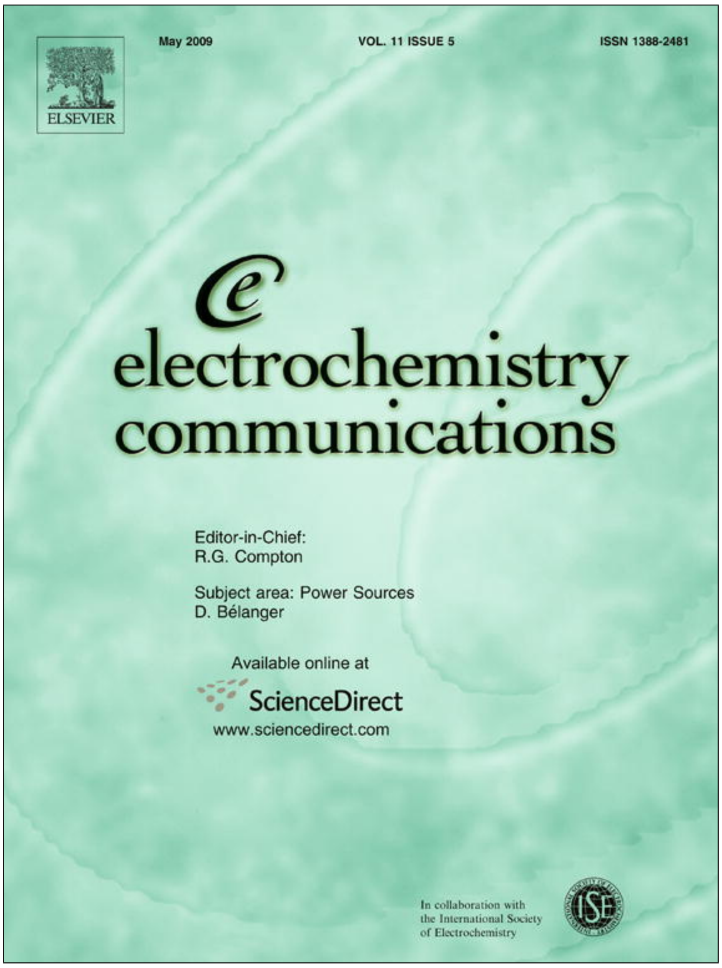
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The behavior of single-molecule junctions predicted by atomistic simulations

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ABSTRACT

Molecular dynamic simulations in combination with energy minimizations are used in order to understand the basis of the novel experiments reported recently by Haiss et al. (W. Haiss, C. Wang, I. Grace, A.S. Batsanov, D.J. Schiffrin, S.J. Higgins, M.R. Bryce, C.J. Lambert, R.J. Nichols, Nature Mater. 5 (2006) 995). Our model suggests that single-molecule junctions produced by the trapping method can be reached when the STM tip – substrate surface separation is smaller than 8 Å. Additionally, our model predicts that the effect of the electric field on the attachment/detachment process can be neglected.

1. Introduction

During the last years the building of molecular switches has motivated many researchers to find a suitable way to connect a single molecule between two metallic electrodes and hence construct nanodevices to be used in molecular electronics [1].

In recent years Tao and co-workers [2,3] have developed a novel technique to obtain single-molecule-contact conductance measurements. They were able to create single-molecular junctions by means of a scanning tunnelling microscope (STM) tip. The method involves a soft mechanical contact between the STM tip and a Au(111) surface in a solution containing the sample molecules (i.e. alkanedithiols). After withdrawal of the Au tip, one or several alkanedithiol molecules can be linked between the end-atoms (from tip and surface) and the conductance is measured at the same time as the system is elongated.

A different approach to measuring conductance of single-molecule junctions was developed by Haiss et al. [4–7] based on trapping alkanedithiol molecules between a STM tip and a substrate without mechanical contact between them. In one type of experiments, the spontaneous attachment and detachment of alkanedithiols was monitored through the time, by means of the observation of current jumps. When the gap between the tip and the surface was bridged by a dithiol molecule, the tunnelling current presented a step as a consequence of the decrease in the resistance of the junction [4]. In another set of experiments, the STM tip was lifted while keeping a constant location on the surface. As a consequence, the tunnelling current decayed presenting a number of plateaux. It is worth pointing out that while the first technique measures a one-molecule event (its attachment/detachment), the second may involve all the molecules trapped in the gap between the STM tip and the substrate.

In the present work we make a first attempt to understand the foundation of the technique developed by Haiss et al. [4–7], specifically to answer the question: *why dithiols molecules are detached from the Au(111) surface to jump towards the tip and/or vice versa*? Our goal is to understand the mechanism at the atomic level in order to suggest or predict different situations, and therefore to help to improve the method.

In the experiments performed by Haiss et al. [4] it has been shown that both sulphur atoms of the alkanedithiol molecule are bonded to the Au(111) surface at low coverage and short times (15 s), whereas only one S atom is linked to the gold surface at high coverage and long immersion times. On the basis of these detailed experimental observations, we have performed a combination of classical molecular dynamics and energy minimization calculations to evaluate activation energies and waiting times for the attachment/detachment events.

2. Model and methods

The model system in our calculations is shown in Fig. 1. Firstly, the alkanedithiol molecule is adsorbed on the Au(111) surface in a flat configuration, through the sulphur(thiolate group)-gold bonds. As we are interested in determining the activation energies of the jump process, we have devised the following procedure. While one of the thiolate terminal groups, for example S_1, remains attached to the surface, the other terminal groups, S_2 for instance, is lifted towards the tip, allowing the whole structure to relax. In Fig. 1b, a rotation angle θ is defined as the angle between the segment

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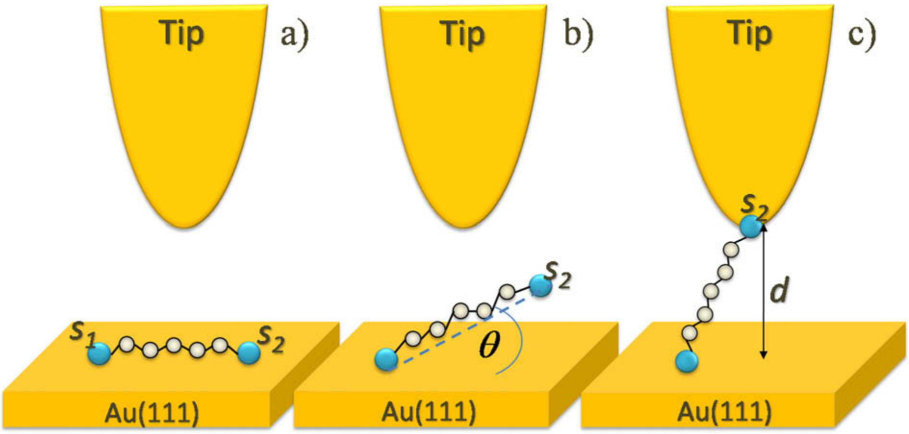

Fig. 1. Model system employed in the simulation. (a) A 1,8-alkanedithiol molecule is initially attached to the Au(111) surface. (b) One of the S atoms of the molecule is subsequently moved towards the tip in small steps. (c) The molecule forms the molecular wire.

joining both S atoms of the molecule and a straight line parallel to the surface.

The 1,8-alkanedithiol molecule was modelled according to the united atom method. On the other hand, the Au(111) surface and the tip were represented by means of metal atoms arranged on an fcc(111) structure with the lattice parameter of bulk Au, remaining fixed during the simulation.

The interatomic potential between atoms was represented by several contributions to the total energy, composed of two-body, three-body and four-body interactions as follows:

$$V_{total} = V_{stretching} + V_{bending} + V_{dihedral} + V_{LJ} + V_{Morse} + V_{Coulomb} \qquad (1)$$

where $V_{stretching}, V_{bending}, V_{dihedral}$ and V_{LJ} represents the stretching of the bond, the angle bending contribution due to three atoms, the torsion potential due to four linked atoms, and the short-range van der Waals interaction, respectively. The last two terms (V_{Morse} and $V_{Coulomb}$) represent the S–Au interaction and the electrostatic interaction, respectively. The bond–stretching interactions are described by means of a harmonic potential:

$$V_{streching} = \frac{1}{2}k_r(r - r_0)^2 \qquad (2)$$

where k_r and r_0 are the force constant and the equilibrium bond length, respectively. The bond-bend term is given by:

$$V_{bending} = \frac{1}{2}k_\theta(\theta - \theta_0)^2 \qquad (3)$$

where θ is the C–C–C or S–C–C angle and θ_0 and k_θ are the equilibrium angle and the force constant, respectively. The torsion interaction is given by the following polynomial:

$$V_{dihedral} = a_0 + a_1\cos(\phi) + a_2\cos^2(\phi) + a_3\cos^3(\phi) + a_4\cos^4(\phi) + a_5\cos^5(\phi) \qquad (4)$$

where ϕ is the dihedral angle between four atoms. The model parameters used have been successfully employed in the literature [8,9] to study a variety of systems. In addition to the stretching, bending and dihedral contributions, short-range van der Waals interactions (12-6 Lennard Jones) were considered between atoms in the chain, and between CH_2 groups with gold atoms.

Finally, and in connection with one of the most important parameters in our model, we considered the interaction between S and Au surface atoms. The Au–S bonding was represented by a pairwise additive Morse potential, with parameters fitted from first-principle calculations [10]:

$$V_{Au-S} = D_e[\exp(2\alpha(r_e - r)) - 2\exp(\alpha(r_e - r))] \qquad (5)$$

where α, D_e and r_e are fitted parameters.

This parameterization predicts correctly the adsorption energy of 1-octanethiol on Au(111) (−3.728 eV compared with −3.609 eV from DFT calculations); the S-surface distance (1.91 Å compared with 2.03 Å from DFT); the S–Au distance (2.53 Å compared with 2.50 Å from DFT); and the angle of alkanethiols with respect to the normal to the surface (73° compared with 60° from DFT) [11].

3. Results

We have performed extensive calculations at different tip-surface distances while computing the potential energy of the system. Fig. 2 shows the potential energy as a function of the thiol group(S_2)-surface distance for several tip-surface distances (from 6 to 15 Å). The calculations show that the detachment of the dithiol molecule is an activated process, which depends on the tip-surface distance. Initially, the molecule lays flat on the substrate, with both sulphur atoms attached to the Au surface. This fact is reflected in the minimum observed at S_2-surface distances close to 2 Å in Fig. 2. As one of the thiol-terminal groups begins to rise, the potential energy increases until a maximum, which will define the saddle-point of the transition state. Finally, when the maximum angle of lifting is reached, the potential energy achieves a second minimum which depends on the tip-substrate distance. Such configura-

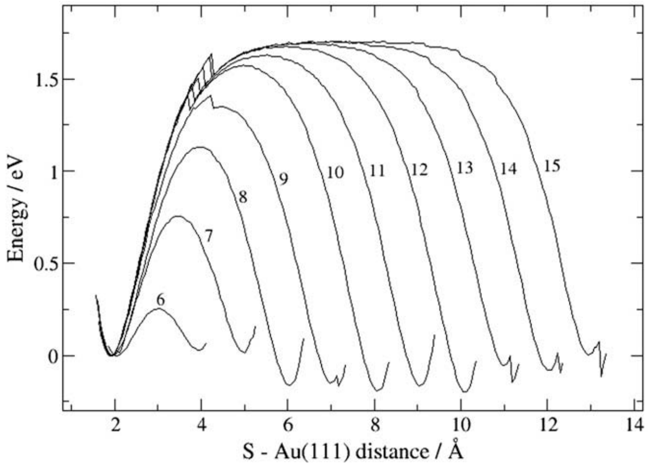

Fig. 2. Potential energy as a function of the S–Au(111) distance for several tip-surface distances (from 7 to 14 Å).

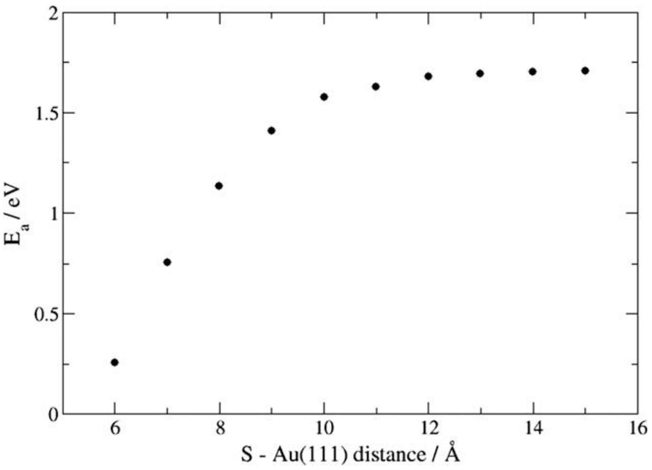

Fig. 3. Activation energies for the detachment process as a function of the tip-surface distance.

tion corresponds to that in which both thiol-terminal groups are linked to Au (one to the planar surface and the other to the tip surface).

It is important to note that at tip-surface distances greater that 9 Å the energy vs. S–Au(1 1 1) distance curves present an abrupt decrease of the potential energy at approximately 4 Å. These jumps on the potential energy were found to be due to conformational changes (through the torsion) in the molecule. At this point we can compute the activation energy of the detachment process as the difference between the energy of the configuration at the saddle-point and the initial (relaxed) configuration. The calculated activation energies for different tip-surface distances are shown in Fig. 3. As can be observed, for a tip-surface distance of 12 Å, which corresponds to the 1,8-octanedithiol length, the activation energy to detach a single molecule is too high (~1.68 eV) to make the process observable within the experimental time. In fact, if we assume the transition state theory to be valid for the problem at hand, we can estimate the waiting time (t_w) for a transition as follows:

$$\frac{1}{t_w} = \nu_0 \exp\left(-\frac{E_a}{RT}\right) \qquad (6)$$

where ν_0 is an attempt frequency. If we take $\nu_0 = 1 \times 10^{12}\ s^{-1}$ at room temperature we obtain $t_w = 1.53 \times 10^{17} s$. Evidently, this time is inaccessible. Therefore, our model suggests that within the present molecular structure, the tip should be very close to the surface (~6–7 Å) so as to detect the jump within the waiting time observed experimentally (~0.1 s).

Finally, and assuming that the tip is close to the substrate surface during the trapping of the alkanedithiol molecules, (i.e., the tip-substrate distance is approximately 7 Å), the electric field (E) at the interface between the tip and the substrate cannot be neglected *a priori*. If a bias potential of +0.3 V is applied (as in the experiment performed by Haiss et al. [4]) the magnitude of the resulting electric field between both electrodes (assuming that the line of forces are all normal to the plane of the substrate) will be of the order of 0.042 V/Å. For the purpose of introducing the effect of E in our model, we have performed Density Functional calculations (DFT) using the SIESTA-package [12] to obtain the net charge on each atom by means of the Mulliken population analysis for the adsorbed molecule. The values obtained for the Mulliken charges were −0.2470, 0.0004 and 0.0260 atomic units for S, Au and the CH_2 group, respectively. These charges were subsequently added to the classical force field as a coulomb term. The effect of the electric field was introduced by simply adding the following contribution to the forces on the atoms:

$$F_e = |E|q_i = \frac{|V|}{h} q_i \qquad (7)$$

where q_i are the electric charges on each atom and V is the bias potential applied between the STM tip and the substrate surface. Image charges were also considered during the calculations of the activation energy of the detachment process. The activation energy for the detachment of a dithiol molecule in the presence of an electric field is a small fraction of an eV, therefore could be omitted from the model. This fact can also be understood in terms of the following qualitative discussion. Let us consider S, the atom with the highest Mulliken charge in absolute value, and a tip-substrate bias of 0.3 V. The application of this bias would produce a change of −0.247 e × 0.3 V = 0.074 eV in the potential energy of the system for the transfer of this S atom from the substrate to the tip. Taking into account that the transition state experiments only a fraction of the total bias, it can be stated that field effects should be negligible. More precisely, it should be emphasized that the changes in the potential energy profiles are given by the potential bias, and not by the electric field.

4. Conclusions

We have presented a simple computational model to understand the physical basis of the trapping method to generate single-molecule junctions as reported by Haiss et al. [4–7]. The model was analyzed by means of molecular dynamic simulations and energy minimizations calculations, and predicts that the STM tip must be very close to the substrate surface in order to catch the molecular linkers (i.e., 1,8-alkanedithiol molecules), as long as their molecular structure is that usually proposed. Finally, the effect of the electric field was introduced to the model, showing that such parameter may be neglected to understand the mechanisms of the method. Further investigations will introduce the effect of mobile gold atoms.

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