Electron transport signature of H$_2$ dissociation on atomic gold wires

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Nonequilibrium Green's functions calculations based on density functional theory show a direct link between the initial stages of H$_2$ dissociation on a gold atomic wire and the electronic current supported by the gold wire. The simulations reveal that for biases below the stability threshold of the wire, the minimum-energy path for H$_2$ dissociation is not affected. However, the electronic current presents a dramatic drop when the molecule initiates its dissociation. This current drop is traced back to quantum interference between electron paths when the molecule starts interacting with the gold wire.

The field of molecular dynamics studied by electronic currents has been continuously expanding in the past two decades [1–8]. Major progress was achieved when electron currents were tailored to detect reactions within a single molecule, prompting the search for single-molecule chemistry [9–11]. In this way, molecules could be studied to dissociate [2], to assemble [4,5], and to desorb [10,11] in the extraordinary conditions of a perfectly known environment. All of these experiments were performed for molecular adsorbates under a scanning tunneling microscope tip. However, an electrical probe has yet to be proposed to study single-molecule chemistry in the gas phase or in solution.

Using the variations of electronic currents in nanowires is a very interesting possibility for reaching the single-molecule limit in gas or liquid chemical reactions. Due to the extreme reduction in the wire's dimensions, nanowires present enhanced reactivity. Thus, the very inert noble metal, gold, becomes chemically active in clusters [12–21] and nanowires [22–29] due to the presence of many dangling orbitals which form bonds with the surrounding molecules. In particular, the

possible dissociation of H$_2$ on gold nanowires has already been reported [30,31]. In order to use the nanowire as a reactivity sensor, the electronic transport properties of the wire should change in the presence of a chemical reaction while the reaction remains unaltered by the flowing electron current. Unfortunately, evidence of the reactivity-sensing properties of atom-size nanowires still needs to be revealed.

In this Rapid Communication, we concurrently evaluate the minimum-energy path (MEP) of a gas-phase H$_2$ molecule that impinges on a gold nanowire and the wire's electron current, using nonequilibrium Green's functions (NEGFs) and density functional theory (DFT). These calculations show that for biases below the stability threshold of the wire, the H$_2$ molecular dynamics is not affected. However, the electronic current presents a dramatic drop when the molecule initiates its dissociation. Hence, atom-size nanowires can be excellent probes for determining the onset of H$_2$ dissociation without perturbation from the measuring current.

Starting from an initial atomic configuration, the MEP is obtained by computing the total potential energy and its gradient as the H$_2$ molecule approaches the atomic wire. The initial configuration corresponds to H$_2$ far from a gold monoatomic wire and the final one corresponds to the chemisorbed species on the wire, forming the usual

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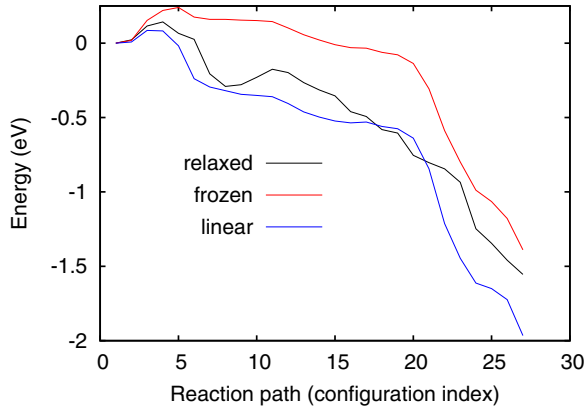[†]nicolas.lorente@cin2.cat

FIG. 1. (Color online) Minimum-energy path (MEP) for three models of a hydrogen molecule impinging on a 4-atom gold wire connected to semi-infinite electrodes. The energy with respect to the initial configuration energy is plotted against the index of the 27 points chosen to describe the dissociation of H_2 on the wire. The initial configuration corresponds to a relaxed molecule and wire distant enough to have no mutual interaction. Black line (relaxed): MEP when the 4-atom chain is also allowed to change its geometry. Red line (frozen): MEP for a frozen 4-atom chain to the initial configuration. Blue line (linear): MEP for an infinite gold atom chain that is allowed to adapt to the evolving H_2 molecule. The realistic case (relaxed) shows two equilibrium situations at the stages $i = 8$ and 27 of the MEP.

Au-H-Au-H-Au double-bridge bond [31]. The energy and corresponding gradients are evaluated using the TRANSIESTA code [32,33] with the Perdew, Burke, and Ernzerhof (PBE96) functional [34]. The whole system can be divided in three distinct regions breaking periodicity along the transport direction. The contact region is a central region composed of a 4-atom free-standing gold chain connected to two electrodes, left and right, each formed by the first five layers of a 3×3 cell of Au (111). The two electrodes were frozen, and kept at a distance of 13.3 Å. The interelectrode distance affects the interatomic distance, which has been analyzed elsewhere [28]. The two other regions are the semi-infinite electrodes formed by periodically repeating three layers of bulk gold in the (111) direction. In this way, bias can be applied between the two asymptotic regions by shifting their Fermi levels, and by self-consistently solving the Poisson and DFT equations for the nonequilibrium density matrix in the central region [33]. Finally, the electron transmission through the central region is evaluated for all cases using standard nonequilibrium Green's functions [33].

Three different models of the wire, of decreasing complexity, have been built to better understand the processes under study, and in each case a MEP has been calculated (Fig. 1). First, the model contact described above has four central gold and the two hydrogen atoms optimized along the MEP (relaxed wire). In the second case, the four central gold atoms are kept frozen in a linear configuration, and only the geometry of the two hydrogen atoms is optimized (frozen wire). Finally, we consider the case of a linear chain of 12 gold atoms (linear wire), repeated periodically, kept frozen, and where only the two hydrogen atoms define the MEP. The MEPs in the three considered cases have been discretized in a set of 27 points, each one corresponding to a different nuclear configuration.

In the three cases, H_2 dissociation on the gold wire is exothermic by 1.4–2 eV. All the cases present a low barrier when H_2 approaches the wire (approximately at $i = 4$). The barrier height is ≈ 0.12 eV for the relaxed and linear wires and ≈ 0.25 eV for the frozen case. Keeping in mind that the zero-point energy of H_2 is ≈ 0.25 eV, it should be easy to overpass. Once on the top of this barrier, the reaction path has been determined by following the gradient. In the case of the relaxed wire, there is a well for $i = 8$, of roughly 0.25 eV below the asymptote given by $i = 1$. In this case, once the two minima were found ($i = 8$ and 27), the saddle point is located by doing several minimizations starting from different geometries. In a previous work [31], it was found that the saddle point corresponds to one hydrogen bonded to two Au atoms, in a Au-H-Au bridge bond, and the second hydrogen on the top of one Au atom. Thus, the initial geometries chosen were all close to this situation. The initial guesses yielded to the chemisorption well ($i = 27$), and the process is ended when a small change in the initial guess leads to the entrance well ($i = 8$). To refine the position of the saddle point, a detailed calculation varying the geometries of the two hydrogen atoms is done. Once the approximate saddle point ($i = 12$) is determined, two final minimizations are performed towards each of the two minima, to extract several points along the path to characterize the MEP. Some characteristic geometries for the relaxed and frozen wires are illustrated in the lateral panels of Fig. 2.

We can now evaluate the electron transmission between electrodes for each of the stages i of the MEP. When H_2 is far from the wire ($i = 1$, bottom panel of Fig. 2), the transmission at the Fermi level is equal to one for the three cases because each system presents one single conduction channel. On the opposite side, for $i = 27$ with the two hydrogen atoms chemisorbed in the wire forming the double-bridge bond, the transmission is reduced, being ≈ 0.75 in the linear model and ≈ 0.5 in the other two cases. At the minimum ($i = 8$) and saddle ($i = 12$) points the transmission is in between 0.8 and 1 in the three cases, all of them showing a rather smooth and similar behavior along the MEP. However, $i = 5$ is a striking point because the three cases show a nearly zero transmission. It corresponds to the initial stage of the H_2 dissociation where a slightly elongated H_2 starts to attach to the gold wire.

Kiguchi *et al.* [35] have found that the electronic transmission dramatically decreases when H_2 inserts in a metallic nanowire, Pt in their case. This situation corresponds to an elongated metallic wire, with a long distance between the two Pt atoms, and a H_2 molecule inserted, behaving as a bridge. Their analysis shows that the H atoms partially saturate the s and d orbitals of the two neighboring Pt atoms, producing a reduction in the electronic transmission. However, in the results presented here, there is no saturation of the s-d orbitals of the gold atoms, which could explain the reduction of the electron transmission. Furthermore, when the two hydrogen atoms reduce the distance to the wire, they form stronger bonds with the surrounding gold atoms, with the result that the transmission increases again.

To analyze this result, and based on the similarity of the three model systems considered here, we use the simplest
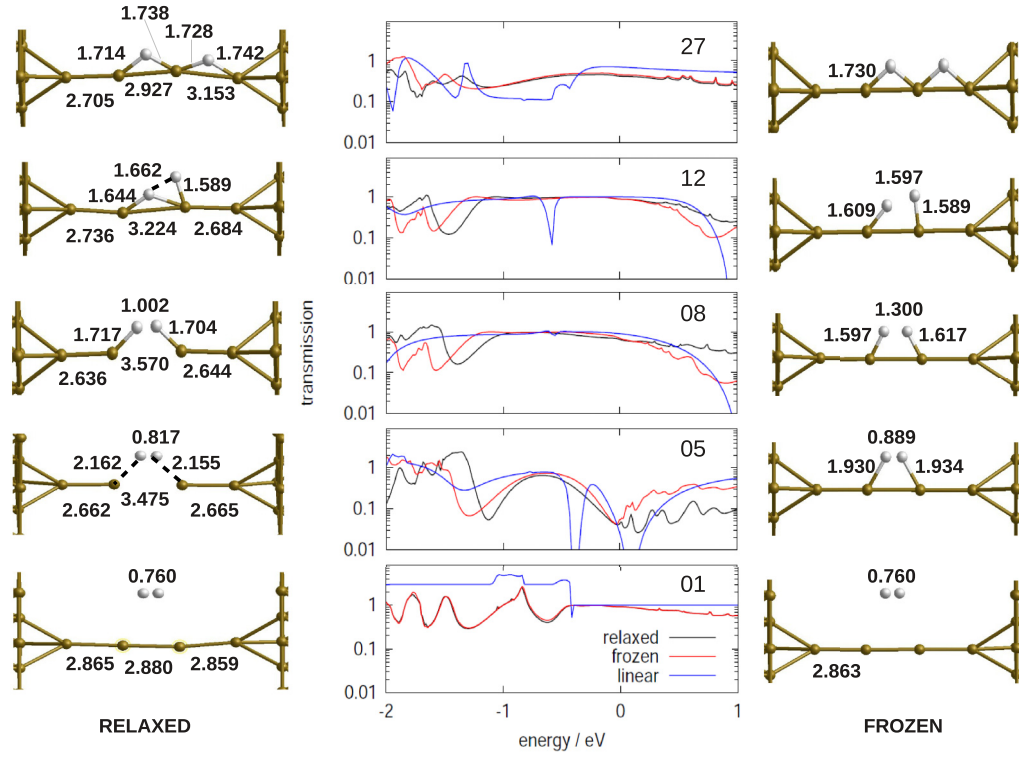
FIG. 2. (Color online) Central panels: Electronic transmission vs electronic energy at significant points along the H$_2$ MEP. The zero of energy is taken at the electrode's Fermi level. In the lateral panels, the geometries of the relaxed (left) and frozen (right) wires are shown. The geometries of the infinite linear gold wire are very similar to those of the frozen wire. Numbers in the geometrical schemes denote distances in Å. The spontaneous H$_2$ dissociation is initiated at stage $i = 5$, where the transmission shows an important decrease at the Fermi level.

linear model. We have calculated its eigenchannels, defined as the nonmixing transmission channels that diagonalize the transmission matrix with eigenvalues $0 \leqslant T_n \leqslant 1$, whose sum provides the total transmission of the system [36–38]. For all the geometries, there is only one conduction eigenchannel contributing to the transmission at the Fermi energy, as expected for gold atomic chains. When H$_2$ is far from the wire ($i = 1$), the conduction channel is located in the wire. As H$_2$ sticks to the wire, part of the electron flux passes through it, either as molecular hydrogen ($i = 8$) or as atomic hydrogen chemisorbed on the wire ($i = 27$). At $i = 5$, however, the amplitude density of the eigenchannel becomes zero at the right edge, indicating that the electron flux is stopped. This reveals an interference effect.

This interference behavior can be rationalized in terms of a four-state tight-binding model composed of two gold and two hydrogen atoms described by one orbital, where the possible electronic paths along the wire and the molecule are jointly solved. The model is defined by the energies $E_{Au} = 0$ and E_H, and by three hopping terms T, $t_a = t_b$, and t (see Fig. 3). The coupling to the rest of the system is characterized by the self-energies $\Sigma_a = \Sigma_b$ associated with the a or b leads; then the wire's transmission $T(E)$ is given by [39]

$$T(E) = \frac{8e^2}{h} |\Sigma_a(E)|^2 |G_{ab}(E)|^2, \qquad (1)$$

where $G_{ab}(E)$ is the ab component of the Green's function associated with the four-atom model described above. Figure 3 shows $T(E)$ for the indicated set of parameters, taking

$\Sigma_a = \Sigma_b = iT$ to guarantee that $T(E = 0)$ becomes 1, for $t_a = t_b = 0$, the case of an ideal Au chain, as in the point $i = 1$. As H$_2$ approaches the wire, t_a grows and the electron can also be transmitted through the Au-H bond with two concurrent electron paths competing, one going through the H atoms and the other one through the Au atoms. These two transmission
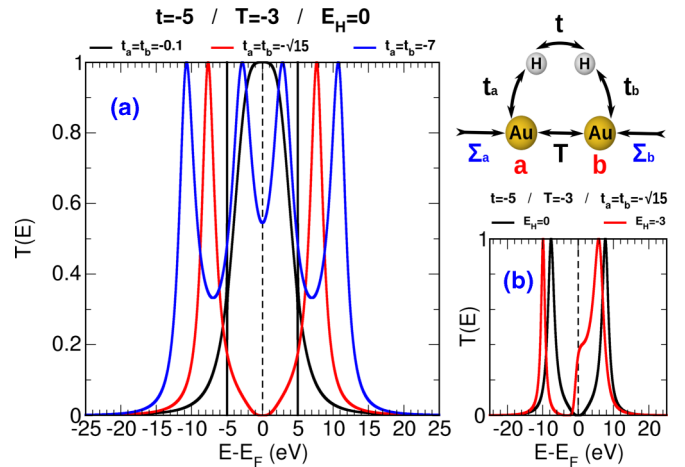

FIG. 3. (Color online) Transmission as a function of energy for the model system shown in the upper right-hand side of the figure, for different values of $t_a = t_b$ and E_H ($E_{Au} = 0$ eV, $T = -3$ eV, and $t = -5$ eV). (a) $E_H = 0$. (b) $E_H = -3$ eV. For $t_a = t_b = \sqrt{15}$, $t_a^2 = Tt$ a dip in $T(E)$ is found.
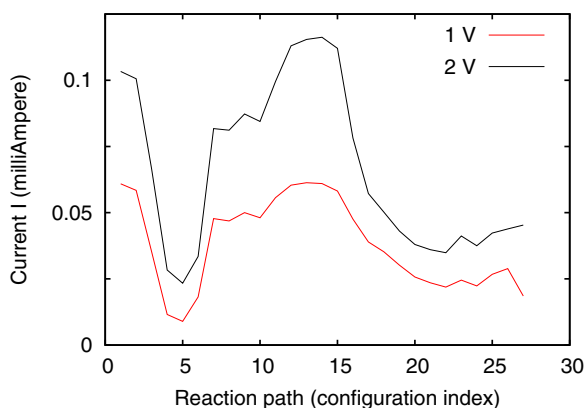
FIG. 4. (Color online) Electron current I for biases of 1 and 2 V, vs the system configurations, which correspond to the zero-bias MEP for the relaxed wire (Fig. 1). At the dissociation onset, stage $i = 5$, there is an important drop in the current due to quantum interference between the through-wire and through-molecule electron paths. The drop is visible at both biases. At 2 V, the wire's stability is compromised and the zero-bias MEP is used to illustrate the robustness of the quantum-interference effect.

paths lead to interferences which manifest in Fano profiles of the electronic transmission [40–43], with a zero occurring when the two paths occur with nearly equal amplitude.

These conditions for the interference are imposed by the atomic geometry found in the MEP for $i = 5$. The connection between geometry and quantum interference in molecular conduction has already been proven experimentally [44]. In the present case, the H_2-wire interactions are strong enough to steer the molecule to become parallel to the wire before dissociation. In this geometry (point $i = 5$ of the MEP), the electronic conditions needed for the above interference are met.

Finite bias changes the above picture only quantitatively. The electronic transmission has been investigated at 0.5, 1, and 2 V. This has been done at the configurations of the MEP calculated for zero voltage. At finite bias, the MEP is ill defined due to the appearance of nonconservative forces [45–47]. However, if the bias-induced changes in the forces are small

enough, we expect the zero-voltage MEP to be an excellent approximation to the molecular path at low temperatures. To check these approximations, the forces were calculated along the MEP for the different bias voltages considered. This was done using the Hellman-Feymann-like method implemented in SIESTA but using the nonequilibrium density matrix and Hamiltonian matrix instead of the equilibrium quantities. We found that for a bias voltage lower than 2 V, the change in the forces was negligible.

Figure 4 shows the wire's currents evaluated from the electron transmissions for 1 and 2 V. As voltage increases, the current increases as well. For all the considered wire models, there is a pronounced decrease of the current intensity for $i = 5$. Again, we retrieve that the decrease is due to the quantum-interference effect at the initial stage of dissociation. These results show that even at biases larger than 1 V, within the stability limit of the wire, the dissociation of the H_2 molecule will cause a measurable decrease in the electron current through the gold wire.

In summary, nonequilibrium Green's function (NEGF) calculations based on density functional theory (DFT) are used to evaluate the minimal energy path (MEP) that an H_2 molecule follows near an atomic-sized gold wire. The molecule dissociates on the wire and the electronic current decrease in the initial stages of H_2 dissociation on a gold atomic wire. This current drop is due to quantum interference between electron paths when the molecule starts interacting with the gold wire. Moreover, no significant dependence of the MEP on applied biases below the wire's stability limit has been found. This suggests that the conductance properties of gold wires can be recorded to acquire information on chemical reactions taking place in the single-molecule limit in a gas or liquid environment.

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