The Smallest Molecular Switch

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Ab initio total energy calculations reveal benzene-dithiolate molecules on a gold surface, contacted by a monatomic gold STM tip to have two classes of low-energy conformations with differing symmetries. Lateral motion of the tip or excitation of the molecule cause it to change from one conformation class to the other and to switch between a strongly and a weakly conducting state. Thus, surprisingly, despite their apparent simplicity, these Au/BDT/Au nanowires are shown to be electrically bistable switches, the smallest two-terminal molecular switches to date.

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Electronic devices that switch between high and low resistance states are at the heart of the modern information technology. As miniaturization of this technology continues to progress, the long-standing fundamental problem of identifying and understanding the smallest physical systems that are capable of switching behavior is attracting growing interest [1–8] . Recently it has been discovered experimentally that some molecular wires (i.e., *single molecules* carrying an electric current between a pair of metal nanoelectrodes) can exhibit electrical bistability and switch between strongly and weakly conducting states, either spontaneously or in response to a change in the applied bias voltage [1–3]. It has been suggested that this intriguing behavior may be due to charging of the molecule and/or changes of the molecular geometry (conformation) [1–4]; however, the complexity of the experimental systems has thus far prevented the development of a quantitative explanation. On the theoretical side, the possibility of making molecular wire switches by introducing a third (gate) electrode into the system has been explored [5–7], as has the possibility of designing two-terminal molecular wires that switch due to electric field-induced conformational changes [8]. In this Letter, we demonstrate theoretically that a much smaller and simpler two-terminal molecular wire can exhibit bistability and switching than has been thought possible until now, and we present a realistic theory of its behavior. We consider a 1,4 benzene-dithiolate (BDT) molecular wire with one sulfur end group bonded to a gold substrate and the other to a monatomic gold scanning tunneling microscope (STM) tip as depicted in Fig. 1. Our *ab initio* total energy calculations [9] demonstrate that this system has low-energy conformations of two distinct types that have different symmetries. Flipping between these conformations is predicted to occur in response to lateral motion of the STM tip, and, also, for some positions of the STM tip, in response to excitation of the wire by a current pulse or spontaneously at nonzero temperatures. The symmetry change when the molecular wire flips results in a large change in its current-voltage characteristic. Thus, its electrical conductance exhibits bistability and switching. Theoretical work [10–15] stimulated by a pioneering molecular wire experiment [16] has elucidated various aspects of electron transport through Au/BDT/Au wires. However, the possibility that wires of this type may be bistable or capable of switching is far from obvious *a priori* and has not been investigated until now [17]. Thus, as well as identifying the smallest two-terminal molecular switch to date and shedding new light on the mechanisms of molecular bistability and switching, the present work reveals an unexpected new dimension of the physics of Au/BDT/Au molecular wires, one of the most important paradigms of molecular electronics. The molecular switch that we describe should be amenable to experimental study with presently available techniques. Thus, our findings also raise the prospect of bridging the gap that has persisted in this field between theory and experiment since molecular switching was first observed.

In our *ab initio* calculations of the energetics of Au/BDT/Au wires [9], the STM tip was represented by a tetrahedron of Au atoms and the Au (111) substrate by a cluster of three Au atoms as shown in Fig. 1. We searched for low-energy molecular wire conformations holding the

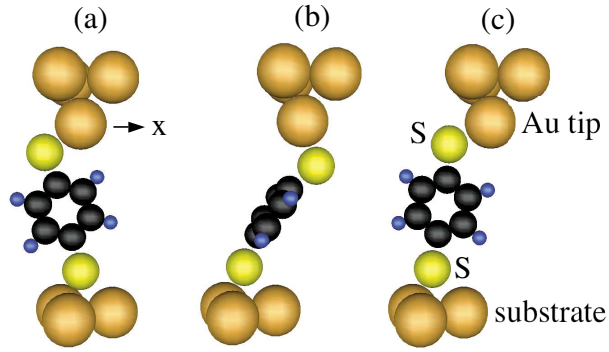

FIG. 1 (color online). Relaxed molecular conformations. (a) Ground state (edge) conformation for STM tip at $x = 0$ Å, over hollow substrate bonding site. (b) Ground state (face) conformation for $x = 3$ Å. (c) Metastable edge conformation for $x = 3$ Å.

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positions of the Au atoms fixed and keeping one of the S atoms of the BDT over the hollow site between the three Au substrate atoms since it is believed that organic thiol molecules bond to Au (111) surfaces via a sulfur atom at this location [18]. All other coordinates of the atoms of the wire were allowed to vary freely. The lowest energy conformation of the molecular wire when the Au tip atom is directly over the hollow bonding site of the substrate and 9.9 Å from the substrate is depicted in Fig. 1(a). The molecule orients itself so that the Au tip atom is approximately coplanar with the benzene ring. We will refer to this as an *edge* conformation of the wire since the Au tip atom faces the edge of the benzene ring. If the Au tip is moved further from the substrate, so that it becomes *geometrically* possible for the molecule to stand perpendicularly to the substrate with the terminal Au atom of the STM tip directly over the upper S atom, we find this upright geometry to be unstable energetically: As long as the tip atom is close enough to the molecule for a chemical bond to form between the Au and S atoms, the molecule relaxes to a tilted position. We note that such nonlinear bonding geometries of Au, S, and C atoms have also been found in recent *ab initio* simulations of monatomic Au wires bonded to other organic thiolate molecules [19].

When the Au tip is moved laterally away from the position over the hollow substrate bonding site, we find the molecular wire's ground state conformation to change dramatically. This is illustrated in Fig. 1(b) where the tip has been displaced laterally by 3 Å in the x direction from its ($x = 0$) position in Fig. 1(a). Interestingly, the molecule adopts an orientation in which it tilts as far from the normal to the substrate as it can while maintaining the chemical bond between the Au tip atom and the upper S atom of the molecule. Most importantly, however, as the lateral tip displacement increases from $x \sim 2$ Å to ~ 3 Å, the molecule rotates about its S-S axis from its edge conformation through an angle of $\sim \pi/2$ to an orientation in which the Au tip atom is over the flat face of the benzene ring, as in Fig. 1(b). We shall refer to this as a *face* conformation. Thus, the ground state conformation of the molecular wire switches from edge to face as the STM tip moves laterally away from the location where the molecule bonds to the substrate. If the tip is moved instead in the opposite (negative x) direction from its position in Fig. 1(a), the ground state conformation of the molecular wire again switches from edge to a strongly tilted face geometry although the substrate and tip both have a pronounced left-right asymmetry. For the $x = 3$ Å position of the tip in Fig. 1(b), we find the molecular wire to also have a metastable conformation that corresponds to a *local* energy minimum. This is the upright edge conformation in Fig. 1(c) whose energy is 0.11 eV above the ground state face geometry of Fig. 1(b) [20].

We now examine the implications of the conformational switching and bistability described above for electrical conduction through the molecular wire. In recent years, much progress has been made developing theories of electron transport through molecules [10–15,21–24]. An important conclusion has been that the current at low bias is carried by molecular π orbitals. The overlap between the π orbitals and the states of the contacts is sensitive to the orientation of the molecule relative to the contacts, which implies a strong orientation dependence of the molecular wire's conductance [14]. Such overlap effects have been found in semiempirical [10,15] and density functional [12] transport calculations. Thus, it is reasonable to expect them to result in a significant change in conductance when an Au/BDT/Au wire switches between an edge and a face conformation, and our calculations show this to be the case. Since semiempirical calculations have been successful in explaining the experimental current-voltage characteristics of a variety of molecular wires consisting of organic thiol molecules bonded to gold electrodes [15,21,23], we adopted this approach here [25]. In Fig. 2, we show the calculated differential conductance [25] of the molecular wire in its *ground state* conformation for a sequence of positions of the STM tip along a linear trajectory over the molecule that passes through the locations that the tip occupies in Fig. 1. [Figs. 1(a) and 1(b) correspond to $x = 0$ Å and 3 Å on the trajectory, respectively.] When the tip is furthest from the center where the molecule bonds to the substrate (i.e., for $x = -4$ Å and 4 Å in Fig. 2), the molecule in its ground state is in the face conformation and is highly conducting at a source-drain bias around 1.5 V. When the tip moves towards the center ($x = -2$, 0, 2 Å in Fig. 2), the molecule's ground state switches to the edge configuration which is seen to be much less conducting in the same range of bias. Our calculations of the dI/dV characteristics of the molecular wire in a variety of face and edge conformations that have energies higher than the ground state [including the metastable edge conformation in Fig. 1(c)] yielded very similar results to those in Fig. 2. That is, all face conformations of the molecular wire

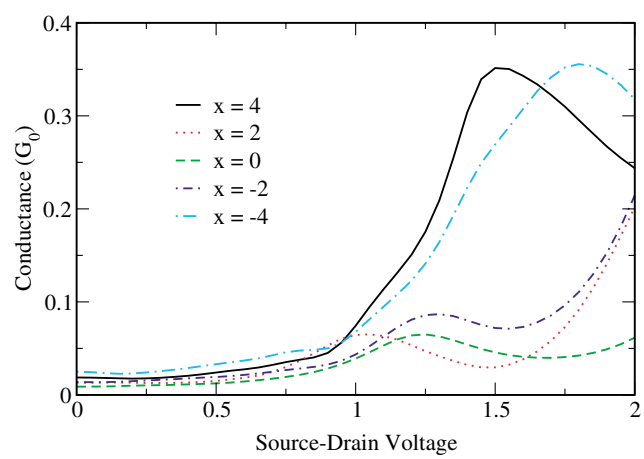

FIG. 2 (color online). Calculated differential conductance for ground state BDT conformations at several STM tip positions. At 1.5 V the molecule is in the "ON" state when the tip is at $x = -4$ and 4 Å and "OFF" at other x values.

were found to be highly conducting at the first conductance peak near 1.5 V while all edge conformations are weakly conducting there. Thus, whenever the molecule is made to flip from a face conformation to an edge conformation, either by displacing the STM tip laterally or by exciting the molecule thermally or by a current pulse, the molecule is predicted to switch from a highly conducting to a weakly conducting state, and vice versa.

This large difference in conductance between the edge and face conformations can be understood within Landauer theory [26] by considering the transmission probabilities T for electrons to scatter through the molecular wire, taking account of π orientational effects [14]. Representative results [25] are shown in Fig. 3 for several face [Fig. 3(a)] and edge [Fig. 3(b)] conformations. The Fermi energy of gold in our semiempirical model is near -10 eV [25]. The transmission peaks immediately below the Fermi energy can be attributed to the highest occupied molecular orbitals (HOMOs) of the BDT and those above to the lowest unoccupied molecular orbital. The Fermi energy lies nearest the HOMO [27], so the onset of conductance is due to electron transmission through the HOMO. In the face conformations, there is a strong overlap between the first HOMO molecular π orbital and the atomic orbitals on the Au tip atom. This results in the strong transmission due to the first HOMO below the Fermi energy (beginning near -10.5 eV) in Fig. 3(a) and in the strong conductance peak seen for the face conformations in Fig. 2. However, in the edge conformations the molecular π orbitals are oriented differently and their overlap with the orbitals on the Au tip atom is weaker. This results in the weaker transmission through the first HOMO below the Fermi energy in Fig. 3(b) and the lower conductance of the edge conformations in Fig. 2.

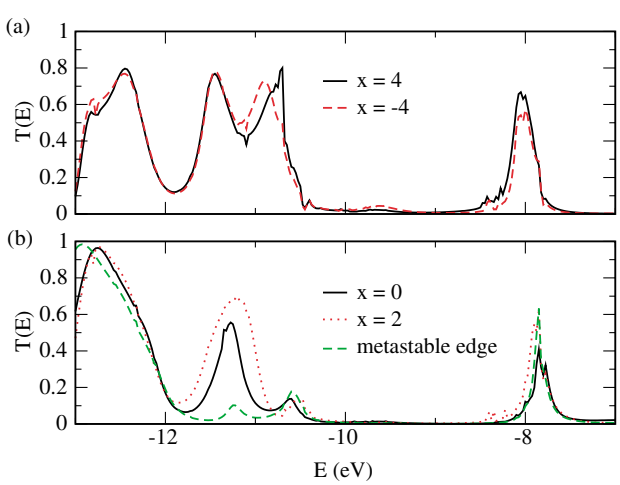

FIG. 3 (color online). Calculated transmission probabilities T vs electron energy E for different tip positions. (a) Transmission for ground state face conformations. (b) Transmission for some edge conformations [the metastable edge conformation is the excited state at $x = 3$ Å in Fig. 1(c)]. The Fermi energy is -10 eV. Resonances due to the HOMO are below the Fermi energy.

Thus, we arrive at the unexpected prediction that a molecule as simple as BDT can be made to switch through its interaction with a suitable STM tip. The ON state corresponds to the molecule oriented in such a way that its ring faces the tip, whereas in the OFF state the edge of the ring faces the tip. The switching can be induced by passing the tip over the molecule [the transition between Figs. 1(a) and 1(b)] or by exciting the molecule to a different conformation for a fixed tip position [the transition between Figs. 1(b) and 1(c)].

We predict an unusual and striking experimental signature of switching induced by the motion of the tip: The conductance should be *low at the center* of the STM image of the molecule where the edge conformation is stable and *high* when the tip moves *away* from the center of the image and the face conformation becomes stable. Experimental observation of switching induced by passing the tip over the molecule may be facilitated at low temperatures where thermal excitation of the higher energy conformations is minimal. [For example, we find the highly conducting excited face conformation obtained by rotating the molecule from the (weakly conducting) ground state edge conformation in Fig. 1(a) through $\pi/2$ about the S-S axis corresponds to an energy saddle point $\sim kT_{\mathrm{room}}$ above the ground state; thus this excited state will be populated significantly at room temperature.] Hysteresis may occur in the STM image of the molecule at low temperatures, as is evident from the greater similarity of the $x = 0$ Å ground state in Fig. 1(a) to the $x = 3$ *excited* state in Fig. 1(c) than to the ground state in Fig. 1(b). This also suggests interesting experiments that may combine scanning by the tip and activation of switching by current pulses.

Experimental studies may employ a conventional STM to contact a molecule adsorbed on a metal substrate [17]. An alternative may be to *self-assemble* a monatomic STM tip for the top probe. Realizing such a system would rely on growing the top electrode epitaxially on a heterogeneous self-assembled monolayer (SAM) of insulating and conducting organic molecules, where the conducting molecule is chosen to be shorter than the insulating one. Such a SAM would have a "divot" at the site of each conducting molecule. It has been suggested [7] that, when the top layer is grown, a metal atom that bonds chemically to the conducting molecule should occupy the divot forming a tip. Our calculations indicate that the top electrode may sit quite high over the insulating part of the SAM (we considered gold contacts with pentanethiol as the insulator and BDT as the conductor). Thus, there is room for the formation of a monatomic tip contacting the conducting molecule. In such systems, the switching rate between the ON (face) and the OFF (edge) states for a fixed tip position would depend on steric constraints imposed by the local environment of the molecule; analogous effects have been observed recently in

STM experiments on more complicated (three-ring) switching molecules in an insulating host matrix [3]. For an insulating host SAM such as an alkanethiol that does *not* bond chemically to the upper metal contact, one may also consider the possibility of sliding the top metal electrode laterally a few angstroms (and the self-assembled tip with it) relative to the substrate and SAM by applying suitable mechanical or electrostatic forces to the metal contacts, thus realizing a *mobile* self-assembled STM tip that could probe switching of the molecule induced by motion of the tip.

In conclusion, we have shown that one of the simplest and most studied molecular wires, surprisingly, becomes a bistable molecular switch if one of its two metal contacts is a monatomic scanning tunneling microscope tip. This is the smallest two-terminal molecular switch to date. The switching mechanism that we have introduced here relies on the coupling between the molecule and contacts and thus should be broadly applicable. We have proposed experiments with a conventional or novel self-assembled STM to test our predictions, and hope that the ideas put forward here will facilitate bridging the gap between theory and molecular switching experiments.

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