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# Bistable molecular conductors with a field-switchable dipole group

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A class of bistable "stator-rotor" molecules is proposed, where a stationary bridge (stator) connects the two electrodes and facilitates electron transport between them. The rotor part, which has a large dipole moment, is attached to an atom of the stator via a single sigma bond. Hydrogen bonds formed between the rotor and stator make the symmetric orientation of the dipole unstable. The rotor has two potential minima with equal energy for rotation about the sigma bond. The dipole orientation, which determines the conduction state of the molecule, can be switched by an external electric field that changes the relative energy of the two potential minima. Both orientations of the rotor correspond to asymmetric current-voltage characteristics that are the reverse of each other, so they are distinguishable electrically. Such bistable stator-rotor molecules could potentially be used as parts of molecular electronic devices.

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## I. INTRODUCTION

The success or failure of molecular electronics (moletronics)[1,2] will largely depend on the development of efficient molecular electric switches. Switches are critical to the ability to store digital information and route signals in moletronic logic circuits. Single-molecule switches (SMS's), in which the switching originates in the physical properties of individual molecules rather than molecular complexes or films, are especially valuable. SMS's will allow the ultimate miniaturization of moletronic devices, where one memory or configuration bit is represented by only one molecule.

For memory applications, the SMS has to be bistable. In principle, the bistability may be realized as two different *electronic* states of the molecule. Then the information can be read out by direct sensing of the charge on the molecule or by measuring its electrical conductance. A strong dependence of conductance on the molecular charge state was reported by several groups.[3–5] However, two electronic states are unlikely to have the same energy and the energy barrier between the states will be low. In a pure electronic mechanism, the higher energy state can only be stabilized by a third electrode, a solid-state gate or electrolyte, that affects the interior of the molecule and actually performs the switching between the two states. While three-terminal switches could potentially be used for signal gain and routing, memory applications will be limited. Given the small physical dimensions of molecules, the provision of a third electrode to every memory bit will be difficult to achieve.

Recently, it was suggested that a bit be stored in the form of *current* flowing through a molecule.[6] Under special circumstances (attractive correlations between electrons on the molecule, and a high degeneracy of the molecular orbital), molecules could be electronically bistable. This is characterized by two very different currents passing through the molecule at the same applied voltage depending on the bias history. The higher-current state is stable *only* at an external bias voltage exceeding some threshold. Thus, this mechanism could be the basis only for volatile molecular memory, even if such special molecules are found.

Alternatively, bistability may be realized as two different *conformational* states of the same molecule. In this case, the two states differ by the spatial positions of one or several atoms. The electric conductance of the two states can be different because: (i) the change in shape causes the current-carrying molecular orbitals to rehybridize, thus changing their energy and electron transmission; or (ii) the redistribution of electrostatic charge significantly alters the current-carrying orbitals through direct Coulomb interactions. An additional constraint is switchability in a two-terminal geometry, which implies some degree of ionicity of mobile groups. At least one class of SMS's that satisfies all these requirements has been reported.[7–9] These are interlocked supermolecular complexes, catenanes, rotaxanes, and pseudorotaxanes, in which the mutual orientation of two structural subunits of the complex have at least two local energy minima. The electrical switching observed in solid-state devices is speculated to be caused by the movement of a positively charged (+4) tetrapyridinium ring [the full chemical name is "cyclobis(paraquat-*p*-phenylene")] back and forth along the molecular backbone. The movement happens when one of the "stations" on the backbone is oxidized or reduced under bias and pushes the ring away or attracts it back. Significant current hysteresis has been observed in some cases, although direct experimental evidence for the ring movement inside the devices is still lacking. This example of ionic molecular switching is not the only possible mechanism. Its main drawback is the slow switching speed, which is about $10^{-3}$ s, due to the large mass of the moving ring. One way to improve the performance of SMS's is to design conformationally bistable molecules with smaller moving parts.

## II. A DESIGN FOR A SINGLE-MOLECULE SWITCH

In this paper, we propose a class of bistable conducting molecules that could be the basis for single-molecule switches, memory bits, and other moletronic devices. The bistability is provided by the formation of one or more hydrogen bonds between the moving and stationary parts of the molecule. The two states are distinguishable by their current-voltage characteristics. The molecules can be flipped be-

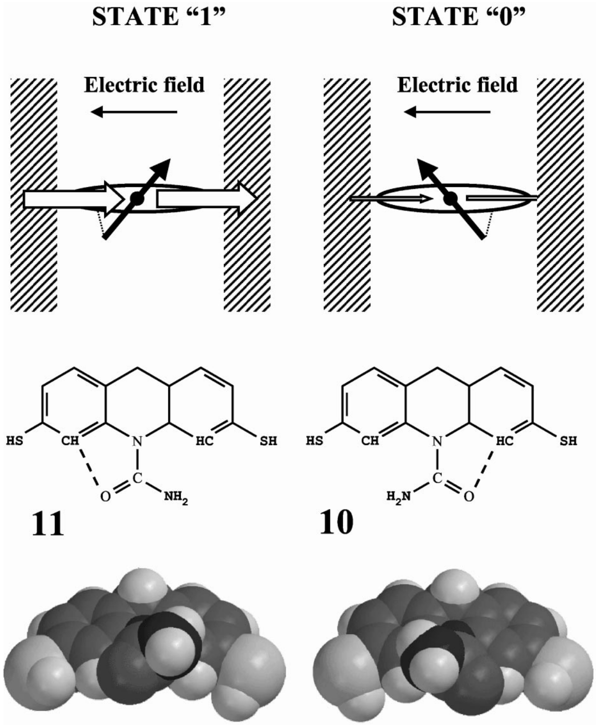

FIG. 1. Top: The operating principle of the stator-rotor single-molecule switch. The stator is the thin oval in the center. The dipole group, represented by the solid arrow, is unstable with respect to one of the two potential minima caused by the formation of hydrogen bonds between the stator and the rotor. Open arrows indicate the direction of the electron flow. For electrons going from left to right, the two states are clearly nonequivalent, which is indicated by different widths of the open arrows. Thus the two states are distinguishable electrically. Middle: A bistable stator-rotor molecule 9-hydro-10-acridinecarboxamide-2,7-dithiol shown in state 1 (11) and in state 0 (10). Hydrogen bonds formed between the oxygen of the amide group (-CONH$_2$) and the hydrogens of the stator are indicated by dashed lines. Bottom: Space-filling model of 11 and 10.

tween the two states with an external electric field, so that only two electrodes are required to operate the device.

The principal scheme of our SMS is shown in Fig. 1 (top). The molecule consists of two major subunits, the stator and the rotor. The stator bridges the two metal or semiconductor electrodes and facilitates electron transfer between them. Thus, it has to be a fairly conductive molecular structure, which implies that the stator is entirely or piecewise conjugated. The rotor is a side group that carries a significant dipole moment. Examples of such dipole rotors are the aldehyde (-COH) and amide (-CONH$_2$) groups. The rotor is attached to one atom of the stator via a single covalent sigma bond, making stator-rotor rotation relatively easy. The key feature of the present design is that for some stator-rotor molecules, the symmetric position of the rotor (that is, when it is roughly perpendicular to the main axis of the stator) is *unstable*. This happens if the polar atoms of the rotor tend to form hydrogen bonds with the hydrogen atoms of the stator, which causes the rotor to tilt out of the symmetric position in either of the two possible directions. As a result, the total energy of the molecule as a function of the stator-rotor angle has *s* double-well shape. In this paper we consider the case of stators that are symmetric with respect to the attachment point of the rotor. In this case, the two equilibrium conformations must be the mirror images of each other. Accordingly, the two potential minima have the same energy. An example of a symmetric-stator molecule is shown in Fig. 1 (middle and bottom). The selection of one of the two equivalent potential minima by the rotor part can be viewed as an example of *discrete symmetry breaking*.

To complete the general description, let us mention the other two important properties of our SMS. First, the dipole moment of the rotor interacts with an external electric field oriented along the stator axis. A field of precisely this direction is generated by a potential difference between the two electrodes. Thus, a strong enough external field (external bias voltage) will change the energy balance between the two states, the population of those states becomes inequivalent and some dipolar groups will flip from one state to the other, performing an act of switching. This process is expected to be thermally assisted. Second, since both equilibrium states are asymmetric with respect to the electrodes, the current-voltage characteristics of *both* states will be asymmetric (although they will be the reverse of each other for a symmetric stator, as here). Therefore, the two states can, in principle, be distinguished electrically, by applying a small test voltage (much smaller than the switching bias) across the electrodes and measuring the current in one particular direction (e.g., left to right in Fig. 1). These two major properties of SMS are discussed in more detail below.

## III. QUANTUM CHEMISTRY CALCULATIONS

We have performed extensive quantum chemistry calculations of several stator-rotor molecules.[10] Since the results are largely similar, we present them for 9-hydro-10-acridinecarboxamide-2,7-dithiol (1) depicted in Fig. 1. The stator comprises three fused rings that can be thought of as a derivative of the fully conjugated anthracene molecule with one middle carbon saturated and another replaced with a nitrogen. The end thiol groups -SH serve the purpose of attaching the molecule to gold or platinum electrodes, a standard design feature in moletronic studies. The rotor is the amide group -CONH$_2$, which has a dipole moment of $d=4.0$ D $\approx 0.8e\cdot$ Å. The symmetric orientation of the rotor (perpendicular to the plane of the stator) is unstable because of the formation of *two* hydrogen bonds with the oxygen and nitrogen of the amide.

The relative energy of 1 as a function of the stator-rotor angle $\theta$ is shown in Fig. 2. It has the shape of a double well with the height of the energy barrier $\triangle E=0.18\pm0.02$ eV. The data were obtained from complete relaxation of the molecule with the positions of the end sulfur atoms fixed. (The latter are supposed to bind strongly to the electrodes and therefore cannot move.) Other useful quantities provided by the quantum chemistry calculations are intramolecular vibrational modes and frequencies. Of most interest to us is the stator-rotor rotation mode around the N-C bond. We identified its frequency to be $\omega=97$ cm$^{-1}=1.8\times10^{13}$ rad/s. This

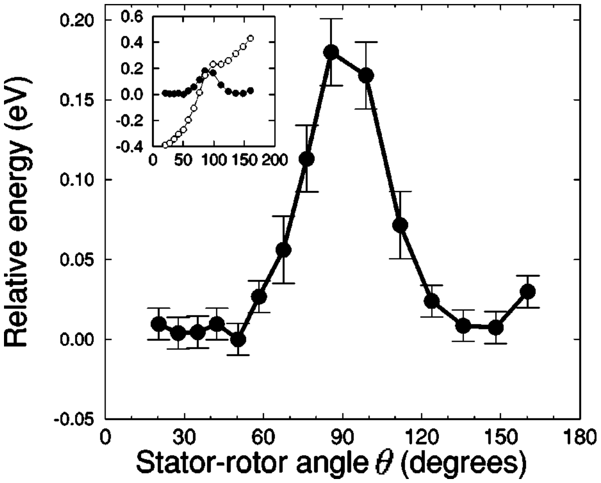

FIG. 2. The relative energy of the molecule shown in Fig. 1, as a function of the stator-rotor angle $\theta$. The height of the energy barrier is $(0.18\pm0.02)$ eV. The error bars have been estimated from the energy variance during geometry minimization. Inset: the same data (solid circles) compared with the energy of the same molecule in an external field of 0.5 V/Å.

information allows us to estimate the stability of the switch against thermal fluctuations. The retention time can be found from Kramers formula,

$$\tau=\frac{1}{\omega}e^{\triangle E/k_BT}. \tag{1}$$

Using the above values, one finds $\tau=58$ ps at room temperature ($T=300$ K), $\tau=33$ ms at $T=77$ K, $\tau=1$ h at $T=54$ K, and $\tau=30$ y at $T=40$ K. With respect to the small retention times at room temperature, we should note that the energy barrier can be systematically increased by enhancing the hydrogen bonds and/or increasing their number. For instance, replacing the -CH segments of the stator with -C-OH brings the hydrogens of the stator closer to the rotor and increases their ionicity. As a result, the barrier increases to 0.6 eV. Such molecules, however, are more difficult to synthesize. We believe it is more appropriate to focus initially on the simplest members of the stator-rotor family. At the same time, we point out that ways to increase the energy barrier and retention times do exist in the framework of the present design.

Another important parameter that can be estimated from the quantum chemistry data is the switching voltage. Taking into account the interaction energy of the dipole moment $d$ with an external electric field $F$, the full $\theta$-dependent energy of the molecule becomes

$$E(\theta)=-Fd\cos\theta+\triangle E(\theta), \tag{2}$$

where the second term represents the function plotted in Fig. 2. At *zero* temperature, switching occurs when the field changes the energy balance of the two states such that the barrier reduces to zero and the system rolls down to the only energy minimum available. This is illustrated in the inset of Fig. 2. Equating the $\theta$ derivative of Eq. (2) to zero and evaluating $\partial\triangle E/\partial\theta$ as finite differences, one finds that the barrier vanishes at field $F=0.5$ V/Å, and the higher-energy state of the rotor becomes mechanically unstable. The nominal length of the molecule (sulfur-to-sulfur) is 10.3 Å. Adjusting for two sulfur-electrode bond lengths, the distance between the two electrodes is about 14 Å. This results in a switching voltage of $\approx 7$ V. At nonzero temperatures, switching occurs at a smaller voltage, namely when the barrier is reduced such that the dipole is quickly flipped by thermal fluctuations. One should mention that these estimates do not take into account interaction of the molecule with other molecules or with the electrodes. We believe, however, that they represent the correct magnitude of the switching voltage.

## IV. TRANSPORT CALCULATIONS

The bistability alone is not sufficient to produce a molecular switch. The two states have to be distinguishable by their current-voltage ($I$-$V$) characteristics. We have performed self-consistent quantum-mechanical calculations of current through molecular films of 1 sandwiched between two semi-infinite gold electrodes. Starting with the equilibrium molecular structure from the quantum-chemical calculations, the end hydrogen atoms were removed and each replaced with a triangle of gold atoms. Together with the sulfur, the gold atoms formed a triangular pyramid with sulfur at the pinnacle. The main axis of the molecule was near perpendicular to the bases of the pyramids and the distance between the bases and the sulfur atoms was 1.9 Å.[11] Then the (gold triangle)-molecule-(gold triangle) complexes were organized in a two-dimensional monolayer commensurate with the Au(111) surface and placed between two semi-infinite gold electrodes. There was one molecule-gold complex per four surface atoms.

The current through the monolayer of 1 was calculated from the Büttiker-Landauer formula,[12]

$$I(V)=\frac{2e}{h}\int_{E_F}^{E_F+eV}dE\,T(E), \tag{3}$$

where $E_F$ is the Fermi energy of one of the electrodes, and $T(E)$ is the transmission probability for an electron with energy $E$ to get through the molecules from one electrode to the other. A tight-binding parametrization of the molecules[13] and the electrodes[14] as well as the details of calculation of $T(E)$ with transport Green's function formalism have been described elsewhere.[15–18]

The calculated $I$-$V$ characteristics of the stator-rotor SMS are shown in Fig. 3. The two curves correspond to the two stable states 11 and 10 of the molecule 1. The curves are *not* exact reverses of each other because 10 was not prepared as a geometrical mirror image of state 11. Instead, the geometries of the two states were optimized independently. Then the molecules were oriented *approximately* perpendicular to the surfaces of the electrodes. As a result, the two geometries slightly differed, which produced different noise in the $I$-$V$ characteristics that can be seen in Fig. 3. We emphasize in this regard that in any real situation the molecules would not be all locked in the same ideal conformational state but rather be distributed over a variety of conformations. Thus, it

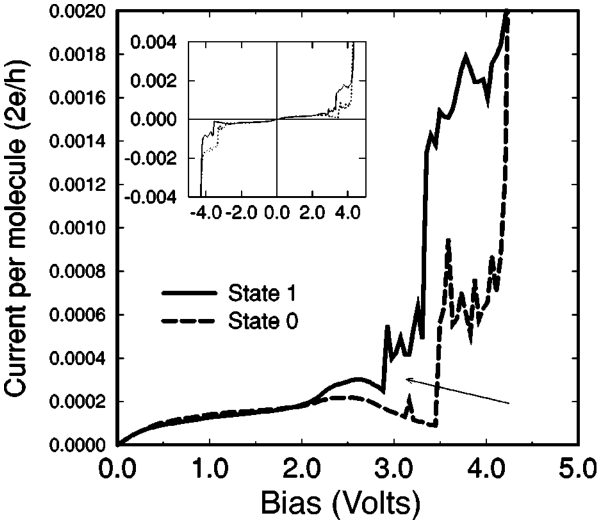

FIG. 3. *I-V* characteristics of the two states 11 and 10 of the stator-rotor SMS 1. The major "window of distinguishability" lies in the interval of 3 to 4 v. An arrow indicates the region where the currents in the two states differ because of the asymmetric localization of the highest occupied molecular orbital, see text. The inset shows the same *I-V* characteristics in a symmetric voltage interval. Note that the two curves are not exact reverses of each other.

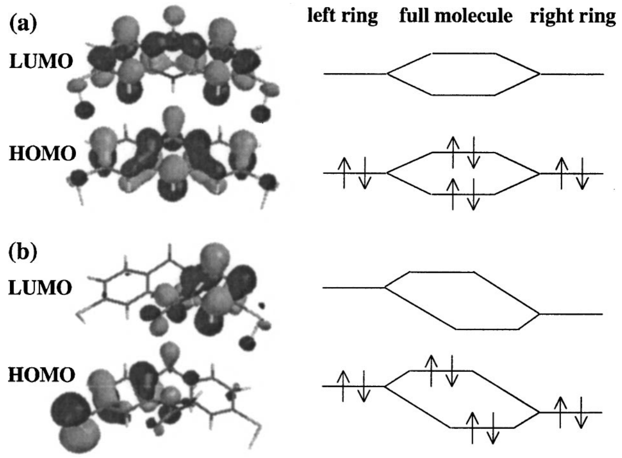

FIG. 4. On the left: the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of (a) relaxed stator, and (b) full stator-rotor molecular switch in state 11. On the right: the electronic structure of the molecules perceived as a hybridization of the electronic structures of two benzene rings. In state 11 (b), the electric field of the dipole moment of the rotor shifts the levels of the left ring upward. As a result, the HOMO (LUMO) of the molecule shifts toward the left (right) benzene ring.

is important to investigate the sensitivity of the *I-V* characteristic to changes in the junction geometry. We have shown earlier that the current through chemisorbed molecules strongly depends on their orientation with respect to the electrodes.[16,17] We shall discuss below that, given the roughness of the electrode and disorder in the film, there will be a spread of the *I-V* characteristics of individual molecules, and the corresponding deterioration in the performance of the molecular device.

The most important feature of the *I-V* characteristic of Fig. 3 is the hysteresis loop at voltages between 3.2 and 4.2 V. Since the currents in the two curves differ by about a factor of two, these data demonstrate that the two states could be clearly distinguishable as long as the current ratio remains stable and is not washed out by fluctuations of various kinds.

We now discuss the physical origins of the observed hysteresis. In both states, the asymmetry of the *I-V* characteristic must originate from the asymmetry of molecular orbitals (MO's), which in turn is caused by the electric field of a dipole. To illustrate this point, we compare in Fig. 4 the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of 11 [Fig. 4(b)] with the HOMO and LUMO of the stator alone (no dipole group) in its fully relaxed geometry [Fig. 4(a)]. It is instructive to view the electronic structure of a full molecule as a hybridization of those of the two benzene rings, see the right half of Fig. 4. In case (a), the molecule is symmetric, the two rings are identical, and the resulting HOMO and LUMO are equally distributed over the two halves of the molecule. Such an electronic structure will produce a symmetric current-voltage characteristic if the two electrodes and molecule-electrode contacts are made the same (which we always assume in this paper). In case (b), however, the electric field of the tilted rotor shifts the electronic structures of the benzene rings with respect to each other. In 11, the electron rich (i.e., negatively charged) oxygen atom of the rotor is closer to the left benzene ring, while the positively charged -$NH_2$ group is closer to the right benzene ring. As a result, the electronic levels of the left ring end up being higher than the right ones by as much as 0.4 eV. After hybridization, the LUMO of the entire molecule is primarily located on the right ring while the HOMO is on the left ring. Clearly, such an electrical structure should produce an *asymmetric I-V* characteristic. The *degree* of asymmetry depends on the energy, conductivity, and spatial structure of the current-carrying molecular orbitals that are closest to the Fermi level of the electrodes.

The mechanism responsible for the asymmetry of the *I-V* characteristic can be understood with the help of Figs. 5 and 6. Figure 5 shows the energy-dependent transmission coefficient $T(E)$ for 11. Of most interest for us are the peaks marked *A*, *B*, and *C*. Peak *A* corresponds to the HOMO. It is the closest molecular orbital to the Fermi level (1.5 eV below) but is less conductive than *B* or *C*. *B* and *C* are almost equidistant from $E_F$ by $\approx 1.75$ eV. It is critically important that the closest conducting level (HOMO in our case) is *spatially* asymmetric. This is the major source of the *I-V* asymmetry, as illustrated in Fig. 6. When an orbital is shifted from the center of the molecule toward one of the electrodes, the total voltage drop will be distributed unevenly between the two contacts. As a result, the condition for resonant tunneling will be met at different external biases for the two opposite polarities, compare (b) and (c) in Fig. 6. This simple argument applies equally well to the HOMO, LUMO, or any other conducting MO. If more than one MO's are involved, the partial asymmetries may cancel. Thus, the main contribution comes from the closest conducting MO. For our SMS, the hysteresis region caused by the HOMO is indicated by an

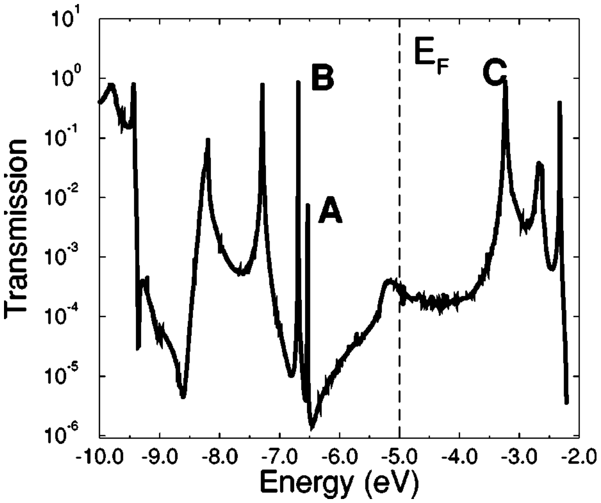

FIG. 5. Transmission through 11. The dashed line indicates the position of the Fermi level of the electrodes (−5.0 eV).

arrow in Fig. 3. It turns out that this region is not the dominant one in the calculated *I-V* characteristic. This is because of the relatively low conductance of the HOMO, compare *A* with *B* and *C* in Fig. 5.

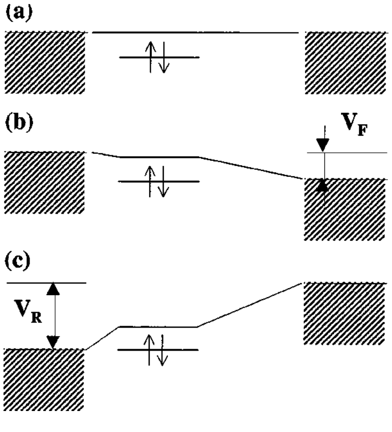

FIG. 6. The mechanism of formation of an asymmetric *I-V* characteristic. (a) A conducting molecular orbital localized closer to the left electrode than to the right. Most of the external bias drops on the right molecule-electrode contact. (b) In the forward direction, the conditions for resonant tunneling are met at a relatively small bias $V_F$. (c) In the reverse direction, the conditions for resonant tunneling are met at a larger bias $V_R$.

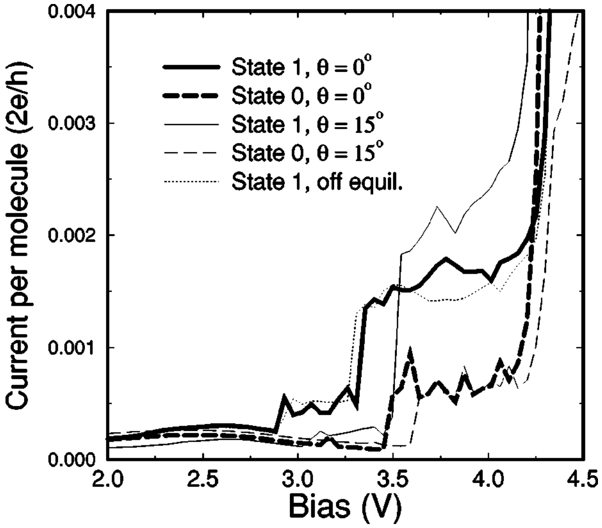

FIG. 7. Sensitivity of the *I-V* characteristic to temperature and orientational disorder. The thick lines are the data from Fig. 3 (the molecule is roughly perpendicular to the surface). The thin solid and dashed lines are the *I-V* characteristic of the same molecule but tilted by 15° from the normal (orientational disorder). The dotted line corresponds to state 11, normal to the surface, but with the dipole swayed from its equilibrium conformation by 15° (temperature disorder). Orientational disorder seems to be more effective in closing the hysteresis region than the temperature one.

Two design rules of how to enhance the hysteresis regions of the *I-V* characteristic follow from the above analysis. The *height* of the hysteresis loop (that is, the current difference in states “1” and “0” at the same voltage bias) depends on the conductivity of the MO closest to the Fermi level. Indeed, the current difference appears because in 11 the carriers tunnel through the molecule resonantly, via a molecular level, while in 10 the carriers must go under the barrier in nonresonant mode. A strongly transmitting MO then produces a larger current difference. The *width* of the hysteresis loop depends primarily on the spatial asymmetry of the conducting MO, as explained above. In turn, the latter depends on the conjugation level of the stator, the length of the insulating bridge of the stator, and the size and orientation of the dipole moment of the rotor. Basically, the same factors determine the bistability of the molecule, which may be affected if the molecule is changed in some way to increase the localization of the orbital. One general way to enhance the asymmetry of the MO is to use an asymmetric stator. Within the present design, when one wants to preserve the bistable potential profile for the dipole group and yet break the symmetry of the backbone, one may, e.g., replace one or two carbon atoms in one of the side rings by nitrogen atoms. These issues will be addressed elsewhere.

Lastly, we discuss the variation of the *I-V* characteristic with changing molecular conformation and with changing geometry of the molecule-electrode contact. In addition to the disorder in the film, an important source of fluctuating geometry of the molecule is temperature. At finite temperature, the rotor fluctuates about its equilibrium position which produces a fluctuating field on the stator and moves the conducting orbitals up and down in energy. We have estimated that at room temperature the rotation amplitude of the rotor of 1 is about 15°. Figure 7 compares 11 with a rotor in its ground state and when it is swayed away by 15°. One can see that the difference in *I-V* characteristics is negligible. One must add that the inelastic tunneling through the molecules is also strongly temperature dependent and may be observed. This mechanism is beyond the scope of the present paper.

The prime source of the fluctuations of the contact geometry is the nonuniformity of the electrode surfaces and molecular films. We investigated this effect by tilting the main axis of the molecule by 15° from the normal to the surface. Such a tilt affects the overlap of molecular orbitals with the wave functions of the electrode.[16,17] As a result, the conductance as well as the *position* of the resonance shift, which might cause the closure of the hysteresis loop. The calculated *I*-*V* characteristics of 1 are shown in Fig. 7. One can see that the changes relative to the normal position are quite significant. We conclude that the nonuniformity of the metal-molecule contact geometry is a serious issue that might impede the observation of the hysteresis and switching, unless the molecule with a wide hysteresis loop is chosen.

## V. EXPERIMENTAL TESTS

The proposed design of the stator-rotor single-molecule switch is based on *three* major effects that should work together within the same molecular-electrode device. These are (i) the bistability of the molecules, (ii) the distinguishability of the two states by their *I*-*V* characteristics, and (iii) the ability to switch the molecules between the states with an external field. It is very possible that within a particular junction, only one or two but not all three effects will work at once. Identification of any one of them would still be important because it would show paths to SMS's with better characteristics. We now briefly discuss the experimental modes that can be used to approach the problem.

(i) *Bistability*. This is the most definite theoretical prediction for the stator-rotor molecules. Of course, not every such molecule is bistable. For instance, the rotor may be so large that the steric hindrance prevents it from rotating and leaves the symmetric orientation as the only stable one. However, for those molecules that *are* predicted to be bistable, the results are uniform across a number of modeling methods ranging from molecular mechanics to density-functional calculations. Thus, while the quantitative numbers (the barrier height, etc.) might carry some uncertainty, the very fact of bistability is robust. The question is whether the bistability is detectable by simpler than moletronic means, such as optical methods. Consider our SMS 1 from Fig. 1. In the gas phase, the two states would be the *exact* mirror images of each other and their infrared (IR) spectra would be indistinguishable. Now, suppose the molecules self-assemble on a gold surface such that they bind with one thiol group only. The presence of the surface will break the symmetry and make the two states inequivalent. As a consequence, some of the IR peaks will split. Moreover, the two states will be split in energy by $\sim 10-100$ K (the scale of dipole-dipole interaction on separation 1–2 nm). Thus the partial intensities of the IR doublets are expected to have a strong temperature dependence.

(ii) *Distinguishability*. It is possible that a molecule is bistable, the energy barrier is low, yet the electric field is too weak to switch it. This may be because of the long length of the molecule, low breakdown threshold, effective screening, and so on. In this case, it will still be possible to detect the current differences between states "0" and "1," where the switching of molecules between the states will be thermally activated. A signature of such behavior would be telegraph noise observed at a *fixed* bias voltage between $V_F$ and $V_R$. The frequency of the telegraph noise would be strongly (exponentially) dependent on temperature and the field. (In interpreting the data, one will have to take into account other possible sources of telegraph noise, such as the diffusive motion of metal atoms near the molecules at the molecule-electrode contact.)

The described approach would be difficult to realize on molecular films because there will be significant fractions of molecules in states "0" and "1" at any given time and the net average would not fluctuate much. Instead, measurements should be performed on single molecules. It would also eliminate the disorder-induced washing out of the hysteresis regions discussed in the preceding section. A number of experimental techniques allowing single-molecule electrical measurements have been developed in recent years.[3–5,19–22]

(iii) *Switchability*. It may happen that the molecule is bistable and switchable by an external electric field, but does not possess a large hysteresis loop because of the weak influence of the dipole on the current-carrying orbitals of the stator. Then, in principle, the switching can be detected by other means such as optical. One possibility is to shine light through one of the electrodes that is IR transparent or made thin enough to let some light through. In this case, the electrodes should probably be made of different materials to make the two states of the switch inequivalent.

Obviously, the best demonstration would be the direct observation of a *I*-*V* hysteresis, preferably in the single-molecule measurement.

## VI. SUMMARY

In this paper, we have proposed a class of bistable stator-rotor molecules that could be used for single-molecule switches and possibly for other moletronic applications. The basic idea is to incorporate into the molecule a rotor with a large dipole moment that performs *three* roles simultaneously. First, the rotor is capable of forming hydrogen bonds with the stator, which makes the entire molecule bistable. These two stable conformational states of the rotor can, in principle, represent the digital "zero" and "one." Second, the rotor makes the two states distinguishable electrically. In either state, the rotor is positioned asymmetrically with respect to the stator, see the bottom of Fig. 1. The electric field of the dipole then lifts the mirror symmetry of the electronic structure of the stator. As a result, the response of the stator to an external bias becomes asymmetric. Thus, the state of the switch can be read out by interrogating it at a small test voltage that is always the same in polarity and magnitude. The two states are distinguished by the current passing through the junction. Third, the rotor provides the means to switch the molecule between the states. The dipole moment of the rotor interacts with a large external electric switching field, which changes the relative energies of the two states and enables the molecules to transfer into the lowest one. Provided that the switching voltage (that is, the writing voltage) is higher than the reading voltage, the entire read-write cycle can be done with only two external terminals.

The rotor performing three simultaneous functions results in an economical design of the molecular switch. The candidate molecules are likely to be as small as three fused benzene rings and relatively simple to synthesize. In fact, several stator-rotor molecules, similar to 1 but without the thiol clips, *are* commercially available[23]. What is needed are the experimental methods that would allow them to be placed between electrodes and test their conformational and electrical properties.

Building in and optimizing three functions within one molecule is a challenging task. However, the proposed switching mechanism applies to a whole class of stator-rotor molecules, rather than to one particular molecular species. There are several ways to manipulate the mechanical and electronic properties of the molecule by changing the chemical composition of the stator and rotor. For instance, increasing the dipole moment of the rotor decreases the switching voltage. Enhancing the insulating bridge in the middle of the stator increases the asymmetry of the $I$-$V$ characteristics, and using an asymmetric stator-rectifier widens up the hysteresis loop in $I$-$V$ curve, etc. We have also identified several experimental tests that could be used to screen out and isolate only one or two functions (see the preceding section). One proposal is to compare infrared spectra of stator-rotor molecule in the gas phase and self-assembled on a surface. If the molecule is bistable, then some IR peaks should split when the molecules are on the surface and their relative intensity should be strongly temperature dependent.

Finally, we mention that only symmetric stators have been discussed in this paper. Stator-rotor molecules with *asymmetric* stators are richer in physical content and potential moletronic applications. Such molecules will be discussed in a separate publication.

## ACKNOWLEDGMENTS

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