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Single-molecule field-effect transistors: A computational study of the effects of contact geometry and gating-field orientation on conductance-switching properties

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The relation of geometric features to the effect of gating electric fields on the conductance through conjugated systems is investigated by electronic transmission calculations employing Green's function based modeling. Switching is only induced if the field is applied in an orientation which results in energy shifting of the molecular orbitals. This is found to depend on the orientation of the field with respect to the plane defined by the molecular conjugation. The switching can be quenched by structural rearrangement of the chemical bonds to the bulk, where the relative position of the electrodes is modified.

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I. INTRODUCTION

Molecular electronics has recently become an exciting and important field of research, as electronic devices are becoming progressively smaller and silicon based technology is reaching its limit. Various molecular systems have been studied both experimentally and theoretically to determine their potential for use in electronic devices. Self-assembled monolayers (SAMs) of a number of large conjugated molecules have already been used as organic semiconducting layers in transistor devices.[1–8] The prospect of fabricating highly efficient electronic devices utilizing the unique properties of *single* molecules[9–16] may offer the ultimate miniaturization and accuracy limit.

Recent experimental work[17–21] has measured the current through single molecules between two gold leads under the influence of an electric field. This work has shown that the current in single molecule devices can, in fact, be modulated by orders of magnitude through the use of an electrochemical gate. Computational studies can complement the experimental work by elucidating the mechanism which underlies the transistor functionality at the molecular level.[22–29] In molecular electronics, orbital delocalization over the span of a molecule, as well as electron density at the contacts, was shown to provide a pathway for the flow of current. Thus, molecules with highly delocalized π conjugated systems are well suited for molecular devices. Changing conditions, such as an electric field or the contact geometry, which affect the molecular orbitals of the organic molecule or their overlap with the orbitals of the metallic lead can either enhance or diminish the current flow through the organic molecule. This is evidenced by the difficulty of reproducing conductivity measurements for identical or similar molecules.[18,30]

Classic silicon semiconductor field-effect transistors (FETs) function by controlling the shape of a channel, through which the major charge carriers (electrons or holes) travel, with an electric field. Thus, the conductivity through the FET can be turned on or off. In molecular electronics, switching can be achieved by shifting the orbital energies of organic molecules in semiconducting layers. When the molecular orbitals are well aligned with the Fermi energy (E_f) of the metal contacts, current can flow through the FET. On the other hand, the current flow is turned off if the molecular orbitals are poorly aligned with E_f. Typically, the electric field in a semiconductor FET is applied through the use of a potential placed across two terminals of the device (gate and source), while current is measured across the source and drain terminals. For single-molecule devices, the fabrication of three terminal devices is a technological challenge. This is due to current limitations in the ability to manipulate molecular scale systems coupled to metal clusters or surfaces. Since it is not generally feasible for a third terminal to be chemically coupled to the molecular device, an external gating electric field is often used instead as the *third terminal*[17–21] for single-molecule devices.

We explore the possibility of changing the conductance of a conjugated system by the application of a gating electric field. Here, we focus on a molecular model which closely resembles the Tour-Reed device[31–33] [Fig. 1(b)]; a related molecule, where the central ring is unsubstituted [Fig. 1(a)], is also studied in detail. In this study, it is shown that switching behavior can be induced in conjugated molecules with specific contact geometries under the influence of a properly aligned gating electric field, where bonding to the electrodes occurs through single gold adatoms. We also note that our observations are general for conjugated systems and have been verified for a number of systems involving a conjugation plane.[34]

II. COMPUTATIONAL DETAILS

Optimized geometries for the organic molecules with one gold atom attached at each sulfur terminal are first obtained from density-functional theory by employing QCHEM 3.0.[35] In all computations, the B3LYP (Refs. 36 and 37) functional

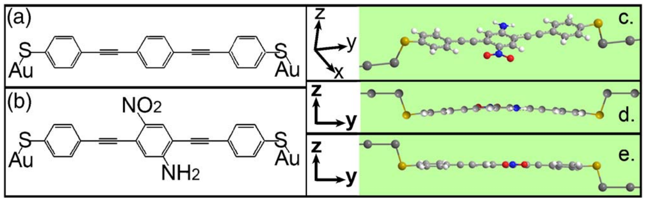

FIG. 1. (Color online) [(a) and (b)] Molecules considered. (c) Axis convention. (d) *Cis* and (e) *trans* conformers of the devices.

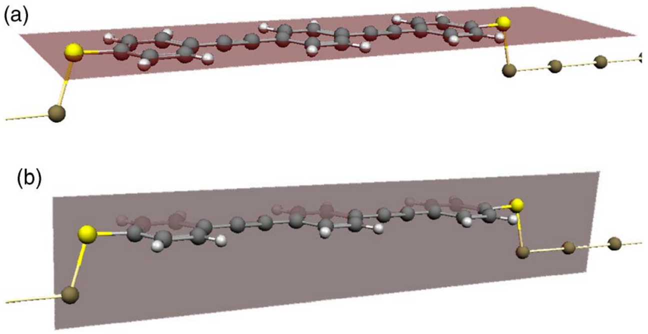

FIG. 2. (Color online) (a) Molecular conjugation plane and (b) plane formed by the Au-S bond of *cis*-1a system.

and the LANL2DZ (Ref. 38) basis set are utilized. The organic molecules are bonded through thiols to two Au leads which are oriented parallel to each other and the molecular axis (along the *y* axis). The molecular plane lies parallel to the *x*-*y* plane, as illustrated in Figs. 1(c)–1(e). At the optimized geometries, the molecular plane is also perpendicular to the plane defined by the two Au-S bonds, as seen in Fig. 2. Two orientations of the gating field, which are perpendicular to the applied bias voltage (V_{ds}) (*y* axis), are considered: aligned parallel (along the *x* axis) and perpendicular (along the *z* axis) to the molecular plane. (Note that a positive magnitude field implies that the positive charge is placed in the positive direction, and the negative charge in the negative direction. A negative magnitude implies the opposite polarity.) Single point energies, overlap matrices, and Fock matrices are computed with various gating-field strengths. We follow the scattering based picture of molecular conductance (Landauer formalism[39–41]) based on the Green's function (GF) formalism to calculate the electronic transmission, as described in detail by others.[11,42–47] These calculations include a representation of the semi-infinite bulk by efficiently solving a tight-binding (TB) model of the bulk at every energy, where the surface and bulk GFs are solved for iteratively and simultaneously.[48–50] The TB parameters are extracted from the electronic structure calculations described above.

Two different models are used to represent the electrodes and their bonding to the organic molecules. The most simple electrode model involves a one-dimensional wire of gold atoms. These models, along with several binding orientations, are shown in Fig. 1. Our observations, as reported below, were also confirmed using a more sophisticated bulk model. This electrode model resembles a Au(111) scanning tunneling microscope (STM) tip, where each layer of the bulk includes six-atoms. Both models involve binding of the molecule to the electrode through thiol groups at a single top site. These models are appropriate for describing experiments where single molecule junctions are formed by driving a STM tip into a gold surface and then pulling it out in a solution of some organic molecule, leaving a single molecule bonded to two gold tips or short wires.[14,16–20] We therefore model the contact between the molecule and the metal lead as through a covalent bond to a single adatom.

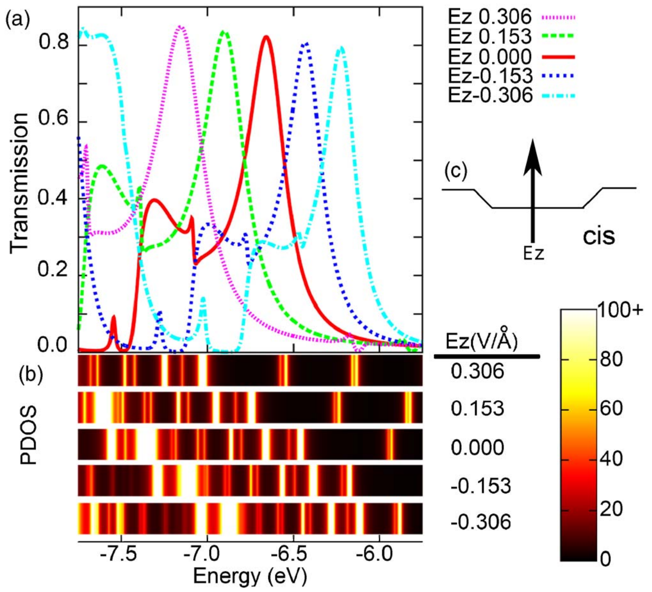

FIG. 3. (Color online) (a) Transmission and (b) PDOS on the organic molecule vs energy in eV for the 1a *cis* conformer in the 1d binding scheme with a field directed perpendicular to the conjugation plane. (c) Cartoon showing the field direction and lead-molecule-lead conformation.

III. RESULTS AND DISCUSSION

The contact geometry of an organic molecule to a metal lead will affect the interaction of the orbitals of the metal and the organic molecule.[32,47,51–53] Therefore, differences in contact geometry must also be considered when studying the effect of an electric field on the transmission through a molecule. The gating-field response to the relative orientation of the two gold-thiol bonds, as depicted in Fig. 1, is investigated in this study. The *cis* (1d) and *trans* (1e) conformations of the Au–organic molecule–Au systems are both minima and are essentially identical in energy (with a difference of less than 0.001 eV). The transmission functions of both conformations (for each molecule) with no external electric field are nearly indistinguishable and feature substantial peaks.

We begin our analysis of the effect of a gating field by considering a field oriented parallel to the conjugation plane of the molecule (*x* directed). The effect of such a gating field on either *cis* or *trans* isomers of 1a and 1b is negligible (for applied fields up to ±0.51V/Å). We find that 1b shows a somewhat stronger response than 1a due to its asymmetry in the *x* direction, yet this response is still inconsequential. Therefore, no significant switching behavior can be induced through the use of an electric field parallel to the conjugation plane defined by the phenyl rings. Electric fields perpendicular to the phenyl rings of the organic molecules (*z* directed) are, however, far more influential.

The transmission functions of the *cis* conformation of 1a under various *z*-directed electric-field strengths (E_z) are shown in Fig. 3(a). A positive *z*-directed field has the effect of shifting the transmission peaks toward more negative energies, while a negative electric field shifts the transmission function in the positive direction. The peaks in the transmis-

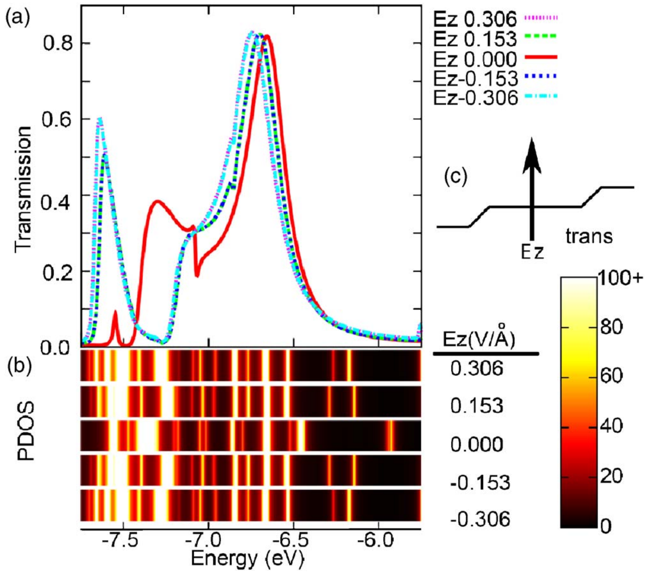

FIG. 4. (Color online) (a) Transmission and (b) PDOS on the organic molecule vs energy in eV for the 1a *trans* conformer in the 1e binding scheme with a field directed perpendicular to the conjugation plane. (c) Cartoon showing the field direction and lead-molecule-lead conformation.

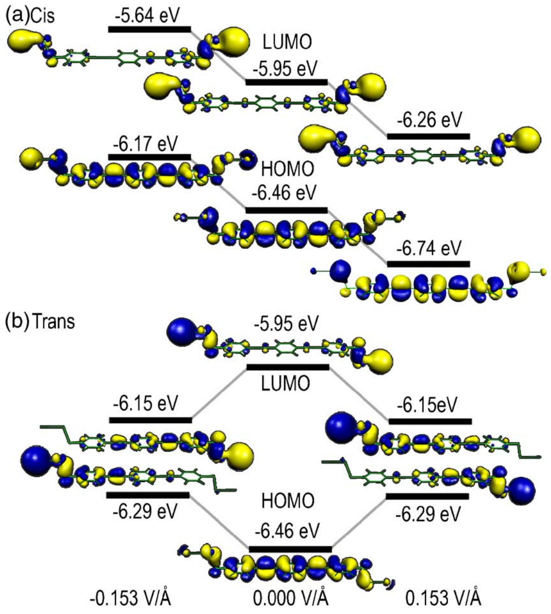

FIG. 5. (Color online) HOMO and LUMO of (a) *cis*-1a and (b) *trans*-1a under a ±0.153 and 0.000 V/Å electric field directed perpendicular to the conjugation plane (Ref. 54).

sion function grow slightly as a negative z-directed field is applied; however, the basic shape and magnitude of the peaks are maintained. Next, we consider the effect of a gating field on the transmission of *trans* conformations.

Figure 4(a) shows the transmission functions for several z-gating fields for the *trans* conformer of 1a. The peak in the transmission function at -6.7 eV moves very little as E_z changes. The peak at ~ -7.3 eV in the zero-field transmission function is, however, split, which causes the peak at -7.5 eV to grow and a small feature at -7.1 eV to appear when an electric field is present. It is interesting to note that this splitting occurs at even the smallest electric-field strength; there is only a small variation to the transmission function as the field strength is increased. The differences in the behavior of the transmission function for the *cis* and *trans* conformers can be explained by analyzing the projected density of states (PDOS).

The PDOSs on the organic portion of the devices are given in Figs. 3(b) and 4(b). From the PDOS plots for *cis*-1a it is clear that the density of states moves consistently lower in energy under a positive gating field and higher in energy under a negative field. This uniform shifting of the PDOS results from the symmetry of the two contacts with respect to the field and leads to the smooth shifting of the transmission function as observed above. An examination of the molecular orbitals of the organic molecule under various field strengths explains this behavior.

Figure 5(a) shows the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of *cis*-1a under no field and ±0.153 V/Å. The orbital energy shift upon application of a field is not correlated with strong relaxation of the orbital shape for the *cis* conformer. In the *cis* conformation the leads are both on the same side of the molecular plane; therefore, the couplings between the molecule and the two leads experience the electric field equivalently. Upon application of a positive electric field, both ends of the device, which have appreciable electron density, are closer to the positive plate of a hypothetical capacitor. The orbitals are thus relatively stabilized, and their energies are shifted to lower values. Since all of the relevant molecular orbitals of the *cis* conformer have electron density on either one or both of the leads, all of the orbitals will be stabilized by a positive field. A negative field will have the converse effect, and the molecular orbitals are all destabilized for the *cis* conformer, yielding the opposite shift. The PDOS and molecular orbitals for the *trans* conformer of 1a, however, respond to the gating field in a more complicated manner, as seen in Figs. 4(b) and 5(b), respectively.

The orbitals of the ungated *cis* and *trans* conformers have identical energies and similar shapes; however, their response to an external electric field is different, as evidenced by the transmission and PDOS trends outlined above. In the *trans* conformations, the couplings to the electrodes are antisymmetrical. The electric field breaks the symmetry between the two coupling regions of the molecular orbitals in the *trans* configuration, where the two leads bind to the molecule from opposite sides of the conjugation plane. Therefore, in this case, the electron density becomes localized on either one or the other side.

Due to these symmetry considerations, the resulting effect of the gating field on the orbitals in the *trans* conformation is more complex than in the *cis* case. For the *trans* case, some of the molecular orbitals are stabilized by either a positive or a negative field, while others are destabilized. This results from the fact that the metallic leads of the device lie on opposite sides of the organic portion of the molecule. Molecular orbitals, which are polarized in such a way that there is more electron density on the end of the device which is close to the positive plate of a hypothetical capacitor, are

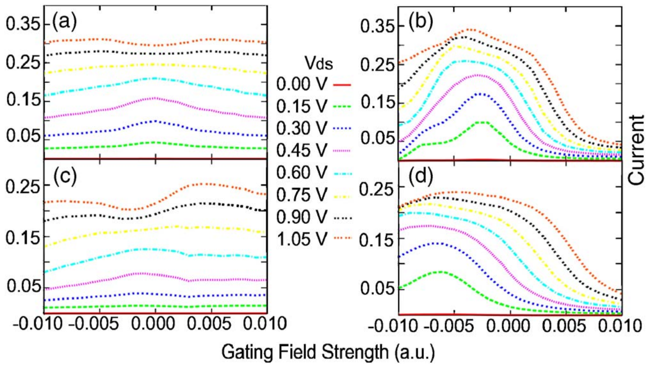

FIG. 6. (Color online) Current (27.211 a.u.) vs field strength (a.u.) for (a) *trans*-1a, (b) *cis*-1a, (c) *trans*-1b, and (d) *cis*-1b.

stabilized, and those with density closest to the negative plate are destabilized. The LUMO and HOMO shown in Fig. 5(b) provide an illustration of this behavior. In general, approximately half of the orbitals are stabilized at each field strength for the *trans* conformer, while the other half are destabilized. Molecular orbitals which are lower in energy than the HOMO are often involved in avoided crossing interactions and thus appear to move very little in the energy spectrum, as is evidenced by the PDOS plot in Fig. 4(b). For example, the energy of the HOMO-1 orbital changes only slightly under the influence of the ±0.153 V/Å fields, from −6.54 eV with no electric field to −6.52 eV at either +0.153 V/Å or −0.153 V/Å. The trends outlined above for the transmission functions, PDOS, and molecular orbitals of 1a are also observed for both *cis*- and *trans*-1b under the influence of a *z*-directed gating field.

The gating-field effect on conductivity at constant bias voltage (V_{ds}) is presented in Fig. 6. In the left panel, the current of the *trans* isomers of 1a and 1b is provided; the right panel contains the current of the *cis* isomers. As expected from the transmission trends, the current through the *trans* conformers is effected very little by the presence of the gating electric field. The switching behavior is apparent only for the *cis* conformers.

IV. CONCLUSIONS

Devices in which the organic molecules are covalently bonded to Au(111) STM tips with semi-infinite leads made up of six-atom layers, instead of the single atom wires, show the same trends for the *cis* and *trans* conformations (for both 1a and 1b) as those described above. It is also important to point out that the gating behavior described above for the Tour-Reed related molecular models is general for other conjugated molecules. This has been confirmed with a variety of conjugated systems including pentacenes, porphyrins, and other variants of the Tour-Reed device.[34] We also note that gating is eliminated when both thiol-Au bonds lie in the molecular plane in either a *cis*, a *trans*, or a linear conformation (in contrast to the perpendicular arrangement of the molecular plane and the thiol-Au plane discussed previously and seen in Fig. 2). In addition, the transmission through a long oligo(phenylene ethynylene) polymer (without any thiol group or metallic lead) is also unresponsive to either an *x*-or *z*-directed electric field. These observations confirm that the variables which determine the switching capacity of the organic system are the relative positions of the Au-S bonds, the relationship between the plane formed by the two bonds and the molecular conjugation plane, and the alignment of the gating field with the molecular plane.

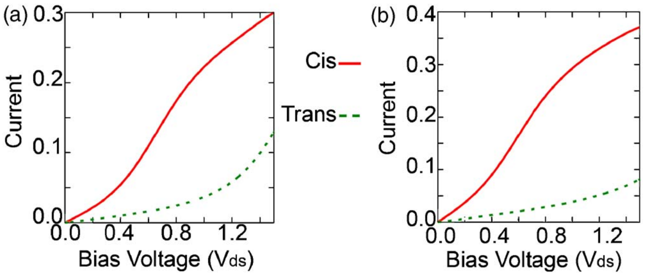

FIG. 7. (Color online) Current (27.211 a.u.) vs V_{ds} (V) for (a) 1a at E_z=0.520 V/Å and (b) 1b at E_z=−0.306 V/Å.

To summarize, for both the *cis* and *trans* conformers, an electric field parallel to the molecular conjugation plane is ineffective at changing the transmission appreciably, while an electric field directed perpendicular to the plane displays a marked effect on the transmission of *cis* conformers, and thus on the current. Therefore, a *z*-directed (out of plane) gating field can be used to switch the current on and off in molecules *cis*-1a and *cis*-1b by modulating the magnitude and direction of the field. Note that this can be realized by using a combination of two electric fields, where one is used to anchor the polarized molecular plane of 1b to a specific orientation, and the other is used as the perpendicular gating field. Furthermore, the ability to change the conductance depends on the relative position of the gold-thiol bonds with respect to the conjugation plane. The observed quenching of the gate-induced switching for the *trans* conformers originates from a symmetry breaking effect. Therefore, the different response of the *cis* and *trans* configurations indicates another possibility for a switching behavior. This is illustrated in Fig. 7 which shows the current versus V_{ds} for both configurations of 1a and 1b at a constant field. The current versus V_{ds} curves are dramatically different for the *cis* and *trans* conformers, suggesting that under a constant external electric field, the current can be altered significantly via a mechanical change between the two contact geometries. Highly conjugated organic molecules thus have potential for use as single-molecule transistors in molecular electronic devices with switching induced via either a specifically oriented electric field or via the combination of an electric field and a conformational change at the contact.

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