Conduction Switching of Photochromic Molecules

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We report a theoretical study of single molecule conduction switching of photochromic dithienylethene molecules. The light-induced intramolecular transformation drives a swapping of the highest occupied molecular orbital and lowest unoccupied molecular orbital between two distinct conjugated paths. The shuffling of single and double bonds produces a significant conductance change when the molecule is sandwiched between metal electrodes. We model the switching event using quantum molecular dynamics and the conductance changes using Green's function electronic transport theory. We find large on-off conductance ratios (between 10 and over 100) depending on the side group outside the switching core.

A photochromic molecule is one that changes its conformation when it is acted upon by light [1]. Such molecules are attractive candidates for use in molecular electronics where molecules are attached to metallic leads and electronic current passes through them. One such photochromic molecule (a dithienylethene derivative) has recently been fabricated as a monomolecular device [2]. A conduction enhancement of more than 2 orders of magnitude was observed for the closed isomer compared to the open (see Fig. 1) which was suggested to agree with theory (see Ref. [2]). The exciting discovery of optically controlled conduction opens up the field of optoelectronic monomolecular switches [3,4]. In this Letter we theoretically study the electronic transport and switching properties of several dithienylethene derivatives. We find on-off switching ratios in agreement with experiment, but these ratios vary considerably depending on the side group. We have simulated light-induced dynamical switching and observe a swapping of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of the molecule.

Dithienylethene derivatives provide a prototype system to study parameters that control photoswitching. However, other molecules have been proposed and studied such as azobenzene [5]. Figure 1 shows dithienylethene in two conformations: open and closed. Upon UV irradiation in solution, the open isomer transforms to the closed (ring closure), while the closed isomer transforms to the open under visible light (ring opening). Starting with the closed molecule, the ring opening reaction on gold was observed [2] to occur as in solution. However, with open molecules, the ring closure reaction was quenched (no reaction) when attached to gold. This unexpected quenching challenges our current understanding of this photochromic molecule; in solution, the ring closure reaction with UV light has a very high yield (transformations per photon) compared to the ring opening reaction. The switching in solution is rapid, with an ear-

lier measurement of the switching time being on a picosecond time scale [3]. However, recent ultrafast transient absorption spectra studies in solution recorded a switching on a sub-200 femtosecond time scale [6,7].

Theoretical work [7–9] has been confined to electronic structure studies of small model systems like model 1a and 1b (see Fig. 1). The calculations were limited to the potential energy profile of static conformations along a reaction coordinate. Here we report a theoretical study of dithienylethene derivatives as monomolecular optical switches between Au contacts and model ring closure by quantum molecular dynamics (QMD). We address the nature of the photo-induced structural changes and ensuing conduction switching phenomena. The main first-principles method used [10] is a local atomic-orbital density functional theory (DFT) based method in the pseudopotential local-density approximation (LDA). To simulate the photo-induced dynamics, we perform QMD
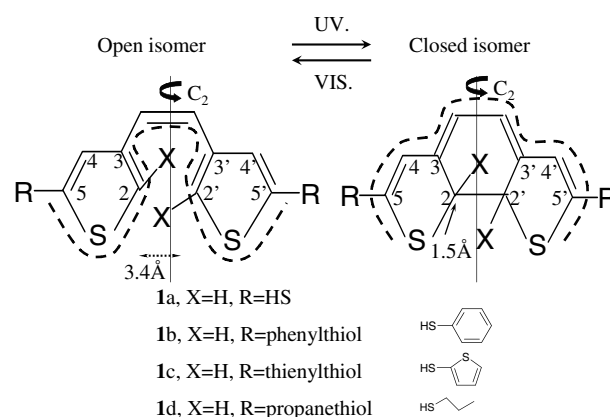

FIG. 1. Open and closed conformers of dithienylethene (C_2 symmetry axis shown). A sulfur (not shown) in the *R* groups bonds the molecule to gold. The dashed lines depict the π-electron conjugation path from inspection of the HOMO and LUMO.

simulation as in a previous study of light-induced phenomena of glassy systems [11], in which the Hellmann-Feynman force is calculated in the excited electronic configuration. The electron conduction calculations employ a Green's function transport kernel within the framework of Landauer theory [12], and use the electronic structure of the entire metal-molecule-metal system. Details on construction of the contacts and the transformation of the electronic Green's functions using gold slabs to semi-infinite contacts using a block recursion technique can be found in Ref. [13].

The frontier HOMO and LUMO orbitals are distributed along the π-conjugation chains shown in Fig. 1. The HOMO has π-bonding character while the LUMO has π^*-antibonding character. The π path of the open isomer has severe distortion along the hexatriene center (clockwise ring from 2 to 2′) due to the nonplanar geometry caused by repulsion between X groups. The frontier orbitals become somewhat localized around the highly strained 2/2′ positions. In the closed isomer, the frontier orbital is more extended and coplanar along the polyene chain shown in Fig. 1 instead of around the cyclohexadiene ring.

The photochemical ring closure reaction follows the Woodward-Hoffmann rule in symmetry-conserved conrotatory mode (twofold axis conserved, see Fig. 1) [14]. The shuffling of the single-double bonds during structural transformations correlates six (π, π^*) orbitals (denoted χ_1-χ_6) of hexatriene in the open isomer to four (π, π^*) plus two (σ, σ^*) orbitals of cyclo-hexadiene in the closed isomer as shown in the orbital correlation diagram of Fig. 2(a). Following Woodward-Hoffman nomenclature[14], we use two sets of orbital notations to distinguish the different characters of the conjugated electronic structures in the two isomers. During the reaction, the two sets of orbitals, including the HOMO and LUMO, undertake an orbital swap, where the HOMO of one becomes the LUMO of the other and vice versa.

We simulate the ring closure reaction and orbital swapping for free molecules by a first-principles QMD calculation [15]. The effect of light is simulated by boosting an electron in the open isomer from the HOMO to the LUMO and allowing the system to evolve as in the dark. The transformation to a new configuration is quite fast (~100 fs), but this does not include the time to absorb the photon. Forces are obtained from the Hellmann-Feynman theorem and electrons follow the Born-Oppenheimer surface. The excitation of a HOMO electron to the LUMO breaks an initial doubly occupied π bond, and the system races to find a new balance in the bonding. Figure 2(b) records the reaction coordinate (the distance between carbon atoms at 2 and 2′) during structural conversion. After 100 fs, the reaction coordinate falls from 3.4 Å to about 2 Å and subsequently drops into oscillations about the single C bond length near 1.5 Å
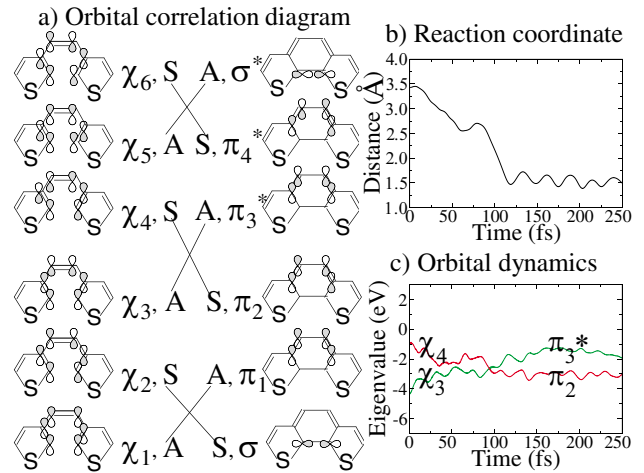

FIG. 2 (color online).   The photo-induced π-orbital swaps of model 1a. The reaction coordinate is the 2-2′ distance (Fig. 1). (a) The orbital correlation diagram by the Woodward-Hoffman rule. Each orbital is classified as S or A from the C_2 symmetry. We use subscripted χ and (π, σ) in the open and closed isomers, respectively. The frontier orbitals are (χ_3, χ_4) for hexatriene (in the open isomer) and (π_2, π_3^*) for cyclo-hexadiene (in the closed isomer). (b) The reaction coordinate evolution in QMD. The simulation time step was 0.25 fs. (c) The orbital dynamics by tracking electronic eigenvalues during QMD. Note the HOMO-LUMO swap (and band gap closing) near 100 fs.

of the closed isomer. Figure 2(c) shows how the two sets of frontier orbitals are correlated during the structural transition. The crossing of the HOMO and LUMO at 100 fs to close the gap is a convenient marker, defining a characteristic switching time after photon absorption. Our observed switching time is in accordance with the experimentally observed sub-200 fs optical switching [6,7] in solution. Other theoretical work indicates that the ring closure reaction is along a largely downhill direction in the energy landscape [8], suggesting that this reaction is not reversed spontaneously. The reverse reaction, i.e., the ring opening, is not yet clearly understood, and likely involves a multiphoton process [16]. We were unable to simulate this process using a single electron excitation.

We now show that the two molecular isomers have distinct electronic transport properties when the molecule acts as a molecular wire. We construct a conceptual device, in which molecules are sulfur-bonded between gold electrodes in a sandwich junction (see Fig. 3). This configuration mimics the often used approach of scanning probe microscopy [17] and has been used in our previous study of carotene [18]. The tunneling current is evaluated from the transmission function of Landauer transport theory [12], neglecting phonons [19] although recent work indicates that electron-phonon coupling may result in some additional structure.
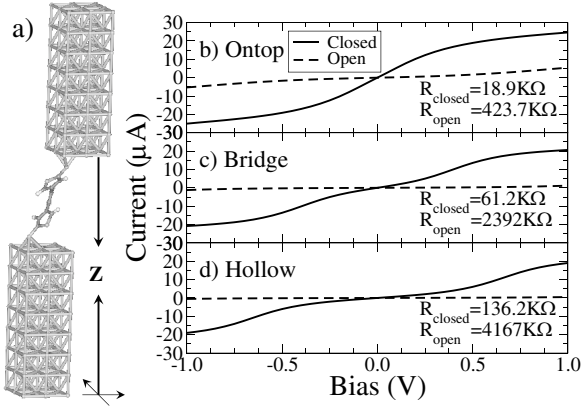
FIG. 3. (a) The sandwich junction model. The gold slab is (3×3) a periodic lattice made up of eight ideal Au(111) layers as in [18]. *I-V* curves of model 1a at (b) on-top, (c) bridge, and (d) hollow Au sites, with the corresponding distances between sulfur and contact sites being 2.42 [20], 2.07 [21], and 1.9 [22], respectively. Each curve is averaged from four molecular orientations. The resistance is calculated from the linear low bias region.

We consider three typical molecule-metal contact sites (on-top, bridge, and hollow sites) to allow for our uncertainty about the interface between dithienylethenes and the gold surface [20–22]. DFT calculations show that the hollow site is the energetically preferred site. We assume that the molecule is tilted $30°$ as inserted in an alkane self-assembled monolayer (SAM) as in the case of carotene [17,18]. *I-V* curves are calculated for contacts at the three bonding sites and our attention is drawn to a conductivity comparison of the open and closed isomers.

The *I-V* curves of model 1a are given in Fig. 3. The closed isomer conducts much better than the open isomer for all considered contacts. The conduction enhancement, defined as the ratio of the low bias conductance of the closed isomer to the open isomer, is relatively similar, being 22, 39, and 31 for on-top, bridge, and hollow sites, respectively, even though the *I-V* curves differ by an order of magnitude. Thus we predict a 20–40 times conduction enhancement between the closed and open isomers during optical switching (other molecules, e.g., 1b, give different results). Such a significant change in the current should be easily measurable (measurements have been performed for the molecule similar to model 1c [2]).

Conduction changes are largely attributed to changes of the frontier orbitals of the isomers. The frontier orbital π path is an electronic tunneling channel from one *R* group to the other *R* group (Fig. 1). The two conformations also produce very distinct alignment of the metal Fermi level within the molecular HOMO-LUMO gap. Table I shows that the metal Fermi level is near the HOMO of the closed isomer, giving an additional enhancement to the current. For the open isomer, the metal Fermi level is midgap leading to a current reduction. The

TABLE I. Fermi-level alignment of model 1a. $\Delta E = $ Au Fermi level with respect to molecule HOMO.

	Open	Closed
	(On-top, Bridge, Hollow)	(On-top, Bridge, Hollow)
ΔE (eV)	(1.168, 1.387, 1.414)	(0.096, 0.131, 0.352)

significant dependence of the *I-V* curves on the contact sites partially reflects a dependence of the self-consistently determined alignment of the metal Fermi level within the HOMO-LUMO gap.

Table II shows that the conduction enhancement can be improved by using different functional groups. The enhancement is improved dramatically in model 1c. The predicted 100 times enhancement for the DFT energetically preferred hollow site contact can be directly compared to the recent measurement of the conduction enhancement on this molecule [2]. This prediction agrees well with the low end of the experimental enhancement range of 100 to 1000.

The alignment of the metal Fermi level for model 1a is shown in Fig. 4 (the alignment is similar for model 1c). The HOMO of the open isomer is buried more than 1 eV beneath the metal Fermi level (near the fast increasing edge of the 3D bands of Au). In contrast, the HOMO of the closed isomer is within the low density of states *s* band near the Au Fermi level. We speculate that observed quenching [2] of the ring closure reaction may result from the Fermi-level alignment in the open isomer. The deep lying HOMO level at a high metal density of states offers the opportunity for many possible electron transfer events, thus reducing the lifetime of the hole. A possible remedy to reduce quenching is to reduce the interaction between the switching π paths and the metal states. In model 1d, alkane chains separate the switching unit from the gold electrode. We find that the electronic states associated with the switching unit in model 1d has a sharper local density of states than in model 1a, indicating less entanglement between switching π orbitals and metal surface states.

Our main theoretical results have been tested with other electronic structure methods. The plane-wave basis

TABLE II. Dithienylethene models with different *R* groups. E_g is the molecular band gap and τ is the switching time from open to closed. Enhancement (Enh.) is the on-off (closed-open) conductance ratios near zero bias. (o-b-h) means the on-top, bridge, and hollow sites.

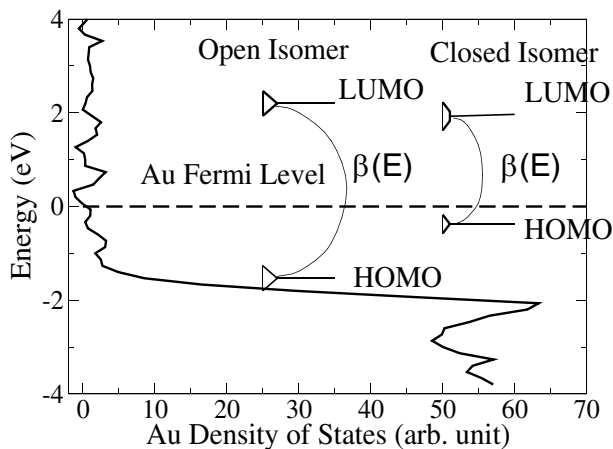| Model	1a	1b	1c	1d
E_g (eV) (Open)	3.3	3.15	3.02	3.09
E_g (eV) (Closed)	2.23	1.70	1.64	2.17
τ (fs)	100	100	88	100
Enh. (o-b-h)	22-39-31	37-29-47	57-53-109	10-11-16

FIG. 4.   The schematic alignment of the Au density of states and the HOMO-LUMO gap of the open and closed isomers of model 1a. The semielliptical $\beta(E)$ curves indicate how the tunneling decay rate ($\propto e^{-\beta L}$, $L =$ length) is expected to change with Au Fermi-level alignment.

DFT method VASP [23] and the Hartree-Fock method GAMESS [24] give the same frontier orbital characteristics of Fig. 1. We also achieved qualitatively the same dynamics [25] and I-V curves using another local orbital DFT code, SIESTA [26]. We use Hartree-Fock relaxed molecule structures[27] in a 6-31G basis within GAMESS as the initial structure of the photo-induced dynamic simulation and in the construction of molecular devices. Our speculation on the quenching mechanism focused only on qualitative considerations on the Fermi-level–HOMO alignment. Predicting this alignment will depend on charge transfer at the interface. The theoretical calculations at zero bias are fully self-consistent and will include these effects, but since we do not know the detailed geometry at the interface they are subject to error. We also use finite metal slabs, so we cannot accurately include image charge effects. Future work will be directed at a quantitative description of quenching to include interactions with image charges and coupling of the transition dipole with the electromagnetic field.

In summary, our results show 1 to 2 orders of magnitude conduction changes due to optical switching of dithienylethene. The process differs from redox switches and from the traditional semiconductor based optoelectronic mechanism in which the photocurrent depends on the photo-induced excess carriers. The molecular switching process is found to produce a swapping of the HOMO and LUMO during the conformational change.

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