Ab initio study of the electron transport in dithienylethene photochromic molecules attached to gold leads

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Abstract. We report a theoretical study of single molecule conduction in open and closed conformations of photochromic dithienylethene molecules attached to metallic leads. Photochromic molecules are attractive candidates for use in molecular electronics because of the switching between different states with different conducting behavior. We also investigate the switching behavior of the molecule based on total energy calculations for intermediate conformations along the reaction path. The results are compared to earlier work.

1. Introduction
In this paper we investigate the switching and conducting properties of photochromic dithienylethene derivatives. Such molecules change their conformation in solution when acted upon by light. The central benzene ring in the closed isomer opens under visible light (400-700 nm) while the reverse ring closure of the open isomer occurs under UV irradiation (<400 nm), Figure 1. The conduction enhancement of the closed isomer compared to the open has been investigated experimentally [1] and theoretically [2-4] and was found to reach orders of magnitude. The possibility of optically controlling the conductance of the molecule attached to leads may lead to new device implementations. However the ring closure reaction has been reported to be quenched when attached to gold leads [1]. Here we present calculations of the potential energy barrier for the switching reaction and the electronic conductance under finite bias.

2. Theory
We use the numerical atomic orbital DFT code Siesta [5] for atomic and electronic structure, and total energies. Core electrons are modeled with norm-conserving, nonlocal Troullier-Martins pseudopotentials [6] and valence electrons are expanded in an optimized basis [7]. The exchange-correlation energy is approximated with LDA [8] for the conductance calculations and GGA [9] for the switching energy barrier. Relaxed structures of the free molecules are obtained with coordinate optimization by conjugate gradients.

For the current-voltage characteristics of the lead-molecule-lead system we use the non-equilibrium Green’s function method Smeagol [10] integrated with Siesta. In this method the system is divided into three regions; left lead, scattering region and right lead. The scattering region is the supercell shown in Figure 4 and is assumed to be the region where all scattering effects take place. It contains four atomic layers of gold on each side of the molecule. The advantage of this method is that both the scattering region (molecule) and the leads are described with the same level of approximation. The
Figure 1. Light induced switching between open (A1) and closed (A2) isomer of the dithienylethene molecule.

electronic Hamiltonian and the electrostatic potential in the scattering region is also solved for self-consistently for each bias voltage point.

3. Switching

To find the potential energy barrier for the motion between the open and closed isomer we interpolated molecular structures between the two respective ground state conformations. These structures were then relaxed for all coordinates except the two central carbon atoms, which were kept fixed. The result is ground state energies for a number of conformations with values between 1.5 and 3.3 Å for the reaction coordinate, shown in Figure 2.

Also shown are earlier work where similar systems and methods have been used. Dulic et. al. [1] used a semi empirical quantum chemical method to investigate the molecule C, as well as measuring the electronic transport properties and absorption spectra for the molecule. They calculated ground and excited states for the motion along the reaction coordinate and concluded that opening and closing reactions goes through excited states. However when the molecule was attached to gold in a break-junction setup, the closing reaction was quenched. They speculated that since the first excited state in the open form is close to the gold Fermi level this molecular state mixes with the lead states inhibiting excitation of the open molecule since the excited electrons will escape into the leads. Hania et. al. [11] investigated the molecule B both experimentally and theoretically with a combination of DFT and
TDDFT. From the obtained excitation spectra and corresponding potential energy curves they concluded that the closing reaction involves motion along excited-state pathways. We obtained very similar potential barriers using another scheme than used here, where the starting conformation for each step was inherited from the previous step with the two central carbon atoms fixed at a slightly larger (or smaller) distance.

Although different molecules have been investigated in all these works the obtained behavior is very similar. This indicates that the properties of these molecules mainly stem from the central switching part, the molecule we have chosen for this work, Figure 1.

We can conclude that there is a large barrier separating the open and closed isomer and that switching between open and closed forms must involve excited states. Many different explanations have been put forward regarding the quenching of the closing reaction when the molecule is attached to gold. We will address this issue in later work.

4. Conduction

Since the same level of approximation is used for all parts of the system and the electronic structure and effective potential is solved for self-consistently for each bias voltage the computational cost is quite large. As a first step to investigate this system we therefore used a reduced valence basis set for the gold atoms: only the 6s electrons were considered in order to reduce the size of the system. This approximation can be justified since the Au 5d electrons are located over 1 eV below the fermi level. For small bias voltages our reduced Au basis set should give the same result as a complete Au basis. The results for the conduction calculations are shown in Figure 4.

Our results agree with earlier calculations [2,3] in magnitude but differ in details. However the level of approximation is also different. Li et. al. [2] calculated the transmission function for zero bias voltage and integrated this for an increasing bias window to get the current at finite voltage. Zhuang and Ernzerhof [3] used a tight-binding approximation for the lead atoms and used model voltage profiles for the electrostatic potential. The experimental result [1] is about one order of magnitude smaller. However we capture the general behavior with a large increase in conductance for the closed isomer compared to the open isomer. Especially at low bias the conductance enhancement is 10 times.

![Figure 3](image-url)

**Figure 3.** Calculated current for the closed and open form and the scattering region used in the calculations (with the closed molecule). The current goes in the Au[100] direction.

The transmission coefficient for zero bias is shown in Figure 4 together with the density of states for the isolated molecule. The states in the isolated molecule give rise to the peaks in the plot of the transmission coefficient, shifted so that the LUMO lies at or just below the Fermi energy. The
molecular states are also broadened in the lead-molecule-lead setup. Here we can see the reason for the lower conductance in the open isomer. At zero bias the transmission is much larger in the closed form than in the open because of the sharp peak centered at the Fermi level for the closed isomer. The large distance between the HOMO and LUMO in the open form 2.5 eV creates a large gap in the transmission function between 0 and 2.3 eV. For the closed isomer the smaller HOMO-LUMO gap of 1.5 eV enables a finite transmission probability even in between the HOMO and LUMO states.

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