

# Computation of the $I$ - $V$ Characteristics of a Molecular Switch

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## INTRODUCTION

We study the single molecule conduction properties of a class of molecular torsional switches whose conformation is sensitive to the electric field perpendicular to the molecular plane and affects the possibility of charge transport from one end of the molecule to the other. In particular, we present a calculation of the current as a function of the internal configuration of the molecule.

## MOLECULAR DEVICE AND COMPUTATIONAL METHOD

The molecular switch we are analyzing is made up of two benzene rings (each with two electron withdrawing chemical groups) connected by an acetylene bridge. A terminal thiol group is placed at each molecular end to act as a clip between the molecule and the gold electrodes (see Fig. 1). The switching functionality in such a class of molecules has already been extensively investigated [1], [2]. The principle of operation is that, under the action of an electric field of appropriate intensity and perpendicular to the ring-ring axis, the two rings counter-rotate: this leads to a disappearance of the conjugation of the molecular  $\pi$  orbitals, resulting in charge localization. Thus the conductance of the molecule is expected to drop significantly when the rings reach the mutually perpendicular position.

The  $I - V$  characteristics of the molecular structure, with the rings coplanar or perpendicular, have been computed using a method developed from the approach recently proposed by Gonzalez *et al.* [3]. Within the framework of the combined Density Functional Theory and Green's function formalisms, the molecule-electrode coupling contributing to the self-energy is taken to be proportional to

the projection of the molecular orbitals onto the terminal thiol fragment. The proportionality constant determines the strength of the molecule-electrode coupling and reflects the physical evidence that strongly coupled molecule and lead result, in the contact region, into spatially extended orbitals. With respect to the method of Ref. [3], we consider only the thiol as a terminal fragment and evaluate the true projection of the molecular orbitals onto the thiol orbitals, thus taking into account the effects of a non-diagonal overlap matrix.

In Fig. 2 we report the transmission function and the molecular projections obtained with our approximate computational method. The transmission function, if determined with the assumption of a diagonal Green's function, is non-zero for both coplanar and perpendicular rings, but in the latter case interference effects that are introduced by the off-diagonal terms do cancel the diagonal contribution, thereby resulting in current suppression. Such a cancellation does not occur for coplanar rings, which leads to a net current flowing through the molecule. The on-off ratio and the  $I - V$  characteristic for the molecular switch are reported in Fig. 3, as computed from the results of Fig. 2 via the Landauer-Büttiker formula.

## REFERENCES

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- [3] C. Gonzales, Y. Simon-Manso, J. Batteas, M. Marquez, M. Ratner, M., V. J. Mujica, *Phys. Chem. B* **108**, 18414 (2004).

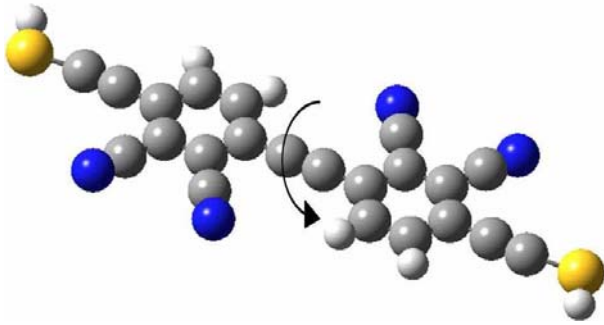


Fig. 1. Sketch of the molecular switch

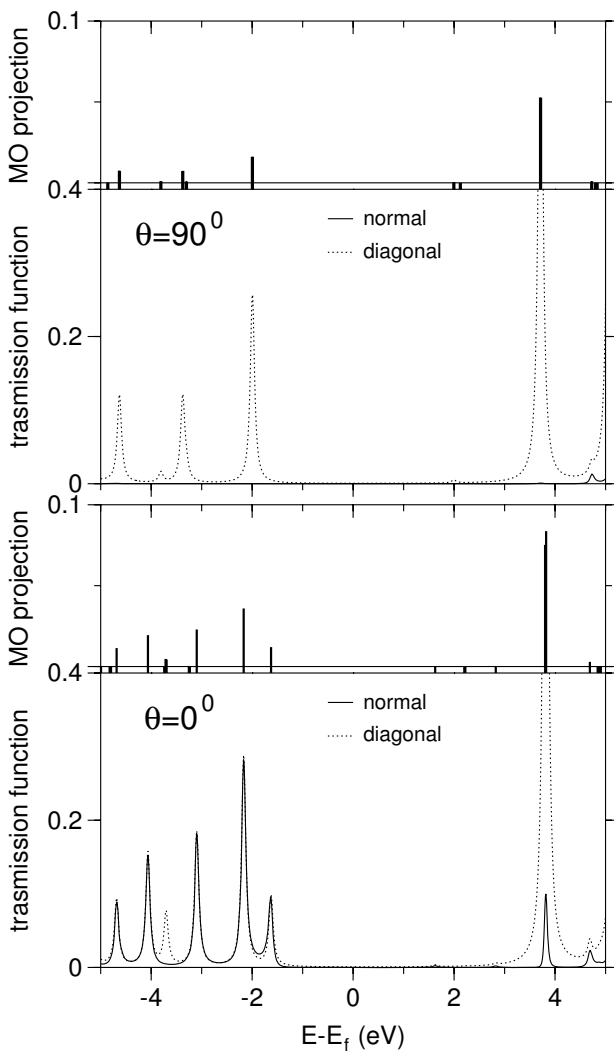


Fig. 2. Molecular orbital projections and transmission function for the configurations with perpendicular and parallel rings.

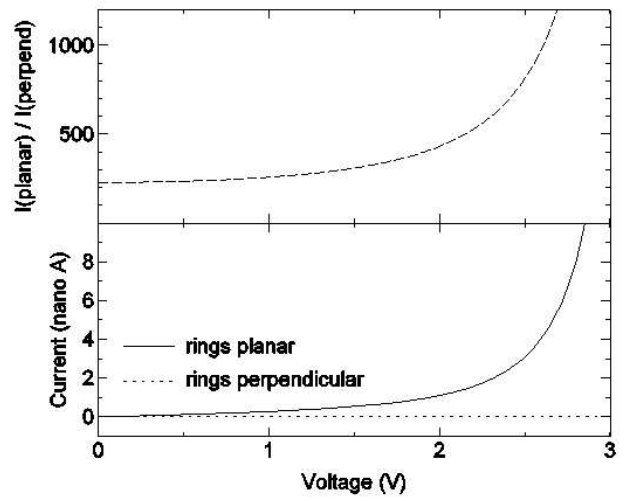


Fig. 3. Computed on-off ratio vs. applied longitudinal bias and  $I - V$  characteristic.