4D08

Theoretical investigation of a N-salicylideneanyline used as a molecular wire.

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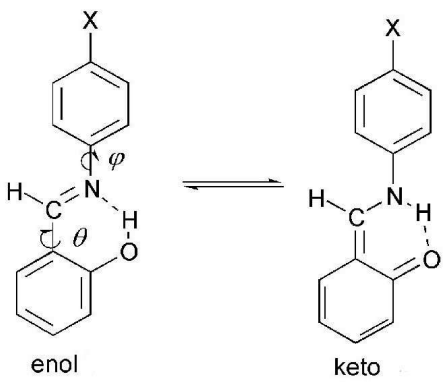
We propose a theoretical study of the N-salicylideneaniline (SDA) used as a molecular junction between gold electrodes. The SDA is one of the most extensively studied photochromic molecule. An intramolecular proton transfer is responsible for the switching properties. The photoexcitation of the *eno*l form leads to a metastable *keto* form (reaction on the first excited singlet surface) then the reverse *keto* to *enol* conversion occurs on the ground state. We investigate wether this phenomenon could be used in the design of single molecule electronic devices.



At first, an exploration of the *keto* to *enol* interconversion is done with an ab-initio molecular dynamics approach. We use the Car-Parinello Molecular Dynamics package CPMD which relies on a plane wave/pseudopotential implementation of Density Functional Theory (DFT). The SDA is bonded with thiolate groups to two gold clusters, each one composed of 11 atoms (see the molecule and the *grey* gold atoms in Fig. 1). We try to reproduce the Mechanically Controlable Break Junction experimental conditions so as to get a realistic microscopic structure. With partially relaxed clusters, the simulation shows that the *keto* to *enol* internal transfer is likely to occur eventhough the SDA is coupled to the metal leads. The molecule stays strongly bonded to the gold atoms, eventhough the sulphur atoms hover between the *on-top*, *bridging* and *hollow* positions.

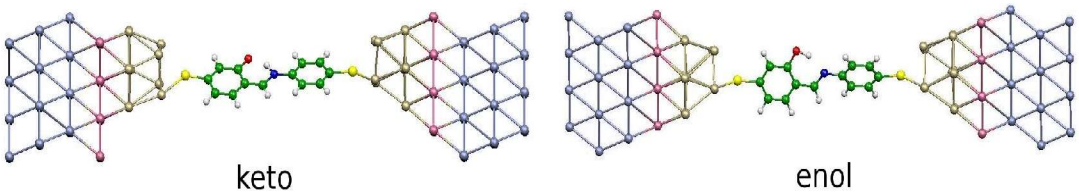


Figure 1: Optimized keto and enol structure. The 22 grey gold atoms are included in the Molecular Dynamics simulation; the 32 gold atoms in red are included in the extended molecule for the transmission calculations; the layers in blue belong to the bulk (see text).

Second, we consider the two Au_{11}-SDA-Au_{11} minimums and perform theoretical calculations of the conduction properties for both the *keto* and *enol* forms. In this model, each Au_{11} clusters is extended with a layer composed of 16 atoms (red atoms in Fig.1), so as to define a large 'extended molecule', which is geometrically connected to semi-infinite bulk electrodes (blue layers in Fig. 1).

The transmission spectra under bias voltage are calculated using a self-consistent method, based on the Non Equilibirum Green's Function (NEGF) formalism and DFT ab-initio calculations.

Differences are found in the transmission spectra for the most stable *keto* and *enol* forms of the SDA (see Fig. 2 and 3), as well as modifications of their current/voltage characteristics, and we discuss wether molecular devices based on the SDA could exhibit switching properties.

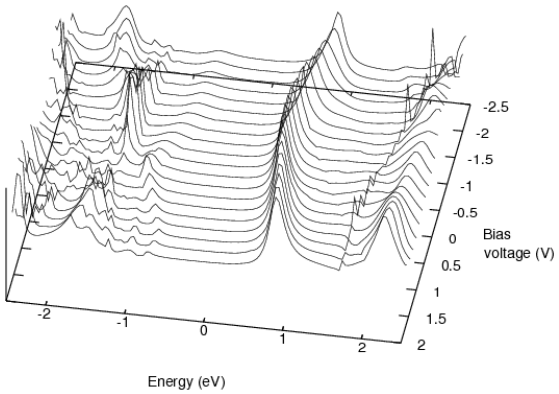


Figure 2: keto transmission spectra

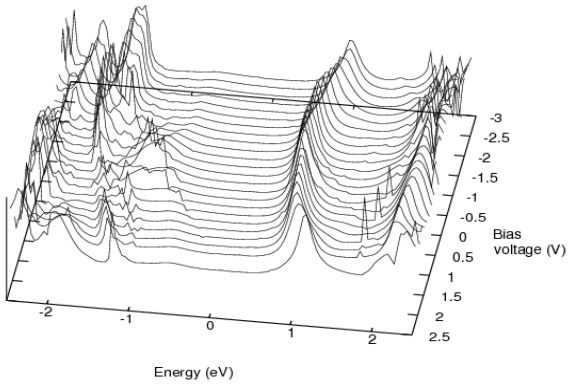


Figure 3: Enol transmission spectra

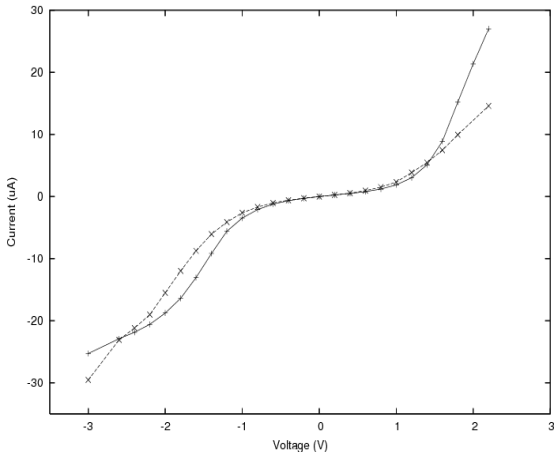


Figure 4: keto and enol current/voltage curves