STM induced molecular dynamics of biphenyl on Si(100) : a theoretical analysis.

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Since its invention in the mid 80's, Scanning Tunneling Microscopy (STM) has become a powerful tool to explore structural and electronic properties of materials at the nanoscopic scale. It has, then, widely been used in surface science as well as in studying single adsorbed molecules, carbon nanotubes or supramolecular organic assemblies. Another of its striking features is the possibility to manipulate individual objects (atoms or molecule). The STM tip can be used to mechanically move these objects, but electronic excitation is emerging as a new promising way to control the molecular dynamics at picometer scale inside a single molecule.

In this context, the work of M. Lastapis et *al.* [1] on individual biphenyl molecules adsorbed on a silicon (100) surface has demonstrated that different reversible molecular movements can be selectively activated by tuning the electron energy injected by the STM tip and by selecting precise locations for the excitation inside the molecule. From a theoretical point of view, no study has been performed on this subject but the investigation of the possible adsorption's configuration of the biphenyl on Si(100). However, the experimentally observed one is still uncertain and electronic excitations mechanisms responsible for the molecular movements remain unclear.

In this work, we present a theoretical analysis of the electronic structure, STM images and STS spectra of a biphenyl molecule adsorbed on Si(100). We chose to study a dissociated twisted biphenyl adsorption (one hydrogen atom dissociates) as it appears to be energetically favourable and to increase switching yields [2,3]. We performed *ab initio* calculations to relax the structure of the system and STM simulations have been performed using our well established model [4,5]. The electronic structure of the system (the chemisorbed molecule + a silicon cluster) has been calculated using the tight binding density functional theory code DFTB [6].

Calculated STM images present a good agreement with experimental data validating the adsorption's configuration. Moreover, local STS spectra have been calculated over both the so-called fixed and mobile parts of the molecules (Figure). Very different results have been obtained which confirms the experimental explanation for the excitation of different electronic states at a precise location inside the molecule, responsible for different dynamics. Simulations allow to clearly identify these electronic states [7].

References:

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Figures:

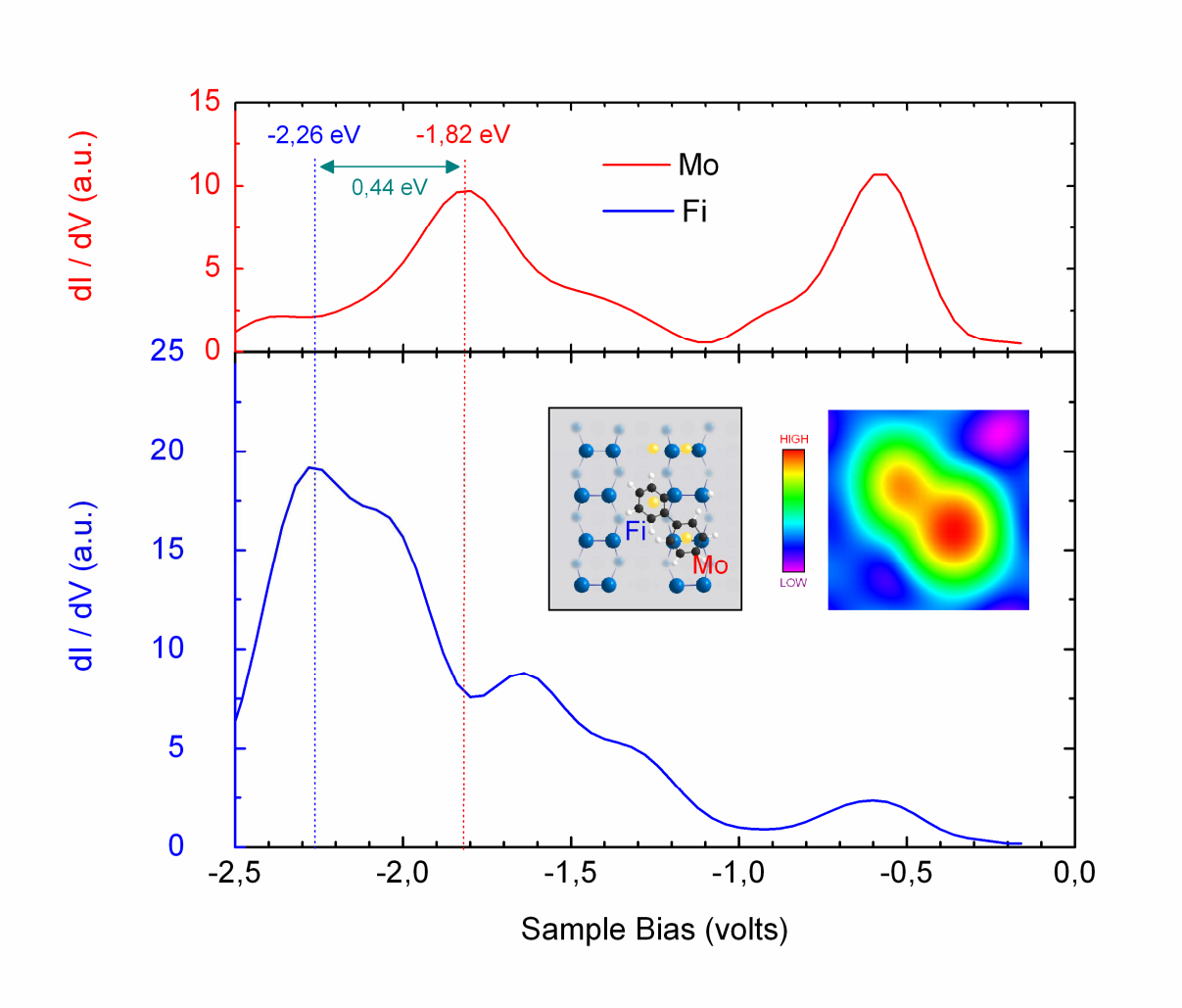

Figure :

Calculated STS spectra over the "fixed" part of the molecule (blue) and over the "mobile" one (red). Insets : positions of the STM tip used for the calculations of the STS spectra, and calculated STM image (applied bias = -1.5 V, current = 0.12 nA)