

## Modelling of AFM manipulation of organic molecules on the TiO<sub>2</sub> (110) surface

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The development of the field of nanoelectronics is closely associated with the problem of manipulation of organic molecules on the surfaces to assemble the elements of nano-circuits and the circuits themselves. A considerable progress has been made in recent years in the manipulation of single porphyrin-based molecules on metal surfaces with the STM tip [1]. However, for the nanoelectronics purposes the ability to manipulate organic molecules on metal oxide surfaces is required. This suggests that Atomic Force Microscopy (AFM) should be used. Studying of complex organic molecules at oxide surfaces with AFM is even more challenging both experimentally and theoretically. The main problem for theory is the absence of reliable description of the interactions of relatively large organic molecules with oxide surfaces. The description of molecule/surface and molecule/surface/AFM tip systems on the ab initio level is hardly possible due to the size of these systems. Consequently, a more realistic description of the interactions in these systems should be achieved on a semi-empirical level, i.e. the force-fields for these systems should be derived.

We propose a combined approach to constructing these force-fields. Instead of the derivation of a force-field for the whole organic molecule containing benzene and its derivatives we have studied the adsorption of small molecules representing its main "building blocks" on the TiO<sub>2</sub> (110) surface at the ab initio level. Since defects are inevitably present on TiO<sub>2</sub> surface, the interaction of small organic molecules with partially reduced TiO<sub>2</sub> surface have also been studied. Different types of oxygen vacancies on the surface and in the second layer have been considered.

We have focused on the adsorption of methane on the clean and reduced TiO<sub>2</sub> surfaces as a model for the adsorption of methyl groups of more complex organic molecules. The adsorption of formaldehyde, which can be used as an 'anchor' to keep the organic molecule at the surface not letting it to stick to the AFM tip due to its higher adsorption energy to TiO<sub>2</sub> surface, was also considered.

Two approaches: the Hartree-Fock and a hybrid Hartree-Fock/Density Functional (B3LYP) methods in a cluster model, and DFT method in a periodic model has been used. The results of ab initio calculations were used for constructing a classical force-field for the molecule-surface interaction. The construction of the force-field for the description of the organic "building blocks"/surface interactions has been done on the basis of the available force fields for the bulk TiO<sub>2</sub> [2] and TiO<sub>2</sub> surface [3].

The obtained force-fields were used for the semi-empirical study of adsorption of C<sub>52</sub>H<sub>72</sub>O<sub>3</sub> molecules on stoichiometric and partially reduced TiO<sub>2</sub> surfaces (Fig.1). Different positions of the molecule on TiO<sub>2</sub> (110) surface have been studied and the most stable conformations as well as the energy barriers for the transitions between them have been identified. The effect of surface oxygen vacancies on the adsorption properties of C<sub>52</sub>H<sub>72</sub>O<sub>3</sub> has also been considered.

To explore the possibility of manipulation of the C<sub>52</sub>H<sub>72</sub>O<sub>3</sub> molecule with an AFM tip the interaction of the molecule with an ionic AFM tip in contact and non-contact modes has been modelled. The results demonstrate the role of molecular deformation and adhesion to the tip. We discuss the mechanism for pushing the molecule along the oxygen rows on the TiO<sub>2</sub> (110) surface.

### References

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2. M. Matsui, M. Akaogi, Mol. Simul. 6, 239 (1991).
3. A. Bandura, J. Kubicki, J. Phys.Chem. B 107, 11072 (2003).

### Figures

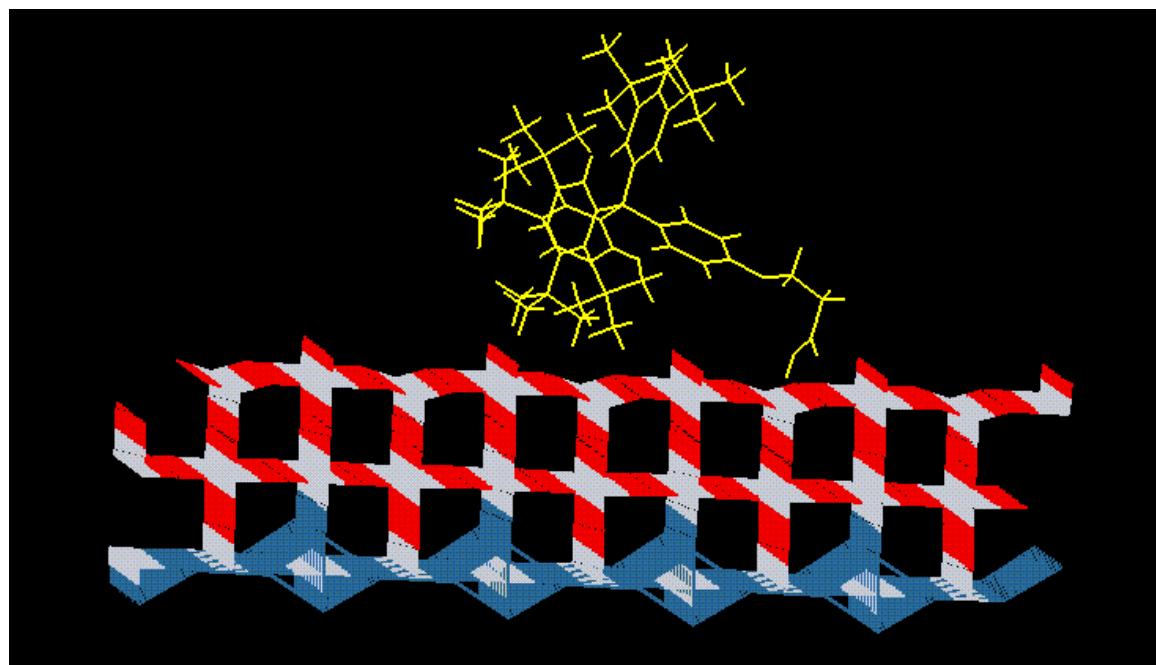


Fig. 1 C<sub>52</sub>H<sub>72</sub>O<sub>3</sub> molecule on TiO<sub>2</sub> surface.