

## DF 3: Focus Session: Interactions of Molecules with Dielectric Surfaces

Time: Monday 14:30–17:20

Location: WIL A317

### Invited Talk DF 3.1 Mon 14:30 WIL A317

**Interaction of molecules with dielectric surfaces: From single molecular adsorption to functional devices** — ●LUKAS M. ENG — TU Dresden, Institut für Angewandte Photophysik, 01062 Dresden

Heterojunctions formed between organic/biological molecules and dielectric/ferroelectric substrates (such as organic FETs [1]) gain rapidly in interest due to the possibility of inducing novel and tunable functionality on the atomic/molecular scale. We report here on high-resolution topographic and surface potential investigations of polar and non-polar organic molecules deposited onto ultrathin dielectric layers of just 1 monolayer in thickness. Dipole formation was measured for several types of molecules resulting in both donor and acceptor-like molecular behavior for different molecule-substrate interactions [2,3]. Our multi-scale modeling [4] of molecular ordering [5] revealed a strong dependence on local electric fields, leading to distinctly different molecular pattern formation for instance at step edges and defect sites [6]. As such a "defect", we purposely introduced ferroelectric thin films having a remnant but switchable surface charge, in order to investigate their applicability as functional gate electrodes in ferroelectric organic field effect transistors. Moreover, we use such ferroelectric templates as templates for the controlled molecular adsorption, as will be demonstrated for nanowires attached along domain walls. - Acknowledgement: DFG. [1] K. Haubner, *Phys. Rev. Lett.* 90 (2003) 430. [2] P. Milde, *NT 19* (2008) 305501-1. [3] U. Zerweck, *NT 18* (2007) 084006. [4] S. Gemming, *J. Comput.-Aided Mater. Des.* 14(S1) (2008) 211. [5] S. Gemming, *EPJ: Special Topics* 149 (2007) 145. [6] C. Loppacher, *NT 17* (2006) 1568.

### 5 min. break

### Topical Talk DF 3.2 Mon 15:05 WIL A317

**Studying terephthalic acid on dielectric surfaces using non-contact atomic force microscopy** — ●PHILIPP RAHE, MARKUS NIMMIRICH, and ANGELIKA KÜHNLE — Fachbereich Physik, Universität Osnabrück, Germany

Self-assembly of organic molecules is a promising route to fabricating devices on the nanometer scale. While the interaction of molecules with metallic surfaces has been investigated extensively, dielectric surfaces have been studied rather rarely due to both experimental as well as theoretical challenges. For obtaining real-space information on insulators, atomic force microscopy has been established as this technique is not limited to conducting substrates compared to scanning tunnelling microscopy.

Here, we have studied the adsorption characteristics and self-assembly of terephthalic acid (TPA) on two different substrates, namely titania and calcite, using non-contact atomic force microscopy operated under ultra-high vacuum conditions.

On the (110) surface of rutile titania we observe an ordered (2×1) structure at coverages of about 1 ML, which we attribute to an upright adsorption geometry of TPA. At lower coverages single molecules are observed. In contrast, on the (10 $\bar{1}$ 4) surface of calcite the molecules are mobile at room temperature at coverages less than a monolayer. Experiments at 115 K reveal stable, well-ordered islands. Upon increasing the coverage to 1 ML, we observe a well-ordered structure, which is stable at room temperature. Comparing these two substrates we can evaluate the influence of the dielectric substrate on molecular self-assembly.

### Topical Talk DF 3.3 Mon 15:25 WIL A317

**Theoretical contributions to the characterization of adsorbates at titania surfaces** — ●THOMAS BREDOW — Universität Bonn, Institut für Physikalische und Theoretische Chemie, Bonn

Titania is one of the most important materials for heterogeneous catalysis, either as active compound or as support. Despite the large amount of theoretical work that has been correspondingly spent on this subject, several issues concerning surface structure, bonding of adsorbates, and catalytic reaction mechanisms at the titania surfaces, have only recently been addressed.

In this contribution a brief overview of quantum-chemical investigations of titania is presented. Starting from basic properties such as relaxation and energy of low-index rutile and anatase surfaces and electronic effects of simple adsorbates, e.g. metal atoms and dimers,

models are presented that take into account solvent effects of titania nanoparticles in aqueous solution, and allow for a spectroscopic characterization of adsorbed species.

### Topical Talk DF 3.4 Mon 15:45 WIL A317

**Accurate Energetics of Ground and Excited States of Molecules on Surfaces** — ●THORSTEN KLÜNER — Universität Oldenburg, Theoretische Chemie, 26111 Oldenburg

Photodesorption of small molecules from surfaces is one of the most fundamental processes in surface photochemistry. Despite its apparent simplicity, a microscopic understanding beyond a qualitative picture still poses a true challenge for theory. While the dynamics of nuclear motion can be treated on various levels of sophistication, all approaches suffer from the lack of sufficiently accurate potential energy surfaces, in particular for electronically excited states involved in the desorption scenario.

In the last decade, we have developed a systematic and accurate methodology to reliably calculate accurate ground and excited state potential energy surfaces (PES) for different adsorbate-substrate systems. These potential energy surfaces serve as a prerequisite for subsequent quantum dynamical wave packet calculations, which allow for a direct simulation of experimentally observable quantities such as velocity distributions.

In this contribution, I will focus on recent results obtained for photodesorption of NO and CO from a NiO(100) surface. In contrast to previous studies, we were able to construct highly accurate potential energy surfaces based on correlated quantum chemical calculations (CASPT-2/CCSD(T)). These potential energy surfaces were used in subsequent wave packet studies which reveal new desorption mechanisms. All results are in good agreement with recent experiments.

### 5 min. break

### Invited Talk DF 3.5 Mon 16:10 WIL A317

**Fluorescence and ordering of aromatic molecules on thin dielectric films** — ●MORITZ SOKOLOWSKI — Institut für Physikalische und Theoretische Chemie der Universität Bonn, Germany

The fluorescence of organic molecules adsorbed on well-defined surfaces constitutes an interesting and powerful probe that completes surface science experiments. In particular, the interplay of structural order and the resulting optical properties due to the intermolecular dipole-dipole coupling is of interest and offers new possibilities to tune the emitting properties. Among the substrate materials, thin epitaxial films of wide-band gap materials are most interesting, since they allow parallel investigations by electron based surface techniques, e.g., low energy electron diffraction or STM, but avoid the ultrafast fluorescence quenching that is otherwise present on metal surfaces. In this talk, the present status of fluorescence experiments on different dielectric thin film (e.g., NaCl, AlO<sub>x</sub>) will be reported.

### Topical Talk DF 3.6 Mon 16:40 WIL A317

**Determination of Molecule Orientation on Oxide Surfaces by Near-Edge X-ray Absorption Spectroscopy** — ●ALEXEI NEFEDOV, MIKHAIL NABOKA, and CHRISTOF WÖLL — Ruhr Universität Bochum, Germany

Recently, the formation of molecular networks on metals has attracted considerable attention [1]. When replacing the supporting metals by their oxides the situation becomes more complex because the interaction with the ionic centers on the substrate will compete with the molecule-molecule interaction. Since most techniques employed to study adsorption on metals are difficult to apply to oxides because of the insulating nature of these substrates only few works focusing on such systems have been reported so far. Recently, Tekiel et al. [2] studied the adsorption of TPA on TiO<sub>2</sub>(110) and an upright orientation was reported, which is incompatible with the formation of a two-dimensional network. We have carried out a systematic investigation on the orientation of the TPA-molecules on a rutile TiO<sub>2</sub>(110) substrate using near-edge x-ray absorption spectroscopy. We have investigated a series of coverages, extending from a few percent of monolayer to saturation corresponding to 1 ML. We find a planar adsorption geometry of TPA molecules up to ~ 0.3 ML, while when saturation coverage is reached the TPA molecules are adsorbed in an upright po-

sition. The latter adsorption geometry implies that one of the carboxyl groups binds to the surface as a bidentate carboxylate.

[1] S. Stepanow et al, J. Phys. Chem. B. 108, 19392, (2004).

[2] A. Tekiel et al, J. Phys. Chem. C, 112, 12606, (2008).

### Topical Talk

DF 3.7 Mon 17:00 WIL A317

**Adsorption of Organic Molecules on Moderately Reactive Substrates** — ●MICHAEL ROHLFING<sup>1</sup>, ANDREAS GREULING<sup>1</sup>, and THOMAS BREDOW<sup>2</sup> — <sup>1</sup>Fachbereich Physik, Universität Osnabrück, Germany — <sup>2</sup>Institute for Physical and Theoretical Chemistry, Universität Bonn, Germany

We discuss the adsorption of organic molecules on crystal surfaces within density-functional theory (DFT), focusing on three examples of moderate molecule-substrate interaction. PTCDI, which is a flat elongated molecule, binds to rutile TiO<sub>2</sub>(110) in a flat-lying configuration with orientation along the rows, showing high mobility along the rows.

TMA, on the other hand, interacts with rutile TiO<sub>2</sub>(110) via COOH groups at preferred sites, resulting in specific, flat-lying configurations. Thirdly, PTCDA adsorbs on Ag(111) by delocalized interaction of its perylene core plus local binding via its oxygen corner groups. All results are discussed in context with available experimental data.

Our studies demonstrate very different relaxation time scales of intramolecular and molecule-substrate coordinates, driven by the much different respective energies. This requires particular care in all optimization procedures. Furthermore, we discuss the validity of various exchange-correlation functionals, in comparison with more advanced adsorption energies from an exact-exchange-and-correlation (EXX+RPA) formalism. Our EXX+RPA and DFT results for PTCDA/Ag(111) demonstrate that the most reliable DFT data are obtained from the local-density approximation (LDA), which we use throughout our DFT studies, therefore.