

O 12: Oxides and insulators: Adsorption

Time: Monday 15:00–17:45

Location: H33

O 12.1 Mon 15:00 H33

Water adsorption on SrTiO₃(001): A density-functional theory study — ●HANNES GUHL^{1,2}, WOLFRAM MILLER¹, and KARSTEN REUTER^{2,3} — ¹Leibniz Institut für Kristallzüchtung Berlin (Germany) — ²Fritz-Haber-Institut Berlin (Germany) — ³TU München (Germany)

SrTiO₃ is a technological oxide, with applications as photo-catalyst, gas-sensor or as substrate for film growth. In many of these applications the surface of SrTiO₃ is deliberately or unintended in contact with water molecules. Aiming for the atomic-scale details of this interaction we perform density-functional theory calculations addressing the adsorption of H₂O on both regular terminations of the SrTiO₃(001) surface. We find that the binding energetics is crucially controlled by long-range surface relaxations. Using this energetics to construct a thermodynamic phasediagram we obtain a different propensity for hydroxylation of the two terminations that is consistent with recent experiments by Iwahori *et. al* [1]. Around room temperature the SrO-termination becomes hydroxylated already at lowest background humidity, whereas the TiO₂-terminated domains stay practically water-free in the range of low and moderate H₂O vapor pressures.

[1] K. Iwahori *et. al* J. Appl. Phys. **93**, 3227 (2007).

O 12.2 Mon 15:15 H33

H and H₂O adsorption on Fe₃O₄(001): Adsorbate induced charge and orbital order — ●NARASIMHAM MULAKALURI^{1,2}, ROSSITZA PENTCHEVA¹, WOLFGANG MORITZ¹, and MATTHIAS SCHEFFLER² — ¹Section Crystallography, Dept. for Earth and Environmental Sciences, University of Munich — ²Fritz-Haber-Institut der MPG, Berlin

Besides potential applications in spintronics, magnetite plays an important role in many environmental redox reactions. Using density functional theory together with an on-site Coulomb repulsion term (GGA+*U*), we investigate the adsorption of H₂O and H on Fe₃O₄(001) surface and its influence on the electronic structure. The surface phase diagram, compiled within the framework of *ab initio* atomistic thermodynamics reveals dissociative adsorption of water especially at surface defect sites. At higher water vapour pressures a partial dissociation sets in, where a chain of hydrogen bonded H₂O and OH groups forms[1]. The adsorbates (H₂O, OH, H) are found to induce a unique charge and orbital ordering in the surface and sub-surface layers. This feature can be used to tailor the catalytic properties as well as half-metallicity of the material.

[1] N. Mulakaluri *et.al*, Phys. Rev. Lett **103**, 176102 (2009).

O 12.3 Mon 15:30 H33

A Classical Potential to Model Protein Adsorption on the Natively Oxidised Titanium Surface — ●JULIAN SCHNEIDER and LUCIO COLOMBI CIACCHI — Hybrid Materials Interfaces Group, BC-CMS, Universität Bremen, 28359 Bremen

In order to investigate the surface properties of metals in a realistic fashion it is crucial to take into account the thin oxide layer that forms spontaneously when the surface is exposed to an oxidising environment. Starting from reference oxide layer structures obtained in extensive first-principles molecular dynamics simulations, we have developed a novel classical potential which is able to reproduce the topological binding features of the amorphous oxide network on Ti as well as the interfacial behaviour of the TiO_x/water interface. The analytic form of the potential has been chosen so that it can be easily combined with well-established biomolecular force fields. This allowed us to perform classical simulations of small organic molecules on the oxide surface and compare the results with those of density functional theory calculations. Ongoing work is focusing on the application of our force field to simulate the adsorption of amino acids, small peptides and larger protein fragments on oxidised Ti surfaces.

O 12.4 Mon 15:45 H33

Anomalous molecular orbital variation upon adsorption on wide band gap insulator: Gluconic acid on MgSO₄·H₂O(001) — ●WEI CHEN¹, CHRISTOPH TEGENKAMP¹, HERBERT PFNÜR¹, and THOMAS BREDOW² — ¹Institut für Festkörperphysik, Leibniz Universität Hannover, Hannover, Germany — ²Institut für Physikalische und Theoretische Chemie, Universität Bonn, Bonn, Germany

The understanding of the interaction between organic molecule and wide band gap insulator is of great importance provided with their elementary roles in organic electronics and optoelectronic devices. It is commonly believed that organic molecules are physisorbed on the ideal non-polar surface of wide band gap insulator with limited variation on the electronic properties of the adsorbate molecule. However, on the basis of first principles calculation on the gluconic acid adsorbed on the (001) surface of a ternary compound MgSO₄·H₂O, we show that the orbitals of the acid molecule could undergo significant changes upon adsorption. The gluconic acid binds strongly to the MgSO₄·H₂O(001) via multiple electrostatic interactions from Mg-O, which is further stabilized by the long range dispersion force. The electrostatic interactions result in a pronounced intra-molecular distortion of the adsorbate, yielding a much smaller HOMO-LUMO gap of the acid due to the geometrical change alone. Furthermore, as manifested by the prominent hybridization between the molecule and the surface, the characteristics of the frontier orbital are modified significantly upon adsorption with respect to the isolated molecule.

O 12.5 Mon 16:00 H33

A comparative study of short-chained alcohols and water adsorbed on TiO₂(110) by He atom scattering and DFT —

●DAVID SILBER¹, FRANZISKA TRAEGER¹, CHRISTOF WÖLL³, PIOTR KOWALSKI², and DOMINIK MARX² — ¹Department for Physical Chemistry I at the university of Bochum — ²Department for Theoretical Chemistry at the university of Bochum — ³Institute of Functional Interfaces Karlsruhe at the Karlsruher Institute of Technology

In this combined experimental and theoretical study the adsorption of methanol and ethanol on well defined TiO₂(110) was investigated. Theoretical and experimental results will prove that methanol adsorbs molecularly in a c(2x2)-superstructure. Heating the surface to 300 K leads to the deprotonation of methanol. Further heating to 350 K (binding energy - 1 eV) leads to a recombinative desorption process in which solely methanol is detected. In additional experiments predosing of D₂O was performed to fill bridge bonded oxygen vacancy sites and to investigate the interaction of water with methanol. TDS reveals that water and methanol compete for adsorption sites, but a pure methanol layer was never formed on water precovered TiO₂. These experimental finding is supported by our DFT calculation, which proves that a mixed methanol and water structure is stable. This work is complemented by the analogue investigation of ethanol adsorption on clean and water precovered TiO₂. On clean rutile solely the desorption of ethanol in a recombinative desorption process was detected. Like methanol ethanol competes with water for adsorption sites, but unlike methanol, ethanol is able to completely replace water in the first layer.

O 12.6 Mon 16:15 H33

Light-induced isomerization of an azobenzene derivate on an insulating surface — ●JÖRG HENZL and KARINA MORGENSTERN

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Azobenzene molecules and its derivatives are highly attractive for switches in molecular electronics and have a high potential in optoelectronic devices as they exhibit a light-induced *cis-trans* isomerization. Recent studies demonstrated the principle feasibility of isomerization in contact with a metal surface. But circuits on metals are of little technological relevance in contrast to insulators. A model system for an insulating surface is a thin NaCl film grown on metal substrates. Recently, the electron-induced isomerization of amino-nitroazobenzene on NaCl/Ag(111) was shown.[1] In this contribution, we present low temperature scanning tunnelling microscopy measurements of p-hydroxy-azobenzene on thin NaCl films on Ag(111). After depositing at 20 K, single molecules are found on the surface. The reversible isomerization can be triggered either with inelastic tunnelling electrons from the STM tip or with photons from a Hg-arc lamp. We characterize the adsorption geometry of both configurations and discuss the wave-length depend light-induced isomerization. [1] A. Safiei, J. Henzl, and K. Morgenstern, O17.8, DPG conference, Dresden 2009

O 12.7 Mon 16:30 H33

Orbital symmetries in Cu(II)-tetraazaphthalocyanine isomers — ●TOBIAS SONNLEITNER, INGMAR SWART, NIKO PAVLIČEK,

CHRISTOF UHLMANN, and JASCHA REPP — Institute of Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany

Ultrathin insulating films on metal substrates facilitate the use of the scanning tunneling microscope to study the electronic properties of individual molecules, which are electronically decoupled from the metallic substrate. To gain a detailed understanding of the molecular properties, it is desirable to systematically vary the electronic structure of molecules step by step without changing the geometrical structure too strongly. Cu(II)-tetraazaphthalocyanine molecules provide such a model system. For these molecules four classes of isomers with different symmetries exist. These symmetries are directly visualized by imaging of the unperturbed molecular orbitals. This allows us to determine the isomer under study, and locate the nitrogen atoms in the molecular structure. DFT calculations substantiate the experimental findings.

O 12.8 Mon 16:45 H33

Interaction of CO₂ and H₂O with Thin NiO Layers on Cu(111) — ●KARIN GOTTERBARM, MICHAEL PETER ANDREAS LORENZ, REGINE STREBER, OLIVER HÖFERT, MARIE-MADELEINE WALZ, CHRISTIAN PAPP, ANDREAS BAYER, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

NiO is an important material in heterogeneous catalysis. Under ambient conditions, reactions with CO₂ and H₂O can lead to the formation of carbonates and hydroxides, which could block active sites and thereby influence the catalytic reactivity. We studied the adsorption of CO₂ and H₂O on thin NiO layers (around 2 ML) on Cu(111) as inert substrate by in-situ XPS applying synchrotron radiation at BESSY II.

Upon adsorption of CO₂, characteristic peaks in the O 1s and C 1s region indicate the formation of carbonate. When the surface is exposed to water, hydroxide and multilayers of water are formed. In-situ XPS during heating revealed an unusual thermal stability of the carbonate as well as hydroxide layers. Experiments on different NiO layers with varying hydroxide precoverages showed that adsorbed OH species effectively block CO₂ adsorption sites, leading to a lower saturation coverage of CO₃.

This work was supported by BMBF (05 ES3XBA/5) and the DFG through the Cluster of Excellence "Engineering of Advanced Materials".

O 12.9 Mon 17:00 H33

Adsorption of cobalt phthalocyanine on rutile TiO₂ (110) surfaces: interface formation. — ●PAVEL SHUKRYNAU, MARIUS TOADER, and MICHAEL HIETSCHOLD — Chemnitz University of Technology, Institute of Physics, Solid Surfaces Analysis Group. D-09107 Chemnitz, Germany.

We have employed variable temperature scanning tunneling microscopy (STM) to follow the adsorption of cobalt phthalocyanine (CoPc) on rutile TiO₂ (110)-1x1 and -1x2 substrates. The coverage of CoPc varied from 0.05 up to 1 monolayer (ML). At room temperature and very low coverage single phthalocyanine molecules either lay flat on the surface over the bridging oxygen atomic lines or stay tilted in troughs between them. Further deposition of CoPc leads to the agglomeration of the molecules and finally results in the formation of irregularly disordered films on both substrates. At a coverage of about 0.75 ML the surfaces are completely covered with roundly shaped 3D

clusters of typical size up to 3 nm. The general structure of the surface, i.e., shape of the step edges, remains unchanged. Subsequent annealing of the samples up to 300°C results in the rearrangement of the adlayer and forms the molecular rows along [001] direction of the substrate. STS spectra taken at different coverages give an information about the electronic properties of the interface, revealing the adsorption mechanism of molecules on this substrate.

O 12.10 Mon 17:15 H33

NEXAFS/XPS Study of the Organic Molecules on Metal-Oxide Surfaces — ●MICHAEL NABOKA^{1,2}, ALEXEI NEFEDOV^{1,2}, and CHRISTOF WÖLL² — ¹Ruhr University of Bochum, D-44780, Bochum, Germany — ²Karlsruher Institute of Technology, D-76344, Eggenstein-Leopoldshafen, Germany

Today the investigation of the electronic properties and orientation of the organic molecules adsorbed on metal-oxide single crystal surfaces attracts considerable attention. The reason for that is a search for the new metal organic systems which may become useful in the rapidly developing area of organic electronics and catalysis. The example of such a system can be a terephthalic acid adsorbed on the TiO₂ (110) surface. This system offers a possibility to create the monolayer of the carboxyl-terminated up-standing molecules which may in future have an application similar to self-assembling monolayers or may also serve as a linker for Metal Organic Frameworks (MOFs). Near Edge X-Ray Adsorption Fine Structure (NEXAFS) spectroscopy and X-ray Photoelectron Spectroscopy (XPS) are the techniques which were developed particularly for the study and understanding of the organic molecules structure on the surface revealing the molecular electronic structure and its orientation. Since nowadays requirements for such kind of research are increased the new NEXAFS/XPS endstation at synchrotron facility BESSY II has been developed and constructed. The machine functionalizes under ultrahigh vacuum conditions and allows to measure NEXAFS/XPS spectra as well as to use the additional surface science methods such as LEED and TDS.

O 12.11 Mon 17:30 H33

Coupled cluster calculations for NO and Au adsorption on CeO₂ using the method of increments — CARSTEN MÜLLER and ●BEATE PAULUS — Physikalische und Theoretische Chemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin

CeO₂ is an active constituent in today's car catalysts where it assists in the reduction of NO_x to N₂. Here we present results from first principles CCSD(T) calculations for NO physisorption on the CeO₂ (111) surface. Many first principles methods fail to describe the physisorption phenomenon. The main binding force is dispersion, which is neglected in the Hartree-Fock theory, not included in common DFT functionals, but recovered by many-body methods such as MP2 or the coupled cluster method. Here we apply this theory in the framework of a local correlation scheme called "The Method of Increments". It was successfully used to determine the adsorption energies for CO and N₂O on the CeO₂ (111) surface [1,2]. Now we extend the method to the adsorption of open-shell molecules like NO and to open-shell atoms like Au.

[1] C. Müller, K. Hermansson, and B. Paulus, Chem. Phys. 362, 91 (2009).

[2] C. Müller, B. Paulus, and K. Hermansson, Surf. Sci. 603, 2619 (2009).