

## O 14: Oxide Surfaces: Adsorption and Reactivity

Time: Monday 15:00–18:00

Location: MA 042

O 14.1 Mon 15:00 MA 042

**Adsorption energies of small molecules on metal oxide surfaces using the method of local increments** — ●WILKE

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Obtaining highly accurate potential energy surfaces is still very demanding and one of the limiting factors in theoretical surface science. Nowadays density functional theory (DFT) with periodic boundary conditions is the most frequently used approach in theoretical surface science. However, the exact form of the exchange correlation functional is unknown and no systematic strategy of improving the results obtained in DFT calculations has been investigated. So far, only conventional quantum chemistry provides a well-defined hierarchy of methods for the systematic treatment of electron correlation effects.

The disadvantage of using high accurate post-Hartree-Fock methods like Moller-Plesset perturbation theory or the coupled-cluster method is the high computational cost of these methods. For example the CCSD method scales very bad with the size of the system. In order to decrease the size of the system, the method of increments was introduced by Stoll to calculate the correlation energy on an accurate level of theory.

In this study, the method of local increments is used in connection with an embedded cluster approach and wave function based quantum chemical ab initio methods [1] to describe the adsorption of small single molecules on the rutile(110) and MgO(001) surfaces.

[1] B. Paulus, Phys. Rep. 428, 1 (2006).

O 14.2 Mon 15:15 MA 042

**The role of defects in the adsorption of CO on Co<sub>3</sub>O<sub>4</sub>** — ●M.ALEXANDER SCHNEIDER<sup>1</sup>, PASCAL FERSTL<sup>1</sup>, LUTZ HAMMER<sup>1</sup>,M.ALIF ARMAN<sup>2</sup>, EDVIN LUNDGREN<sup>2</sup>, JAN KNUDSEN<sup>3</sup>, SASCHA MEHL<sup>4</sup>, ARAFAT TOGHAN<sup>4</sup>, YAROSLAVA LYKHACH<sup>4</sup>, and JÖRG LIBUDA<sup>4</sup> — <sup>1</sup>Solid State Physics, FAU Erlangen-Nürnberg, Germany — <sup>2</sup>Division of Synchrotron Radiation Research, Lund University, Sweden — <sup>3</sup>The MAX IV Laboratory and Division of Synchrotron Radiation Research, Lund University, Sweden — <sup>4</sup>Physical Chemistry II, FAU Erlangen-Nürnberg, Germany

We studied the adsorption of CO on 3 nm thick Co<sub>3</sub>O<sub>4</sub>(111) films grown on Ir(100) by means of XPS, IRAS and STM under ultrahigh vacuum conditions. At full saturation of the surface at 100 K both XPS and IRAS suggest that CO is bound in three different configurations. We find two distinctly different adsorption sites in which the molecule is weakly bound and desorbs from Co<sub>3</sub>O<sub>4</sub> well below 300 K. A third stronger bound minority configuration resides at the surface even beyond room temperature. The latter might be related to surface defect sites which are investigated in detail by STM for the clean films. Possible configurations for the weakly bound CO molecules on the Co<sub>3</sub>O<sub>4</sub> surface are also discussed.

O 14.3 Mon 15:30 MA 042

**Adsorption of carbon dioxide onto an iron oxide** — ●PETR DEMENTYEV, CASEY O'BRIEN, FRANCISCO IVARS, SWETLANA SCHAUERMANN, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Carbon dioxide is likely to play one of the key roles in clean energy technologies. Its conversion into methanol or other chemicals is a promising way for renewable energy storage. Since carbon dioxide molecules are inert, an important issue is to activate them. Herein we employ a combination of single-crystal adsorption calorimetry (SCAC) and infrared reflection-absorption spectroscopy (IRAS) to study carbon dioxide adsorption on iron oxide Fe<sub>3</sub>O<sub>4</sub>. SCAC is a method for probing energetics of adsorbate-surface interactions, while IRAS allows identifying chemical nature of surface species. Both instruments contain molecular beams what enables to conduct careful adsorption experiments under clean UHV conditions.

We probe two well-defined Fe<sub>3</sub>O<sub>4</sub> (111) and (100) thin films. Both substrates as well as FeO film are grown epitaxially on Pt single crystal. Low-temperature SCAC measurements reveal that carbon dioxide transiently sticks to Fe<sub>3</sub>O<sub>4</sub> whereas it does not interact with oxygen-terminated FeO and bare Pt. IRAS confirms that CO<sub>2</sub> does react with the iron oxide. There are many features in the region of C-O stretching vibrations indicating coexistence of different species such as

physisorbed CO<sub>2</sub> and carbonates. Surface chemistry of CO<sub>2</sub> seems to be strongly kinetically limited. Co-adsorption experiments show that water surface species block CO<sub>2</sub> adsorption.

O 14.4 Mon 15:45 MA 042

**High chemical activity of a perovskite surface: adsorption of CO and H<sub>2</sub>O on Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub>** — ●FLORIAN MITTENDORFER, BERNHARD STÖGER, DANIEL HALWIDL, WERNFRIED MAYR-SCHMÖLZER, JOSEF REDINGER, MICHAEL SCHMID, and ULRIKE DIEBOLD — Institut f. Angewandte Physik, TU Wien

In the recent years, complex transition metal oxide surfaces have received enormous attention, both due to the fundamental properties as well as their potential for applications in the field of energy storage and conversion. Yet only little is known about the chemistry of these materials. On the basis of density functional theory (DFT) calculations, I will present a theoretical study on the surface chemistry of Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub>, supported by experimental STM measurements. Surprisingly, the STM study shows a high chemical activity of the Sr<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub> surface [1]. We conclude that these observations are related to the facile adsorption of carbon monoxide (CO), which can easily be converted to a carboxylate-like COO species at the surface. With an adsorption energy of -2.2 eV, the latter structure shows a high chemical stability. We also find that H<sub>2</sub>O can be readily adsorbed at the surface, resulting in the dissociation of the water molecule. Yet the fragments display an attractive interaction, leading to complex adsorption patterns.

[1] B. Stoeger et al., Phys. Rev. Lett. 113 (2014) 116101

O 14.5 Mon 16:00 MA 042

**Surface chemistry of magnetite (001) surface: Adsorption of Formic Acid and Methanol.** — ●OSCAR GAMBA<sup>1</sup>, HESHMAT NOEI<sup>2</sup>, JIŘÍ PAVELEC<sup>1</sup>, ROLAND BLIEM<sup>1</sup>, MICHAEL SCHMI<sup>1</sup>, ULRIKE DIEBOLD<sup>1</sup>, ANDREAS STIERLE<sup>2</sup>, and GARETH PARKINSON<sup>1</sup> — <sup>1</sup>Institute of Applied Physics, Vienna University of Technology, Wien, Austria — <sup>2</sup>DESY Nanolab & Physics Department, University of Hamburg, Hamburg, Germany

Understanding the surfaces of metal oxides and their interactions with organic molecules is a crucial aspect in research topics such as catalysis, and environmental science. Formic acid (HCOOH), and methanol (CH<sub>3</sub>OH), are often used as probe molecules to test the reactivity of metal oxide surfaces (1). Adsorption of both species can be molecular, as in the low temperature regime, but is frequently dissociative on surfaces that expose pairs of undercoordinated cations (2).

In this talk, the study of adsorption of formic acid and methanol on the Fe<sub>3</sub>O<sub>4</sub>(001) surface using XPS, LEED, IRRAS, and STM will be described. Both molecules adsorb molecularly at low temperature, and dissociatively at room temperature, yielding adsorbed formate and methoxy species respectively, together with surface hydroxyl groups. Formate adsorbs in a bidentate configuration at regular iron lattice sites producing a (1X1) overlayer. Methoxy adsorption is restricted to step edge and other defect sites where the coordinative undersaturation of the surface atoms is higher.

1. J. M. Vohs, Chemical Reviews 113 (6), 4136-4163 (2012). 2. J. M. Vohs and M. A. Barteau, Surface Science 176 (12), 91-114 (1986).

O 14.6 Mon 16:15 MA 042

**Carboxylic Acid Deprotonation on MgO(100)** — ●QURATULAIN TARIQ, MATTHIAS FRANKE, MICHAEL RÖCKERT, HANS-PETER STEINRÜCK, and OLE LYTKEN — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, 91058 Erlangen, Egerlandstraße 3, Germany

Chemical functionalization of surfaces provides unique routes to obtain nanoscale supramolecular architectures, for novel technological applications. Only few attempts have been made to functionalize metal oxide surfaces by adsorption of organic molecules. A promising class of molecules to form supramolecular structures are aromatic carboxylic acids. Such species have been studied previously, on a variety of surfaces and both flat-lying and upright-standing adsorption configurations are possible. In the present work, we investigate the adsorption of phthalic acid (C<sub>6</sub>H<sub>4</sub>(COOH)<sub>2</sub>) on MgO(100) thin films on Ag(100), as a function of temperature and coverage, by X-ray photoemission spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), near-edge X-ray absorption fine structure (NEXAFS) and tempera-

ture programmed desorption (TPD). We find deprotonation of both carboxyl groups of the phthalic acid molecule upon heating and formation of a bidentate species with an upright standing orientation, stable between 350 and 500 K. The project is supported by the DFG through FOR 1878 (funCOS).

O 14.7 Mon 16:30 MA 042

**Density Functional Theory study of adatom and metal cluster adsorption on metal supported thin Zirconia films** — ●WERNFRIED MAYR-SCHMÖLZER, FLORIAN MITTENDORFER, and JOSEF REDINGER — Center of Computational Materials Science, TU Vienna

Zirconium dioxide is a material with many interesting properties, which make it useful for various technological applications, for example as a solid electrolyte in solid-oxide fuel-cells or as an oxygen gas sensor. Therefore a detailed understanding of adsorption on zirconia films is crucial for these applications.

We present results of DFT calculations of adsorption of metal adatoms and clusters on a thin zirconium oxide film supported by a Pt<sub>3</sub>Zr substrate. This alloy is very stable and can be used to experimentally grow thin ZrO<sub>2</sub> films by oxidation. The calculations were performed using the Vienna Ab-Initio Simulation Package (VASP) employing standard PBE and van-der-Waals density functionals.

The binding mechanism and interaction of adsorbed transition metal adatoms such as gold, silver, nickel and palladium was investigated. For gold we only find weak physisorption while the other metals show significantly higher adsorption energies. Additionally we present results of the adsorption of larger transition metal clusters on the oxide film and an analysis of their charged state.

This work has been supported by the Austrian Science Fund under the project number F4511-N16.

O 14.8 Mon 16:45 MA 042

**Surface etching of single crystalline ZnO by phosphonic acid based SAMs** — ●ALEXANDRA OSTAPENKO and GREGOR WITTE — Molekulare Festkörperphysik, Philipps-Universität Marburg, Renthof 7, 35032 Marburg, Germany

Self-assembled monolayers (SAMs) attachment have proven to be an effective way of tuning electronic interfacial properties or specifically link dye-molecules to transparent metal oxides. Organic-inorganic hybrid systems based on the latter approach have recently attracted significant research interest because of their promising use in photovoltaic application. The resulting device performance is expected to depend critically on the microstructure of the film. Widely used phosphonic acid based SAMs form surprisingly robust films on ZnO surfaces. However, it was found that during the film deposition phosphonic acid anchoring causes surface damaging resulting from dissolution-precipitation of ZnO. For the extended immersion times we observe the formation of star shaped surface defects of crystalline needles on single crystalline ZnO substrates. We show that the etching rate can be tuned directly by variations of pH-value during the immersion. Structure and composition of surface precipitations and their thermal stability were investigated combining atomic force spectroscopy, X-ray diffraction spectroscopy and thermal desorption spectroscopy. Preparative routes to optimize film formation avoiding surface etching were elucidated as well.

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**Formation of 1D adsorbed water structures on CaO(001)** — XUNHUA ZHAO, ●SERGEY V. LEVCHENKO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Berlin, DE

Understanding the interaction of water with oxide surfaces is of fundamental importance for basic and engineering sciences. Recently, a spontaneous formation of one-dimensional (1D) adsorbed water structures have been observed on CaO(001) [1]. Interestingly, at other alkaline earth metal oxides, in particular MgO(001) and SrO(001), such structures have not been found experimentally. We calculate relative stability of adsorbed water structures on the three oxides using density-functional theory with the hybrid functional HSE06 and *ab initio* many-body dispersion interaction correction [2], combined with the *ab initio* atomistic thermodynamics. Low-energy structures at coverages up to one monolayer are obtained with a first-principles genetic algorithm. Finite-temperature anharmonic vibrational spectra are calculated using *ab initio* molecular dynamics. We find a range of (*T*, *p*) conditions where 1D structures are thermodynamically stable on

CaO(001). The orientation and vibrational spectra of the 1D structures are in agreement with the experiments [1]. The formation of the 1D structures is found to be actuated by a symmetry breaking in the adsorbed water tetramer, as well as by a balance between water-water and water-substrate interactions, determined by the lattice constant of the oxide.—[1] X. Shao, Y. Fujimori, M. Sterrer, H.-J. Freund, and N. Nilius, to be published; [2] A. Tkatchenko, R. A. DiStasio, Jr., R. Car and M. Scheffler, Phys. Rev. Lett. **108**, 236402 (2012).

O 14.10 Mon 17:15 MA 042

**Formation of dendritic structures due to water ice on oxide surfaces under ambient conditions** — ●OĞUZHAN GÜRLÜ<sup>1</sup>, KIVANÇ ESAT<sup>1</sup>, and ÖZGÜR BİRER<sup>2</sup> — <sup>1</sup>Istanbul Technical University, Istanbul, Turkey — <sup>2</sup>Koç University, Istanbul, Turkey

We have studied the chemical and morphological properties of nanoscale chromium oxide particles on glass and silicon oxide surfaces. Furthermore we investigated their interaction with water from the ambient atmosphere. We found out that dendritic structures due to water on these surfaces can form spontaneously. Our systematic studies of dosing such surfaces with humidified air revealed formation of further fractal structures due to water condensation and evaporation. The growth of these structures was observed under an ambient optical microscope in real time. When these samples were transferred to an atomic force microscope (AFM), dendrites due to water ice could still be observed, also under ambient conditions. AFM data showed that these structures could be as high as several hundredths of nanometers, proving them to be three-dimensional. Depending on the density of the oxide particles on glass or silicon oxide surfaces, shapes and sizes of the dendrites were observed to differ. Despite the counter intuitive nature of such formations, an explanation could be brought to their formation by use of Electrostatic Force Microscopy (EFM).

O 14.11 Mon 17:30 MA 042

**The interaction of water molecules with hematite(0001) surface** — ●ROMAN OVCHARENKO and ELENA VOLOSHINA — Humboldt-Universität zu Berlin, Institut für Chemie, Brook-Taylor-Str. 2 12489 Berlin, Germany

The interaction of water with oxide surfaces is ubiquitous, as water is always present either as a reactant or just an "innocent spectator". The wetting process is predominantly govern by several factors, such as ambient conditions, surface termination and valence band structure. The precision *ab initio* calculation of the latter two properties of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> surface is a serious challenge posed to theory due to Fe 3d electrons, unusual hybridisation, huge surface relaxations, big super cells and magnetism. The situation becomes even more complicated since taking into account on-site Coulomb interactions drastically changing the structure of the valence band top, that allows anyone to consider hematite as charge-transfer insulator in contrary to the prediction of pure GGA approach.

In this study we present the detailed *ab initio* theoretical investigation of the single water molecule behaviour on the hematite(0001) surface. The electronic structure has been treated within DFT approach with PBE-GGA exchange-correlation functional. To take into account Fe 3d strong electronic correlation we adopt DFT+U approach formalised by Dudarev and D2 theory proposed by Grimme has been applied to account for dispersion interaction between water molecule and the surface termination.

O 14.12 Mon 17:45 MA 042

**Water adsorption on non-polar ZnO surfaces: from single molecules to multilayers** — ●STEPHANE KENMOE and P. ULRICH BIEDERMANN — Max-Planck-Institut für Eisenforschung GmbH Max-Planck-Straße 1 D-40237 Düsseldorf

The interface between water and ZnO plays an important role in many domains of technological relevance. Following the vital role of adsorbed water on substrate properties and the fascinating properties of interfacial water, there is a great interest in characterizing this interface. We use DFT to study the possible aggregation regimes that can form on the ZnO non-polar low-index (10-10) and (11-20) surfaces. We study the adsorption of water monomers, small water clusters like water dimers, water chains, ladder-like water structures, water thin films and water multilayers. Based on this, trends in binding energy as well as the binding mechanisms are analyzed to understand the driving forces and the nature of the fundamental interactions that stabilize the adsorbed layers.