O 54 Adsorption an Oberflächen VI

Zeit: Mittwoch 10:45–13:00 Raum: TU EB202

O 54.1 Mi 10:45 TU EB202

Dissociation of Oxygen at Al(111): The Role of Spin Selection Rules — •Jörg Behler[1], Bernard Delley[2], Sönke Lorenz[1], Karsten Reuter[1], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin — [2]Paul-Scherrer-Institut, CH-5232 Villigen PSI

The description of the dissociative adsorption of molecular oxygen at the Al(111) surface remains a most basic and puzzling enigma in surface science. The very low sticking probability of thermal oxygen molecules found experimentally is in strong conflict with the results of state-of-the-art first-principles calculations. We show that this is caused by hitherto unaccounted spin selection rules, which give rise to a highly non-adiabatic behavior in the oxygen-aluminium interaction. As a consequence, the molecular trajectory does not follow the barrier-free adiabatic potential energy surface (PES), but maintains the diabatic triplet state up to close distances to the surface. Detailed density-functional calculations within an appropriate spin-constrained formulation clearly show that the latter PES exhibits sizeable energy barriers, yielding a sticking curve in agreement with experiment. Problems caused by the insufficient accuracy of present-day exchange-correlation functionals and the effects of electronic transitions are also discussed.

O 54.2 Mi 11:00 TU EB202

The relevance of sub-nanometer thin oxide films in the CO oxidation on Pd(100) — •Jutta Rogal, Karsten Reuter, and Matthias Scheffler — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin

There is an increasing awareness that oxides may form at the surface of transition metal (TM) catalysts under the oxygen-rich environmental conditions of oxidation catalysis. What is, however, still an open question is, if the metal is fully oxidized or if only nanometer thin surface oxide films are formed and which of these different phases are crucial for the catalytic activity of the material.

On Pd(100) the oxidation of the surface proceeds through several different stages, including a $(\sqrt{5}\times\sqrt{5})R27^{O}$ surface oxide structure. The stability of this surface oxide and other oxidation states of Pd(100) in an O_2 gas phase up to ambient pressures was recently analyzed in a combined experimental and theoretical study [1]. We now use density-functional theory and atomistic thermodynamics to also account for the other reactant in CO oxidation catalysis by considering the surface structure and composition in a *constrained* equilibrium with an O_2 and CO gas phase. Under gas phase conditions typical of technological CO oxidation the surface oxide results then as the most stable structure. However, this may be significantly affected by the on-going reactions, which continuously drive the system away from equilibrium. Such kinetic effects under steady-state conditions are discussed on the basis of preliminary kinetic Monte Carlo simulations.

[1] E. Lundgren *et al.*, Phys. Rev. Lett. **92**, 046101 (2004)

O 54.3 Mi 11:15 TU EB202

NO laserdesorption of excited C_{60} — •Tim Hoger[1], Carsten Marzok[2], and Helmut Zacharias[1] — [1]Uni Münster Wilhelm-Klemm Str. 10 48149 Münster — [2]Uni Tübingen

Motivated by long living excited states (exiton states) of a fullerene surface we investigated the desorption of NO rotationally and vibrationally resolved. In a pump / probe experiment we excited the NO covered C_{60} surface with 355 nm ns pulses and detected desorbed NO by (1+1)REMPI. The spectra yield two desorption channels with different characteristics: a 'fast' desorption channel produces a typical non thermal laser desorption spectrum with highly excited rotational and vibrational states ($T_{rot} \sim 430\,K$, $T_{vib} \sim 610\,K$, $E_{kin}(J) \sim 1500\,m/s$) and a second 'slow' desorption channel with low rotational temperatures ($T_{rot} \sim 110\,K$) as well as an extremily delayed arrival time.

O 54.4 Mi 11:30 TU EB202

Adsorption-Induced Distortion of F_{16}CuPc on Cu(111) and Ag(111): An X-ray standing wave study — •A. Gerlach[1], F. Schreiber[1], S. Sellner[2,3], H. Dosch[2,3], I. A. Vartanyants[4], B. C. Cowie[5], T.-L. Lee[5], and J. Zegenhagen[5] — [1]Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, OX1 3QZ, United Kingdom — [2]Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, 70569 Stuttgart, Germany — [3]ITAP, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany — [4]HASYLAB, DESY, Notkestr. 85, 22607 Hamburg, Germany — [5]ESRF, 6 Rue Jules Horowitz, B.P. 220, 38043 Grenoble Cedex 9, France

The adsorption geometry of perfluorinated copper-phthalocyanine molecules (F_{16}CuPc) on Cu(111) and Ag(111) is studied using X-ray standing waves. A detailed, element-specific analysis taking into account non-dipolar corrections to the photoelectron yield shows that the molecules adsorb in a lying down configuration, but with a significant distortion of the molecule on both surfaces. While on copper (silver) the central carbon rings reside 2.61 Å (3.25 Å) above the substrate, the outer fluorine atoms are located 0.27 Å (0.20 Å) further away from the surface. We propose that the outer carbon atoms in F_{16}CuPc undergo a rehybridization ($sp^2 \rightarrow sp^3$) which results in a non-planar adsorption.

O 54.5 Mi 11:45 TU EB202

Influence of the alkyl-chain length on the electronic structure and interface properties of 1,4-octasubstituted Zinc Phthalocyanine thin films on gold — •Indro Biswas[1], Heiko Peisert[1], Sonja Dick[1], Danilo Dini[2], Michael Hanack[2], and Thomas Chassé[1] — [1]Institut für Physikalische und Theoretische Chemie, Universität Tübingen, Auf der Morgenstelle 8, 72076 Tübingen — [2]Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen

We compare the interface properties of various 1,4,8,11,15,18,22,25-octa-alkyl-substituted zinc phthalocyanines [$(But)_8$PcZn, $(Hep)_8$PcZn, $(Dec)_8$PcZn] with those of unsubstituted zinc phthalocyanine (PcZn) on gold using X-ray photoemission spectroscopy (XPS) and valence band ultraviolet photoemission spectroscopy (UPS). Although the separation between the aromatic cores in the evaporated thin films clearly depends on the alkyl chain length, it is found that the nature of the substituents causes only minor changes of electronic properties, such as optical gap and ionization potential. It is shown that the observed small energetic shifts for film thicknesses larger than the molecule size cannot be understood in terms of a band bending-like mechanism. Influences of a different orientation of the molecules at the interface and in thin films are discussed. We are grateful for helpful discussions and the synthesis of organic materials to M. Cook and I. Chambrier.

O 54.6 Mi 12:00 TU EB202

Self-assembled two-dimensional supramolecular structures: Rubrene on Au(111) — •Marie-Christine Blüm, Elizabeta Ćavar, Marina Pivetta, François Patthey, and Wolf-Dieter Schneider — Institut de Physique des Nanostructures, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

We report on the study of the polycyclic aromatic hydrocarbon rubrene (5,6,11,12-Tetraphenylnaphthacene) deposited on a reconstructed Au(111) surface by means of low-temperature STM and STS under UHV conditions. The topographic images measured at 5K reveal a surprising variety of 2D self-assembled structures with different geometries and sizes ranging from dimers up to large ordered islands. A striking feature of this formation is the coexistence of 5- and 6-fold symmetries, i.e. the bonding of the molecules into pentagons, hexagons, honeycomb patterns and hexagonal close packed islands. Furthermore, the molecular pentagons act as new building blocks and line up into chains with lengths of up to 100 nm. The differential conductance spectra acquired on top of a molecule exhibit characteristic peaks which reflect the occupied and unoccupied molecular orbitals and show the presence of an energy bandgap between the HOMO and the LUMO of rubrene adsorbed on Au(111).

O 54.7 Mi 12:15 TU EB202

STM and STS studies of planar and non-planar Naphthalocyanines (Nc) on Graphite (0001) — •T. G. Gopakumar and M. Hietschold — Chemnitz University of Technology, Institute of Physics, Solid Surfaces Analysis Group, D-09107 Chemnitz, Germany.

Adsorption of base free naphthalocyanine (Nc), planar molecule and tin-naphthalocyanine (SnNc), non-planar molecule were studied using a STM on freshly cleaved highly oriented pyrolytic graphite (HOPG) surface at low temperature (50 K) in UHV conditions. Planar Nc molecules form large areas of defect free ordered superstructure [1] with larger molecular packing density (0.3 molecule/nm2) while the non-planar molecules show different phases of adsorption with comparatively less molecular packing density (0.18 molecule/nm2). Tip-sample distance dependent current voltage spectroscopy has been conducted and its normalized differential conductivities have been characterized. The general current voltage curves show an asymmetrical diode like nature. A distant dependent HOMO-LUMO gap shrinking have been observed in the case of Nc, in which it is shown that the HOMOs of the molecules are pinned and the LOMOs are moving towards the Fermi energy. But there is no subsequent HOMO-LUMO gap shrinking in the case of SnNc but an increased current of almost one order of magnitude has been observed in the current voltage characteristics.

[1]. M. Lackinger, T. Müller, T. G. Gopakumar, F. Müller, M. Hietschold, G. W. Flynn, J. Phys. Chem. B. 2004, 108, 2279-2284.

O 54.8 Mi 12:30 TU EB202

Rasterkraftmikrokopie und Mikroquarzwaage: Vergleichende Untersuchungen zur Adsorptionskinetik von Proteinen — •Martin Görlich[1], Peter Schön[2], Lorenz Walder[3] und Marika Schleberger[1] — [1]Universität Duisburg-Essen, Fachbereich Physik, 45117 Essen — [2]Radboud University Nijmegen, Institute for Molecules and Materials, 6525 ed Nijmegen — [3]Universität Osnabrück, Fachbereich Chemie, 49069 Osnabrück

Das Adsorptionsverhalten des Proteins von F_1-ATPase auf Gold ist *in situ* mit einem Rasterkraftmikroskop (*Atomic Force Microscope, AFM*) und einer Mikroquarzwaage (*Quarz Crystal Microbalance, QCM*) untersucht worden. Die Ergebnisse wurden quantitativ ausgewertet und gegenübergestellt. Dabei zeigten die beiden Techniken unterschiedliche Adsorptionskinetiken. Die Gründe dafür sind in den verschiedenen Messmethoden zu suchen: Im AFM-Experiment sorgen spitzeninduzierte Deformationen für einen scheinbar langsameren Adsorptionsverlauf, während im QCM-Experiment der scheinbar schnellere Verlauf auf Wassereinlagerungen in der Proteinschicht zurückzuführen ist.

O 54.9 Mi 12:45 TU EB202

Adsorption isotherms and capillary waves of molecularly thin liquid films - an x-ray reflectivity study — •Michael Paulus[1], Christian Gutt[2], Michael Sprung[3], Christoph Krywka[1], and Metin Tolan[1] — [1]Experimentelle Physik I, Universität Dortmund, Maria-Goeppert-Mayer Str. 2, 44227 Dortmund — [2]Department of Physics 0350, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0350, USA — [3]c/o 8ID/IMMY-XOR-CAT, APS/ANL, Argonne, IL, 60439, USA

We present an x-ray reflectivity study of molecularly thin films of liquid iso-butane adsorbed on bulk liquid glycerol. The glycerol-isobutan interface serves as a model system to study the influence of the substrate-adsorbate interactions on both adsorption isotherms and capillary wave fluctuations. The low condensation pressure of isobutane (approximately 1.6bar at 288K) allows to adsorb thin liquid isobutane layers on the glycerol surface. The layer thickness is adjustable between monolayer coverages and 2-3 nm by varying the gas pressure at constant temperature. A special sample cell has been designed which guarantees the high degree of pressure and temperature stability needed for these experiments. From the x-ray reflectivity data film thickness and the capillary wave induced surface roughness as a function of pressure have been determined. A strong coupling between the first monolayers of isobutan and the glycerol surface leads nearly to a complete suppression of capillary waves in the monolayer.