

O 17: Adsorption on Metal Surfaces

Time: Monday 15:00–18:15

Location: H6

O 17.1 Mon 15:00 H6

Self-assembly of Ni-TPP on the Cu (100) surface: electronic and geometric structure — ●GIOVANNI ZAMBORLINI¹, VITALIY FEYER¹, ANDREA GOLDONI³, MIRKO PANIGHEL³, GIOVANNI DI SANTO³, MARGHERITA MARSILI^{4,5}, PAOLO UMARI⁴, BERND KOLLMANN⁶, DANIEL LÜFTNER⁶, PETER PUSCHNIG⁶, and CLAUD M. SCHNEIDER^{1,2} — ¹Peter Grünberg Institute (PGI-6), Research Center Jülich, 52425 Jülich, Germany — ²Universität Duisburg-Essen, D-47048 Duisburg, Germany — ³Elettra Sincrotrone Trieste, 34012 Basovizza, Trieste, Italy — ⁴Dipartimento di Fisica e Astronomia, Università di Padova, 35141 Padova, Italy — ⁵S3, Istituto Nanoscienze, CNR, 41125 Modena, Italy — ⁶Institut für Physik, NAWI Graz, Karl-Franzens-Universität Graz, 8010 Graz, Austria

In this work the adsorption of the Ni-TPP on the Cu(100) surface was studied by a multi-technique approach combining STM, LEED and ARPES complemented by DFT. STM measurements show the presence of two rotational domains oriented with an angle of 16 degrees respect to each other, leading to a simulated superstructure which is in good agreement with the measured LEED pattern. Molecular orbital tomography was employed to determine the azimuthal orientation of the molecules as well as the molecule-substrate interaction and the charge transfer phenomena between adsorbed molecules and a metal surface. The valence band spectra of Ni-TPP/Cu(100) system show two features originating from the ionization of low energy molecular orbitals of adsorbed Ni-TPP. The experimental data are compared with DFT calculations.

O 17.2 Mon 15:15 H6

Is Cu₂N/Cu(100) a good insulator? An STM/STS study of a metal-organic monolayer — ●PASCAL R. EWEN^{1,2}, CRISTIAN A. STRASSET², ALEXANDER A. KHAJETOORIANS², and DANIEL WEGNER² — ¹Radboud Universiteit, Nijmegen, The Netherlands — ²Westfälische Wilhelms-Universität, Münster, Germany

The study of molecules by scanning tunneling microscopy (STM) and spectroscopy (STS) also includes probing molecule-substrate interactions, which can change physical properties from hybridization to charge transfer and even to drastic effects such as decomposition. A thin insulating film can significantly decouple the adsorbate leading to a behaviour comparable to the isolated molecule. But it turns out that the decreased interaction with the substrate often causes drawbacks in the sample preparation or scanning conditions due to lower sticking coefficients or higher mobilities even at low temperature. In that respect, Cu₂N layers have recently gained increasing interest.

We investigate Pt(II) complexes that are used as emitters in prototypical OLEDs. Previously, we have shown that Pt-based orbitals are strongly influenced even by a Au(111) surface, which is commonly considered to show weak adsorbate-substrate interactions. Therefore, we have chosen to investigate the decoupling capability of Cu₂N/Cu(100) for these complexes. We found that the molecules self-assemble into a well-ordered monolayer. We determined adsorption geometry by STM and carefully analysed the spatial and energy distribution of molecular orbitals via STS-based spectral mapping to evaluate the impact of the substrate on the molecule.

O 17.3 Mon 15:30 H6

CO adsorption on graphene supported Pt, Rh and Pt-Rh nanoparticles — ●MARCUS CREUTZBURG^{1,2}, HESHMAT NOEI¹, and ANDREAS STIERLE^{1,2} — ¹Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, Hamburg, Germany — ²Fachbereich Physik, Universität Hamburg, Jungiusstraße 9, Hamburg, Germany

Small metal nanoparticles dispersed on porous substrates have gained increasing interest in surface science because of their widespread applications, especially in heterogeneous catalysis. It was previously shown that nanoparticles grown by UHV vapor deposition of material form ordered arrays on graphene substrates using the moiré of graphene/Ir(111) as a template. The size and shape of these nanoparticles can be carefully controlled with diameters smaller than 2 nm on graphene/Ir(111) by the amount of deposited material. In this contribution, we study the adsorption of CO on Pt, Rh and Pt-Rh core-shell nanoparticles on graphene/Ir(111) using vibrational spectroscopy under UHV conditions. The UHV-IRRAS data demonstrate one adsorption site for the two-layered Pt and Rh nanoparticles, which is assigned

to CO on-top edge sites of the nanoparticles, while for the three-layered Pt and Rh nanoparticles the adsorption of CO on-top edge sites is only preferred at low CO coverages. For higher CO coverages a second (additional) adsorption site with higher wavenumbers is observed, which is interpreted as on-top adsorption sites on nanoparticle terrace atoms. Three-layered Pt-Rh core-shell nanoparticles show CO adsorption on-top of Rh edge and corner atoms at low CO coverages and on-top of Pt terrace sites at higher CO coverages.

O 17.4 Mon 15:45 H6

STM study of tower-shaped tripodal molecules on a Au(111) surface — ●TIMO FRAUHAMMER¹, LUKAS GERHARD¹, KEVIN EDELMANN^{1,3}, MAXIMILIAN KRISTEN¹, MARCIN LINDNER¹, MICHAL VALASEK¹, MARCEL MAYOR^{1,2}, and WULF WULFHEKEL^{1,3} — ¹Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT) — ²Department of Chemistry, University of Basel — ³Physikalisches Institut, Karlsruhe Institute of Technology

We examined three different tetraphenylmethane derivatives deposited on a Au(111) surface using scanning tunneling microscopy (STM) at 5 K. The molecules are designed as tripodal tower-shaped molecules with a platform that specifically binds to the Au surface and molecular rods of one to three phenyl rings pointing away from the surface with a nitrile end group to allow contact formation to the STM tip. We deposited the molecules from a solution with Dichloromethane by using a spray technique.

It is shown that up to a height of at least three phenyl-rings the molecules indeed stand upright on their tripodal sulfur-feet with the head group arranged away from the surface. For the three investigated molecules, the apparent height, the shape in constant current images and the conductance at constant height are compared.

O 17.5 Mon 16:00 H6

Line shapes of C₆₀ vibrational modes in inelastic electron tunnelling spectroscopy — ●STEFAN MEIEROTT, NICOLAS NÉEL, and JÖRG KRÖGER — Institut für Physik, Technische Universität Ilmenau, D-98693 Ilmenau, Germany

Tunnelling contacts comprising W tips coated with Pb and terminated by single C₆₀ molecules as well as pristine and C₆₀-covered Pb(111) surfaces were investigated with a low-temperature scanning tunnelling microscope. The junctions exhibited C₆₀ vibrational signatures, which were previously observed [1]. While Pb-coated W tips led to peak-like line shapes of the vibrational modes in inelastic tunnelling spectra [1] C₆₀-terminated tips gave rise to Fano-type profiles. In agreement with previous calculations [2] we assign the Fano-type line shape to the electronic structure of the C₆₀-terminated tip. The lowest unoccupied molecular orbital (LUMO) of C₆₀ at the tip apex covered the range of vibrational energies, which was identified as a prerequisite for observing Fano-type line shapes [2]. To test the proposed scenario, the LUMO energy of C₆₀ attached to the tip was deliberately modified, presumably owing to different adsorption geometries at the tip apex [3]. Upon moving the LUMO energy farther away from the Fermi level and concomitantly avoiding its overlap with vibrational energies, the peak-like structures in the vibrational spectra were recovered. Financial support by the DFG through KR 2912/7-1 is acknowledged.

[1] K. J. Franke et al., *J. Phys. Chem. Lett.* **1**, 500 (2010).[2] A. Baratoff et al., *J. Vac. Sci. Technol. A* **6**, 331 (1988).[3] G. Schull et al., *New J. Phys.* **10**, 065012 (2008).

O 17.6 Mon 16:15 H6

Controlled Intermolecular Coupling in Charging Processes of Molecular Assemblies — ●NEMANJA KOCIĆ¹, DOMINIK BLANK¹, SILVIO DECURTINS², SHI-XIA LIU², and JASCHA REPP¹ — ¹Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany — ²Department of Chemistry and Biochemistry, University of Bern, 3012 Bern, Switzerland

In a recent study, we found that electron-acceptor molecules located at the edges of the self-assembled islands on the Ag(111) surface can be switched in their charge state by means of the electrostatic field inside a scanning tunneling microscope junction [1]. Here, we show that controlled vacancy formation by means of STM-based manipulation techniques allows to convert molecules inside the islands to edge-like molecules and thereby to create different pattern of molecules

that show charge switching. Whereas simple electrostatic effects lead to different switching fields for different arrangements, in addition, very complex charging pattern originate from strong coupling between charge states of the molecules. Thereby, our work demonstrates that very complex functionality can be encoded into only few interacting molecules and might be a first step towards molecule-based cellular automata.

[1] N. Kocić et al., *Nano Lett.* 15, 4406 (2015)

O 17.7 Mon 16:30 H6

Reversible light-induced spin-state switching in Fe(II) spin-crossover films on Au(111) studied with NEXAFS and PES — ●SEBASTIAN ROHLF¹, MATTHIAS KALLÄNE¹, ARNDT QUER¹, HOLGER NAGGERT², FELIX TUCZEK², and KAI ROSSNAGEL¹ — ¹Institut für Experimentelle und Angewandte Physik, Universität Kiel, 24098 Kiel, Germany — ²Institut für Anorganische Chemie, Universität Kiel, 24098 Kiel, Germany

Fe(II) coordination complexes are model systems for organic molecules whose electronic, magnetic, and structural properties can be manipulated by external stimuli. Moreover, the temperature- and irradiation-dependent spin transitions observed in a number of these materials may provide a suitable testbed for the development of future spintronic devices. Light-induced spin-state trapping (LIESST) in thin molecular films of these complexes is well established. Here, we present a combined near edge X-ray absorption fine structure (NEXAFS) and photoelectron spectroscopy (PES) study of the LIESST and, for the first time, of the reverse LIESST of thin films of the spin-crossover complex Fe(H₂bpz)₂(phen) adsorbed on Au(111). The NEXAFS spectra reveal two different stable molecular spin states after green and infrared light irradiation at low temperatures. The PES results confirm these observations and, furthermore, provide information on the efficiencies of the light-induced transition processes.

O 17.8 Mon 16:45 H6

The interaction of deuterium with AgPd/Pd(111) surface alloys — ●THOMAS DIEMANT, JAN MARTIN, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Albert-Einstein-Allee 47, Ulm University, D-89081 Ulm

AgPd/Pd(111) surface alloys, which consist of a reactive and an inert metal, represent an ideal test case for the study of ensemble effects on bimetallic surfaces. In the present contribution, we have studied their deuterium adsorption properties by temperature-programmed desorption (TPD) measurements. The structural properties (surface contents and atom distribution) were determined already earlier by high-resolution scanning tunnelling microscopy (STM) [1], which enables us to correlate the structural properties of these surface alloys to their adsorption behaviour. Most prominently, a steady decrease of the adsorbate coverage with increasing Ag content is observed. The results will be compared to findings on the interaction of CO with these surface alloys [2].

[1] R. Rötter, Diplomarbeit Ulm University (2009).

[2] Y. Ma et al., *Surf. Sci.* 603 (2009) 1046, *Phys. Chem. Chem. Phys.* 13 (2011) 10741.

O 17.9 Mon 17:00 H6

Water - Hydroxyl Overlayers on Rh(111) — ●CHRISTINE McMAHON, ALAN MASEY, ANDREW HODGSON, and GEORGE DARLING — Surface Science Research Centre University of Liverpool Liverpool L69 3BX

At metal surfaces, water ice structures are determined by a competition between optimising the bonding of molecules to the surface and optimising the hydrogen bonding within the layer. On some metals the water overlayer is partially dissociated, this can be induced by preadsorbing oxygen, leading to a mixed OH+H₂O overlayer on metals where dissociation is not spontaneous. We have used Density Functional Theory calculations to examine partially dissociated overlayers produced on Rh(111). Specifically we are looking to address questions that cannot be definitively answered by experiment: what is the optimum ratio of OH to H₂O, and do the resultant structures favour Bjerrum defects (defects where H atoms point to each other rather than participating in hydrogen bonding or pointing into/away from the surface), as found on Cu surfaces.

O 17.10 Mon 17:15 H6

Adsorption of isolated nickelocene on Cu(100) — ●MARISA FARAGGI¹, NICOLAS BACHELIER², MAIDER ORMAZA², BENJAMIN VERLHAC², MARTIN VEROT³, TANGUI LE BAHERS³, MARIE LAURE

BOCQUET¹, and LAURENT LIMOT² — ¹Ecole Normale Supérieure, Département de Chimie, ENS-CNRS-UPMC UMR 8640, 75005 Paris, France — ²IPCMS, Université de Strasbourg, UMR CNRS 7504, 67034 Strasbourg, France — ³Université de Lyon, Université Claude Bernard Lyon 1, CNRS, ENS Lyon, 69007 Lyon, France

In this work we focus on the study of nickelocene in gas phase and deposited on Cu(100). We concentrated on the theoretical description of the system by implementing Density Functional Theory (DFT) using the VASP code. We performed an energetic analysis of the adsorption of nickelocene in three high-symmetric sites by centering the Cp ring in a top, bridge and hollow site of Cu(100). We move within different theoretical approximations (PBE, Grimme, optPBE) to better describe the main characteristics of the system. Our results show that the hollow site appears to be energetically more stable in all approaches, in agreement with the STM experiments. Nickelocene is moderately chemisorbed. The atomic-orbital projected density of states were also studied. The lowest unoccupied molecular orbital (LUMO) of Nc is clearly spin polarized, giving a magnetic character to the molecule. Hence, the entire Nc molecule is magnetic and the magnetization is shared by the two Cp rings and by the dyz, dxz shells of the Ni atom. Upon adsorption the magnetic moment of nickelocene is therefore preserved.

O 17.11 Mon 17:30 H6

Chemo-mechanical coupling from first principles: On the strain dependency of oxygen adsorption on Pd(111) — ●GREGOR FELDBAUER, ANJA MICHL, and STEFAN MÜLLER — Hamburg University of Technology, Institute of Advanced Ceramics, Denickestr. 15, D-21073 Hamburg

Mechanical deformation can affect the adsorption and reaction processes of reactants on surfaces. Thus, by straining catalytically active surfaces their reactivity as well as selectivity can be influenced, which is of high importance in the field of heterogeneous catalysis.

Here, the adsorption of atomic oxygen on Pd(111) is used as a model system. At first, the dependence of the adsorption energetics on various oxygen adsorption sites and coverages is investigated within the framework of density functional theory (DFT). Furthermore, vibrational frequencies, work functions and densities of states are studied. Using the DFT results as input data a cluster-expansion Hamiltonian is constructed to scan exhaustively the configuration space of the examined model system. This allows to identify the most favourable adsorption configurations. Additionally, for various configurations biaxial strain is applied in the surface plane to obtain the response of the adsorption energetics. Particularly, the coupling parameter between the strain and adsorption energies is of interest to allow for a comparison with experiments.

O 17.12 Mon 17:45 H6

Methanol oxidation on nanoporous gold — ●WILKE DONONELLI¹, LYUDMILA MOSKALEVA², and THORSTEN KLÜNER¹ — ¹IfC, CvO Universität Oldenburg, 26111 Oldenburg — ²IAPC, Universität Bremen, 28359 Bremen

Nanoporous metals, such as nanoporous gold (np-Au), have recently attracted considerable interest due to their potential use in catalysis. These Au-based catalysts can be used for fuel cells, the synthesis of esters or the selective oxidation of alcohols, where the selectivity of gold to partial oxidation products is higher than the selectivity of other metal catalysts. For this study, a kinked Au(321) surface first introduced by Moskaleva [1] represents one of the surfaces of the nanoporous gold. It consists of (111) terraces and zigzag-shaped steps, which may be favorable as possible adsorption positions for methanol in partial oxidation reactions. These catalytic surface reactions are analyzed using the exchange-correlation functional PBE and rPBE-D3 implemented in the plane-wave based Vienna ab initio simulation package (VASP) within the supercell approach. The aim is the elucidation of the detailed mechanisms for total and partial oxidation of methanol on this model surface. We will calculate the adsorption geometries for the reaction intermediates and transition states in order to identify the energetically most favorable reaction paths. Beyond that the effect of adsorbed active oxygen species like atomic oxygen, molecular oxygen or hydroxo and hydroperoxo species on the reaction mechanisms will be considered. [1] L.V. Moskaleva, V. Zielasek, T. Klüner, K.M. Neyman, M. Bäumer, *Chem. Phys. Lett.* 525 (2012) 87.

O 17.13 Mon 18:00 H6

A quantum chemical study of adsorption and catalytic activity on nanoporous gold (np-Au) surfaces — ●GABRIELE

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The Nanotechnology is one of the most important future technology fields. The fact, that nanoparticles show an extraordinary relation between size and the properties of the material, allows us to use them in a variety of catalytic applications. The np Au as an example shows a remarkable catalytic activity even though bulk gold is catalytically inert. The reason for this is the high specific surface area and a high density of low coordinated surface atoms in the np Au surface. Various theoretical studies of the Au(111) and Au(321) [1] surfaces could well

represent the catalytic behavior of the np Au ligaments. The Au(310) surface with steps, kinks and sinks in the terraces is an additional surface which has a lot of adsorption sites and thus can also very well describe the np Au surface. We represent the theoretical study of the methanol oxidation on the Au(310) model-surface with the purpose to find the feasible adsorption sites for different adsorbates and the favorable reaction pathways. In this study, we use the plane-wave based Vienna ab initio simulation package (VASP) [2] with the exchange-correlation functional PBE [3]. [1] L.V. Moskaleva, V. Zielasek, T. Klüner, K. M. Neyman, M. Bäumer, Chem. Phys. Lett. 525 (2012) 87. [2] G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251. [3] J. P. Perdew, K. Burke, M. Erzenhof, Phys. Rev. Lett. 77 (1996) 3865.