

O 25: Metal substrates: Adsorption of organic / bio molecules III

Time: Tuesday 10:30–13:00

Location: H36

O 25.1 Tue 10:30 H36

Tuning molecule-mediated spin coupling in bottom-up fabricated vanadium-TCNE nanostructures — ●DANIEL WEGNER^{1,2}, RYAN YAMACHIKA², XIAOWEI ZHANG², YAYU WANG², TUNNA BARUAH³, MARK R. PEDERSON⁴, BART M. BARTLETT², and JEFFREY R. LONG² — ¹Physikalisches Institut & CeNTech, WWU Münster, Germany — ²University of California, Berkeley, and Lawrence Berkeley National Laboratory, Berkeley, CA, USA — ³University of Texas, El Paso, TX, USA — ⁴Naval Research Laboratory, Washington, DC, USA

We have fabricated hybrid organic/inorganic magnetic molecules based on vanadium atoms and tetracyanoethylene (TCNE) ligands in an atom-by-atom fashion using a cryogenic scanning tunneling microscope. By means of local tunneling spectroscopy we observe spin-polarized molecular orbitals as well as a structure-dependent Kondo resonance. For complexes having two V atoms, the Kondo behavior can be switched on and off by a minute structural change that leaves the spin-containing orbital essentially unchanged. This can be explained by a tunable, structure-dependent change in the vanadium spin-spin coupling strength through the TCNE molecule, as confirmed by density functional calculations. The present findings offer a new route for designing molecular spin nanostructures with atomic-scale precision.

O 25.2 Tue 10:45 H36

Positioning Co atoms with organic molecular templates — ●WOLFGANG KRENNER¹, DIRK KÜHNE¹, FLORIAN KLAPPENBERGER¹, SVETLANA KLYATSKAYA², MARIO RUBEN², and JOHANNES V BARTH¹ — ¹Physikdepartment E20, TU München, München, Germany — ²Institute of Nanotechnology, Forschungszentrum Karlsruhe, Karlsruhe, Germany

In this work the adsorption of atomic Cobalt onto organic molecular templates is investigated by means of low-temperature scanning tunneling microscopy under UHV conditions. When evaporated onto a Ag(111) surface held at room temperature, diphenyl oxalic amides can be grown into strings across the surface at submonolayer coverages or as densely packed monolayers. Co is evaporated at low temperatures around 140 K onto submonolayers and monolayers, displaying different behavior depending on the coverage, which will be discussed.

The presence of the molecular layer prevents the formation of Co-clusters and instead leads to an adsorption of atomic Co onto the phenyl rings of the oxalic amides. Annealing the sample leads to a redistribution of the Co atoms on the monolayer. At coverages well below a single monolayer a bending of the molecular strings in the presence of Co is observed, which is no longer the case for coverages just below a monolayer. Through annealing it is found, that diffusion of Co atoms away from the molecular strings takes place. In both cases it is possible to assemble ordered arrays of single Co atoms sitting on top of the phenyl rings of the oxalic amides, therefore forming chains of ferromagnetic atoms.

O 25.3 Tue 11:00 H36

Scanning Tunneling Microscopy investigation of different porphyrins on a Ni-prestructured Cu(111) surface — ●MICHAEL RÖCKERT, FLORIAN BUCHNER, ELISABETH ZILLNER, STEFANIE GLÄSSEL, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen

The assembly of organic molecules on single-crystal surfaces is an approach towards the creation of novel materials with outstanding properties. Porphyrins appear to be ideal candidates to generate functional molecular devices, due to their self-assembly properties and their versatile functionality. In the present work we study the possibility to locally anchor or functionalize porphyrins on a prestructured surface, namely a composite Ni/Cu(111) surface, by scanning tunneling microscopy (STM) in ultra-high vacuum at room temperature. Based on scanning tunneling micrographs and movies the dynamics, assembly and intramolecular conformation of the corresponding porphyrins (2HTPP, CoTPP, OEP) as well as the role of molecule-molecule and molecule-substrate interactions are discussed. The obtained findings indeed indicate the possibility to locally anchor and/or functionalize

(e.g. metalate [1-2]) the porphyrins on a Cu(111) surface prestructured either with atomically flat Ni- or oxygen-islands. This work has been funded by the DFG through Sonderforschungsbereich 583.

[1] F. Buchner et al., ChemPhysChem, 2007. 8(2): p. 241-243 [2] T.E. Shubina et al., JACS, 2007. 129(30): p. 9476-9483.

O 25.4 Tue 11:15 H36

Dynamics of Tetraphenylporphyrins on a Copper (111) surface: A Scanning Tunneling Microscopy Study — ●STEFANIE GLÄSSEL, FLORIAN BUCHNER, ELISABETH ZILLNER, MICHAEL RÖCKERT, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II and Interdisciplinary Center for Molecular Materials (ICMM), Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058

The understanding of the properties of large organic molecules at surfaces is a requirement to utilize their functional properties either in single-molecule devices or in organized supramolecular architectures. Here we concentrate on the investigation of the dynamics and self-assembly of tetraphenylporphyrins (TPP) on Cu(111) using scanning tunneling microscopy (STM) in ultra-high vacuum (UHV). STM images of ordered molecular arrays and individual molecules with submolecular resolution enable to determine the supramolecular and intramolecular conformation of the porphyrins. Interestingly, 2HTPP molecules exhibit a mainly one dimensional diffusion along the main crystallographic axes of Cu(111) at room temperature, whereas CoTPP molecules form ordered arrays. Based on STM movies acquired at varying sample temperatures fundamental parameters of the molecular motion of 2HTPP on Cu(111), like the activation energy for diffusion and rotation could be estimated. These results allow a deeper understanding of the corresponding molecule-molecule and molecule-substrate interactions and thus the assembly of the observed porphyrins.

Funded by the DFG through Sonderforschungsbereich 583.

O 25.5 Tue 11:30 H36

Vibrational spectroscopy of 4-mercaptopyridine on Au(111): A comparison of scanning tunneling spectroscopy and calculations — ●NORBERT MAURER¹, ANNA TSCHETSCHETKIN¹, BERNDT KOSLOWSKI¹, PAUL ZIEMANN¹, INGA RESPONDEK², and DAVID M. BENOIT² — ¹Institut für Festkörperphysik — ²Nachwuchsgruppe Theorie SFB 569, Universität Ulm, Albert-Einstein-Allee 11, D-89081 Ulm

Notion of the adsorption structure and vibrational properties is essential to understand electronic transport across molecules and, therefore, is an essential issue in the field of molecular electronics. Scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and especially inelastic electron tunneling spectroscopy (IETS) is ideal to investigate these properties on a single-molecular basis. We employ these techniques to reveal the properties of 4-mercaptopyridine (4MPy) on Au(111) and compare those to, e.g., DFT calculations. We put emphasis on IETS where we find about 20 excitations in the energy range 0-200 meV. Results are compared to calculations based on the vibrational self-consistent field method [1] and earlier experimental results [2,3]. We conclude that 4MPy adsorbs at elbow sites, in the fcc region, and at step edges preferentially in a bridge configuration thereby ruling out a model proposed earlier which suggests that adsorption of a single 4MPy is accompanied by a Au ad-atom.

[1] I. Respondek and D.M. Benoit, J. Chem. Phys 131, 054109 (2009). [2] Yu, et al., Nano Lett. 8 (7), 1923 (2008). [3] Zhang, et al., J. Raman. Spec. 38, 1106 (2007).

O 25.6 Tue 11:45 H36

The local structure of the methoxy reaction intermediate on Cu(110): a scanned-energy mode photoelectron diffraction study — ●DAGMAR KREIKEMEYER LORENZO¹, WERNER UNTERBERGER¹, DAVID DUNCAN², TSENOLO LEROTHOLI², MATT BRADLEY², JIM ROBINSON², and DAVID PHILIPP WOODRUFF¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — ²University of Warwick, Great Britain

Scanned-energy mode photoelectron diffraction (PhD) is a well-established method to determine quantitatively the local structure of adsorbates at surfaces. We apply this method to study the adsorption on a copper surface, Cu{110}, of the methoxy species, an interme-

diates in the catalytic decomposition of methanol. Previous STM [1] and XPD [2] studies have concluded that methoxy bonds to Cu {110} through the oxygen atom on a three-fold coordinated site. However, our O1s PhD spectra show the strongest modulation at 30° and 40° polar emission angles in the azimuth, consistent only with a short bridge adsorption site. More quantitative analysis, as well as a parallel DFT study, identifies the structure as involving two distinct short-bridge adsorption sites, one on Cu adatoms, with slightly different bond-lengths to the copper atoms below. The results indicate a tilt of the O-C axes of 37° in the azimuth, with the carbon atoms pointing in opposite directions at alternate adsorption site. This tilt is consistent with the XPD results, and creates a zig-zag structure that accounts for the STM images [1]. [1] F.M. Leibsle et al., Surf. Sci. 318 (1994)46 [2] E. Holub-Krappe et al., Surf. Sci. 173 (1986)176

O 25.7 Tue 12:00 H36

Planar chain structure of formic acid on Au(111) surfaces studied by Micro-Channel Plate (MCP)-LEED — ●MIRKO MÜLLER, MICHEL KAZEMPOOR, and GERHARD PIRUG — Institut für Bio- und Nanosysteme (IBN 3) and JARA-FIT, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

Vibrational spectroscopy (HREELS) indicates that formic acid adsorbs in a molecular reversible manner on Au(111) surfaces. (1) The vibrational signature points to the formation of flat lying chains of H-bonded formic acid molecules. This hypothesis could not be proven by structure investigations using conventional LEED systems. The electron beam sensitivity of the adsorbed layer prevents from the observation of clear LEED patterns. On the contrary bright LEED spots could be observed using a micro-channel plate (MCP) LEED system which allows a more gentle examination with reduced electron beam current in the pA regime. Consistent with the weak chemical interaction of physisorbed formic acid molecules the reconstruction of the Au(111) surface is not lifted. In addition an incommensurate rectangular superlattice could be identified. Missing (0,2n+1) spots indicates the presence of mirror glide plane symmetry p2mg consistent with the formation of zig-zag chains containing links of cis formic acid molecules oriented accordingly.

(1) M. Kazemipoor, and G. Pirug, Appl. Phys. A 87, 435-441 (2007)

O 25.8 Tue 12:15 H36

Oxidation of Formic Acid on Pt(111) — ●WANG GAO and TIMO JACOB — Universität Ulm, Albert-Einstein-Allee 47, D-89069 Ulm, Germany

Oxidation of formic acid (HCOOH) on Pt(111) surfaces, which can be considered a benchmark reaction to probe the corresponding electrocatalytic HCOOH conversion in fuel cells, has been studied using density functional theory. The effects of water and adsorption coverage on the process from HCOOH to CO₂ were investigated in detail. For each reaction pathway we evaluated relative energies under different environmental conditions, including activation barriers, reaction energies, and intermediate and transition state structures. Our results indicate that while the direct conversion is energetically unfavorable both HCOO and COOH could be reactive intermediates. Moreover, surrounding or co-adsorbed water turned out to play a key role in the whole process, which drastically influences the stability of reactants and products on Pt(111), as well as the correlated reaction barriers. Meanwhile, the entire catalytic process additionally varies with surface

coverage, making the formic acid oxidation a rather complex reaction. Based on our energetics, future analysis of the reaction kinetics will elucidate preferred reaction mechanisms.

O 25.9 Tue 12:30 H36

Joint experimental and theoretical studies of complex adsorption structures: Adsorption versus Interaction Strength — ●J. HAUBRICH¹, D. LOFFREDA², F. DELBECQ², P. SAUTET², Y. JUGNET³, C. BECKER¹, and K. WANDEL¹ — ¹Inst. f. Phys. und Theo. Chemie, Universitaet Bonn — ²Lab. de Chimie, Ecole Normale Supérieure de Lyon, France — ³Inst. de Rech. sur la Catalyse et Env., Villeurbanne, France

Model catalysis studies in UHV represent a crucial strategy to identify surface species, reaction mechanisms, and separate the roles of the catalysts, promoters and supports in heterogeneous catalysis. Combining powerful experimental tools with theoretical methods, surface processes can be studied nowadays in atomic level detail. Here we present a combined HREELS and DFT study of the adsorption and interaction of multifunctional molecules, crotonaldehyde and prenal, on Pt(111) and two Pt-Sn surface alloys. The identification of adsorption structures is a fundamental step towards understanding of the molecule-surface bonding and the reaction mechanisms in the selective hydrogenation of α, β -unsaturated aldehydes. We identified the stable adsorption structures on the three model surfaces and surprisingly find that the tin-induced changes in the vibrational properties disagree with the electronic modifications of the surfaces and the adsorption energies. Our detailed energetic analysis of the molecule-surface bonding reveals that the interaction energies of complex molecules with the substrate are very different than the adsorption energies and allow us to rationalize the vibrational frequencies.

O 25.10 Tue 12:45 H36

Nitrogen Adsorption on Graphite: Defying Physisorption — ●ALEXANDRE TKATCHENKO and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Faradayweg 4-6, 14195 Berlin, Germany

The adsorption of a nitrogen molecule at the graphite surface can be considered a paradigm of molecular physisorption [1]. The binding of N₂ can be phenomenologically described in terms of a competition between quadrupole-quadrupole and van der Waals dispersion energies. Of particular interest is the relative stability of the so-called "in-plane", "out-of-plane" and "pin-wheel" monolayer structures, in which the nitrogen molecules alternate between parallel and perpendicular configurations on the surface. By combining state-of-the-art electronic structure methods, such as dispersion-corrected density-functional theory and Møller-Plesset second-order perturbation theory along with high-level coupled cluster [CCSD(T)] calculations, we are able to gain quantitative insight into the adsorption mechanism of N₂@graphite and achieve very good agreement with experimental desorption enthalpy. We challenge the commonly held view of a closed-shell adsorbed N₂ molecule, finding a noticeable charge-density polarization for nitrogen in a perpendicular configuration on the surface. We map out the N₂@graphite potential energy surface as a function of sliding and orientation and discuss the influence of quantum zero-point energy for different adsorption sites. [1] D. Marx and H. Wiechert, Adv. Chem. Phys. **95**, 213 (1996).