

## O 10: New Methods and Developments II: Scanning Probe, Spectroscopic, and Diffraction Techniques

Time: Monday 15:00–18:00

Location: H3

O 10.1 Mon 15:00 H3

**Interaction between a metallic STM tip and a single CO molecule adsorbed on a copper surface** — ●NORIO OKABAYASHI<sup>1,2</sup>, ANGELO PERONIO<sup>2</sup>, SONIA MATENCIO<sup>2</sup>, FERDINAND HUBER<sup>2</sup>, THOMAS FREDERIKSEN<sup>3</sup>, MAGNUS PAULSSON<sup>4</sup>, and FRANZ J. GIESSIBL<sup>2</sup> — <sup>1</sup>Kanazawa University, Kanazawa, Japan — <sup>2</sup>University of Regensburg, Regensburg, Germany — <sup>3</sup>Donostia International Physics Center, San Sebastián, Spain — <sup>4</sup>Linnaeus University, Kalmar, Sweden

In order to investigate the interaction between a CO molecule and the metallic tip of a scanning probe microscope, we have combined inelastic electron tunneling spectroscopy (IETS) and non-contact atomic force microscopy (AFM) with a qPlus sensor. We have found that the higher the tip-molecule interaction, the more the vibrational modes of the molecule are perturbed. These findings have been rationalized by a classical model describing the molecule as a double pendulum, where the presence of the tip weakens the tip-surface chemical bond [1]. However, in our previous research, the lower limit of a tip molecule distance for an IETS measurement was restricted owing to the method to measure a tunneling current with an interaction force. We have improved our method to understand what happens at smaller tip molecule distances, confirming the validity of our previous findings for both the Cu(111) and Cu(110) surfaces. In addition, bistable configurations are observed at very small tip-molecule distances for both surfaces. [1] N. Okabayashi, A. Peronio, M. Paulsson, T. Arai, and F. J. Giessibl, PNAS 115, 4571 (2018).

O 10.2 Mon 15:15 H3

**DFT-based forces on a CO tip approaching Fe, Cu, Si adatoms on Cu(111) in an atomic force microscope** — ●SVITLANA POLESYA<sup>1</sup>, SERGIY MANKOVSKY<sup>1</sup>, FERDINAND HUBER<sup>2</sup>, FRANZ GIESSIBL<sup>2</sup>, and HUBERT EBERT<sup>1</sup> — <sup>1</sup>Dept. Chemistry, LMU Munich, D-81377 Munich, Germany — <sup>2</sup>Inst. Expt./Appl. Physics, University of Regensburg, 93053 Regensburg, Germany

We present the results of a DFT-based investigation on the forces experienced by a CO tip approaching different types of atoms deposited on Cu(111) surface: Cu, Fe and Si. A similar behaviour has been found for the forces as function of distance of CO molecule from Cu and Fe adatoms: they show two attractive minima with a repulsive 'barrier' in-between. In contrast to this, in case of a Si adatom the force on a CO tip is always repulsive at distances  $d \leq 400$  pm from the adatom. These findings are discussed using similar arguments as in the discussion of chemical and physical adsorption on a surface. In particular, attractive forces in the vicinity of Fe and Cu adatoms are explained by the formation of bonding states giving a significant energy gain in these cases, while charge redistribution in the vicinity of Si adatom is responsible for a strong Coulomb repulsion at these distances. Similar arguments are used to explain the variation of the force upon a lateral motion of the tip at constant distance from the surface, that was found in a good agreement with experiment. Based on these results we conclude about the crucial role of the quantum-mechanical contribution to the forces between the Fe and Cu adatoms and a CO tip responsible for experimentally observed AFM image.

O 10.3 Mon 15:30 H3

**In-situ characterization of O-terminated copper tips for high-resolution atomic force microscopy** — ●ALEXANDER LIEBIG and FRANZ J. GIESSIBL — University of Regensburg, Regensburg, Germany

The use of chemically inert tips allows to directly probe the repulsive interaction regime and thus to obtain high spatial resolution. Gross *et al.* found in 2009 [1] that CO-terminated metal tips enable intramolecular resolution imaging of organic molecules. Later, it was found that terminating the tip apex with noble gas atoms [2] achieves a similar spatial resolution. Recently, Mönig *et al.* [3] proposed to use oxygen-terminated Cu tips that apparently are also quite inert, but are stiffer in lateral directions than CO tips. So far, to verify tip functionalization with oxygen, the STM and AFM contrast of copper oxide domains has been compared to calculated images for different tip models. Here, we apply the COFI method [4] and force spectroscopy to characterize O-terminated Cu tips *in-situ* on a Cu(110) surface. Our approach is

an efficient way to experimentally determine both the structural composition as well as the chemical species of the tip apex. Knowledge of these properties is of crucial importance, especially if the tips are used for experiments on other sample systems. The experimental data about the tip structure and composition is expected to improve the precision of theoretical studies about the interaction between tip and sample. [1] L. Gross *et al.*, Science **325**, 1110 (2009). [2] F. Mohn *et al.*, Appl. Phys. Lett. **102**, 073109 (2013). [3] H. Mönig *et al.*, ACS Nano **10**, 1201 (2016). [4] J. Welker *et al.*, Science **336**, 6080 (2012).

O 10.4 Mon 15:45 H3

**Atomic-scale inelastic electron tunnelling spectroscopy with superconductive tips** — ●ANGELO PERONIO and FRANZ J. GIESSIBL — Institut für Experimentelle und Angewandte Physik, Universität Regensburg, 93040 Regensburg, Germany

Inelastic electron tunnelling spectroscopy with a scanning tunnelling microscope (STM-IETS) enables the measurement of excitations with atomic spatial resolution, such as vibrational and rotational modes of single molecules, and flip of single spins. The intrinsic lineshape of molecular vibrations carries information on the electron-vibration coupling, the hybridization of the molecule with its environment, and the degree of vibrational damping by electron-hole pair excitation. On the other hand, the measured lineshape is usually dominated by extrinsic effects, such as temperature, modulation, and instrumental radio-frequency broadening. The temperature broadening originates from the finite width of the Fermi edge of the electronic density of states of the tip apex. We circumvent the temperature broadening by using the gap of a superconductive STM tip to probe the vibrational modes of carbon monoxide adsorbed on copper, and deconvolving the density of electronic states of the tip from the resulting spectra.

O 10.5 Mon 16:00 H3

**Single molecule nanotribology: understanding friction and adhesion at a single molecule level.** — ●J.G. VILHENA, REMY PAWLAK, and ERNST MEYER — Department of Physics, University of Basel

Understanding the motion/dynamics of a single molecule over a surface is a problem of a paramount importance in the design of advanced molecular nanostructures/assemblies capable of meeting specific needs. Nevertheless, to date, understanding the interplay between molecule mechanics, surface displacements and dynamics at a atomic level is a highly challenging task since it requires the knowledge of not only the forces needed to manipulate them but also to relate them with particular molecular/atomic motion. Here we bridge this gap by combining MD simulations, scanning probe microscopy and force spectroscopy to investigate the manipulation of two different molecules (ssDNA and poly-pyrene) over a Au(111) surface in UHV at 5K. Our experiments/simulations revealed a contrasting on-surface dynamics of these molecules. The high ssDNA adhesion to Au(111) enabled us to chart the unexplored nano-Newton tensile force regime which allowed to quantify for the first time the stretching stiffness of a single DNA nucleotide. In the other extreme, the low adhesion and superlubric behavior of the poly-pyrene revealed a surprising complex on-surface dynamics of the molecule. Our simulations/experiments reveal a dynamic balancing between the intra-molecular mechanics and surface commensurability which result in a snake like motion of the molecule over the surface.

O 10.6 Mon 16:15 H3

**Sensing in-plane and out-of-plane nanomechanical Surface and Subsurface Properties of Polymers** — ●ANNA LISA HAWLITSCHKEK — TU Darmstadt

Bimodal atomic force microscopy enables the quantitative nanomechanical analysis of heterogeneous polymers. The technique is based on the simultaneous excitation and detection of two different cantilever eigenmodes. Depending on the type of the oscillation modes (flexural or torsional), out-of-plane elastic and dissipative sample properties or the in-plane shear behavior can be analyzed. Here, a trimodal approach was developed where in addition to the first flexural eigenmode, the second flexural eigenmode as well as the first torsional eigenmode were excited. The indentation depth of the tip into the sample surface

could be controlled by the first flexural oscillation amplitude used for the topographical feedback. The frequency shifts of the second flexural and the first torsional eigenmode provided measures for the elastic moduli and the shear forces, respectively, using a frequency modulation setup in constant amplitude mode. Thus, dissipative interactions could be derived from the drive amplitudes of the second flexural and the first torsional eigenmodes. It was demonstrated that differences in the elastic behavior in in- and out-of-plane direction can be examined on heterogeneous polymers (elastomeric polypropylene and polystyrene-block-polybutadiene diblock copolymer) using this trimodal approach with high lateral and depth precision.

O 10.7 Mon 16:30 H3

**Soft x-ray RIXS-Imaging of thin microstructured VO<sub>2</sub>** — ●JAN OLIVER SCHUNCK<sup>1,2</sup>, FLORIAN DÖRING<sup>3</sup>, BENEDIKT RÖSNER<sup>3</sup>, JENS BUCK<sup>1</sup>, SANJOY MAHATHA<sup>1</sup>, MORITZ HOESCH<sup>1</sup>, CHRISTIAN SCHÜSSLER-LANGEHEINE<sup>4</sup>, ADRIAN PETRARU<sup>5</sup>, HERMANN KOHLSTEDT<sup>5</sup>, KAI ROSSNAGEL<sup>1,6</sup>, CHRISTIAN DAVID<sup>3</sup>, and MARTIN BEYE<sup>1,2</sup> — <sup>1</sup>Deutsches Elektronen-Synchrotron DESY, Hamburg — <sup>2</sup>Physics Department, Universität Hamburg — <sup>3</sup>Paul Scherrer Institut, Villigen, Switzerland — <sup>4</sup>Helmholtz-Zentrum Berlin — <sup>5</sup>Nanoelektronik, Technische Fakultät, CAU Kiel — <sup>6</sup>Institut für Experimentelle und Angewandte Physik, CAU Kiel

This contribution presents the results of imaging Resonant Inelastic X-ray Scattering (RIXS) measurements performed on vanadium dioxide samples at the soft x-ray synchrotron beamline P04 at PETRA III in Hamburg, where a new experimental setup was employed [1]. Instead of averaging over  $\mu\text{m}$ -sized x-ray spot foci on the sample, the incident x-rays were focussed to a vertical line, along which the photon energy varied due to the dispersion of the beamline. Furthermore, an off-axis Fresnel zone plate was employed, dispersing the emitted photon energies in horizontal direction onto a CCD camera while imaging the sample in vertical direction. This enables the in-parallel recording of RIXS maps of emitted intensities depending on incident and emitted photon energies. Additionally, scanning the 1D imaged line focus across the sample in perpendicular direction facilitates the recording of 2D images of electronic properties with a spatial resolution of about  $2\ \mu\text{m}$ .

[1] F.Marschall *et al.*, Scientific Reports **7**, 8849 (2017).

O 10.8 Mon 16:45 H3

**Using X-Ray Cavities for the Enhancement of RIXS Signal Levels** — ●ROBIN YOËL ENGEL<sup>1</sup>, LARS BOCKLAGE<sup>1</sup>, SIMO HUOTARI<sup>2</sup>, HASAN YAVAS<sup>3</sup>, MARCO MORETTI SALA<sup>4</sup>, PETER MIEDAMA<sup>1</sup>, GYÖRGY VANKO<sup>5</sup>, RALF RÖHLSBERGER<sup>1</sup>, and MARTIN BEYE<sup>1</sup> — <sup>1</sup>DESY, Hamburg, Germany — <sup>2</sup>Dep. of Phys., University Helsinki, Finland — <sup>3</sup>LCLS, SLAC, Menlo Park, USA — <sup>4</sup>Dep. of Phys., Politecnico di Milano, Italy — <sup>5</sup>Wigner RCP, Budapest, Hungary

While Resonant Inelastic X-ray Scattering (RIXS) is a powerful analytic tool for the analysis of material functionality, achieving adequate signal levels is one of the main challenges for experiments. This difficulty lies in the low probability of the inelastic scattering process (J. Synchrotron Rad. (2018). 25, 580-591) combined with the fact that most spectrometers only cover a small part of the solid angle opposed to the quasi-isotropically emitted fluorescence photons. Here, we show a method to significantly increase signal levels by embedding probe layers, in this case thin iron and iron oxide, into a grown multilayer system, which acts as a resonant cavity at specific incident angles. This brings two advantages: First, the standing waves within the cavity exhibit strongly enhanced electric field amplitudes, thus increasing the total fluorescence yield correspondingly. Further, the cavities resonance condition focuses the fluorescence photons into specific emission angles. This talk presents preliminary results of an experiment performed at the ESRF, demonstrating the expected resonant cavity effects, leading to a five-fold enhancement in signal due to the focusing of fluorescence photons on top of the effect of enhanced excitation.

O 10.9 Mon 17:00 H3

**Three-dimensional atomic image reconstruction by means of high kinetic energy electron holography** — ●CHRISTOPHER KOHLMANN<sup>1,2</sup>, MATTHIAS GIANFELICE<sup>1</sup>, GERT NOLZE<sup>3</sup>, LUKAS KESPER<sup>1,2</sup>, RICHARD HÖNIG<sup>1,2</sup>, and CARSTEN WESTPHAL<sup>1,2</sup> — <sup>1</sup>Experimental Physics I - TU Dortmund University, Otto-Hahn-Str. 4a, D-44221 Dortmund — <sup>2</sup>DELTA - TU Dortmund University, Maria Goeppert-Mayer-Str. 2, D-44221 Dortmund — <sup>3</sup>BAM, Unter den Eichen 87, D-12205 Berlin

The determination of the atom locations in crystalline structures is of

great importance for numerous systems and applications. Without a detailed knowledge of the atomic structure, the creation of synthetic systems with pre-determined properties, or the calculation of electronic properties would not be possible. For structures directly located at the surface, scanning-probe microscopy is an applicable method determining the surface structure.

One way to gain direct information about the three-dimensional structure in the subsurface region is the holographic approach as proposed by D. Gabor in 1948. The small wavelength of the electron wave is perfectly suited for imaging atoms. In the past electron holography was not as successful as imagined.

We present an electron holography method, which is able of three-dimensional atom image reconstruction with chemical sensitivity in the subsurface regime. Furthermore we will present new approaches of data processing for the experimental execution of this method.

O 10.10 Mon 17:15 H3

**Total Reflection High-Energy Positron Diffractometer at NEPOMUC** — ●MATTHIAS DODENHÖFT, ARTUR ELOVSKII, SEBASTIAN VOHBURGER, and CHRISTOPH HUGENSCHMIDT — Heinz Maier-Leibnitz Zentrum (MLZ) and Physik Department E21, Technische Universität München, 85748 Garching, Germany

Total Reflection High-Energy Positron Diffraction (TRHEPD) has been established as an ideal technique to determine the crystalline structure of topmost and immediate subsurface atomic layers. In contrast to Reflection High-Energy Electron Diffraction (RHEED), TRHEPD features an outstanding surface sensitivity, which stems from the repulsive crystal potential for positrons and the phenomenon of total reflection.

We have developed a new positron diffractometer that is coupled to the high-intensity positron source NEPOMUC ( $10^9$  moderated  $e^+$  per second) at the research reactor FRM II. The setup features UHV down to  $10^{-10}$  mbar, sample temperatures up to  $1000^\circ\text{C}$  and a RHEED system for complementary measurements. The positron beam is accelerated and focused by an electrostatic lens system. We simulated the particle trajectories to optimize the beam properties in order to obtain a parallel, slightly converging beam with a small diameter of around  $1\text{mm}$ . First experimental results are expected in spring 2019.

The project has been supported by the BMBF (funding number 05K16WO7).

O 10.11 Mon 17:30 H3

**Graphene-Enhanced Raman Spectroscopy of CoOEP molecules** — ●SIMON RAULS, STEPHAN SLEZIONA, TOBIAS FOLLER, LEONHARD CHRISTEN, PHILLIP ERNST und MARIKA SCHLEBERGER — Universität Duisburg-Essen, AG Schleberger, Germany

Graphene-enhanced Raman spectroscopy (GERS) has been shown to be a powerful tool for ultra-sensitive detection of adsorbed molecules [1]. As a possible mechanism charge transfer is often suggested, which depends on the Fermi-level of the graphene, the HOMO-LUMO levels of the molecules and the excitation laser energy [2, 3]. Therefore, a combination of changing the fermi level in a graphene-based field effect device (GFET) and the excitation laser energy is tempting. To exploit this approach several methods have to be combined: (i) preparation of the GFET by photolithography, (ii) controlled deposition of molecules and characterization by measuring the interplay of the transport characteristics and Raman spectra of (iii) the pristine device and (iv) after deposition of molecules. We will present first results from evaporated Cobalt Octaethylporphyrin (CoOEP). This system allows to investigate if the magnetic properties of the molecule may be manipulated with the help of the GFET through Coulomb or quantum mechanical coupling [4].

[1] X. Ling *et al.*, Small, **6** (2010), pp. 2020\*2025

[2] E.B. Barros *et al.*, Phys. Rev. B, **90** (2014), 035443

[3] Q. Hao *et al.*, Appl. Phys. Lett., **102** (2013), 011102

[4] C. Crevetti *et al.*, Nat. Mater., **15** (2016), pp. 164\*168

O 10.12 Mon 17:45 H3

**Probing atomic site-specific electronic and catalytic properties of bimetallic surfaces by tip-enhanced Raman spectroscopy** — ●JINHUI ZHONG<sup>1,2</sup>, HAI-SHENG SU<sup>1</sup>, XI JIN<sup>1</sup>, XIANGUANG ZHANG<sup>1</sup>, DE-YIN WU<sup>1</sup>, and BIN REN<sup>1</sup> — <sup>1</sup>State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, China — <sup>2</sup>Institute of Physics, Carl von Ossietzky University Oldenburg, 26129 Oldenburg, Germany

Revealing site-specific electronic and catalytic properties of catalysts

is highly desirable for an atomic and molecular level understanding of heterogeneous catalysis. We demonstrated the use of tip-enhanced Raman spectroscopy (TERS) to chemically and spatially resolve site-specific electronic and catalytic properties of bimetallic catalyst surfaces [1,2]. We first investigated an atomically well-defined Pd(sub-monolayer)/Au(111) bimetallic model catalyst surface using phenyl isocyanide as a probe molecule. We obtained local nanospectroscopy at a spatial resolution of 3 nm in real space, which revealed a weakened NC bond and enhanced reactivity of phenyl isocyanide adsorbed at the

Pd step edge compared with that at the Pd terrace site. We further studied a sub-10 nm sized Pt nanoisland deposited on Au(111) surface. Site-specific properties of Au terrace, Pt terrace, step edge, corner and kink sites with varying coordination numbers on the Pt nanoisland/Au(111) bimetallic surface were observed. Our results pushes important steps towards the (in-situ) probing and understanding of local structure correlated catalytic activity and selectivity of real catalysts at truly atomic and molecular level.