

## O 100: Surface Dynamics II

Time: Friday 10:30–13:00

Location: PHY C 213

O 100.1 Fri 10:30 PHY C 213

**A short-pulse facility for time and angle-resolved photoemission experiments at the synchrotron light source DELTA** — ●SVEN DÖRING<sup>1,2</sup>, STEFAN CRAMM<sup>1,2</sup>, MATHIAS GEHLMANN<sup>1,2</sup>, LUKASZ PLUCINSKI<sup>1</sup>, MARKUS HÖNER<sup>2</sup>, HOLGER HUCK<sup>2</sup>, MARYAM HUCK<sup>2</sup>, ROBERT MOLO<sup>2</sup>, PETER UNGELENK<sup>2</sup>, SHAUKAT KHAN<sup>2</sup>, and CLAU M. SCHNEIDER<sup>1</sup> — <sup>1</sup>PGI-6, Forschungszentrum Jülich — <sup>2</sup>Zentrum für Synchrotronstrahlung, DELTA, TU Dortmund

At the synchrotron light source DELTA (TU Dortmund), a short-pulse facility is under commissioning. The U250 undulator of the storage ring is used to generate coherent sub-ps pulses at higher harmonics of a seeding laser. The VUV beamline BL5 operated by a group from PGI-6 (FZ Jülich) guides those pulses into an end-station that is optimized for angle and spin-resolved photoemission spectroscopy experiments. A part of the seeding laser pulse is brought into the end-station via a separate beamline and can be used as a pump beam for pump-probe experiments. With those time and angle-resolved photoemission experiments that are now feasible with this unique setup we will, in the near future, study magnetization dynamics of thin ferromagnetic films on metal surfaces.

The modifications of the photoemission setup that were necessary to conduct time-resolved experiments and the current status of the short-pulse facility will be described.

O 100.2 Fri 10:45 PHY C 213

**Time-resolved two-photon photoemission of NiO(100) ultrathin films** — ●KONRAD GILLMEISTER<sup>1</sup>, MARIO KIEL<sup>1</sup>, and WOLF WIDDRA<sup>1,2</sup> — <sup>1</sup>Martin-Luther-Universität Halle-Wittenberg, Halle, Germany — <sup>2</sup>Max-Planck-Institut für Mikrostrukturphysik, Halle, Germany

Although NiO is one of the most important models for a correlated electron system, not much is known about the electron dynamics across its charge-transfer band gap. Here we focus on the dynamics of unoccupied states for well-ordered NiO ultrathin films. The films with thicknesses up to nine monolayers (ML) have been grown via molecular beam epitaxy on Ag(001).

Based on two-photon photoemission spectroscopy, we find for all films unoccupied Ni 3d states in the range of 1.5 to 2.8 eV above  $E_F$ . The lifetimes of these states are well below 20 fs. This ultrafast dynamics in the presence of the large NiO bandgap points towards the importance of electron correlation for the decay mechanism. At higher energies a series of image potential states is present starting from one NiO monolayer up to nine ML. The states are identified from their parabolic dispersion. With increasing film thickness, the lifetime of the  $n=1$  image state decreases non-monotonically from 30 to 9 fs.

O 100.3 Fri 11:00 PHY C 213

**Electronic structure and exciton formation dynamics at the ZnO(10 $\bar{1}$ 0) surface** — ●JAN-CHRISTOPH DEINERT, DANIEL WEGKAMP, MICHAEL MEYER, CLEMENS RICHTER, JULIA STÄHLER, and MARTIN WOLF — Fritz-Haber-Institut der MPG, Abt. Physikalische Chemie, Faradayweg 4-6, 14195 Berlin

Zinc oxide (ZnO) is a promising electrode material for optoelectronic applications. It is transparent to visible light (band gap of 3.4 eV), natively n-type doped and abundant. Notably, the electronic properties of its interfaces with - possibly functional - organic molecules are not well understood, e.g. only recently the effect of ZnO metallization by hydrogen adsorption and formation of a surface charge accumulation layer (SCA) has been elucidated in detail. We employ a pump-probe technique to gain insight into the dynamics of excited carriers at hydrogen-terminated ZnO surfaces: time-resolved two-photon photoelectron spectroscopy (2PPE). Above band gap excitation at the (10 $\bar{1}$ 0) surface leads to the population of states in the conduction band (CB). These states decay on a few ten fs timescale via LO phonon scattering, where scattering rates show no distinct temperature dependence. At energies below the bulk CB, however, the excited electron dynamics deviate strongly from that ultrafast behaviour. We observe exciton formation within two ps after excitation, 50 meV below the Fermi energy. These surface excitons exhibit lifetimes exceeding several hundred ps. Remarkably, the signature of the surface excitons is quenched by increasing the charge density in the SCA. This is due to enhanced screening as the charge density approaches the Mott limit.

O 100.4 Fri 11:15 PHY C 213

**Ultrafast Water Dynamics at the Water-Surfactant-Air Interface** — ●RUTH A. LIVINGSTONE, MISCHA BONN, and ELLEN H. G. BACKUS — Department of Molecular Spectroscopy, Max Planck Institute for Polymer Research, 55128 Mainz, Germany

Time resolved spectroscopy has revealed exciting new insights into how energy is transferred in interfacial water. The surfactant SDS (sodium dodecyl sulfate) is an important constituent of cleaning products, and has been widely used as a model in surface and colloidal chemistry. At the water-air interface the SDS solution forms a self assembled surfactant monolayer. Our recent study looks at the interaction of water with SDS at this interface on a molecular level. By using time-resolved two-dimensional sum-frequency generation spectroscopy (2DSFG) we found that there are two distinct types of water present at the air-SDS-water interface. In one type, the water molecules are strongly interacting with the SDS layer; while in the other, the water molecules behave more like bulk water. Interestingly, we observed extremely fast energy transfer between these two different types of water.

O 100.5 Fri 11:30 PHY C 213

**2D-Polymer superstructure dynamics on graphene mapped by ultrafast low-energy electron diffraction** — ●MAX GULDE, SIMON SCHWEDA, SASCHA SCHÄFER, and CLAU ROPERS — IV. Physical Institute, University of Göttingen, Germany

Time-resolved diffraction methods currently serve as powerful tools to elucidate the ultrafast structural dynamics of bulk media. Corresponding experimental developments for the investigation of transient processes on surfaces and other 2D systems have proven to be challenging. Here, we present the implementation of ultrafast low-energy electron diffraction (ULEED) in a laser pump / electron probe setup allowing for a temporal resolution of few picoseconds.

The surface sensitivity of ULEED is utilized to investigate the dynamical behavior of an ultrathin bilayer system, composed of a polymethyl methacrylate (PMMA) superstructure on a freestanding, single layer graphene substrate. In particular, ultrafast partial melting of two-dimensional folded chain crystals is observed, paralleled by the appearance of an expanded amorphous phase. The structural evolution of the crystallites and the amorphous phase are mapped, showing characteristic time constants between 50 ps and 300 ps.

O 100.6 Fri 11:45 PHY C 213

**Rotation and translation in surface diffusion of pentacene on pentacene: Extracting different processes from Helium-3 spin echo measurements.** — ●PAUL ROTTER<sup>1</sup>, ANTONIA MORHERR<sup>1</sup>, BARBARA LECHNER<sup>2</sup>, DAVID CHISNALL<sup>2</sup>, ANDREW JARDINE<sup>2</sup>, JOHN ELLIS<sup>2</sup>, WILLIAM ALLISON<sup>2</sup>, BRUNO ECKHARDT<sup>1</sup>, and GREGOR WITTE<sup>1</sup> — <sup>1</sup>Fachbereich Physik, Philipps-Universität Marburg, 35032 Marburg, Germany — <sup>2</sup>Cavendish Laboratory, Cambridge, CB3 0HE, UK

We advance surface diffusion investigation to comparatively large organic adsorbates on organic surfaces. In this study a coplanar monolayer of pentacene chemisorbed on Cu(110) was used as a well characterized organic surface on which isolated pentacene molecules diffuse. Helium-3 spin echo measurements provide a complete statistical description of the adsorbate motion at adequate length scales (nm) and time scales (ps). The potential energy landscape is explored via molecular mechanics and is used for molecular dynamics simulations to compare to experimental results for different azimuthal surface directions. An analytical model is derived, which links our observations to known diffusion characteristics and explains key features of the measurements. It turns out that a diffusing molecule lies flatly on the surface but rotates its long axis between two preferred orientations. Thereby the anisotropy of a pentacene molecule considerably impacts its movement across the surface.

O 100.7 Fri 12:00 PHY C 213

**Dynamics of O<sub>2</sub> on Pd(100) – Unfreezing the surface** — ●VANESSA JANE BUKAS<sup>1</sup>, ANGELA DEN DUNNEN<sup>2</sup>, JÖRG MEYER<sup>1</sup>, LUDO JUURLINK<sup>2</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Technische Universität München, Germany — <sup>2</sup>Universiteit Leiden, The Netherlands

Despite its progress, state-of-the-art quantitative modeling in the field of gas-surface dynamics still faces considerable challenges when it comes to faithfully reproducing experimental data. We find such a dis-

crepancy upon comparing measured sticking curves for O<sub>2</sub> on Pd(100) with our first-principles results. Within the latter approach, we perform molecular dynamics simulations on a neural network interpolated potential derived from density-functional theory and accounting for all six molecular degrees of freedom [1]. Suspecting as source for the discrepancy the prevalent frozen surface approximation (FSA) underlying this approach, we extend our model to additionally include surface mobility in the form of a surface oscillator (SO), and a generalized langevin oscillator (GLO). While following the same dissociation mechanism, even a simple SO model significantly enhances the system's reactivity and already yields remarkable agreement to experiment. Allowing for energy dissipation to the bulk within the GLO approach further reproduces molecular chemisorption at low surface temperatures as also suggested by electron energy loss spectroscopy [2]. Overall, our results thus underscore the importance of overcoming the FSA for adsorbates heavier than the prototypical H<sub>2</sub>.

[1] V. J. Bukas *et al.*, *Z. Phys. Chem.*, **227**, 1523 (2013).

[2] C. Nyberg *et al.*, *Solid State Commun.* **44**, 251 (1982).

O 100.8 Fri 12:15 PHY C 213

**Vibrational properties of O<sub>2</sub> on Ag(100): multiple adsorption sites vs. Fermi resonances?** — DANIEL STROBUSCH, JÖRG MEYER, and CHRISTOPH SCHEURER — TU München, Garching, Germany

Adsorption of molecular oxygen on the Ag(100) surface is commonly believed to occur competitively on *both* hollow and bridge sites. A double peak for the oxygen stretch mode observed in high-resolution energy electron loss spectroscopy (HREELS) in combination with semi-empirical cluster calculations [1,2] have been invoked as evidence. However, recent density functional theory (DFT) calculations question this picture [3]. In this work, we propose that side-on adsorption of the oxygen molecule on the fourfold hollow site *alone* can reconcile the DFT results with the experimentally measured vibrational properties. We calculate the latter with a full quantum dynamical treatment at the vibration configuration interaction (VCI) level of theory [4] based on a six-dimensional DFT potential energy. This yields excellent agreement with the observed overtone and combination bands [2]. Guided and supported by electronic structure calculations, we propose a model based on the occurrence of a Fermi resonance to explain the HREELS double peak and its coverage dependence. We will discuss implications for other surfaces and larger adsorbates.

[1] L. Vattuone *et al.*, *Surf. Sci.* **377**, 671 (1997).

[2] F. Buatier de Mongeot *et al.*, *J. Chem. Phys.* **106**, 9297 (1997).

[3] V. J. Bukas *et al.*, *Z. Phys. Chem.*, **227**, 1523 (2013).

[4] D. Strobusch, M. Nest and C. Scheurer, *J. Comp. Chem.* **34**, 1210 (2013).

O 100.9 Fri 12:30 PHY C 213

**Vibrational properties of alkali nitrate solutions: from clus-**

**ters to the water/vapor interface** — GANG HUANG<sup>1</sup>, MARIE-PIERRE GAIGÉOT<sup>2</sup>, and MARIALORE Sulpizi<sup>1</sup> — <sup>1</sup>Institute for physics, Johannes Gutenberg University, Staudingerweg 7,55099, Mainz, Germany — <sup>2</sup>LAMBE UMR8587, University of Evry Val d'Essonne, Blvd F. Mitterrand, Bat Maupertuis, 91025 EVRY, France

The structure of ions at the vapor/aqueous interface, as well as their influence on the water's hydrogen bond network is of special interest to the atmospheric chemistry community. We use Density Functional Theory-based molecular dynamics to investigate the structure and dynamics of solvated alkali nitrate in water clusters and at the vapor-aqueous interface.

Vibrational density of states (VDOS) are calculated to extract the vibrational signatures for the ions and the surrounding water molecules. We find that in the clusters alkali-nitrate induces a redshift of hydrogen-bonded O-H stretch peaks while in the full water/vapor interface there is an overall blueshift of the hydrogen bonded OH-stretching band. Results are rationalized in term of contact vs water separated ion pairs and confronted with recent surface specific vibrational spectroscopy experiments [1].

[1] A. M. Jubb, W. Hua, and H. Allen, *Ann. Rev. Phys. Chem.* **63**, 107 (2012)

O 100.10 Fri 12:45 PHY C 213

**Rotational Excitation Spectroscopy with the Scanning Tunneling Microscope** — FABIAN DONAT NATTERER, FRANÇOIS PATTHEY, and HARALD BRUNE — Institute of Condensed Matter Physics, École Polytechnique Fédérale de Lausanne (EPFL), Switzerland

The great potential of inelastic electron tunneling spectroscopy with the scanning tunneling microscope (STM) is based on its unmatched spatial resolution that allows for a study of the magnetic, electronic and vibrational properties of individual atoms and molecules. Complementary information about surface processes could be harvested from rotational excitations of molecules, but hitherto remained elusive. Here we show rotational excitation spectroscopy (RES) with the STM for hydrogen, its isotopes, and mixtures thereof, physisorbed on graphene and on hexagonal boron nitride. In consequence of strict symmetry requirements for molecules with identical nuclei (Pauli principle), a certain alignment of nuclear spins demands a specific set of rotational levels  $J$ . For this reason, the molecular nuclear spin states can be derived from the measured rotational levels. We observed excitation energies at 44 and 21 meV, corresponding to rotational transitions  $J = 0 \rightarrow 2$  for hydrogen and deuterium. Notably, these values identify the nuclear spin isomers para-H<sub>2</sub> and ortho-D<sub>2</sub>. For H<sub>2</sub>:HD:D<sub>2</sub> mixtures, we observe RES transitions of all three isotopes, irrespective of where the spectra were recorded; a sign of a collective excitation. Our results mark the potential of STM-RES in the study of nuclear spin states of homonuclear molecules with unprecedented spatial resolution.