

## O 78: Surface Dynamics I

Time: Thursday 16:00–19:15

Location: H42

O 78.1 Thu 16:00 H42

**"Pick-up" mechanism in the scattering of hyperthermal N atoms off N-covered Ag(111)** — ●MARÍA BLANCO-REY<sup>1</sup>, ESTÍBALIZ DÍAZ<sup>1</sup>, GISELA BOCAN<sup>2</sup>, LUDOVIC MARTIN-GONDRE<sup>1,3,4</sup>, RICARDO DÍEZ-MUIÑO<sup>1,3</sup>, MAITE ALDUCIN<sup>1,3</sup>, and J. IÑAKI JUARISTI<sup>1,3,5</sup> — <sup>1</sup>Donostia International Physics Center, 20018 Donostia-San Sebastián, Spain — <sup>2</sup>CONICET and CNEA, 8400 S.C. de Bariloche, Argentina — <sup>3</sup>Centro de Física de Materiales, Centro Mixto CSIC-UPV/EHU, 20018 Donostia — <sup>4</sup>Institut des Sciences Moléculaires, CNRS UMR 5255 / Université Bordeaux I, 33405 Talence, France — <sup>5</sup>Dept. de Física de Materiales, Facultad de Químicas UPV/EHU, Ap. 1072, 20018 Donostia

An ab-initio 3D potential energy surface (PES) and classic molecular dynamics (MD) are used to study the reflection and adsorption dynamics of N atoms on N-covered Ag(111). We find that the surface N species modify the PES dramatically, adding corrugation and an attractive well above the adsorbed N, but MD shows that the scattered N angular distributions change little upon N adsorption, in agreement with molecular beams experiments. However, this level of theory fails to reproduce the experimental final-to-initial average energy ratios,  $\langle E_f \rangle / \langle E_i \rangle$ , at grazing angles. From a close examination of N sticking, we infer that gas N is likely to "pick-up" adsorbed N species to form N<sub>2</sub>. This mechanism is active mainly at low energies. With this in mind, the experimental energy ratios are explained by the surface being partially cleaned as the experiment is being conducted. Simulations with a 6D PES support the "pick-up" process efficiency.

O 78.2 Thu 16:15 H42

**Adsorption & dissociation of O<sub>2</sub> on Ag(100) – How much do we really know?** — ●VANESSA BUKAS, JÖRG MEYER, and KARSTEN REUTER — Technische Universität München, Germany

Despite the considerable attention it has received over the past decades, the adsorption of oxygen on silver surfaces remains elusive of an exact *microscopic* description [1,2]. Connecting and elucidating past results, the present theoretical work revisits the O<sub>2</sub>-Ag(100) interaction from a density-functional theory (DFT) perspective – starting from the interpolated potential energy surface (PES) constructed by Alducin *et al.* within a recent dynamical study [2]. An extensive global search on this PES allows us to obtain all stable molecular adsorption configurations, corresponding vibrational modes as well as minimum energy paths leading from the former towards dissociation. While barriers of more than 1.2 eV do rationalize the low dissociative sticking probability [2], a conclusive assignment for the two species of adsorbed O<sub>2</sub> reported by Vattuone *et al.* [3] cannot be reached. Re-interpolation of the existing DFT data with a different technique [1] fails to account for potential shortcomings of the PES. Aiming to go beyond the limits of the previously employed pseudo potentials [2] in future dynamical studies, we will finally present first results of highly-accurate all-electron DFT calculations using the FHI-aims code [4].

[1] I. Goikoetxea *et al.*, *New J. Phys.* **14**, 013050 (2012).[2] M. Alducin *et al.*, *J. Chem. Phys.* **129**, 224702 (2008).[3] L. Vattuone *et al.*, *Surf. Sci.* **377**, 671 (1997).[4] V. Blum *et al.*, *Comp. Phys. Comm.* **180**, 2175 (2009).

O 78.3 Thu 16:30 H42

**Non-adiabatic vibrational damping of O<sub>2</sub> on Ag(100): implications for light-enhanced heterogeneous catalysis?** — ●SIMON P. RITTMAYER, JÖRG MEYER, and KARSTEN REUTER — Technische Universität München, Germany

The dissociation of oxygen molecules is the rate limiting step in various surface catalyzed oxidation reactions like e.g. the industrially important epoxidation of ethylene. To this end, Linic and coworkers reported a remarkable improvement of the energy efficiency of cubic silver nano-catalysts upon irradiation with visible light, and attributed this to a selective enhancement of the O<sub>2</sub> dissociation step [1]. In their explanation, the non-adiabatic damping of the O-O stretch vibration of adsorbed O<sub>2</sub> plays a crucial role. As going beyond the Born-Oppenheimer approximation for the description of metal-adsorbate interactions is still an emerging field of first-principles based modeling, we will subject the latter to a perturbative treatment rooted in time-dependent density-functional theory, extending an ansatz originally developed to obtain electron-hole pair excitation spectra during ad-

sorption processes (see e.g. [2] and references therein). Within this new approach, we will present estimates for the vibrational lifetime of O<sub>2</sub> adsorbed at various stable sites of the Ag(100) surface and critically discuss the implications for the model proposed by Linic and coworkers.

[1] P. Christopher, H. Xin, and S. Linic, *Nature Chem.* **3**, 467 (2011).[2] J. Meyer and K. Reuter, *New J. Phys.* **13**, 085010 (2011).

O 78.4 Thu 16:45 H42

**Surrogate Hamiltonian study of laser induced desorption of CO/NiO(100) and CO/TiO<sub>2</sub>(110)** — ERIK ASPLUND and ●THORSTEN KLÜNER — Institut für Reine und Angewandte Chemie, Carl von Ossietzky Universität Oldenburg, Germany

In this study, microscopic models for electronic relaxation in femtosecond laser induced desorption experiments are presented. The surfaces in desorption experiments constitute environments for the molecules studied. Due to interactions between an adsorbed molecule and the surface, energy and phase exchange emerge. The photodesorption process consists of three steps: first the adsorbed molecule is excited by an external laser field, thereafter the relaxation process transfers energy to the surface and finally desorption. A theoretical investigation of laser induced desorption must hence treat all involved process, i.e. excitation, excited state dynamics and relaxation, on equal footing. This can be realized within the Surrogate Hamiltonian approach [1]. Furthermore, the Surrogate Hamiltonian method enables a microscopic description of excitation and relaxation process for open quantum systems. The Surrogate Hamiltonian approach is applied to electronic relaxation of CO adsorbed on NiO(100) and TiO<sub>2</sub>(110). Ab initio electronic potential energy surfaces are combined with microscopic descriptions of the interactions between the adsorbed molecule with the surfaces in order to gain insight in the desorption mechanism. Furthermore, life times, desorption probabilities, and velocity distributions for the desorbing molecules are presented.

[1] R. Baer, and R. Kosloff, *J. Chem. Phys.* **106**, 8862 (1997).

O 78.5 Thu 17:00 H42

**The effect of vibrational amplitude on electronic energy dissipation via electron-hole pair-vibrational coupling** — ●MICHAEL GROTEMEYER and ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, Universität Kiel, Germany

Time-dependent density functional calculations for vibrational highly excited HCl molecules in front of an Al(111)-surface have revealed a large non adiabatic energy dissipation. At the first glance this may appear to be in contrast to observations from scattering experiments for HCl/Au(111), which yield only a small energy dissipation into electron-hole pairs in case of low initial vibrational excitation of incoming molecule [1]. To explain this, we have studied the non adiabatic energy transfer by *ab initio* molecular dynamics simulations as a function of initial vibrational excitation energy, thereby filling the gap between experiment and previous calculations. We find a strong increase of dissipation with vibrational energy, which increases faster than linear and clearly deviates from the prediction by the linear friction ansatz. Results are further elucidated by means of a 1D tight binding model.

[1] I. Rahinov *et al.*, *J. Chem. Phys.* **129**, 214708 (2008).

O 78.6 Thu 17:15 H42

**Calculation impossible – how far can we push electronic friction theory?** — FRANCESCO NATTINO<sup>1</sup>, ●JÖRG MEYER<sup>2</sup>, GEERTJAN KROES<sup>1</sup>, and KARSTEN REUTER<sup>2</sup> — <sup>1</sup>Leiden University, Netherlands — <sup>2</sup>Technische Universität München, Germany

One of the prevailing challenges for modeling the motion of molecules on metal surfaces is to go beyond the Born-Oppenheimer approximation in order to account for the potential influence of the continuum of electron-hole pair excitations [1]. Amongst other approaches rooted in time-dependent density functional theory [2], electronic friction theory has the compelling advantage of being a computationally convenient enhancement of classical dynamics for the nuclei – if friction coefficients can be easily and accurately calculated. Along those lines, results obtained within the local density friction approximation (LDFA) applied independently for each atom of a diatomic have fueled a controversial discussion only recently [3]. In an attempt to disentangle

both the LDFA and independent atom approximation for the friction coefficients, we will illustrate a new idea of how to obtain the full-dimensional molecular friction tensor, which is easy to combine with the mapping of high-dimensional potential energy surfaces. First results will be presented using H<sub>2</sub> on Cu(111) as a showcase.

[1] G.-J. Kroes, *Science* **321**, 794 (2008).

[2] J. Meyer and K. Reuter, *New J. Phys.* **13**, 085010 (2011).

[3] J. I. Juaristi *et al.*, *Phys. Rev. Lett.* **100**, 116102 (2008), A. C. Luntz *et al.*, *ibid.* **102**, 109601 (2009), J. I. Juaristi *et al.*, *ibid.* **102**, 109602 (2009).

O 78.7 Thu 17:30 H42

**Helium-3 spin echo measurements and simulation of pentacene on pentacene surface diffusion** — ●PAUL ROTTER<sup>1</sup>, ANTONIA MORHERR<sup>2</sup>, BARBARA LECHNER<sup>3</sup>, DAVID CHISNALL<sup>3</sup>, ANDREW JARDINE<sup>3</sup>, JOHN ELLIS<sup>3</sup>, WILLIAM ALLISON<sup>3</sup>, BRUNO ECKHARDT<sup>1</sup>, and GREGOR WITTE<sup>2</sup> — <sup>1</sup>Komplexe Systeme, Philipps-Universität Marburg, 35032 Marburg, Germany — <sup>2</sup>Molekulare Festkörperphysik, Philipps-Universität Marburg, 35032 Marburg, Germany — <sup>3</sup>Cavendish Laboratory, Cambridge, CB3 0HE, UK

With the Helium-3 spin echo technique (3HeSE) surface diffusion processes can be directly observed at their characteristic length scales (nm) and time scales (ps). While previous experiments focused on small adsorbates and metal surfaces, we advance to comparatively large organic diffusing adsorbates and 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. 3HeSE measurements which contain a complete statistical description of the adsorbate motion were carried out for different azimuthal directions of the surface. To extract the different processes that contribute to the diffusion, we use molecular dynamics simulations to compare to and reproduce key features of the experimental results. The potential energy surfaces needed for those simulations are constructed via molecular mechanics.

O 78.8 Thu 17:45 H42

**Spatial dependence of vibronic excitations** — ●NIKO PAVLÍČEK<sup>1</sup>, INGMAR SWART<sup>2</sup>, JUDITH NIEDENFÜHR<sup>3</sup>, GERHARD MEYER<sup>4</sup>, and JASCHA REPP<sup>1</sup> — <sup>1</sup>Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg, Germany — <sup>2</sup>Debye Institute for Nanomaterials Science, Utrecht University, Utrecht, the Netherlands — <sup>3</sup>Physikalisches Institut, Westfälische Wilhelms-Universität, Münster, Germany — <sup>4</sup>IBM Research-Zurich, 8803 Rüschlikon, Switzerland

In organic and molecular electronics the electrons are much more spatially confined as compared to inorganic semiconductors, leading to a much stronger electron-vibron ( $e$ - $\nu$ ) coupling.  $e$ - $\nu$  coupling therefore gives rise to substantial dissipation in such systems. When an electron tunnels into a given molecule (electron attachment), the nuclei will relax giving rise to the so-called reorganization energy, a process that is usually treated in the Franck-Condon picture.

Here, we show that even for an effective single-level system, the spatial position of the electron injection as well as the wave function strongly affect the  $e$ - $\nu$  coupling strength. These findings can be rationalized by symmetry arguments, thereby shedding new light onto  $e$ - $\nu$  coupling in organic and molecular electronics.

To this end, we performed low temperature scanning tunneling spectroscopy experiments on individual pentacene molecules adsorbed on ultrathin insulating films.

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**Deposition of model chains on surfaces: anomalous relation between flux and stability** — ●PRITAM KUMAR JANA<sup>1</sup> and ANDREAS HEUER<sup>2</sup> — <sup>1</sup>Westfälische Wilhelms-Universität Münster, Institut für Physikalische Chemie, Corrensstr. 28/30, 48149 Münster, Germany — <sup>2</sup>Westfälische Wilhelms-Universität Münster, Institut für Physikalische Chemie, Corrensstr. 28/30, 48149 Münster, Germany

We have investigated model chains which are deposited on the surface with a fixed flux via Monte Carlo simulations. They are supposed to mimic stiff lipophilic chains with a head group and tail groups, reflecting an alkyl chain. After some subsequent fixed simulation time we determine the final energy as a function of flux and temperature. Surprisingly we observe that in some range of temperature and flux the final energy increases with decreasing flux. The physical origin of this counterintuitive observation is elucidated. In contrast, when we are performing equivalent cooling experiments no such anomaly is observed. Furthermore, it is discussed whether flux experiments produce

configurations with lower energies as compared to cooling experiments. These results are related to recent experiments by the Ediger group[1] where very stable configurations of glass-forming systems have been generated via flux experiments.

Reference:

1. K. L. Kearns, S. F. Swallen, M. D. Ediger, T. Wu, Y. Sun, and L. Yu, *J. Phys. Chem. B* **112**, 4934 (2008).

O 78.10 Thu 18:15 H42

**Laser triggered desorption of noble gases from tungsten tips studied by laser-assisted field ion microscopy (FIM)** — ●ARMIN FEIST, SASCHA SCHÄFER, CARSTEN NOWAK, and CLAUDIUS ROPERS — Materials Physics Institute and Courant Research Centre, University of Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen

Field ion microscopy (FIM) is the oldest experimental technique to characterize surface structures of sharp tips on an atomic level. In the related technique of laser-assisted atom probe tomography (APT), ultrashort laser pulses are used for layer-by-layer surface atom removal and the reconstruction of three-dimensional structures. While being a powerful method, the actual dynamics of surface processes cannot be revealed in this approach, and the full capabilities of ultrafast spectroscopy are usually not exploited. Combining FIM with ultrafast pump-probe techniques carries the potential to study surface dynamics with atomic precision, provided that image gas desorption can be induced in a controlled way within ultrafast time intervals. In order to explore such concepts, using tunable femtosecond laser pulses, we study the photo-induced desorption of noble gas atoms from sharp tungsten tips by time-of-flight spectroscopy. The ionization rate is characterized as a function of static electric field, temperature, incident wavelength and laser fluence for various gases (He, Ne and Ar), yielding insights into the respective microscopic desorption mechanisms. We find highly stable and repeatable desorption rates under quasi-steady state conditions. Two-pulse correlation measurements allow for a time-resolved analysis and the disentanglement of thermal from nonthermal effects.

O 78.11 Thu 18:30 H42

**Turning on and off the rotational oscillation of a single porphine molecule by molecular charge state** — ●SHICHAO YAN<sup>1,2</sup>, ZIJING DING<sup>1</sup>, NAN XIE<sup>1</sup>, HUIQI GONG<sup>1</sup>, YANG GUO<sup>1</sup>, XINYAN SHAN<sup>1</sup>, SHENG MENG<sup>1</sup>, and XINGHUA LU<sup>1</sup> — <sup>1</sup>Beijing National Laboratory for Condensed-Matter Physics and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China — <sup>2</sup>Max Planck Research Group-Dynamics of Nanoelectronic Systems, Center for Free-Electron Laser Science, Hamburg

The rotation dynamics of single magnesium porphine (MgP) molecules on ultrathin NaCl bilayer is investigated with low temperature scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. It is observed that the rotational oscillation between two stable orientations can be turned on and off by the molecular charge state, which can be manipulated with the tunneling electrons. The features of the charge states and the mechanism of molecular rotational on/off state control are revealed at the atomic scale. The dependence of molecular orientation switching rate on the tunneling electron energy and the current density illustrates the underlying resonant tunneling excitation and single electron process. The drive and control of molecular motion with tunneling electrons demonstrated in this study suggests a novel approach towards electronically controlled molecular rotors and motors.

O 78.12 Thu 18:45 H42

**Surface Dynamics of Sb(111) Measured with Helium Atom Scattering** — ●MICHAEL MAYRHOFER-REINHARTSHUBER, ANTON TAMTÖGL, PATRICK KRAUS, MARKUS POLANZ, and WOLFGANG E. ERNST — Institute of Experimental Physics, Graz University of Technology, Graz, Austria

Especially due to its appearance in a group of compounds belonging to the lately discovered class of topological insulators, the semimetal antimony (Sb) is an interesting candidate for investigations of its surface properties. Recently the surface phonon dispersion curve of Sb(111) was calculated using density functional perturbation theory [1], but there has been a lack of experimental data.

First Helium Atom Scattering measurements of the Sb(111) surface were performed by our group, showing sharp diffraction peaks in good agreement with the already known surface structure. The analysis of resonance features in our spectra revealed three bound states. The best fit helium-surface interaction potential shows a pure van der Waals

character. By using time-of-flight measurements the surface phonon dispersion was obtained. The acoustic modes are in good agreement with ab-initio calculations. In analogy to measurements on Bi(111) [2, 3], vibrations of the electron corrugation originating in displacements of atoms in the second bilayer were detectable. These subsurface modes can only be observed by HAS because of the electron phonon coupling.

[1] D. Campi et al., Phys. Rev. B. 86 (2012) 075446

[2] M. Mayrhofer-Reinhartshuber et al., JPCM 24 (2012) 104008

[3] T. Tamtögl et al., Phys. Rev. B., submitted 2012

O 78.13 Thu 19:00 H42

**Switching dynamics in laser-driven phase change materials probed by time-resolved X-ray diffraction** — •FLORIAN QUIRIN<sup>1</sup>, AZIZE KOC<sup>1</sup>, MATTHIEU NICOUL<sup>1</sup>, PETER ZALDEN<sup>2</sup>, JAN SIEGEL<sup>3</sup>, MARIANO TRIGO<sup>4</sup>, PERERIK ANDREASSON<sup>5</sup>, HENRIK ENQUIST<sup>5</sup>, MICHAEL SHU<sup>4</sup>, TOMMASO PARDINI<sup>6</sup>, MATTHIEU CHOLLET<sup>7</sup>, DILING ZHU<sup>7</sup>, HENRIK LEMKE<sup>7</sup>, AARON LINDENBERG<sup>4</sup>, DAVID REIS<sup>4</sup>, JÖRGEN LARSSON<sup>5</sup>, STEFAN HAU-RIEGE<sup>6</sup>, MATTHIAS

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Phase change materials (PCMs) exhibit rapid and reversible phase transitions between an amorphous and a crystalline state, which can be triggered by short light pulses. Since the structural changes are associated with large differences in the optical properties of the two phases, PCMs are widely used in rewritable optical data storage technology (e.g. RW-DVDs). We have used time-resolved X-ray scattering at the Linear Coherent Light Source (LCLS) to directly probe the structural dynamics in PCMs (GeSb, GST, AIST) after fs laser irradiation over an extended time range from fs to  $\mu$ s, thus obtaining complete information on the phase transition dynamics. All transitions (amorphous-to-crystalline and vice versa) seem to involve melting of the material. Depending on the excitation strength melting can occur on a sub-ps time-scale as a non-thermal process. However, it takes ns up to  $\mu$ s for the material to resolidify and to reach the final state.