

O 14: Surface Chemical Dynamics

Time: Monday 15:00–18:00

Location: S053

O 14.1 Mon 15:00 S053

The Importance of Meta-Stable Structures and High Spin States for Oxygen Activation on Small Gas-Phase Silver Clusters from First Principles — ●WEIQI WANG, LUCA M. GHIRINGHELLI, and MATTHIAS SCHEFFLER — *Fritz-Haber-Institut der MPG, Berlin.*

At finite temperature, the silver-cluster catalysts could have transient meta-stable structures with spin states higher than those of zero kelvin stable structures (singlets for an even number of silver atoms). These transient structures could be crucial in activating adsorbed species like O_2 . In this work, the temperature-dependent relative stability of Ag_n and Ag_nO_2 ($n = 4, 8$) systems are simulated at different finite temperatures, by means of replica-exchange *ab initio* molecular dynamics (REMD) and efficient Boltzmann-reweighting based methods (e.g., Weighted Histogram Analysis Method, WHAM, and multi-state Bennett acceptance ratio estimator, MBAR). The multi-spin-state free energy surfaces are visualised with the help of Sketch-Map [1]. The results show that meta-stable structures and the spin-polarized states can synergistically influence the activation of the adsorbed O_2 molecule. [1] M. Ceriotti, G. A. Tribello, M. Parrinello, J. Chem. Theory Comput. 9, 1521 (2013)

O 14.2 Mon 15:15 S053

Long-lived reactive trapped electrons on amorphous ice surfaces — ●SARAH KING¹, DANIEL WEGKAMP^{1,2}, MICHAEL MEYER¹, MARTIN WOLF¹, and JULIA STÄHLER¹ — ¹Department of Physical Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany — ²ICFO - Institute of Photonic Sciences, Mediterranean Technology Park, Av. Carl Friedrich Gauss 3, 08860 Castelldefels (Barcelona), Spain

Trapped electron states have been observed for the first time at the amorphous solid water (ASW)/vacuum interface with relaxation times fourteen orders of magnitude longer than previously observed in bulk ASW. The formation, relaxation and decay pathways, and reactivity of trapped electrons was investigated using time-resolved two-photon photoemission of ≥ 15 bilayers of D_2O on the Cu(111) surface. We find that the decay time of the trapped electron is 15.74 ± 0.12 s, independent of ASW thickness, suggesting an electron hopping mechanism, as opposed to tunneling, for electron recombination with the Cu surface. An increase in the ASW/Cu effective work function of approximately 0.5 eV, concomitant with a decrease in the photo-stationary trapped electron population, is also observed upon repeated irradiation of the ASW/Cu surface with ultraviolet femtosecond pulses. This is consistent with a reaction between the trapped electrons and the ASW at the vacuum interface producing an anionic species, and highlights the possible role of these trapped electrons as reactive intermediates.

O 14.3 Mon 15:30 S053

Reaction-diffusion modeling of hydrogen in beryllium — ●MIRKO WENSING, DMITRY MATVEEV, and CHRISTIAN LINSMEIER — Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung - Plasmaphysik, 52425 Jülich, Germany

Beryllium will be used as first-wall material for the future fusion reactor ITER as well as in the breeding blanket of DEMO. In both cases it is important to understand the mechanisms of hydrogen retention in beryllium. In earlier experiments with beryllium [1] low-energy binding states of hydrogen were observed by thermal desorption spectroscopy (TDS) which are not yet well understood. Two candidates for these states are considered: beryllium-hydride phases within the bulk and surface effects. The retention of deuterium in beryllium is studied by a reaction rate approach using a coupled reaction diffusion system (CRDS)-model relying on *ab initio* data from density functional theory calculations (DFT). In this contribution we try to assess the influence of surface recombination. [1] M. Reinelt, A. Allouche, M. Oberkofler, C. Linsmeier, New J. Phys. 11 043023 (2009)

O 14.4 Mon 15:45 S053

Deuterium/Wasserstoff-Isotopenaustausch an Beryllium und Berylliumnitrid — ●PETRA DOLLASE, MICHAEL EICHLER, MARTIN KÖPPEN, TIMO DITTMAR und CHRISTIAN LINSMEIER — Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung - Plasmaphysik, 52425 Jülich, Germany

In den Fusionsexperimenten JET und ITER besteht die erste Wand im Hauptraum aus Beryllium (Be). Zur Strahlungskühlung im Divertor wird der Einsatz von Stickstoff diskutiert. Dieser kann mit der Oberfläche der ersten Wand zu Berylliumnitrid (Be_3N_2) reagieren. Als Brennstoff werden die Wasserstoffisotope Deuterium und Tritium eingesetzt, die in der Fusionsreaktion zu Helium und einem Neutron reagieren. Da der magnetische Einschluss des Plasmas nicht perfekt ist, treffen auch Deuterium- und Tritiumionen auf die Berylliumwand auf und können sich dort anreichern. Das soll aufgrund der Radioaktivität von Tritium unbedingt vermieden werden. Daher wird zur Regenerierung der ersten Wand der Isotopenaustausch mit Deuterium untersucht. Wir untersuchen den Isotopenaustausch von Deuterium und Protium, um nicht mit radioaktivem Tritium arbeiten zu müssen. Der Ionenbeschuss wird dabei mit einer Ionenquelle simuliert. Mit Spannungen bis maximal 5 kV werden Deuterium- und protische Wasserstoffionen in polykristallines Be bzw. Be_3N_2 implantiert. Die Proben werden dann *in-situ* mit Röntgenphotoelektronenspektroskopie (XPS) und thermischer Desorptionsspektroskopie (TDS) analysiert. Anschließend werden unter den gleichen Bedingungen hergestellte Proben *ex-situ* mittels nuklearer Reaktionsanalyse (NRA) charakterisiert.

O 14.5 Mon 16:00 S053

Untersuchung der Rückhaltemechanismen von Wasserstoff in Beryllium Wolfram Verbindungen — ●MICHAEL EICHLER, TIMO DITTMAR und CHRISTIAN LINSMEIER — Forschungszentrum Jülich GmbH, Institut für Energie- und Klimaforschung - Plasmaphysik, 52425 Jülich, Germany

In den experimentellen Fusionsreaktoren JET und zukünftig auch ITER besteht die erste Wand im Hauptraum aus Beryllium (Be). In Bereichen der höchsten Wärmelasten (Divertor) wird zusätzlich Wolfram (W) verwendet. Als Brennstoff werden die Wasserstoffisotope Deuterium (D) und Tritium (T) eingesetzt. Durch den Kontakt der Reaktorwand mit den D- und T-Ionen wird unter anderem das Oberflächenmaterial erodiert und an anderen Stellen deponiert. Dadurch entstehen Be-W Verbindungen. Da das radioaktive T während des Reaktorbetriebs in der Wand eingelagert wird, ist die Untersuchung des Wasserstoffinventars, insbesondere der Rückhaltemechanismen in Be-W Legierungen von besonderem Interesse. Dazu wird das Ultra Hoch Vakuum Experiment namens ARTOSS vorgestellt, welches verschiedene Oberflächenanalytiken vereint und somit die *in situ* Präparation und Analyse entsprechender Materialien unter wohldefinierten Bedingungen ermöglicht. Der Ionenbeschuss im Reaktor wird hier mit einer Ionenquelle simuliert. Mit Spannungen bis maximal 20 kV werden D und Wasserstoffionen in Be-W Verbindungen implantiert. Ausserdem werden erste Untersuchungen mittels Röntgenphotoelektronenspektroskopie (XPS), thermischer Desorptionsspektroskopie (TDS) und nuklearer Resonanzanalyse (NRA) gezeigt.

Invited Talk

O 14.6 Mon 16:15 S053

In-situ Studies of the Reactivity of Pt Model Catalysts: from Flat Surfaces to Nanoparticles — ●CHRISTIAN PAPP — Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg

Nanocluster arrays on supported graphene are intriguing model systems for catalysis, modeling the highly dispersed particles on real catalysts. We studied the adsorption and oxidation of CO and the chemistry of the catalyst poison SO_2 on Pt/Gr/Rh(111) with synchrotron-based high-resolution X-ray photoelectron spectroscopy.

On the Pt nanoclusters, we resolved CO adsorbed at three different sites, that is, on-top, bridge and step. The C 1s spectra exhibit remarkable similarities to those on single crystal surfaces: Similar to the case for stepped Pt(111) surfaces, a clear preference for the adsorption on the step sites is found, while the preference for the adsorption on the on-top site over the bridge site on the terraces is less pronounced than on Pt(111). Temperature-programmed X-ray photoelectron spectroscopy revealed an enhanced binding energy for the cluster step sites, similar to the situation on stepped Pt surfaces. The oxidation of CO follows roughly pseudo first order kinetics. The activation energy determined from an Arrhenius analysis was found to be smaller than for stepped and flat platinum crystals.

SO_2 adsorbs in two geometries, perpendicular and parallel to the surface, on both cluster facets and steps. While we again find a remarkable similarity to the adsorption situation on single crystals at low temperature, the reactivity of the nanoclusters is strongly increased.

Support by the DFG through SFB 953 is gratefully acknowledged.

O 14.7 Mon 16:45 S053

Temperature induced change in aliphatic monolayers observed by vibrational sum-frequency generation spectroscopy

— ●ANDRE BEIER-HANNWEG¹, KATHARINA MAUS¹, MICHAEL LACKNER¹, THORSTEN BALGAR², JAN WEBER¹, and ECKART HASSELBRINK¹ — ¹Institut für Physikalische Chemie, Universität Duisburg-Essen — ²Junior Uni-Wuppertal

The conformational order in long, aliphatic calcium-carboxylate Langmuir-Blodgett (LB) monolayers on solid glass supports is investigated by means of vibrational sum-frequency generation spectroscopy (VSFS). The C-H stretching vibrations of both the terminal methyl and the methylene groups are utilized to monitor the chain conformation at various sample temperatures. With increasing temperature, the LB-films exhibit structural changes, which can be probed by VSFS due to a difference in the corresponding signal-intensities at given temperatures. We will discuss how thermodynamic properties can be evaluated from the spectra.

O 14.8 Mon 17:00 S053

Reaction mechanisms by direct imaging of individual intermediates stabilized by surface dissipation and entropy

— ●ALEXANDER RISS^{1,2}, ALEJANDRO PÉREZ PAZ³, SEBASTIAN WICKENBURG^{2,4}, HSIN-ZON TSAI², DIMAS G. DE OTEYZA^{5,6}, ANGEL RUBIO^{9,10,3}, FELIX R. FISCHER^{4,7,8}, and MICHAEL F. CROMMIE^{2,4,8} — ¹Physik-Department E20, Technische Universität München, Germany — ²Department of Physics, UC Berkeley, USA — ³Nano-Bio Spectroscopy Group and ETSF, Universidad del País Vasco, CFM CSIC-UPV/EHU-MPC & DIPC, San Sebastián, Spain — ⁴Materials Sciences Division, LBNL, Berkeley, USA — ⁵Donostia International Physics Center, San Sebastián, Spain and Ikerbasque, Basque Foundation for Science, Bilbao, Spain — ⁶Centro de Física de Materiales CSIC/UPV-EHU-Materials Physics Center, San Sebastián, Spain — ⁷Department of Chemistry, UC Berkeley, USA — ⁸Kavli Energy NanoSciences Institute at the UC Berkeley and the LBNL, Berkeley, USA — ⁹Max Planck Institute for the Structure and Dynamics of Matter, Hamburg, Germany — ¹⁰CFEL, Hamburg, Germany

We have directly determined the microscopic mechanisms underlying complex bimolecular coupling and cyclization reactions of enediynes through real-space imaging of the precise bond configuration of intermediate species using noncontact atomic force microscopy (nc-AFM). Supported by extensive theoretical calculations, we reveal that the observed transient intermediates along the reaction pathway are stabilized by efficient energy dissipation to the substrate and changes in molecular entropy along the reaction pathway.

O 14.9 Mon 17:15 S053

Exciting phonons: When molecules meet surfaces — ●VANESSA JANE BUKAS and KARSTEN REUTER — TU München, Germany

Exothermic surface chemical reactions may easily release several electron volts of energy. This challenges first-principles based dynamical simulations to account for adequate energy dissipation channels. Focusing on phononic dissipation, a novel embedding scheme for metallic substrates (QM/Me [1]) allows for energy to be dissipated out of a quantum-mechanically described reaction zone and into a computationally undemanding, yet reliably described, extended bath. In the application to oxygen dissociation over Pd(100) this approach predicted “hot” O adatoms traveling ballistically over several lattice constants as a consequence of non-immediate energy transfer to the surface [1].

Despite being similarly exothermic, a much shorter transient mobility was measured for the O₂/Pd(111) reaction [2]. We reconcile this

apparent intricacy by quantitatively analyzing the underlying phonon excitations directly from QM/Me trajectories. This identifies certain groups of localized surface modes as the dominant dissipation channels, while comparing the Pd(100) and Pd(111) systems offers important trend understanding into the influence of surface symmetry. The thus obtained first-principles perspective on non-equilibrium adsorbate-phonon dynamics questions prevalent assumptions about energy sinks made in commonly used model Hamiltonians.

- [1] J. Meyer and K. Reuter, *Angew. Chem. Int. Ed.* **53**, 4721 (2014).
[2] M.K. Rose *et al.*, *Surf. Sci.* **561**, 69 (2004).

O 14.10 Mon 17:30 S053

Inelastic Hydrogen Atom Scattering: Role of Electron-Hole Pair Excitations — ●OLIVER BÜNERMANN, HONGYAN JIANG, YVONNE DORENKAMP, and ALEC WODTKE — Universität Göttingen, Institut für Physikalische Chemie, Tammannstr 6, 37077 Göttingen

Obtaining an atomic-level understanding of the dynamics of energy conversion at surfaces remains a complex and challenging area of modern research in physical chemistry. A general strategy to this field follows the lessons of gas-phase bimolecular chemical dynamics, where simple model systems are studied experimentally with great care while theoretical simulations are developed. One of the simplest systems to think of is Hydrogen atom scattering from a single crystalline surface. We built a new apparatus to experimentally investigate this model system with extraordinary precision. Laser photolysis is employed to produce a monochromatic H-atom beam. The H-atom beam strikes a single crystalline surface held in UHV. The kinetic energy and angular distributions of the scattered H-atoms are measured with extraordinary resolution employing Rydberg Atom Tagging.

Experimental results for scattering H-atoms from metal and insulator surfaces will be presented. In case of an insulator the scattering is nearly elastic while in case of metals strongly inelastic scattering is observed. Our results reveal that electron-hole-pair excitation is the dominate relaxation channel for H-atom translation in case of a metal surface, an interpretation supported by theoretical calculations [1].

- [1] Buenermann, O *et al.*, *Science*, DOI:10.1126/science.aad4972 (2015)

O 14.11 Mon 17:45 S053

Adatom Diffusion on Metal Surfaces: Disentangling Phononic and Electronic Energy Dissipation — ●SIMON P. RITTMAYER, PATRICK GÜTLEIN, and KARSTEN REUTER — TU München

The role of electron-hole pair excitations during dynamical surface processes on metal substrates has been controversially discussed. While adiabatic first-principles calculations often provide a satisfactory description, an abundance of such excitations is generally suggested by the continuum of electronic states around the Fermi level. With high-level non-adiabatic calculations still untractable for extended metal surfaces, the concept of electronic friction within the local density friction approximation (LDFA) offers numerically efficient, but approximate insight.

We have recently shown this approach to yield reasonable results for the vibrational damping of high-frequency adsorbate vibrations on various metal surfaces [1]. With this confidence we now apply it for surface diffusion, where non-adiabatic energy losses compete with energy losses due to phononic coupling. We compare our LDFA-based molecular dynamics simulations for various alkali-metal adsorbates on Cu(111) to experimental signatures obtained from ³He spin echo measurements [2]. This comparison allows to decompose empirically obtained friction coefficients into electronic and phononic contributions for the first time.

- [1] S.P. Rittmeyer *et al.*, *Phys. Rev. Lett.* **115**, 046102 (2015).
[2] D.J. Ward, PhD thesis, University of Cambridge (2013).