O 16: Surface Dynamics & Electron-Driven Processes

Time: Monday 15:00–17:30 Location: MA 141

O 16.1 Mon 15:00 MA 141

Role of hydration and electrostatics in salt precipitation — •Adyant Agrawal[1], Simon Gravelle[2], Christian Holm[1], and Alexander Schlaich[3] — [1]Institute for Computational Physics, University of Stuttgart — [2]Univ. Grenoble Alpes, CNRS, LIPhy, 38000 Grenoble, France — [3]SC SimTech, University of Stuttgart

The precipitation of salt leading to the formation of a salt crust is a crucial process in the environment, yet it is still not fully resolved at the molecular scale. We perform an extensive molecular dynamics simulation study of supersaturated solutions of simple salts in contact with their crystal surface to understand the precipitation mechanism. For NaCl, we found that the sodium ions have a larger preference to be adsorbed at a crystal surface than the chloride ions, which results in a buildup of positive charge on the crystal. An excess of sodium ions then drives the adsorption of chloride ions at the surface. This leads to a depletion in the charge distributions above the surface as the crystal grows. This mechanism is different from other common salts we tested. We also obtain the dependence of the free energy for adsorbed ions on the defect topology to capture the thermodynamics of crystal surface formation. We identify a complex competition between hydration and electrostatic interactions at the interface that controls the precipitation process and the interfacial topology. The grown surface can be anomalously patterned since some sites can be more favourable for water molecules than ions. We discuss these competing effects in the context of different common salts.

O 16.2 Mon 15:15 MA 141

Unraveling the Intricacies of Surface Salt Formation on Mg(0001): Implications for Chloride-Ion Batteries — •Kanchan Sarkar[1] and Axel Gross[1,2] — [1]Institute of Theoretical Chemistry, Ulm University, 89069 Ulm, Germany — [2]Helmholtz Institute Ulm (HIU), Electrochemical Energy Storage, 89081 Ulm, Germany

We present a density functional theory study of the initial steps of chlorine deposition on the Mg(0001) surface. Such processes occur in chloride-ion batteries in which lithium and magnesium are used as anode materials. In addition, it is also of fundamental interest, as halide adsorption on metal electrodes is an important process in interfacial electrochemistry. We discuss the adsorption properties and determine the stable adsorption structures, both with respect to the free chlorine molecule but also as a function of the electrode potential. We find indications of the immediate formation of the $MgCl_2$ surface salt structure upon exposure of Cl to a Mg surface. These findings are discussed with respect to the conversion of the Mg anode to a $MgCl_2$ configuration which provides the thermodynamical driving force for the discharge of a Cl-ion battery.

O 16.3 Mon 15:30 MA 141

Copper Surface Electro-Oxidation via Large-Scale Atomistic Simulations — •Felix Riccius, Nicolas Bergmann, Simon Wengert, Nicolas G. Hörmann, Hendrik H. Heenen, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin

Copper (Cu) is a versatile electrocatalyst material. However, the catalytically active metal phase is susceptible to oxidation either during electrode preparation or within the reaction environment. The degree of oxidation and the concomitant structural and morphological transformations are presently still largely unclear, let alone how these changes affect the electrocatalytic performance. With the formed surface structures certainly far from ideal, determining atomistic structural models requires an efficient sampling in vast configurational spaces. We address this challenge by capturing predictive-quality density-functional theory calculations using a MACE machine learning interatomic potential. Enabled by the resulting fast energetics, parallel tempering is employed to sample a large surface phase space of Cu surface structures at increasing degree of oxidation. Combining the resulting data within *ab initio* thermodynamics we arrive at surface phase diagrams that point to amorphous Cu(I)O-like sites as a key to understand the reactivity and stability changes.

O 16.4 Mon 15:45 MA 141

Exploring dynamic catalyst restructuring with adaptive kinetic Monte Carlo: Oxidation of the Pd(100) surface — •Patricia Poths, King Chun Lai, Christoph Scheurer, Sebastian Matera, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin

Modern operando catalyst characterization approaches have revealed that even single crystal model catalysts are not static, but adapt their surface morphology and composition in response to applied reactions conditions. One such adaption is the possible formation of surface oxides, for which the mechanism and kinetics must be regarded as largely unknown. In this talk, we take the first steps towards explicit dynamic modeling of this process employing a newly developed adaptive kinetic Monte Carlo (AKMC) approach. This technique automatically determines the complex reaction mechanism on-the-fly instead of relying on human intuition. Employing machine-learned potentials as the basis for AKMC, we investigate for the first time the explicit kinetics of surface oxide formation on the highly debated Pd(100) surface. We discuss key aspects of surface restructuring during the initial phase of oxide formation.

O 16.5 Mon 16:00 MA 141

Realistic Representations of IrO2 Catalyst Surfaces through Extensive Sampling — •Hao Wan, Hendrik H. Heenen, Christoph Scheurer, and Karsten Reuter — Fritz-Haber-Institut der MPG, Berlin

Iridium oxide catalyzes the oxygen evolution reaction with unparalleled activity and stability, even under harsh acidic conditions. However, this performance is sensitively correlated to strong structural, compositional and morphological changes of the working catalyst. At the atomic level little is presently known about the true active state, if only that it is unlikely ideal rutile IrO2.

This situation spans a vast configurational space, the extensive sampling of which e.g. by means of parallel tempering would be intractable with direct predictive-quality first-principles calculations. Training of a machine-learning interatomic potential (MLIP) as an efficient surrogate is in turn challenged by an unprecedented required diversity of training structures if not even the bulk structure and composition can be assumed known. To this end, we create a comprehensive training set by first assembling prototype bulk structures for various IrO* stoichiometries from existing databases. In an active learning loop, this set is then augmented through extensive sampling of diverse surface structures created from the prototypes. The thus trained MLIP successfully reproduces the known stability reversal of the rutile (110) and (111) facets with increasing potential, while its computational efficiency allows to rapidly probe the activity and stability of the plethora of sampled surface sites using established descriptors.

O 16.6 Mon 16:15 MA 141

Nonadiabatic quantum dynamics of molecules scattering from metal surfaces — •Riley Preston[1], Yaling Ke[1], Samuel Rudge[1], Reinhard Maurer[2], and Michael Thoss[1] — [1]Institute of Physics, University of Freiburg, Germany — [2]Department of Physics, University of Warwick, UK

A precise theoretical understanding of reactivity at metal surfaces has the possibility of providing valuable theoretical insights into the dynamical processes which emerge due to the coupling of a molecule to a surface, as well as the prospect of profound consequences to a range of applications. However, the modelling of molecular scattering off metal surfaces is a theoretical challenge, since a single scattering process will traverse regimes of both strong and weak coupling, while there is no guarantee of a time-scale separation between electronic and nuclear degrees of freedom, rendering perturbative approaches invalid [1].

We simulate the scattering of molecules off metal surfaces using the hierarchical equations of motion approach in the framework of a matrix product state formulation, which aids the computational efficiency [2]. The approach constitutes a numerically exact, quantum approach which includes all nonadiabatic and quantum nuclear effects. The method is applied to a system described by a Newns-Anderson Hamiltonian, from which we derive valuable insights about the behaviour of important observables such as the adsorption probability to the surface under different conditions.

[1] A. M. Wodtke, Chem. Soc. Rev. 45, 3641-3657 (2016).

[2] Y. Ke, R. Borrelli, M. Thoss, J. Chem. Phys. 156, 194102 (2022).

O 16.7 Mon 16:30 MA 141

Electronic Friction of Interacting Systems Near Metal Surfaces — •Martin Mäck, Samuel Rudge, and Michael Thoss — Institute of Physics, University of Freiburg, Germany

Mixed quantum-classical methods are an efficient way of modeling the dynamics of molecules near metal surfaces, such as in molecular junctions or scattering problems. Since a full quantum mechanical description of the vibrational degrees of freedom is numerically expensive, semiclassical methods such as Langevin dynamics based on electronic friction can greatly reduce the computational cost.

Until now, however, a description based on electronic friction was either limited to noninteracting systems or position independent metal-molecule couplings. In this contribution, we further develop the hierarchical equations of motion (HEOM) approach to electronic friction [1] to systems with a position dependent molecule-metal coupling. We derive new expressions for the Markovian friction tensor. Moreover, we apply our approach to a system with strong intrasystem interactions. Here, we demonstrate the usefulness of our extended approach, since the HEOM remains numerical exact [2], even for interacting systems. Our extended approach could be useful for the semiclassical description of a wide variety of problems, such as desorption dynamics and quantum shuttles.

[1] S. L. Rudge, Y. Ke and M. Thoss, Physical Review B **107**, 115416 (2023)
[2] C. Schinabeck, A. Erpenbeck, R. Härtle and M. Thoss,
Physical Review B **94**, 201407 (2016)

O 16.8 Mon 16:45 MA 141

How a long-range attraction influences desorption kinetics — •Florian Schneider[1], Lukas Höltkemeier[1], Andrea Floris[2], Lev Kantorovich[3], Ralf Bechstein[1], and Angelika Kühnle[1] — [1]Physical Chemistry I, Bielefeld University, 33615 Bielefeld, Germany — [2]School of Chemistry, University of Lincoln, Brayford Pool, Lincoln LN6 7TS, UK — [3]Department of Physics, Kings's College London, London WC2R 2LS, UK

Desorption of molecules from surfaces is omnipresent both in nature and technology. Despite its omnipresence and conceptual simplicity, fundamental details can be surprisingly complex and are often poorly understood. Here, we study the desorption of a submonolayer film of 3-nitrophenol from the natural cleavage plane of calcite kept in ultrahigh vacuum. Interestingly, two distinctly different desorption regimes are observed during isothermal desorption monitored by dynamic atomic force microscopy. Initially, at high coverages, the coverage decreases almost linearly in time, indicating a constant desorption rate. Beyond this linear regime, at low coverages, a drastic increase in desorption rate is observed until the surface is completely empty. The transition between these two regimes is associated with a critical island width. The increase in desorption rate when falling below a critical island width indicates that a long-range attractive interaction between the molecules is present. The herein observed phenomenon of two different desorption regimes is expected to be of general significance when interactions beyond next-neighbor attraction are present.

O 16.9 Mon 17:00 MA 141

Supercooled 1D-metal nanocrystallites prepared by orbital-selective photodoping — •Hannes Böckmann[1,2], Jan Gerrit Horstmann[1,2], Felix Kurtz[1,2], Stefan Wippermann[3], and Claus Ropers[1,2] — [1]Max Planck Institute for Multidisciplinary Sciences, Göttingen, Germany — [2]4th Physical Institute, University of Göttingen, Göttingen, Germany. — [3]Faculty of Physics, Philipps University of Marburg, Marburg, Germany.

Photochemical reactions in molecules are brought about by targeted transitions into reactive electronic states. Much like molecular levels, the electronic bands of a material are formed due to the hybridization of atomic orbitals at different energies. In this sense, the most fundamental solid state state analogy is described by the optical quench of a Peierls insulator, in which the periodic dimerization of a one-dimensional atomic chain is lifted by resonant transitions between electronic states at the accompanying band gap. However, in real materials, their light-induced occupation is typically mediated by delocalized higher energy bands, effectively rendering structural transformations independent of the light frequency and polarization. Here, we use orbital-selective photodoping to drive the quench of a prototypic quasi one-dimensional Peierls insulator, formed by atomic indium wires on the (111) face of silicon. Polarized excitation exploits the anisotropic interactions along specific crystallographic directions to directly address electronic states at the cdw gap. The targeted excitation minimizes excess energy, leading to an unprecented control over the nanoscale phase texture and metastable lifetime.

O 16.10 Mon 17:15 MA 141

A continuous-wave/pulsed X-band electron spin resonance spectrometer operating in ultra-high vacuum for the study of low dimensional spin ensembles — Franklin Cho[1,2], Juyoung Park[1,2], Soyoung Oh[1,2], Jisoo Yu[1,2], Yejin Jeong[1,2], Luciano Colazzo[1,2], Lukas Spree[1,2], Caroline Hommel[1,2], Arzhang Ardavan[3], Giovanni Boero[4], and •Fabio Donati[1,2] — [1]IBS Center for Quantum Nanoscience, South Korea — [2]Department of Physics, Ewha Womans University, South Korea — [3]Clarendon Laboratory, University of Oxford, UK — [4]Microsystems Laboratory, EPFL, Switzerland

Surface-adsorbed molecular spin qubits have been attracting growing interest as a new platform for coherently controlled phenomena at the atomic scale. The localization at the surface of the molecular spins imposes to employ specifically designed setups to achieve sufficient spin sensitivity and operate in ultra-high vacuum. In this work, we report the development of a UHV continuous-wave and pulsed X-band electron spin resonance (ESR) spectrometer operating down to 10 K. The use of a half-wavelength microstrip line resonator made of epitaxially grown copper films on single crystal Al_2O_3 substrates allows achieving a sensitivity of 6.5×10^{10} spins G^{-1} $Hz^{-1/2}$ on a surface of about 1 mm^2. Surface characterizations using atomic force microscopy, low-energy electron diffraction, and scanning tunneling microscopy show that the Cu surface is atomically clean, flat, and single crystalline. Advanced pulsed ESR experimental capabilities including dynamical decoupling and electron-nuclear double resonance are demonstrated.