

## O 9: Solid-Liquid Interfaces: Structure, Spectroscopy I

Time: Monday 10:30–13:00

Location: WIL C307

O 9.1 Mon 10:30 WIL C307

**Self-Diffusion Mechanisms of Surface Defects at Copper-Water Interfaces** — ●SURESH KONDATI NATARAJAN and JÖRG BEHLER — Lehrstuhl für Theoretische Chemie, Ruhr Universität Bochum, Germany

The self-diffusion mechanisms of surface defects at metal-water interfaces have to be studied for understanding heterogeneous catalysis, electrochemistry and corrosion. Although a number of studies in the literature have been dedicated to the investigation of these mechanisms at metal-vacuum interfaces, there are hardly any studies for metal-water interfaces. Here, we unravel the surface adatom and vacancy diffusion mechanisms at several copper-water interfaces using a high dimensional neural network potential based on density functional theory [1]. In case of the low index surfaces such as (111), (100) and (110), the adatom diffusions by means of a simple hop and an exchange with a surface atom are investigated and we find that the free energy barrier to the hopping mechanism is much smaller than the barrier to the exchange mechanism. We find that the interfacial water molecules assist in the adatom diffusion processes. The adatoms at stepped surfaces like (311) and (211) hop along the step edge more frequently compared to the hop across the step edge. Finally, the vacancy hop at (100) surface is found to be twice as probable as the hop at (111) and (110) surfaces in the presence of water.

[1] S. K. Natarajan and J. Behler, Phys. Chem. Chem. Phys. 18, 28704 (2016).

O 9.2 Mon 10:45 WIL C307

**Force Implementation for the Modified Poisson-Boltzmann Solvation Model in FHI-aims** — ●CHRISTOPH MUSCHIELOK, STEFAN RINGE, HARALD OBERHOFER, and KARSTEN REUTER — Technische Universität München, Germany

Implicit solvation approaches represent a numerically appealing route to account for solvation effects in first-principles electronic structure calculations. These effects comprise both energetic and structural changes induced by the surrounding medium. Among a plethora of implicit solvation methods, the size-modified Poisson-Boltzmann (MPB) approach thereby combines an account of the dielectric solvent response with a mean-field description of solvated finite-sized ions.

Using a function-space based solution scheme MPB implicit solvation functionality has recently been implemented into the all-electron, numeric-atomic-orbital based density-functional theory (DFT) package FHI-aims.[1] This implementation fully exploits the specialised atom-centered integration grids of FHI-aims. To also allow for structural relaxation under the electrolyte influence, we now derived analytic nuclear derivatives for this MPB functionality. In this contribution we will present the individual terms and their efficient numerical implementation. As a showcase application we investigate conformer stabilities of biomolecules in electrolytes.

[1] S. Ringe *et al.*, J. Chem. Theory Comput. 12, 4052 (2016).

O 9.3 Mon 11:00 WIL C307

**Towards the Understanding of the Water/Zinc Oxide Interface Employing Artificial Neural Networks** — ●VANESSA QUARANTA, MATTI HELLSTRÖM, and JÖRG BEHLER — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Bochum, Germany

The interaction of liquid water with zinc oxide (ZnO) is important in different fields like corrosion protection, electrochemistry and heterogeneous catalysis. To date, theoretical studies have mainly addressed single water monolayers while the reactivity of this material in presence of water multilayers is still poorly investigated due to the required large simulation cells which strongly limit the applicability of *ab initio* techniques. Here a reactive DFT-based neural network potential (NNP) for the liquid water/ZnO interface will be presented. We demonstrate that this potential allows to perform extended simulations enabling to unravel the properties of the interfacial water molecules and the proton transfer (PT) events occurring at the non-polar ZnO surfaces.

O 9.4 Mon 11:15 WIL C307

**Optical fingerprints of solid-liquid interfaces: a joint ATR-IR and first principles investigation** — ●LEI YANG<sup>1</sup>, FANG NIU<sup>1</sup>, STEFANIE TECKLENBURG<sup>1</sup>, MARC PANDER<sup>1</sup>, SIMANTINI NAYAK<sup>1</sup>, ANDREAS ERBE<sup>1</sup>, STEFAN WIPPERMANN<sup>1</sup>, FRANCOIS GYGI<sup>2</sup>, and GIULIA

GALLI<sup>3</sup> — <sup>1</sup>MPI Eisenforschung — <sup>2</sup>UC Davis — <sup>3</sup>U Chicago

Despite the importance of understanding the structural and bonding properties of solid-liquid interfaces for a wide range of (photo-)electrochemical applications, there are presently no experimental techniques available to directly probe the microscopic structure of solid-liquid interfaces. To develop robust strategies to interpret experiments and validate theory, we carried out attenuated total internal reflection (ATR-IR) spectroscopy measurements and *ab initio* molecular dynamics (AIMD) simulations of the vibrational properties of interfaces between liquid water and well-controlled prototypical semiconductor substrates. We show the Ge(100)/H<sub>2</sub>O interface to feature a reversible potential-dependent surface phase transition between Ge-H and Ge-OH termination. The Si(100)/H<sub>2</sub>O interface is proposed as a model system for corrosion and oxidation processes. We performed AIMD calculations under finite electric fields, revealing different pathways for initial oxidation. These pathways are predicted to exhibit unique spectral signatures. A significant increase in surface specificity can be achieved utilizing an angle-dependent ATR-IR experiment, which allows to detect such signatures at the interfacial layer and consequently changes in the hydrogen bond network. Funding from DOE-BES Grant DE-SS0008939 and the DFG (RESOLV, EXC 1069) are acknowledged.

O 9.5 Mon 11:30 WIL C307

**Influence of lithium ions onto water structures on Au(111)** — ●IRENE WEBER and KARINA MORGENSTERN — Chair of Physical Chemistry I, Ruhr-Universität Bochum

Providing information about solvation effects near the liquid-solid interface is of tremendous importance for the understanding of electrochemical processes, i.e. in electrocatalysis. However, the understanding of ions influencing water structures and dynamics near metal surfaces on the atomic scale is far from complete. In our study amorphous water and lithium ions are used to mimic fluid water and circular cations, respectively. We found that lithium ions do not adsorb at specific sites on Au(111) during adsorption at around 215 K and that water nucleation starts predominantly at the elbow sites of the herringbone reconstruction. Contrary to the weak interaction of water with Au(111), water molecules bind strongly to lithium ions on Au(111). Depending on the water-lithium ions-ratio, several types of interactions between water, lithium ions and the Au(111) substrate were determined. In this contribution we will review our recent variable-temperature Scanning Tunneling Microscopy (STM) studies of the influence of lithium ions onto amorphous ice structures on Au(111).

O 9.6 Mon 11:45 WIL C307

**Stability and Structure of TiO<sub>2</sub> Rutile (011) Surface Exposed to Liquid Water** — ●JAN BALAJKA, MARTIN SETVÍN, MARTIN ČALKOVSKÝ, ZDENĚK JAKUB, MATTHIAS MÜLLNER, STIJN MERTENS, MICHAEL SCHMID, and ULRIKE DIEBOLD — Institute of Applied Physics, TU Wien, Austria

Understanding the interface between titanium dioxide (TiO<sub>2</sub>) and liquid water is important for many practical applications such as photocatalytic water splitting.

The (011) termination of TiO<sub>2</sub> rutile is the second lowest energy facet and exhibits a (2x1) reconstruction when prepared in UHV. Based on DFT predictions [1] the (2x1) structure should no longer be favorable in a liquid water environment.

A TiO<sub>2</sub> rutile (011) sample, prepared and characterized in UHV, was exposed to liquid water and consequently analyzed with STM, XPS, LEIS and LEED. For this purpose a dedicated UHV system was used that allows controlled and clean transfer of the samples between the UHV and an electrochemical cell.

The results indicate a surface restructuring upon contact with liquid water. An overlayer of dissociated water is formed with a c(2x1) symmetry. As the splitting of the LEED spots corresponding to the (2x1) structure was observed while the bulk (1x1) spots did not change it is likely that the (2x1) substrate is also affected by the presence of liquid water. By combining XPS and LEIS the possibility of contaminant-induced restructuring was excluded.

[1] U. Aschauer, A. Selloni, PRL 106 (2011), 166102.

O 9.7 Mon 12:00 WIL C307

**Understanding water relaxation at interfaces** — ●DOMINIKA LESNICKI and MARIALORE SULPIZI — Department of Physics, Johannes Gutenberg University, Staudingerweg 7, 55128 Mainz, Germany

Advances in ultrafast spectroscopy allow to study vibrational energy transfer of water molecules at interfaces. In the case of water-air interface, it has been shown that the vibrational energy relaxation dynamics is significantly different from that of bulk water.

Here we propose a method to understand vibrational energy relaxation time scales and pathways of the OH stretching mode of water, which is based on the calculation of vibrational response function and the direct simulation of the energy relaxation processes using density functional theory based molecular dynamics (DFTMD) simulations, where a consistent treatment of the electronic structure of solvent and surface is provided.

We apply our method to the fluoride/water interface as function of pH. This system shows a fast relaxation, at low pH, similar to that of bulk water, and a slow relaxation at high pH. Direct comparison to the experimental results is also possible thanks to the collaboration with the molecular spectroscopy group of E. Backus at MPIP.

O 9.8 Mon 12:15 WIL C307

**Ions at hydrophobic interfaces** — ●YURY FOROV<sup>1</sup>, MICHAEL PAULUS<sup>1</sup>, SUSANNE DOGAN<sup>1</sup>, PAUL SALMEN<sup>1</sup>, CHRISTOPHER WEIS<sup>1</sup>, MIRKO ELBERS<sup>1</sup>, SIMON EGGER<sup>2</sup>, ELENA ZWAR<sup>2</sup>, and METIN TOLAN<sup>1</sup> — <sup>1</sup>Fakultät Physik/DELTA, TU Dortmund, 44221 Dortmund, GER — <sup>2</sup>Physikalische Chemie, TU Dortmund, 44221 Dortmund, GER

The investigation of the microscopic structure of water is one of the important areas of modern research [1]. In particular, the understanding of the behavior of water at interfaces is essential for the explanation of interfacial phenomena in several natural and technological environments [2]. Hereby, one important research area is the behavior of ions at hydrophobic interfaces [3]. Much pioneer work has been done to describe the interactions between ions and hydrophobic surfaces, but a complete description of the physical mechanism of the hydrophobic interaction is still pending [4]. We investigated the adsorption behavior of ions of aqueous salt solutions at hydrophobic interfaces as a function of different ionic radii and concentrations by means of x-ray reflectivity at ambient conditions. The use of high energy x-rays allows the analysis of buried interfaces in-situ and thus can be used for studying the properties of multilayer systems, such as layer thickness, roughness, and electron density. We observed changes in the shape of the hydrophobic interface both with rising salt concentrations and ion radii for different salt types. [1] A. Nilsson and L.G.M. Pettersson, Chem. Phys. 389, 1 (2011); [2] D. Chandler, Nature 437, 640-647 (2005); [3] P. Jungwirth and B. Winter, Annu. Rev. Phys. Chem. 59, 343-366 (2008); [4] S. H. Donaldson et al., Langmuir 31, 2051-2064 (2015)

O 9.9 Mon 12:30 WIL C307

**Calcium-Silicate Phases Explained by High Temperature Resistant Phosphate-Probe Molecules** — ●NICOLAS GIRAUDO and PETER THISSEN — Karlsruher Institut für Technologie (KIT), Institut für Funktionelle Grenzflächen (IFG), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

In this work, high temperature resistant phosphate molecules are applied to characterize ultrathin (100 nm) Calcium-Silicate (C-S) phases. These C-S phases are synthesized on silicon wafers, and the interaction of phosphates with the C-S phases is studied by means of in-situ transmission Fourier Transform Infrared (FTIR) spectroscopy. At room temperature the chemistry of the system is dominated by the formation of Calcium-Phosphates (C-P). In case of temperatures rising up to 1000 °C, the C-S phases are regenerated. FTIR results are analyzed on the basis of first-principles calculations and further supported by complementary Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) experiments. This study provides a detailed and self-consistent picture of the chemical and structural properties of interfaces like the one between the atmosphere and ultrathin C-S phases (gas/C-S) and the one between them and silicon wafers (C-S/Si bulk). The material combination of ultrathin C-S phases grown on silicon wafers might in the future have great potential in selective chemistry, catalysis and sensing technology as well as in the semiconductors manufactory.

O 9.10 Mon 12:45 WIL C307

**Characterization of anion layering and steric anion hydration repulsion on positively charged surfaces in aqueous media** — ●QINGYUN HU<sup>1</sup> and MARKUS VALTNER<sup>1,2</sup> — <sup>1</sup>Max-Planck-Institut fuer Eisenforschung, Duesseldorf, Germany — <sup>2</sup>TU Bergakademie Freiberg, Freiberg, Germany

How anions influence the structure at positively charged solid/liquid interfaces is much less understood. Here we measured force versus distance profiles on mica using Atomic Force Microscopy with SiO<sub>2</sub> terminated tips. We characterized steric anion hydration forces for a set of common anions at pH = 1 in 100 mM concentration, where protons are the only positive counter ion. Steric anion hydration effects strongly depend on the anion type and their structuring within the Stern layer. Anions with low hydration energies such as Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> strongly structure within the first 1-2 nm of a positively charged surface due to specific adsorption effects leading to full charge screening within the Stern layer. In contrast strongly hydrated ions such as multivalent anions do not lead to significant structural forces at distances below 1-2 nm showing thermally disordered structuring in accordance with expected Debye screening lengths. In contrast, in perchlorate based electrolytes interfacial protonation of the anionic species leads to an effective increase of the Debye length. In summary, this work highlights that anion structuring in the inner double layer is very ion specific and correlates with hydration free energies, which may play a vital role in understanding processes where positive charge is screened by anions within an electrolyte, including protein folding or colloidal stability.