O 96: Structure of Solid/Liquid Interfaces II

Time: Friday 10:30–13:00 Location: S052

O 96.1 Fri 10:30 S052

Adsorption and desorption of water on protein-repelling self-assembled monolayers — •Mustafa Sayin[1], Alexei Nefedov[2], and Michael Zharnikov[1] — [1]Institute of Applied Physical Chemistry, University of Heidelberg, Im Neuenheimer Feld 253, 69120 Heidelberg, Germany — [2]Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

We studied kinetics and thermodynamics of water adsorption and desorption as well as wetting and nucleation behaviors of water on a series of model organic surfaces, formed by oligo(ethylene glycol) substituted alkanethiolate (OEG-AT) self-assembled monolayers. The ultimate goal of the study was to get a better understanding of the mechanism behind the inertness of poly(ethylene glycol) and OEG based organic surfaces with respect to biofouling and protein adsorption. Varying the water coverage and the capability of surface hydration, by suitable design of the of the OEG-ATs molecules and respective self assembled monolayers, we monitored transfer from the hydration to wetting regime, distinguishing between the hydration and interfacial phases and deriving specifically their parameters. The bonding character of the hydration phase as well as the structure and morphology of the interfacial phase were investigated by high resolution X-ray photoelectron spectroscopy, in situ infrared reflection absorption spectroscopy, and near edge X-ray absorption fine structure spectroscopy. The kinetics of the water desorption was studied by thermodesorption spectroscopy.

O 96.2 Fri 10:45 S052

A High-Dimensional Neural Network Potential for Water at Zinc Oxide: First Applications to Non-Polar Interfaces — •Vanessa Quaranta, Matti Hellström, and Jörg Behler — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Germany

Zinc oxide (ZnO) is an important material in surface science, which has many applications in different fields [1]. In most of these applications, water is ubiquitous playing a crucial role. To understand these processes at the atomic level, realistic structural models of water/ZnO interfaces are crucial. However, the required large systems often containing thousands of atoms dramatically limit the application of *ab initio* techniques. In recent years, artificial neural networks (NNs) have emerged as a powerful efficient method to provide accurate PESs for a variety of systems [2]. Here, we report first results for a DFT-based NN potential constructed for liquid water/ZnO interfaces. In particular, the structural and dynamical properties of interfacial water molecules interacting with non-polar ZnO surfaces will be presented.

[1] Ch. Wöll, *Progr. Surf. Sci.* **82**, 55 (2007).
[2] J. Behler, *Phys. Chem. Chem. Phys.* **13**, 17930 (2011).

O 96.3 Fri 11:00 S052

Ab-initio molecular dynamics simulations on wet alumina-/isopropanol solid/liquid interfaces — •Paul Schwarz und Bernd Meyer — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

The solid/liquid interface of wet and hydroxylated α-alumina/isopropanol is studied using ab-initio Car-Parrinello molecular dynamics (CPMD) simulations. For the alumina slab three different surface models are taken into account: a termination with a full hydroxyl layer (**hyd**), an aluminum termination with dissociated water molecules to saturate undercoordinated surface sites (**w1**) and a third termination with adsorbed water molecules between the OH groups of the **w1** structure (**w2**).

Simulations of the **w2** slab show that the additional water molecules induce recombinations events on the surface, leading to the protonation of several OH groups and thereby to the formation of water molecules on top of the aluminum atoms. The occurrence and distribution of these newly formed water molecules is analyzed, as well as proton hopping events on the surface. We show that the proton hopping is energetically driven and correlates with an increased number of H-bonds. Recombination events are also found for the **w1** slab after adding isopropanol, whereas the **hyd** surface remains unchanges. Finally, the influence of the surface termination on the structure of the isopropanol liquid will be discussed.

O 96.4 Fri 11:15 S052

A joint *first principles* and ATR-IR study of the vibrational properties of interfacial water at semiconductor-water solid-liquid interfaces — •Lei Yang[1], Stefanie Tecklenburg[1], Fang Niu[1], Andreas Erbe[1], Stefan Wippermann[1], Francois Gygi[2], and Giulia Galli[3] — [1]Max-Planck-Institut für Eisenforschung — [2]University of California, Davis — [3]University of 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. We carried out joint ATR-IR spectroscopy measurements and *ab initio* molecular dynamics simulations of the vibrational properties of interfaces between liquid water and prototypical semiconductor substrates. In particular, the Ge(100)/H_2O interface is shown to feature a reversible bias potential dependent surface phase transition. Our study highlights the key role of coupled theory-experimental investigations on well controlled and characterized interfaces, in order to develop robust strategies to interpret experiments and validate theory. The authors wish to thank T. A. Pham for helpful discussions. G. G. and F. G. acknowledge DOE-BES Grant No. DE-SS0008939.

O 96.5 Fri 11:30 S052

A first-principles study on the phase stability of ZnO(0001)-Zn surfaces — •Suhyun Yoo, Mira Todorova, and Joerg Neugebauer — Department of Computational Materials Design, Max-Planck-Institut fuer Eisenforschung GmbH, Duesseldorf, Germany

Zinc oxide is a wide bandgap semiconductor, which is intensively studied due to its applications in different fields, such as (photo-)catalysis, protective coating, optoelectronics and others. Knowledge of the surface structures which form when ZnO surfaces come into contact with different environments (gas phase, liquid) and are thermodynamically stable is important in the context of most of these applications. Focusing on the polar Zn terminated ZnO(0001) surface we combine density functional theory (DFT) calculations with thermodynamic concepts to study how the stability of surface phases forming on ZnO(0001)-Zn surfaces [1] is influenced by (i) the improved description of the band gap, as achieved by DFT-HSE calculations and (ii) the contact with an aqueous environment. Modelling liquid water by an implicit solvation model [2], we utilize our recent electrochemical approach [3] to construct a surface Pourbaix diagrams for this surface.

[1] M. Valtiner, M. Todorova, G. Grundmeier, and J. Neugebauer, Phys. Rev. Lett. 103, 065502 (2009).
[2] K. Mathew, R. Sundararaman, K. Letchworth-Weaver, T.A. Arias, and R.G. Hennig, J. Chem. Phys. 140, 084106 (2014).
[3] M. Todorova and J. Neugebauer, Phys. Rev. Applied 1, 014001 (2014).

O 96.6 Fri 11:45 S052

Water adsorption on clean bimetallic Pt-Ru(0001) surfaces - a low-temperature UHV-STM investigation — •Martin Schilling, Sylvain Brimaud, and R. Jürgen Behm — Ulm University, Institute of Surface Chemistry and Catalysis, 89069 Ulm

A detailed understanding of the elementary electrochemical/-catalytic processes on catalytically relevant electrode surfaces requires the characterization of the solid | liquid interface, including the water-metal interaction and the influence of coadsorbed species. The water-metal interaction has been studied in detail earlier, using model systems consisting of ice layers adsorbed on monometallic single crystal surfaces [1].

Here, we present results of a scanning tunnelling microscopy (STM) study on the structure of H_2O on 2D bimetallic PtRu model electrodes. H_2O was deposited under well-defined conditions in ultrahigh vacuum (UHV) at low sample temperatures (100 - 130 K) on Pt modified Ru(0001) single crystal surfaces. In addition to adsorption on the clean metal surfaces, also structural effects of pre- or coadsorbed species on the overlayer structure were investigated. The structures were characterized by STM in the temperature range of 100 K to RT. Depending on the Pt-Ru surface structure, the conditions of H_2O dosing and the presence of coadsorbates we identified different trends for the resulting molecular arrangements of the adsorbate. The influence

of substrate-molecule and molecule-molecule interactions is discussed based on the Pt modified Ru(0001) substrate.

[1] J. Carrasco *et al.*, *Nat. Mater.* **11** (2012) 667

O 96.7 Fri 12:00 S052

Water adsorption on Pt(111): water-water vs. water-metal interaction — •Maryam Naderian and Axel Gross — Institute of Theoretical Chemistry, Ulm University, D-89081 Ulm/Germany

Adsorbed water layers typically form hydrogen-bonded networks at surfaces at low temperatures. The stability of these water layers at solid surfaces is thus governed by a delicate interplay between water-substrate and water-water interactions [1]. Using density functional theory (DFT) calculations, we address the importance of water-water vs. water-metal interactions in the adsorption of water on Pt(111). To get a reliable description of the water-metal system, it is crucial to include dispersion effects in the DFT calculations [2].

The initial steps of the formation of hydrogen-bonded networks have been studied using ab initio molecular dynamics simulations of water adsorption on water-precovered Pt(111). The water-metal interaction has been modified by using Pt-terminated bimetallic surfaces. Ligand and strain effects lead to a variation of the reactivity of the Pt atoms which also influences the balance between water-water and water-metal interaction. The consequence of this variation on the resulting water structures will be discussed in detail.

[1] A. Groß *et al.*, J. Electrochem. Soc. **161**, E3015 (2014).
[2] K. Tonigold and A. Groß, J. Comput. Chem. **33**, 695 (2012).

O 96.8 Fri 12:15 S052

Mapping the stabilities of two-dimensional water polymorphs using dispersion-corrected DFT — •Tanglaw Roman and Axel Gross — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

The properties of the contact layer of water or ice on solid surfaces are still not fully understood. The questions that require answers include: How ice-like is water close to a solid surface? How realistic are hexagonal bilayer-based models in describing interfaces with water, both on hexagonal close-packed surfaces and on surfaces of other symmetries? How dense is water at these interfaces? What is the most stable form of ordered water in two dimensions? How different is 2D from 3D crystalline water, and how does the transition go? Which physical factors may contribute to the formation of a water lattice with another symmetry? In response to these, we present a systematic sweep of structural possibilities of water in two dimensions using density functional theory with dispersion corrections, screening one and two-layer structures over different symmetries. Starting with free-standing models, calculations yield structures that differ from those previously reported using classical molecular dynamics, and include several structures which we find more stable than the traditional hexagonal bilayer. Results are discussed with respect to observed water structures confined within graphene sheets, and on how these impact our understanding of water structures at solid surfaces of varying symmetries and interaction strengths.

O 96.9 Fri 12:30 S052

Water adsorption at different noble metal/solution interfaces — •Yujin Tong, Martin Wolf, and R. Kramer Campen — Fritz-Haber-Institut, Abt. Physikalische Chemie, 14195 Berlin, Germany

In aqueous electrochemistry water molecules at the electrode/solution interface determine the structure of the electric double layer, mediate charge transfer mechanisms, and are the reactive species in water electrolysis. Hence gaining a molecular level picture of water structure at the electrode/solution interface, and following its change as a function of electrode potential, is of both fundamental and practical importance. However, achieving such insight via most experimental techniques is challenging. Vibrational sum frequency spectroscopy, owning to its unique selection rules, can selectively probe the structure of water molecules at the electrode/solution interface. Using VSF spectroscopy we here show that: 1). On gold electrodes over a wide range of potentials there are hydrophobic water molecules oriented in such a way that one of their OH groups point towards the gold. 2). After partial oxidation of the gold surface, apparent via cyclic voltammetry and ex-situ characterization via VSF spectroscopy of low frequency Au-O modes, the gold surface becomes hydrophilic and this population of water disappears.

O 96.10 Fri 12:45 S052

Understanding the Structure of Liquid Water at Copper Surfaces — •Suresh Kondati Natarajan and Joerg Behler — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Germany

Solid-liquid interfaces are of fundamental importance in many fields like electrochemistry, corrosion science and heterogeneous catalysis. While in experiment it is often very challenging to obtain detailed information at the atomic level, a wealth of knowledge is in principle available from molecular dynamics (MD). Ab initio MD simulations provide the most reliable description of these systems, but they are severely limited due to the high computational costs associated with studying large "realistic" interfaces. In this talk, a neural network (NN)-based potential for the copper-water interface fitted to density functional theory (DFT) data will be presented which enables to overcome this limitation. Employing this NN potential, we demonstrate that sufficiently long simulations can be carried out allowing to analyze the structural and dynamical properties in detail.