

O 15: Solid-Liquid Interfaces 2: Structure and Spectroscopy

Time: Monday 15:00–18:00

Location: S054

Topical Talk

O 15.1 Mon 15:00 S054
Hydration Layer Mapping at Solid-Liquid Interfaces —
 ●ANGELIKA KÜHNLE — Physical Chemistry I, Department of Chemistry, University Bielefeld, Universitätsstraße 25, 33615 Bielefeld, Germany

Solid-liquid interfaces are omnipresent in nature and technology. Under ambient conditions, the properties of many materials are governed by a thin layer of water at the interface. Understanding processes occurring at the solid-liquid interface thus almost always requires a detailed knowledge of the hydration structure at the interface. Recent improvements in atomic force microscopy (AFM) instrumentation now enable molecular-level insights into the three-dimensional (3D) solvation structure at the interface.

In this talk, the capability of 3D AFM will be presented by discussing the hydration structure at the gypsum-water interface. Gypsum, the dihydrate of calcium sulfate, is an abundant rock-forming mineral in the Earth's crust. It is composed of alternating bilayers of calcium sulfate and water. Upon cleavage, the crystal water is exposed. What is the fate of this crystal water at the aqueous interface? Comparing 3D AFM data with water density maps derived from molecular dynamics simulations allows for elucidating molecular-level details of the gypsum-water interface. Our findings indicate that the crystal water at the interface remains tightly bound, even when in contact with bulk water. Thus, the interfacial chemistry of gypsum is governed by the crystal water rather than the calcium or sulfate ions.

O 15.2 Mon 15:30 S054
Self-assembly and thin film growth dynamics of an ionic liquid on Au(111) investigated in real space — MANUEL MEUSEL¹, MATTHIAS LEXOW¹, AFRA GEZMIS¹, SIMON SCHÖTZ¹, MARGARETA WAGNER², ●SIMON JAEKEL¹, ANDREAS BAYER¹, FLORIAN MAIER¹, and HANS-PETER STEINRÜCK¹ — ¹Chair of Physical Chemistry II, University of Erlangen-Nürnberg (FAU), Germany — ²Institute of Applied Physics, Technical University of Vienna, Austria

Ionic liquids (IL) are organic salts with low melting points, often at or even below room temperature. They have shown promise as solvents and electrolytes, but have also become part of novel catalytic concepts involving solid metal catalysts.

In this context, our group studied the self-assembly and growth dynamics of thin films of 1,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([C₁C₁Im][Tf₂N]) on the model surface of Au(111) using scanning probe microscopy[1,2,3]. Our experiments show that the film undergoes distinct phases between the growth of the wetting layer and subsequent multilayers. Further, 2D film growth is shown to be in competition with the growth of a metastable 3D droplet phase, with the dominant growth mode determined by a combination of temperature and nucleus formation.

[1] Meusel et al. ACS Nano 14 (2020) 9000-9010

[2] Meusel et al. Langmuir 36 (2020) 13670-13681

[3] Meusel et al. J. Phys. Chem. C 125 (2021) 20439-20449

O 15.3 Mon 15:45 S054
Hydration layers at the graphite-water interface: Attraction or confinement? — HAGEN SÖNGEN¹, YGOR MORAIS JAQUES², LIDIJA ZIVANOVIC², SEBASTIAN SEIBERT¹, ●RALF BECHSTEIN¹, PETER SPIJKER², HIROSHI ONISHI³, ADAM S. FOSTER^{2,4}, and ANGELIKA KÜHNLE¹ — ¹Physical Chemistry I, Bielefeld University, Germany — ²COMP Centre of Excellence, Department of Applied Physics, Aalto University, Helsinki, Finland — ³Department of Chemistry, Kobe University, Japan — ⁴Division of Electrical Engineering and Computer Science, Kanazawa University, Japan

Water molecules at solid surfaces typically arrange in layers. The physical origin of the hydration layers is usually explained by (1) the attraction between the surface and the water and/or (2) the confinement of water due to the presence of the surface. While attraction is specific for the particular solid-solvent combination, confinement is a general effect at surfaces. A differentiation between the two effects is critical for interpreting hydration structures. At the graphite-water interface, the solid-solvent attraction is often considered to be negligible. Nevertheless, we observe hydration layers using three-dimensional atomic force microscopy at the graphite-water interface. We use Monte Carlo simulations to explain why confinement alone could cause the forma-

tion of hydration layers. With molecular dynamics simulations, we show that at ambient conditions, there is a significant graphite-water attraction which is pivotal for the formation of layers at the graphite-water interface.

[1] H. Söngen et al., Physical Review B, 100 (2019) 205410

O 15.4 Mon 16:00 S054
Investigation of the wetting layer of [C1C1Im][Tf2N] on Pt(111) by variable temperature scanning tunneling microscopy — ●AFRA GEZMIS, SIMON JAEKEL, MANUEL MEUSEL, ANDREAS BAYER, FLORIAN MAIER, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

With the introduction of Ionic liquids (IL) novel catalytic concepts like the Solid Catalyst with Ionic Liquid Layer (SCILL) approach have emerged. In a SCILL system, a high surface area solid substrate is covered with a thin IL film, and this film modifies catalytically active surface sites at the support. In order to gain better insights in the underlying effects, it is crucial to obtain a detailed understanding of the IL/solid interface. Due to the low vapor pressure of ILs, these interfaces can be investigated in ultra-high vacuum by surface science methods. Herein, we present our first study on the adsorption behavior of 1,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([C1C1Im][Tf2N]) on the reactive Pt(111) surface by variable-temperature scanning tunneling microscopy. We investigated the effect of temperature for coverages up to a closed wetting layer, in particular the formation of 2D islands and their temperature-dependent size. Interestingly, we were even able to detect mobile, single ion pairs on the surface, while for the 2D structures only limited mobility was seen.

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O 15.5 Mon 16:15 S054
bias-dependent switching of molecular nanostructures at the liquid-HOPG interface: the influence of concentration — ●BAOXIN JIA¹, MIHAELA ENACHE¹, SANDRA MIGUEZ-LAGO², MILAN KIVALA², and MEIKE STÖHR¹ — ¹Zernike Institute for Advanced Materials, University of Groningen, Netherlands — ²Institute of Organic Chemistry, University of Heidelberg, Germany

Here we discuss the influence of concentration on the bias-dependent switching of a carboxy-functionalized triarylamine derivative at the nonanoic acid-HOPG interface studied by STM. For a fully saturated solution, a porous phase (chickenwire) was observed for negative sample bias and a close-packed phase for positive sample bias. For a 50% saturated solution, a second porous phase (flower) coexisted with the chickenwire phase at negative sample bias, while the close-packed phase was observed at positive sample bias. For a 20% saturated solution, the two porous phases and the close-packed phase coexisted at positive sample bias, while the two porous phases were observed at negative bias. For all concentrations investigated, a reversible phase transformation between the porous phases and the close-packed phase was accomplished by changing the bias polarity. Additionally, the switching behaviour for a 10:1 mixture of the triarylamine derivatives and 1,3,5-tris(4-carboxyphenyl) benzene molecules at the interface was studied. No intermixed structures were observed. Instead, both molecules formed networks separately but still showed a bias-induced phase transformation. However, the switching occurred for each molecule separately and no effect of cooperativity was detected.

O 15.6 Mon 16:30 S054
In-situ investigation of surface band-bending in the ZnO(0001)-OH/electrolyte interface via the excitonic response. — ●LUIS ROSILLO-OROZCO, CHRISTOPH COBET, and KURT HINGERL — Johannes Kepler University, Linz, Austria

In recent years, the effects of adsorbates on the surface band-bending in ZnO have been studied in UHV and characterized by Valence-Band XPS [1],[2]; showing an alteration of the space-charge region due to the electron transfer that occurs in the adsorption processes. In this work we aim to understand the surface optical properties of a hydroxide stabilized ZnO(0001)-OH surface, previously obtained by chemical etching by Valtiner et al. [3], in contact with 0.1M NaClO₄ as an

electrolyte at a certain applied potential. By changing the cell applied potential, we can, in principle, produce any form of band bending at the semiconductor surface [4] including the flat-band condition. We use in-situ spectroscopic ellipsometry while varying the cell applied potential in order to study the response of the discrete excitons due to the inner electrical fields created by the band bending. We can identify the flat-band potential (V_{fb}) as the one where the imaginary part of the pseudo-dielectric function shows no change at the energy corresponding to the discrete exciton transition. By modulating the potential barrier at the interface we are able to investigate the response of the excitons at any given applied potential. Furthermore, given the significant sensibility of the band-bending to a surface dipole change, it is possible to use this technique to look into the effects of a modification of the surface such as adsorbates.

O 15.7 Mon 16:45 S054

Dynamic Polymorph Formation of a Trimesic Acid Derivative at Solid-Liquid Interface — ●RICHAR ARJARIYA¹, VIPIN MISHRA¹, GAGANDEEP KAUR¹, SANDEEP VERMA¹, MARKUS LACKINGER², and THIRUVANCHERIL G GOPAKUMAR¹ — ¹Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur, UP-208016, India — ²Department of Physics, Technical University of Munich, James-Frank-Strasse 1, Garching 85748 and Deutsches Museum, Museuminsel 1, Munich 80538, Germany

In this work we show the self-assembly of a tricarboxylic acid derivative of trimesic acid (BTA) at heptanoic acid-, nonanoic acid-graphite interface. At both interfaces BTA forms a trimer based-self-assembly, super-flower (SF) pattern. The spontaneously formed SF pattern is observed to be dynamically converting to a dimer-based assembly, chicken-wire pattern (CW), at heptanoic acid-graphite interface while scanning. Interestingly, at nonanoic acid-graphite interface, SF pattern remains stable and not converted to CW pattern. We attribute that the formation energy of both SF and CW patterns is comparable. The difference in the stability of different patterns in heptanoic acid and nonanoic acid is most likely related to the solubility of BTA in these solvents.[1,2]

1) T. N. Ha, T. G. Gopakumar, M. Hietschold, J. Phys. Chem. C, 2011, 115, 21743.

2) M. Lackinger, S. Griessl, W. M. Heckl, M. Hietschold and G. W. Flynn, Langmuir, 2005, 21, 11, 4984-4988

O 15.8 Mon 17:00 S054

in-situ optical probe of chloride-induced surface states in Cu(110)/liquid interfaces — ●SAUL VAZQUEZ-MIRANDA¹, KURT HINGEL¹, and CHRISTOPH COBET^{1,2} — ¹Johannes Kepler Universität Linz Altenberger Straße 69 4040 Linz, Austria — ²Johannes Kepler Universität, Linz School of Education, A-4040 Linz, Austria

While surface states (SSs) appearance and role in metal-electrolyte interfaces are still a controversial debate. The existence of SSs, permits control and tunability of electronic properties of metal-electrolyte interfaces. Resonant excitations among them could enhance, e.g. photocatalytic reactions. SSs and other properties are readily adjustable via an applied electrical potential that is, by promoting changes in the adsorption of ionic species. The electrolyte induces additional scattering and screening effects, so that the electron charge distributions can differ considerably in the presence of high electric fields. We report, by means of electrochemical impedance spectroscopy (EIS) jointly with in-situ reflectance anisotropy spectroscopy (RAS), which aimed to assess the evolution of surface properties and SSs occurring at Cu (110) in contact with an HCl solution. Thereafter, by modeling the RAS response and in comparison with EC-STM measurements, specific surface structures have been identified and ascribed to the optical response. In a specific potential range, three additional resonances are detected in RAS that can be explained by two-dimensional confined SSs.

O 15.9 Mon 17:15 S054

In-situ electrochemical X-ray photoelectron spectroscopy as laboratory technique to study the electrified interface — ●CHRISTOPH GRIESSER, DANIEL WINKLER, TONI MOSER, and JULIA

KUNZE-LIEBHÄUSER — Department of Physical Chemistry, University of Innsbruck, Innrain 52c, Innsbruck, Austria

The interface between a charged metal and an aqueous electrolyte is the most commonly studied in electrochemical surface science, as its properties determine the reactivity of many systems relevant for technological applications. More specifically, in the electrocatalytic conversion of energy, the activity, selectivity and efficiency are determined by the charge transfer between electrolyte and electrode, which is governed by the interfacial properties of the system. Therefore, a fundamental understanding of the interplay between applied potential and surface/interface chemistry is pivotal to further advance energy conversion and storage technologies. While there are several in-situ methods, to characterize the surface structure under reaction conditions, the surface chemistry (i.e. the elemental composition of the surface and the oxidation state of the components) itself is still most often investigated via ex-situ X-ray photoelectron spectroscopy (XPS). This work presents first in situ electrochemical XPS results obtained with a laboratory near ambient pressure (NAP-) XPS system. We show, that it is possible to track the oxidation state of a bulk gold (Au) electrode under reaction conditions, i.e. during anodic oxidation.

O 15.10 Mon 17:30 S054

Structure dependent product selectivity of the CO electroreduction on Au(111) electrodes modified with Cu adatoms — ●DANIEL WINKLER, TONI MOSER, CHRISTOPH GRIESSER, MATTHIAS LEITNER, and JULIA KUNZE-LIEBHÄUSER — University of Innsbruck, Innrain 52c, 6020 Innsbruck, Austria

The efficient conversion of carbon dioxide (CO₂) into valuable hydrocarbons could be a promising solution for storage of excess energy and carbon neutral transportation. The electrochemical reduction of CO₂ has been extensively studied on different monometallic surfaces, where Cu remains the only metal providing a sufficient formation activity to value-added products, such as methane or ethylene. Despite this beneficial behavior, further strategies to increase the product selectivity must be found. This can be accomplished by understanding the exact CO₂ reduction reaction (CO₂RR) mechanism, which remains one of the most challenging problems. Here we focus on the carbon monoxide (CO) reduction on Au(111) electrodes modified with different coverages of Cu adatoms to address this issue. Differential electrochemical mass spectrometry (DEMS) shows an increase in selectivity for the formation of ethylene at low Cu coverages. *In situ* electrochemical scanning tunneling microscopy (EC-STM) and X-ray photoelectron spectroscopy results suggest that two different neighboring CO adsorption sites present at the interface between the metallic Cu islands and the Au(111) surface, which is maximized at low coverages, provide ideal conditions for a facilitated CO-CO coupling reaction resulting in an enhanced formation of ethylene.

O 15.11 Mon 17:45 S054

Electrochemical reflection anisotropy spectroscopy for time-resolved interface structures in aqueous and non-aqueous electrolytes — ●MATTHIAS M. MAY^{1,2}, MARGOT GUIDAT^{1,2}, MARIO LÖW², FLORIAN KELLER², JUSTUS LEIST², and JONGMIN KIM^{1,2} — ¹Universität Tübingen, Institute of Physical and Theoretical Chemistry, Tübingen, Germany — ²Universität Ulm, Institute of Theoretical Chemistry, Ulm, Germany

The microscopic structure of electrochemical interfaces determines many properties that are decisive for the performance of applications in catalysis or batteries. Yet access to this solid-liquid interface at sufficient temporal and spatial resolution is challenging and limits the understanding of this complex interface. Electrochemical reflection anisotropy spectroscopy (RAS) is a powerful emerging tool in spectro-electrochemistry [1], which we apply to a number of systems relevant for energy and matter conversion. Here, we present initial results on InP and Au in aqueous systems as well as select post-Li battery systems. For InP, we can directly observe stability windows with respect to applied potentials and electrolyte composition. We highlight the potential and challenges of electrochemical RAS from a perspective of both computational and experimental spectroscopy.

[1] May and Sprik, New. J. Phys. 20 (2018) 033031.