

CPP 24: Focus session: Structure, chemistry, and ion solvation at solid-liquid interfaces I (joint session O, CPP)

Time: Tuesday 10:30–12:30

Location: HE 101

Topical Talk CPP 24.1 Tue 10:30 HE 101

Water adsorption on Ru(0001): A molecular perspective — ●SABINE MAIER — Department of Physics, FAU Erlangen-Nürnberg, Germany

Water and its dissociation products play an important role in many areas of fundamental science and technological applications. The water molecules at the interface with metal surfaces are arranged differently than those in the bulk liquid or ice due to their strong bonding to the surface. Here, molecular level studies are presented using low temperature scanning tunneling microscopy, that offer new insights into the formation of a wetting layer and the water dissociation process on Ru(0001). We found a bonding motif of the first water layer consisting of rotated hexagonal molecular domains connected by pentagons and heptagons, which deviates significantly from the conventional ice-like water model.[1] Above 150K, we observed the formation of mixed water-hydroxyl structures following partial dissociation. The reaction path for the dissociation process and its energetics will be discussed.[2]

[1] S. Maier et al. Phys. Rev. B 85, 155434 (2012)

[2] S. Maier et al. Phys. Rev. Lett. 112, 126101 (2014)

CPP 24.2 Tue 11:00 HE 101

Probing Water Structure at the α -Al₂O₃(0001) Surface Using Interface Specific Vibrational Dynamics — YUJIN TONG, HARALD KIRSCH, MARTIN WOLF, and ●R. KRAMER CAMPEN — Fritz-Haber-Institut, Abt. Physikalische Chemie, 14195 Berlin, Germany

α -Al₂O₃(0001) surfaces exposed to water are ubiquitous in engineered applications and a useful model for more complicated aluminosilicate surface/water interaction omnipresent in the environment. Despite this ubiquity, gaining a molecular level understanding of water α -Al₂O₃(0001) interaction has proven challenging. It has recently been proposed, based partly on simulation, that the first layer of water on this surface is essentially hydrophobic: while hydrogen bonding occurs within this first layer, neither surface aluminols nor the first layer of molecular water donate a hydrogen bond to overlying bulk liquid. Direct experimental evidence for such a non-wetted water layer has thus far proven elusive. Here we probe the existence of this layer using interface specific vibrational relaxation as a probe of surface water structure. We find, using an ultrafast time resolved infrared pump - vibrational sum frequency probe scheme, that the T₁ of OH groups at the α -Al₂O₃(0001) surface is \approx 8 ps: intermediate between that of surface aluminols in contact with excess water (< 1 ps) and that of isolated surface OH groups on oxide surfaces (> 100 ps). This intermediate T₁ is the first direct experimental insight consistent with a non-wetted interfacial water layer on the α -Al₂O₃(0001) surface.

CPP 24.3 Tue 11:15 HE 101

A joint *first principles* and ATR-FTIR study of the vibrational properties of interfacial water at Si(100):H-H₂O solid-liquid interfaces — ●LEI YANG¹, STEFANIE TECKLEBURG¹, ANDREAS ERBE¹, STEFAN WIPPERMANN¹, FRANCOIS GYGI², and GIULIA GALLI³ — ¹Max-Planck-Institute for Iron Research, Duesseldorf, Germany — ²University of California, Davis, Davis, United States — ³University of Chicago, Chicago, United States

Understanding the structural and bonding properties of solid-liquid interfaces is crucial for a wide range of (photo-)electrochemical applications, such as e. g. solar water splitting and electrolysis. However, there are no experimental techniques presently available allowing one to directly probe the microscopic structure of solid-liquid interfaces. We present a joint investigation of the vibrational properties of interfaces between liquid water and prototypical semiconductor substrates,

i.e. hydrogenated silicon surfaces. We carried out (ATR-FTIR) spectroscopy measurements and *ab initio* molecular dynamics simulations. The latter allowed us to interpret the experiments and to unravel specific bonding configurations and interactions of water molecules with the solid surfaces. 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. This work provides a solid basis for investigating ion solvation and chemical processes at the interface. G. G. and F. G. acknowledge DOE-BES Grant No. DE-SS0008939.

Topical Talk CPP 24.4 Tue 11:30 HE 101

Using resonant inelastic soft x-ray scattering maps to study liquids, gases, and their interfaces — ●LOTHAR WEINHARDT — IPS, Karlsruhe Institute of Technology (KIT), Eggenstein-Leopoldshafen, Germany — ANKA Synchr. Radiation Facility, KIT, Eggenstein-Leopoldshafen, Germany — Dep. of Chem., University of Nevada, Las Vegas, U.S.A. — ITCP, KIT, Karlsruhe, Germany

X-ray emission spectroscopy (XES) and Resonant Inelastic X-ray Scattering (RIXS) have recently been applied to study liquid and gaseous systems. Such experiments became possible with new specialized experimental setups and given a unique insight into the electronic and vibrational structure of these systems. In this way, information on solvent/solute interactions, hydrogen bonding, molecular symmetries, excited-state dynamics, and many other aspects could be gathered. Finally, interfaces between solids and a gas/liquid can be studied in an in-situ fashion, which is of particular relevance for a wide range of applied systems including catalysis, electrochemistry, or the influence of environmental conditions on surfaces. In this presentation, we will report on our recent progress on studying such systems using XES and RIXS. By the development of a high-transmission soft x-ray spectroscopy setup we are able to measure complete Resonant Inelastic soft X-ray Scattering (RIXS) maps. These maps give a comprehensive picture of the electronic structure of occupied as well as unoccupied electronic states of the studied system. We will demonstrate the power of this approach by discussing the results obtained on selected liquids, gases, solutions, as well as gas/solid- and liquid/solid interfaces.

Topical Talk CPP 24.5 Tue 12:00 HE 101

Effect of flow on water organization at solid interfaces — ●MISCHA BONN — Max Planck Institute for polymer research, Mainz, Germany

At the surface or interface of water, the water hydrogen-bonded network is abruptly interrupted, conferring properties on interfacial water different from bulk water. Owing to its importance for disciplines such as electrochemistry, atmospheric chemistry and membrane biophysics, the structure of interfacial water has received much attention.

We elucidate the structure and structural dynamics of interfacial water using ultrafast surface-specific sum-frequency generation (SFG) vibrational spectroscopy. We make use of the fact that the SFG signal depends critically on the interfacial organization of water molecules. We attempt to bridge continuum models of laminar flow along interfaces, with molecular-level descriptions of the Stern and diffuse layer, which describe the near-surface distribution of ions.

For water at two different mineral interfaces, we report a dramatic effect of water flow along the mineral surface on the organization of water at the interface. Our observations can be explained by considering the coupling between the flow and the dissolution chemistry at the interface. Even for low-soluble quartz at neutral pH, dissolution plays a key role in determining the interfacial water organization.