O 4: Solid-Liquid Interfaces: Structure

Time: Monday 10:30–13:00 Location: H4

O 4.1 Mon 10:30 H4

The Impact of the Gold Interface on the Structure and Properties of Aqueous Sodium Citrate Solution — •Elspeth Smith and Marialore Sulpizi — Ruhr-Universität Bochum, Bochum, Germany

Gold nanoparticles (AuNPs) are used widely, with many commercial applications due to their being well suited for catalysis. Owing to the method of production/stabilisation, AuNPs are often suspended in a solution of aqueous sodium citrate, a system with complicated interplays which we seek to elucidate in this work.

Through the use of a previously developed polarisable gold model we have performed all atom classical molecular dynamics simulations of a variety of systems and concentrations of sodium citrate solution, employing the SPC/E water model and a CHARMM based citrate model, with and without a gold interface. In order to better understand the dual effect of both the gold interface and sodium citrate on the water's structure, we employ a number of widely used order parameters for water. As the structure of water in close proximity to AuNPs is difficult to observe experimentally and has possibly large applications for their use in catalysis, we hope to obtain a better understanding of this elusive phenomenon.

O 4.2 Mon 10:45 H4

Rationalizing the "Anomalous" Electrochemical Stark Shift of CO at Pt(111) Through Vibrational Spectroscopy and Density-Functional Theory Calculations — •Elias Diesen[1], Mehmet Ugur Coskun[2], Sergio Díaz-Coello[2], Vanessa J. Bukas[1], Julia Kunze-Liebhäuser[2], and Karsten Reuter[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Department of Physical Chemistry, University of Innsbruck, Austria

We employ infrared reflection absorption spectroscopy (IRRAS) and first-principles density-functional theory (DFT) to revisit the reported "anomalous" negative Stark shift of the CO stretch frequency at Pt(111) in aqueous electrolyte [1]. Our measurements confirm the existence of a potential region with negative Stark shift around 0.5 V vs. RHE at sufficiently high CO concentration in the electrolyte. As these are exactly the same conditions for the occurrence of a phase transition from a (2×2)–3CO to a $(\sqrt{19} \times \sqrt{19})$R23.4°–13CO adsorbate structure [2], we explicitly compute the Stark shift for these two phases using DFT. Neither phase exhibits a negative Stark shift, but the absolute stretch frequencies of atop CO in the two structures are slightly shifted with respect to each other. Remeasuring IRRAS with high resolution indeed reveals a doublet character of the absorption band in the potential region corresponding to the negative Stark shift. Separate fits of the two components then yield positive Stark shifts in quantitative agreement with the calculated values.

[1] Stamenkovic et al., J. Phys. Chem. B 109, 678 (2005); [2] Wei et al., J. Phys. Chem. C 125, 3066 (2021)

O 4.3 Mon 11:00 H4

Adatom Dynamics at Water/Pt(111) Interface from Ab Initio Free Energy Analysis — •Sung Sakong[1], Jonas Lindner[2], Ulrich Ross[3], Michael Seibt[3], Christian Jooss[2], and Axel Gross[1] — [1]Institute of Theoretical Chemistry, Ulm University, 89081 Ulm, Germany — [2]Institute of Materials Physics, University of Göttingen, 37077 Göttingen, Germany — [3]4th Institute of Physics Solids and Nanostructures, University of Göttingen, 37077, Göttingen, Germany

Recent electron diffraction experiments investigated the local structures of the water/Pt(111) interface, a selected model system for investigating the structural properties of the electric double layer (EDL). The reconstructed phase signals of the diffraction data yield the time average of the interface structures with Angstrom resolution and observe the static Pt lattice and dynamic particles above the lattice. Since the time-averaged signals from experiments are often challenging to relate to the corresponding atomic structures of dynamic particles, we probe the interface structure by including Pt adatoms using the ab initio molecular dynamics (AIMD) method. The free energy of Pt adatoms is analyzed by including the vibrational entropy calculated from the AIMD trajectories using the two-phase thermodynamics method. While the dynamics of water molecules are captured within the AIMD trajectories, the relatively slow Pt adatom dynamics are estimated by a free energy analysis, Blue Moon ensemble sampling. By comparing the Water/Pt(111) and Vacuum/Pt(111) models, we will discuss the role of surrounding water molecules and try to relate the model EDL configurations to the experimental findings.

O 4.4 Mon 11:15 H4

Effect of the damping function in dispersion corrected density functional theory on properties of liquid water — •Knut Nikolas Lausch[1,2], Redouan El Haouari[1,2], Daniel Trzewik[1,2], and Jörg Behler[1,2] — [1]Theoretische Chemie II, Ruhr-Universität Bochum, Germany — [2]Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, Germany

Accounting for non-local dispersion interactions is essential to achieve chemical accuracy when applying approximate density functional theory (DFT) to large molecular or condensed systems. A popular approach is to add a damped correction potential, based on the London formula, after convergence. Damping is required to avoid the diverging short-range behavior of the London formula and double counting of interactions treated locally by the exchange-correlation (xc) functional. Often two forms of damping, known as zero- and Becke-Johnson-damping, are employed and it is generally assumed that the choice has only a minor impact on performance even though the resulting correction potentials differ quite dramatically. Here, we demonstrate that the choice of damping function can have a major impact on properties obtained from molecular dynamics simulations of liquid water suggesting that the significance of damping in dispersion corrected DFT needs to be reevaluated.

O 4.5 Mon 11:30 H4

Elucidating the double layer structure of protic ionic liquid electrolytes for next-generation fuel cells — •Christian Rodenbücher, Yingzhen Chen, Federico Parisi, Piotr M. Kowalski, and Carsten Korte — Forschungszentrum Jülich GmbH, Institute of Energy Technologies (IET-3 & IET-4), 52425 Jülich, Germany

Polymer electrolyte membrane fuel cells (PEMFCs) are the backbone of a future hydrogen-based renewable energy system. Increasing their operation temperature to 100–160 °C would allow for a simpler water management and the use of waste heat. In this temperature range, conventional proton conducting polymers such as Nafion are not applicable, since they rely on the presence of water. Hence, we study immidazolium-based protic ionic liquids, which provide a high thermal and chemical stability and a high proton conductivity. We present experimental investigations using impedance spectroscopy, infrared spectroscopy, and atomic force microscopy combined with atomistic simulations by molecular dynamics and density functional theory. Our results reveal that depending on the electrode charge, a dense layered structure of alternating anion and cation layers is formed. Upon the addition of water, which is naturally produced during fuel cell operation, the structuring becomes distorted resulting in the accumulation of water at the interface and the increase of the onset potential of the oxygen reduction reaction. Our findings illustrate that the kinetics of the fuel cell reactions is influenced not only by bulk properties of the electrolyte but also by the adsorption at the electrode, which may be tuned by designing ionic liquids with bespoke properties.

O 4.6 Mon 11:45 H4

Polarizable model of graphite and its applications to nanotechnology — Krishan Kanhaiya[1], Hendrik Heinz[2], and •Marialore Sulpiziz[3] — [1]Ruhr-Universität Bochum — [2]University of Colorado Boulder — [3]Ruhr-Universität Bochum

Graphitic materials are of significant importance in the research and industrial community due to their tunable electrical conductivity, band gap, thermal property and high strength to mass ratio. They are used in battery or fuel cells as electrodes, refractory material, lubricant, aerospace, water purification, and bio-sensing etc.. We present a realistic, all-atom polarizable model of graphite with flexible dummy electrons to model the polarizable nature of electron cloud, similar to the approach which was used to describe image charge effects for ions approaching metal surfaces. The models predict density, lattice parameters, surface energy, hydration energy, water contact angle and elastic constants within 1%, 1%, 5%, 5%, 5% and ~15 % respectively as per the Interface Force Field protocol. Additionally, the model also reproduces experimental and DFT data on binding energies and profiles for cations , anions and neutral molecules (water, amino acids, and organic molecules). We further discuss friction coefficient across the graphene surface and nanotubes in order to model flow characteristics of water over such surfaces . An accurate description of such systems is key to design improved functional materials and devices for water desalination and blue energy (electric energy from salinity gradient in two different electrolyte solutions).

O 4.7 Mon 12:00 H4

Elucidating the interaction of small organic pollutants at ice surfaces with sum-frequency generation spectroscopy — •Gurivi reddy Yettapu[1,2], Luca B. Manning[2], and Jenee D. Cyran[2] — [1]University of Duisburg-Essen, Duisburg, Germany — [2]Boise State University, Boise, USA

Small organic pollutants interacting with ice and water surfaces in the troposphere are relevant for atmospheric compositional changes.[1] Their interactions with hexagonal basal-plane oriented single crystalline ice have been scarcely revealed.[2] Methanol and acetone are two smallest organic molecules that interact differently with single crystalline ice surfaces. Herein, we probed their direct interaction on ice and water interfaces with surface-specific, mode selective sum-frequency generation spectroscopy. Our results show significant difference in the frequency of H-bonding O-H oscillators of water molecules present at the ice interface.[3] The distinct behavior of the adsorption of these molecules could explain their relevant atmospheric compositions. [1] F. Dominé and P. B. Shepson, Science, 297, 1506-1510 (2002). [2] J. D. Cyran et al., Angew. Chem. Int. Ed., 58, 3620-3624 (2019). [3] G. R. Yettapu et al., Faraday Discussions, just accepted (2024).

O 4.8 Mon 12:15 H4

Exploring Charged Aqueous Interfaces with Depth-Resolved SFG/DFG Vibrational Spectroscopy — •Sarabjeet Kaur, Álvaro Díaz Duque, Alexander Fellows, Martin Wolf, and Martin Thämer — Department of Physical Chemistry, Fritz Haber Institute of the Max Planck Society

Charged aqueous interfaces are crucial in biological, atmospheric, and chemical processes, where surface electric fields influence ion distributions and interfacial dynamics. Water mediates these interactions, with effects spanning nanometers. The Gouy-Chapman (GC) model and variants describe ion distributions but oversimplify water as a continuous medium, neglecting molecular-level behaviors like impact of structure, orientation, and hydrogen-bonding dynamics. This omission leaves important aspects of interfacial phenomena unexamined. We address these gaps using depth-resolved vibrational spectroscopy combining phase-resolved sum- and difference-frequency generation (SFG and DFG). This technique reveals depth-dependent water responses and connects electric potential anisotropy with molecular reorientation. Our findings identify two distinct interfacial layers, challenging the single-layer GC model. Spectral analysis shows structural differences between the compact and diffuse layers. Additionally, concentration-dependent studies highlight discrepancies between the observed decay length of orientational anisotropy and the predicted Debye length. These results underscore the limitations of the GC variant model and continuum solvent approaches in capturing water's molecular-level behavior at charged interfaces.

O 4.9 Mon 12:30 H4

Resolving the water structure at iron-oxide/water interface — •Harsharan Kaur[1], Moritz Zelenka[1,2], and Ellen Backus[1,2] — [1]University of Vienna, Faculty of Chemistry, Institute of Physical Chemistry, Währinger Str. 42, 1090 Vienna, Austria — [2]University of Vienna, Vienna Doctoral School in Chemistry (DoSChem), Währinger Str. 42, 1090 Vienna, Austria

Among different iron-oxide polymorphs, Fe3O4 is utilized as a catalyst for industrial-gas shift and photocatalytic water splitting reactions, where it often encounters water. [1] Fe3O4 surface is known to protonate and deprotonate on contact with pH-variant aqueous media. [1] However, less is known about the interfacial species and their molecular orientation under ambient condition. Herein, we explore these attributes at the magnetite-water interface as function of solution pH with macroscopic amount of water. Magnetite films of ~50 nm thick were prepared using magnetron sputtering and were found to sustain Fe3O4 phase combined with FeO or γ-Fe2O3 state. The interface was examined with SFG vibrational spectroscopy. Due to its selection rule, a vibrational spectrum of only the interfacial species is obtained in case of centrosymmetric bulk materials like Fe3O4 and water. We observed a pH-dependent variation in the H-bonding strength of the interfacial water molecules and the presence of Fe-OH groups at alkaline pH. Besides, the water orientation varies with pH. By comparing the results for Fe3O4 to Fe2O3, a detailed molecular picture of interfacial water at these relevant iron oxides will be presented. [1]. Z. Bielan, S. Dudziak, A. Kubiak, E. Kowalska, Appl. Sci. 11 (2021) 10160.

O 4.10 Mon 12:45 H4

Structural and dynamical properties of the Solvated Electron From Ab Initio Molecular Dynamics Simulations — •Anna Karolyna Macieira Silva Gomes and Marialore Sulpizi — Ruhr-University Bochum, Bochum, Germany

The solvated electron is a critical species in plasma/liquid and plasma/solid/liquid interfaces, serving as the primary reducing agent generated at plasma electrodes in contact with liquids. Recently, experimental studies have revealed differences in the properties of solvated electrons formed via plasma compared to other methods, such as water radiolysis. It has been proposed that the unique conditions at plasma interfaces, including electric fields, may alter the electron's solvation properties.

Despite extensive investigations into solvated electrons, their behavior in the presence of electric fields remains unexplored. This project employs atomistic molecular dynamics simulations to explore the influence of electric fields on the structure and dynamics of solvated electrons in aqueous solutions. Ab Initio Molecular Dynamics (AIMD), utilizing hybrid functionals, have been shown to offer a accurate approach to modeling the electronic properties of this system, while remaining computationally feasible for capturing relevant time and length scales.