## O 87: Solid-liquid interfaces: Structure, spectroscopy

Time: Thursday 15:00–17:15 Location: TRE/PHYS

O 87.1 Thu 15:00 TRE/PHYS

**Interfacial Enrichment and Reactivity of Organic Molecules in Ionic Liquids** — •Alisson Ceccatto Santos[1], Luciano Sanchez Merlinsky[2,3], Luis M. Baraldo[2,3], Federico J. Williams[2,3], Florian Maier[1], and Hans-Peter Steinrück[1] — [1]Lehrstuhl für Physikalische Chemie 2, Friedrich-Alexander-Universität Erlangen-Nürnberg — [2]Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires — [3]Instituto de Química Física de los Materiales, Medio Ambiente y Energía, CONICET- Universidad de Buenos Aires

Controlling the surface composition of metalloporphyrins in ionic liquids (ILs) is crucial for designing photoactive materials. Here, we investigate the interfacial behavior of zinc-didodecylporphyrin molecules (Zn-DDP) dissolved in the 1-butyl-3-methylimidazolium hexafluorophosphate [C4C1Im][PF6] IL using angle-resolved X-ray photoelectron spectroscopy (ARXPS). Upon mild heating, Zn-DDP undergoes spontaneous demetallation, evidenced by the appearance of aminic (-NH-) and iminic (=N-) nitrogen XPS signals. Our measurements reveal extremely high surface enrichment of porphyrins at the IL/vacuum interface, with the dodecyl chains oriented toward the vacuum. ARXP spectra reveal that the surface enrichment increases with increasing temperature. Our findings provide molecular-level insights to guide the design of photoactive interfaces in IL systems. Acknowledgements: Alexander von Humboldt Foundation for a Humboldt Research Fellowship for postdocs

O 87.2 Thu 15:15 TRE/PHYS

**How is the hydrophobic force modified by an oscillation frequency in saline conditions?** — •Chiara Wagner, Paul Stöcher, Laura Mears, and Markus Valtiner — Vienna University of Technology, Vienna, Austria

There have been many investigations over the years regarding the mechanism behind the hydrophobic force and over how long a range it can be felt [1]. We present a detailed set of AFM force measurements of hydrophobic SAM modified surfaces, with varying salt concentration and oscillation frequency (0-2kHz). We observe dynamic changes in the force curve characteristics with both salt concentration and oscillation frequency. The changes lead to a reduction of the average force with increasing applied frequency, while multiple distinct characteristic curves are present and enhanced by certain conditions. We also notice changes in the range of the force away from the surface. Altogether, the results we will present bring new insight into the mechanism of hydrophobic interactions.

[1] W. A. Ducker and D. Mastropietro, Current Opinion in Colloid & Interface Science, 2016, 22, 51*58.

O 87.3 Thu 15:30 TRE/PHYS

**Interfacial non-Markovian friction determines non-linear spectral shifts at the water-graphene interface** — •Johannes Schröter, Louis Lehmann, Shane Carlson, and Roland R. Netz — FU Berlin, Fachbereich Physik, Arnimallee 14 14195 Berlin

Understanding the behavior of aqueous interfaces is crucial for various applications. In particular, the graphene water interface plays a key role for energy storage and energy conversion, however, its properties remain poorly understood. Using DFT molecular dynamics simulations we show that the sum-frequency signal of non-hydrogen bonded OH bonds is significantly red-shifted at the water-graphene compared to the water-air interface, in agreement with recent experiments. The red shift is demonstrated to be caused by non-Markovian friction between the graphene surface and interfacial water, which offers a direct method to extract solid-water interfacial friction properties from nonlinear spectroscopy.

O 87.4 Thu 15:45 TRE/PHYS

**Structural Stability of NaCl and KCl Cleavage Surfaces in the BMIM-PF6 Ionic Liquid** — •Ebru Cihan[1], Natalia Janiszewska[2], Kamil Awsiuk[2], Qingwei Gao[3], Rong An[4], Ronen Berkovich[5], and Enrico Gnecco[2] — [1]TU Dresden, Dresden, Germany — [2]Jagiellonian University, Krakow, Poland — [3]Shanghai University of Electric Power, Shanghai, China — [4]Nanjing University of Science and Technology, Nanjing, China — [5]Ben-Gurion University of the Negev, Beer-Sheva, Israel

An investigation was conducted into the evolution of freshly cleaved NaCl(100) and KCl(100) surfaces exposed to the ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-PF6). The surfaces were repeatedly scraped using AFM, resulting in contrasting responses from the two surfaces to the IL. In the case of NaCl, the cleavage step edges are slightly eroded, and the surface is progressively smoothed by the AFM tip. These changes are accompanied by a continuous increase in the friction force. In the case of KCl, a pronounced dissolution of the surface is evident immediately following contact with the IL. The surface is then smeared in the area scratched by the tip and even beyond. An increase in the friction force is also observed but only at the onset of the surface modification process. Crystallites (100-200 nm in size) are observed across the unscratched areas of KCl, but not of NaCl. This result was corroborated by MD simulations and Raman spectroscopy, which revealed that IL exhibits a stronger interaction with the KCl surface, ultimately forming a BMIM-PF6 adlayer. [1] E. Cihan et al., Langmuir 41, 13793 (2025)

O 87.5 Thu 16:00 TRE/PHYS

**How Water Controls Ion Adsorption at Aqueous Interfaces via Entropic and Dielectric Interplay** — •Florian Altmann[1], Matteo Olgiati[1], Moritz Zelenka[2], Joanna Dziadkowiec[3], Andreas Kretschmer[1], Alper T. Celebi[1], Laura L.E. Mears[1], Ellen H.G. Backus[2], and Markus Valtiner[1] — [1]Vienna University of Technology, Institute of Applied Physics, Wiedner Hauptstrasse 8-10, A-1040, Vienna, Austria — [2]University of Vienna, Faculty of Chemistry, Institute of Physical Chemistry, Währinger Straße 42, 1090 Vienna, Austria — [3]NJORD Centre, Department of Physics, University of Oslo, Oslo 0371, Norway

Ion-specific behavior at aqueous interfaces remains poorly understood. Using $Li^+$, $Ca^{2+}$, and $Cs^+$, we combine quantitative atomic force microscopy on muscovite mica with molecular dynamics simulations and sum-frequency generation spectroscopy to resolve interfacial thermodynamics at molecular resolution. Pair correlation functions link ion-water-surface organization to entropy and electrostatics. Small or highly charged ions compact interfacial water, creating entropic penalties and strong dielectric screening, whereas larger ions deplete interfacial water, lower screening, and promote overadsorption. This interplay between entropy and screening governs inner double-layer formation and provides a molecular framework for ion-specific adsorption in complex electrolytes.

O 87.6 Thu 16:15 TRE/PHYS

**Accessing interfaces of ionic liquids in vacuum** — •Florian Maier and Hans-Peter Steinrück — Lehrstuhl Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg

About one decade ago, the perspective "Surface science goes liquid" described possibilities of investigating surfaces and interfaces of vacuum-stable liquids with surface science tools under ultrahigh vacuum (UHV).[1]

Since then, new experimental concepts and setups have been developed considering the special requirements for handling ionic liquids (ILs) in vacuum in order to push the boundaries of surface science experiments further.

In this presentation, some of our experimental developments including key showcases will be presented demonstrating at which level molecular properties of IL interfaces can be accessed under ultra-clean and well-defined UHV conditions.

References [1] H.-P. Steinrück, 2010, Surf. Sci. 604, 481-484 / DOI: 10.1016/j.susc.2009.12.033.

O 87.7 Thu 16:30 TRE/PHYS

**Beyond the Electric Dipole Approximation: Electric and Magnetic Multipole Contributions Reveal Biaxial Water Structure from SFG Spectra at the Air-Water Interface** — •Louis Lehmann[1], Maximilian R. Becker[1], Lucas Tepper[1], Alexander P. Fellows[2], Álvaro Díaz Duque[2], Martin Thämer[2], Martin Wolf[2], and Roland R. Netz[1] — [1]Department of Physics, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Sum-frequency generation (SFG) analysis has been hindered by the lack of quantitative predictions for higher-order multipole contributions. Magnetic dipole and electric quadrupole terms, though determined by bulk properties, appear in all SFG spectra and obscure connections to interfacial structure. We present a simulation-based framework that predicts all multipole contributions and provides depth-resolved spectra for precise localization of features. Applied to the air-water interface, it reproduces experimental spectra across polarization combinations in both bending and stretching regions. Higher-order multipoles are essential: in the bending band, electric and magnetic dipoles are comparable, while the quadrupole dominates; in the OH-stretch region, the quadrupole accounts for the 3600/cm shoulder. Isolating the true second-order electric-dipole susceptibility reveals pronounced biaxial ordering of interfacial water and enables reliable interfacial structure determination from SFG spectra.

O 87.8 Thu 16:45 TRE/PHYS

**Heat transfer across nanometre-sized water meniscus** — •Oscar Mateos[1], Ruben Lopez[2], Pablo Martinez[1,3], Guilherme Vilhena[1], Nicolas Agrait[2,4], and Juan Carlos Cuevas[3,4] — [1]Instituto de Ciencia de Materiales de Madrid (ICMM-CSIC), 28049 Madrid, Spain — [2]Departmento de Física de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Madrid, Spain — [3]Departamento de Física Teórica de la Materia Condensada, Universidad Autónoma de Madrid, 28049 Madrid, Spain — [4]Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049 Madrid, Spain

Heat transfer in nanoscale gaps is of key relevance for a variety of technologies. Recent experiments have reported contradictory results shedding doubts about the mechanisms for heat exchange in nanometre-sized gaps. We aim at resolving this controversy by measuring the thermal conductance of gold atomic-sized contacts with a custom-designed scanning tunnelling microscope that incorporates a novel thermal probe, enabling the measurement of thermal and electrical conductance in different transport regimes. When the electrodes are separated by a nanometre-sized gap, we observe thermal signals which cannot be explained with standard heat transfer mechanisms. Through non-equilibrium molecular dynamic simulations, we elucidate that these anomalous signals are due to thermal conduction through water menisci that form between tip and sample under customary operation conditions.

O 87.9 Thu 17:00 TRE/PHYS

**Charging dynamics of the electrical double-layer in nanometre sized channels** — •Marco Schönig, Serge Lemay, and Marc Koper — Leiden University, Leiden, The Netherlands

Nanoporous electrodes play a crucial role in modern energy storage and conversion technologies. However, despite their ubiquitous usage, the impact of nanoscale geometrical confinement on their electrochemical properties remains poorly understood. This is particularly relevant when the pore dimensions become so confined that the double layers of opposing sides overlap. A key challenge in studying this phenomenon in a systematic manner is the necessary precise control of the experimental dimensions[1]. We aim to bridge this gap by utilizing modern nanofabrication techniques to fabricate model gold slit electrodes[2].

In this contribution, we present the charging behaviour of electrodes with 5 - 20 nm wide slits, under confined and unconfined conditions. We further explore the usage of ATR-IR spectroscopy to probe the electrolyte in the slit electrodes by using micro-grooved Si wafers as substrate[3].

References [1] J. Wordsworth et al. Angew. Chem. Int. Ed. 2022, 61, e202200755; [2] L. Rassaei et al. J. Phys. Chem. C 2012, 116, 10913; [3] T. A. Morhart et al. Anal. Chem. 2017, 89, 11818.