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Putting the spotlight on water: Local thermodynamics and local electrostatic fields at interfaces

Electrode-electrolyte interfaces are decisive in electrochemical energy conversion. Model concepts have been defined over decades. Yet, a microscopic insight into the local solvation motifs, into local pK_a values, and a molecular description of the details of the transport of ions at electrochemical interfaces under non-equilibrium conditions are still a scientific challenge to be addressed. There is a clear need to go beyond the classical electrochemical double layer picture based on the Gouy-Chapman-Stern model and disclose the molecular underpinnings to foster rational advances and manipulation at electrified interfaces.

Solvents greatly impact non-equilibrium charge transfer processes as well as chemical transformation at electrified interfaces. While the impact of the electrode size and electrode material has been subject to a wealth of studies, the role of the interfacial hydration and the contribution to free energy barriers under a potential are yet to be explored. Harnessing our recent advances on local solvation we have addressed these questions by experiment and in simulations. We have set-up up novel spectroscopic tools to probe the role of the solvent in chemical and biological processes. The THz frequency range – which has been technological challenging in the past to access- can be fully explored now with FT spectroscopy, but also with novel ps THz sources (average power of > 1 mW), which will extend the experimental possibilities in this technically challenging frequency range [1]. THz spectroscopy allows to probe most sensitively interfacial hydration. The low frequency spectrum gives access to desolvation and resolvation processes at the interface, which contribute to the free energy cost of prototype reactions. Applications range from electrified interfaces up to protein condensate formation [2]. In the past years, we have developed Terahertz (THz)-calorimetry, i.e., the science of measuring low frequency spectra to derive the solvation free energy changes associated with biological and chemical processes. It is well known that the solvation free energy can be expressed by a sum of the free energy changes owing to cavity formation (hydrophobic solvation) and solute insertion (hydrophilic interactions): $\Delta G_{solvation} = \Delta G_{cavity} + \Delta G_{insertion}$. The fundamental idea behind THz-calorimetry is that spectroscopic observables, which can be quantitatively measured in the THz frequency range, hold information on the influence of the solute and local environment on solvation free energies. We could show that measures of the partial contribution of two distinct water populations are linearly correlated with the changes in solvation entropy and enthalpy. These two populations are: water molecules forming a 2-dim H-bond network at the interface or around a cavity (*hydrophic hydration*) and the water molecules which are hydrogen bonded to a solute or an interface (*hydrophilic hydration*). The linear correlation factors are very general; they are found to be temperature and solute-independent scaling quantities [2]. THz calorimetry allows to probe changes in entropy and enthalpy not only under equilibrium, but in real time (ps time resolution) and in inhomogeneous environments [2].

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Beyond Gouy-Chapman-Stern

The specific arrangement of the water hydrogen-bond (H-bond) network in contact with metal surfaces was recently recognized to confer unique solvation properties to metal–aqueous interfaces, characterized by the coexistence of local hydrophobic and hydrophilic solvation environments, and by large spatial variations in solvation free energies within a few ångströms from the surface [3, 4] Fascinating implications of such a rapidly changing, spatially dependent solvation environment for interfacial chemistry continue to emerge in recent studies, including, effects on the adsorption and transport of reactive species and ions [2, 4-6] across the interface, acid–base chemistry [6], transport properties of interest in nanofluidics [8], as well as the outcome of several chemical reactions [9, 10].

By combining THz spectroscopy and constant-potential molecular dynamics simulations, we showed [3, 7] for Au/water interfaces that strong metal–water interactions template a highly ordered water adlayer physisorbed on the surface, where intra-layer water–water H-bonds between adlayer molecules and interactions with the surface are both maximized.

The hydrophobic solvation layer shows large density fluctuations which reduce the free-energy cost required to form a cavity in the liquid that can host a solute, which we directly comput-

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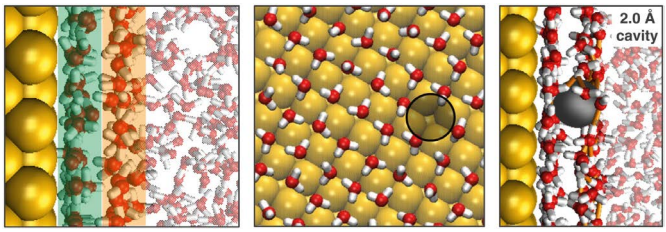

Fig. 1: Displayed is the interfacial water layer at the gold surface. In the first layer (shown in green), water is H-bound to the surface and forms an ordered 2D hydrogen bond network with 2.9 hydrogen bonds/molecule on average. Please note that most H_2O molecules lie flat on Au(100). The next layer is hydrophobic in the sense that typically only 0.4 H-bonds/molecule formed to the 1st layer, promoting the formation of cavities (grey sphere in the side-view snapshot). (Copyright S. Pezzotti)

ed from our MD simulations [3]. The decrease in local density fluctuations implies that the free energy cost to form a cavity increases within the adlayer compared to bulk water thereby creating a solvation driving force that disfavors the adsorption of hydrophobic and amphiphilic species in direct contact with the surface (i. e., inner-sphere adsorption) and favors the localization in between the first and second layer. This free energy barrier is size-dependent but not voltage-dependent.

The high H-bond connectivity within the adlayer leaves few sites available for hydrogen bonding with the adjacent water layer. Hence, next to the hydrophilic metal–adlayer interface, where density fluctuations are suppressed, a water–water interfacial region with low H-bond density is formed, in which density fluctuations are enhanced and (outer-sphere) adsorption of hydrophobic or amphiphilic species is promoted, as typical of hydrophobic interfaces.

These two sides of the interface are confined within less than one nanometer from the metal surface, giving rise to large variations in the cavity contribution to solvation free energies as a solute (or ion) traverses the interface. We quantified this effect by directly computing the cavity formation free energy profile across the interface from MD simulations. By numerically evaluating the effects of the size, shape, and position of the cavity formed by ideal hard-sphere solutes, we showed how these spatial variations give rise to new physics of hydrophobic solvation compared to what is known in bulk systems and encoded in existing solvation theories, such as the Lum–Chandler–Weeks theory [3]. For example, while the free energy of cavity formation is dominated by volume effects for small solutes in the bulk, we show that at the interface the size dependence of hydrophobic solvation becomes markedly different and is modulated by the position, shape, and orientation of the cavity. Even for small cavities that can host molecules such as CO_2, H_2, N_2, O_2, and small alkanes and alcohols – relevant to electrocatalysis and renewable energy technologies – these variations in solvation free energies are large, up to ~0.5 eV, and thus sufficient to significantly alter the outcome of electrochemical processes.

THz ATR: Probing experimentally structural hydration motifs at the interface

The two-dimensional extended network of intra-adlayer H-bonds – parallel to the surface – that covers the metal surface provides a prominent spectroscopic signature in the THz spectroscopic range, which directly probes the intermolecular modes and thus the radial and angular part of the potential energy surface. The intramolecular stretch of the 2-dim H-bond network is centered around ~175 cm^{-1}, which is red-shifted relative to the H-bond stretching band of bulk water (~190 cm^{-1}) due to a loss of cooperativity in the interaction energy [1, 7].

Moreover, the direct interaction of adlayer water molecules with the surface, together with excluded-volume effects due to proximity to the interface, constrains their librational motions, i.e., the hindered rotation of water molecules. This results in a blue shift of the librational mode, which is most sensitive to orientational hindrance. As a consequence, we observe a partial decrease in the range of soft librational modes (~400 cm^{-1}) and a partial increase in the frequency range probing hard librations (~600 cm^{-1}) with respect to bulk water, leading to an approximately linear increase in Δα (from negative to positive values) across the 400–600 cm^{-1} range [1, 7].

In Bochum, we have set-up an Attenuated Reflection Set-up in the THZ frequency range which allows to probe changes

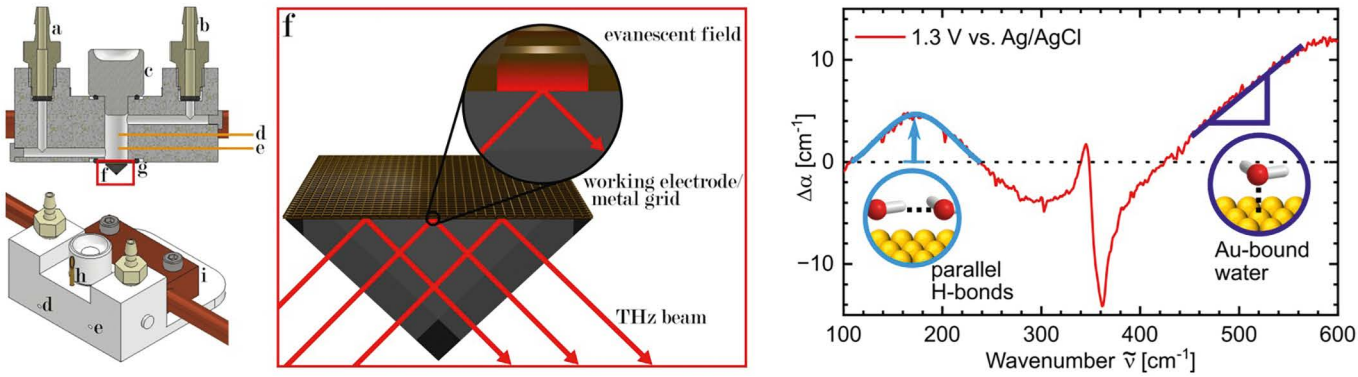

Fig. 2: Displayed is the set-up of our THz ATR electrochemical cell and the change in absorption (Δα) at a voltage of 1.3 V vs the reference of Ag/AgCl. We clearly observe the changes in the H-bond motifs: Around 160 cm^{-1} we observe an increase in the intensity and thus in the number of parallel H-bonds. Please note, then when forming a 2- dim network with a decreased intermolecular interaction compared to bulk water the center frequency will be around 160-170 cm^{-1} (and thus center frequency). The steep linear increase of absorption between 400 and 600 cm^{-1} is indicative of the presence of bound water molecules with a more restricted angular rotation compared to bulk water, i.e. a blue shifted librational mode. The third spectral observable, the sharp feature around 370 cm^{-1} is assigned to a frequency shift of the intermolecular band of the TBA upon formation of an interfacial TBA-Cl ion-pair network. (Copyright N. Wichmann)

of the interfacial hydration in the frequency range of the intermolecular water modes while applying a voltage, i.e. in an electrochemical cell [11]. This is experimentally challenging, since even a monolayer of gold or any conducting material will absorb the THz radiation and would be opaque. Thus, we designed a spectro-electrochemical ATR cell for the THz range with a gold mesh as a semi-transparent working electrode pressed to a diamond ATR crystal, which is coupled to a FT spectrometer. The three-electrode setup uses platinum wires as semi-reference and counter electrode. This is run under stable conditions. We are able to record simultaneously the changes in the spectra and Cyclic Voltammetry (CV).

In our combined experimental/simulation study we observe the following two competing mechanisms, which dictate the molecular details at the interface: *Hydrophobic hydration*: Large hydrophobic TBA+ cations are preferentially enriched at a Au/aqueous interface, forming a TBA-rich film covering the electrode. *Electrostatic repulsion and attraction*: Due to electrostatic repulsion, we observe a partial TBA+ desorption when applying a positive voltage, and a subsequent surface rehydration, which increased both water populations, those forming a 2- dim network as also those which are H-bound to the surface. Cl^- is attracted to the electrode for positive voltages, the increase close to the surface leads to ion-pairing with TBA^+ and thus to a stabilization. The presence of a film was recently hypothesized to explain the catalytic performances of TAA^+ based electrolytes for HER, but is now observed first time! The massive accumulation and the formation of the TBA-film and its resistance to applied voltage variations are optimal to cause a site-blocking effect for underpotential-deposition of H* as proposed e.g. in Koper et al [12] to explain the increased efficiency of Hydrogen Evolution Reaction using TAA^+ based electrolytes. The unrevealed molecular mechanism goes beyond predictions taking into account only electrostatic interactions (e.g., from Gouy–Chapman–Stern model). It is a balance between hydrophobic solvation at the unique molecular environment of metal/water interfaces- and electrostatic interactions which dictates the efficiency and outcome of a reaction. Hydrophobicity and electric fields can both be tuned by adjusting the metal surface and applied voltage, respectively, offering promising, but still unexplored paths to regulate reactivity. These findings highlight the need for a molecular understanding of the complex EDL structure in order to rationally tune electrolyte composition for designing and optimizing electrochemical processes. Solvation matters !

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Martina Havenith received her PhD at the University of Bonn in 1990 and was appointed Chair of Physical Chemistry at Ruhr University Bochum in 1998. She is the founder and spokesperson of the Cluster of Excellence Ruhr Explores Solvation (RESOLV) since 2012 and the director of the Center of Molecular Spectroscopy and Simulation of Solvent Controlled Processes. In 2014, she was appointed as Visiting Miller Professorship UC Berkeley; in 2016, she received the ERC Advanced Grant. She is a member of the German National Academy of Sciences Leopoldina and the Academia Europaea.