DY 24: Focus Session: Water – from Atmosphere to Space II (joint session CPP/DY)

Time: Tuesday 11:15–12:45 Location: ZEU/LICH

DY 24.1 Tue 11:15 ZEU/LICH

Microscopic diffusion and reactivity in aqueous solutions: photogenerated nascent halogen atoms, solvated electrons and subsequent dihalide formation — •Zhangatay Nurekeyev[1,2], Hyein Hwang[1,2], Fernando Rodriguez Diaz[1], Mei Bai[3], Michael Thorwart[3], Michaela Schäfer[4], Carmen Herrmann[4], and Christian Bressler[1,2,5] — [1]Inst. of Exp. Physics, Universität Hamburg — [2]The Hamburg Centre of Ultrafast Imaging (CUI) — [3]I. Inst. of Theor. Physics, Universität Hamburg — [4]Dept of Chemistry, Universität Hamburg — [5]European XFEL, Schenefeld

The solvent plays an important role in the assembly, stability and reactivity of (bio)chemical molecules. Small changes of the caging solvent can alter the reaction outcome, but little is known about the atomic-scale solvation shell dynamics. Our approach utilizes aqueous mono-atomic halide solutes, which are transformed into nascent neutral halogen atoms upon femtosecond optical excitation together with a separated solvated electron. Combining X-ray absorption with transient optical absorption spectroscopies we monitor the subsequent diffusion-driven atom-electron recombination, each focusing on the halogen atom and on the solvated electron, respectively. We also monitor the appearance of dihalides on the tens of picosecond time scale. Using all x-ray and laser observables we deliver a new picture of the ensuing dynamics, for which the existence of the long-lived (X:e) contact pair is not required. Next steps aim to trace more complex guest-host scenarios towards functional proteins in solution.

DY 24.2 Tue 11:30 ZEU/LICH

Surface Propensity of Halide Ions in Water: New Evidence from LJ-XPS — •Daniela Torres-Díaz[1], Shirin Golami[1], Tillmann Buttersack[1], Qi Zhou[1], Rémi Dupuy[2], Bernd Winter[1], Chistophe Nicolas[3], and Hendrik Bluhm[1] — [1]Fritz Haber Institute of the Max Planck Society, Berlin, Germany — [2]Laboratoire de Chimie Physique - Matière et Rayonnement (Sorbonne Université, CNRS), Paris, France — [3]Synchrotron SOLEIL, Saint-Aubin, France

The surface propensity of halide ions in water is still a matter of debate. While the famous Onsager&Samaras model indicates that charged species should avoid the interface, more recent Molecular Dynamics simulations that take into account the polarizability of the ions indicate notably that iodide and bromide prefer the interface while chloride and fluoride avoid it. Different models, however, differ in how strong this effect is, while experimental studies have reported contradictory results. Here I will discuss recent results obtained using Liquid-Jet X-Ray Photoemission Spectroscopy on water interfaces for potassium halide solutions. In particular, the measurement of the photoelectron angular distributions allow for a higher spatial resolution than classic XPS measurements.

DY 24.3 Tue 11:45 ZEU/LICH

Ion Correlations Drive Collective Adsorption of Hydronium Ions at the Air-Electrolyte Interface — •Elena Köhler Ruiz, Maximilian Becker, Louis Lehmann, and Roland Netz — Fachbereich Physik, Freie Universität Berlin, Germany

Acids exhibit distinct interfacial behavior at the air-water interface compared to simple monoatomic salts. While monoatomic ions are largely repelled from the interface, hydronium ions preferentially reside at the interface due to formation of an interfacial hydrogen-bond network. To investigate these contrasting behaviors, we perform molecular-dynamics simulations with thermodynamically optimized force fields, analyzing ionic distributions at the interface as well as resulting surface tensions and potentials. The simulated surface potentials reproduce the concentration-dependent trends observed in SFG experiments: At high concentrations, interfacial hydronium promotes co-adsorption of counterions, which results in a decrease of the surface potential with rising concentration, consistent with experimental observations. These findings highlight the critical role of ion-ion correlations at interfaces, which are not accounted for by modified Poisson-Boltzmann models.

DY 24.4 Tue 12:00 ZEU/LICH

Calcium-amino acid complexation in water probed by Intermolecular Coulombic Decay — •Michele Pugini, Nicolas Velasquez, Harmanjot Kaur, Florian Trinter, Qi Zhou, Lukas Tomaník, Uwe Hergenhahn, and Bernd Winter — Fritz-Haber-Institut, Berlin

The Ca2+ ion is the most abundant metal ion in the human body, playing essential roles in numerous biological processes, many of which involve interactions with proteins. Gaining molecular-level insight into the nature of the interaction between Ca2+ ions and solvated amino acids is therefore crucial for understanding calcium's biological function. Intermolecular Coulombic decay (ICD), a non-local autoionization process, offers unique sensitivity to the local chemical environment and can selectively probe interactions within the first solvation shell of solvated Ca2+ ions.

Here, we demonstrate the sensitivity of resonant ICD3 to the chemical composition of the solvation shell, enabling the identification of Ca2+ associations with specific amino acids. Our model system is the amino acid proline. The interaction, if present, is revealed via the ICD electrons resulting from the ionization of the biomolecule upon the 2p to 3d excitation of Ca2+.

Our results unequivocally identify Ca2+-proline interactions, indicating substitution of water molecules in the ion's coordination shell by proline. These findings establish ICD as a sensitive probe of metal-biomolecule interactions and highlight its potential as a powerful spectroscopic tool for investigating biomolecular structure in solution.

DY 24.5 Tue 12:15 ZEU/LICH

Distinguishing cavity and non-cavity solvation structures of the hydrated electron — •Sy Dat Ho and Benjamin Philipp Fingerhut — Department of Chemistry and Centre for NanoScience, Ludwig-Maximilians-Universität München, 81377 München, Germany

Solvated electrons in water are prototypical low-dimensional quantum systems that are coupled to a fluctuating, many-body environment. However, their hydration structure is still a matter of debate, with both cavity and non-cavity models having been suggested. First-principles molecular dynamics simulations are performed of excess-electron localization in liquid water, using hybrid-meta-GGA and hybrid-GGA density functionals that accurately reproduce bulk water structure. Perturbations to the local hydrogen bond structure of water due to interaction with the excess charge are identified, giving rise to specific signatures in transient radial distribution functions. These patterns are then compared with preliminary liquid-phase MeV-UED data obtained during an early science campaign at SLAC. In order to distinguish the structural changes induced by excess electrons in the diffraction patterns, long-time simulations at an unprecedented level of theory are required in order to minimise statistical noise. Our results clarify the coupling of hydrated electrons to solvent fluctuations and provide microscopic insight into polaron formation in disordered condensed phases.

DY 24.6 Tue 12:30 ZEU/LICH

Mesoscopic Structures in Water/HFIP based Electrolytes — •Sophie Zeilinger[1,2] and Markus Mezger[1] — [1]Center for Nano Structure Research, Faculty of Physics, University of Vienna, AT-1090 Vienna — [2]Institute of Physical Chemistry, Faculty of Chemistry, University of Vienna, AT-1090 Vienna

Previous studies have shown that binary water/hexafluoroisopropanol (HFIP) mixtures exhibit nanoscale heterogeneties that strongly affect properties such as reaction rates. The complex hydrogen bonding network of the binary mixture together with the amphiphilic character of the HFIP molecule provides a sensitive environment in which subtle changes in interactions can generate nanoscale heterogeneities. Here, we study the structure formation in water/HFIP under the influence of hydrophilic and hydrophobic ions by Small Angle X-Ray Scattering (SAXS). Depending on water content, pH, salt concentration and temperature we observe monotonous and oscillatory density correlations with structural parameter on the nanometer length scale. These structures are explained by the coupling of coulombic interactions between charged hydrophilic and hydrophobic ions vs. local fluctuations in water/HFIP concentrations.