ULTRAFAST SPECTROSCOPY

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We aim to understand the structural and dynamical properties of dynamical complex aqueous systems, and how these properties are governed by the interactions on the molecular scale, in particular the interactions with water molecules. These systems include proteins in water, hydrogels and membranes, and reactive systems like electrochemical systems and water nanodroplets and water nanochannels containing protons. To this purpose we study the structural dynamics of water molecules and of molecules interacting with water with femtosecond (two-dimensional) vibrational spectroscopy, surface sum-frequency generation and GHz-THz dielectric relaxation spectroscopy.

Highlights

- Adding the neutral surfactant C12E6 to water enhances the hydrogen bond strength of water close to the surface, and creates a ~3 nm deep interface with a large electric field of ~1 V/nm.
- In water nanodroplets with a diameter of ~7 nm, proton hopping is 4 times slower than in bulk water, for droplets <4 nm, proton hopping is even more than 10 times slower.
- The hyperactive anti-freeze protein RmAFP retains its hydrating water molecules upon adsorption to the ice surface with a hydrogen-bond structure different from the ice surface, thereby inhibiting the insertion of water layers in between the protein and the ice surface.
- The surface of water ice is covered with a quasi-liquid water layer that persists down to 245 K, far below the melting point.

Plans

In the coming years we will study the molecular mechanism of proton transfer reactions at the surfaces of water and ice and in nanoconfined water. We will also study the role of water in the self-assembly and visco-elastic properties of supramolecular hydrogels, and the molecular-scale properties of electrolyte solutions near electrode surfaces in the electrochemical reduction of CO_2, and in the electrochemical generation of H_2. To probe the ultrafast structural dynamics at surfaces, we will develop time-resolved surface sum-frequency generation.

Key research items

1. B. Antalicz, J. Versluis and H.J. Bakker, *Observing Aqueous Proton-Uptake Reactions Triggered by Light*, J. Am. Chem. Soc. 145, (12), 6682-6690 (2023)
2. C.J. Moll, J. Versluis and H.J. Bakker, *Direct Evidence for a Surface and Bulk Specific Response in the Sum-Frequency Generation Spectrum of the Water Bend Vibration*, Phys.Rev.Lett. 127, (11), 116001: 1-6 (2021)
3. O.O. Sofronov and H.J. Bakker, *Slow Proton Transfer in Nanoconfined Water*, ACS Cent. Sci. 6, (7), 1150-1158 (2020)
4. G. Giubertoni, O.O. Sofronov and H.J. Bakker, *Observation of Distinct Carboxylic Acid Conformers in Aqueous Solution*, J. Phys. Chem. Lett. 10, (12), 3217-3222 (2019)
5. W.J. Smit and H.J. Bakker, *The surface of ice is like supercooled liquid water*, Angew. Chem. Int. Ed. 56, (49), 15540-15544 (2017)

Schematic picture of a femtosecond mid-infrared study of proton transfer of in water nanodroplets covered with surfactants and embedded in an apolar matrix.