

Seminar

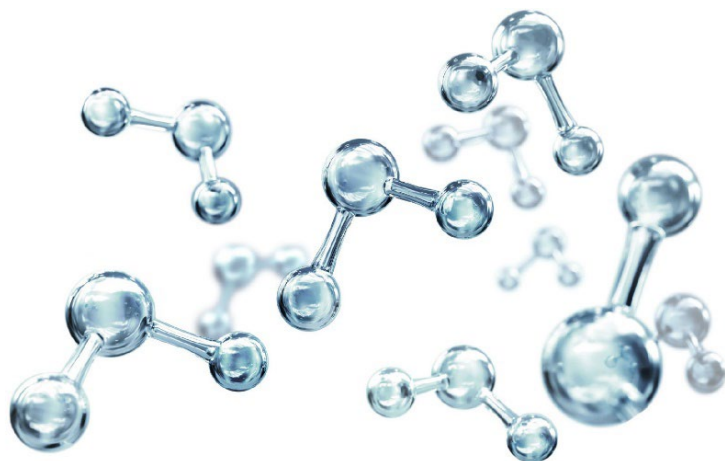
8th of June 2023
12:00 h (CEST)

Zoom Virtual Meeting:

<https://tuhh.zoom.us/j/82631283465>

Meeting-ID: 826 3128 3465

Password: 978444



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Water in confinement and water at the interface

Water in confinement exhibits altered properties in molecular arrangement, bonding, and interaction with its neighboring environment, as compared to its bulk counterpart. We investigated periodically arranged D₂O nano droplets of ~1 nm size on top of a graphene/iridium moiré superstructure by Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) under ultrahigh vacuum conditions at ~120 K. The IR bands of D₂O clusters differ significantly from those observed for bulk D₂O amorphous solid water or crystalline ice phases. Blue-shifted symmetric and asymmetric stretching bands with narrower band widths and modified band intensity ratios were observed, pointing to an enhanced internal order and a reduced nearest neighbor distance. Furthermore, two IR bands of “dangling” deuterium atoms were detected originating from threefold coordinated water molecules at the surface of the clusters and at their interface to the graphene layer. The latter arose only with the transition from the water clusters to an amorphous solid water layer. We propose that upon coalescence, opposing local dipoles trigger a hydrogen bond rearrangement at the interface. Our results represent a first step toward an atomistic understanding of water in confinement.

Furthermore, in a femtosecond time-resolved optical pump-soft x-ray probe photoemission study at FLASH, we follow the dynamics of charge transfer at the interface of water and anatase TiO₂(101). By combining the transient oxygen O 1s core level peak shifts at submonolayer water coverages with Ehrenfest molecular dynamics simulations we find that ultrafast interfacial hole transfer from TiO₂ to molecularly adsorbed water is completed within the 285 fs time resolution of the experiment. This is facilitated by the formation of a new hydrogen bond between an O_{2c} site at the surface and a physisorbed water molecule. The calculations further suggest that this process is preceded by the efficient trapping of the hole at the surface of TiO₂ by hydroxyl species (-OH), that form following the dissociative adsorption of water. At a water coverage exceeding a monolayer, interfacial charge transfer is suppressed. Our findings are directly applicable to a wide range of photocatalytic systems in which water plays a critical role.

