

# Enhancing reactivity in nanoconfined water

## Structure, Spectroscopy and Chemical Reactivity of Intercalated Fluids

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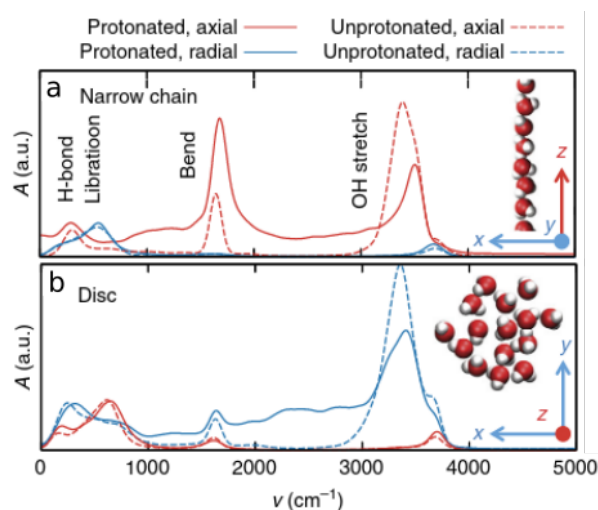
### In Short

- Intercalated fluids display behavior which fundamentally differs from their behaviour in bulk or at interfaces.
- Anisotropic infra-red absorption spectroscopy allows to probe the microscopic water structure as well as surface structure.
- *Ab-initio* molecular dynamics simulations, which predict nuclear motion with very high accuracy using quantum chemistry, quantitatively reproduce experimental infra-red vibrational spectra and also provide detailed information about the fluidic atomic-scale structure.
- Nanoconfinement allows to apply large electric fields between the confining surfaces, which can be used to enhance or trigger chemical reactivity.
- In this project we will investigate the properties of confined water in electric fields and the effect of strong oriented electric fields on chemical reactions in confinement.

Recent experimental advances allow to produce single cylindrical and planar fluid-filled structures at the nanometer scale and to study in detail how the fluid dielectric and flow properties deviate from bulk as the confinement becomes stronger. These structures currently attract considerable interest due to a broad variety of technological and scientific applications. It was shown that strong confinement alters the properties of water. Depending on the dimensionality and strength of confinement, this has implications on the interactions of water with the confining surfaces, ionic absorption as well as chemical reaction equilibria. For example, nanoconfined water shows nearly frictionless transport through graphene sheets and carbon nanotubes, but not through the same structures consisting of boron-nitride. Nanoconfinement of water has also been shown to cause enhancement of cycloaddition reactions in microdroplets, although the precise mechanism remains unclear.

While simulations and theoretical studies utilizing force-field MD based approaches have demonstrated how some of the deviations from bulk fluid behaviour can be understood and predicted by accounting for the discrete molecular properties in

ultra-confinement [1], we intend to employ *ab-initio* molecular dynamics simulations based on quantum chemical density functional theory in order to have a better description of the water interface interactions, taking into account important aspects such as water polarizability, chemical reactivity or surface metallicity.

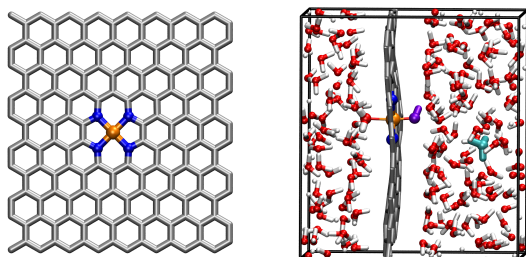


**Figure 1:** Anisotropic absorption spectra calculated from *ab-initio* simulations of a narrow chain of water (a) and a two-dimensional water disk (b). Figure from J. O. Daldrop et al., *Orientation of non-spherical protonated water clusters revealed by infrared absorption dichroism*, *Nature Communications*, published in 2018, Springer Nature.

*Ab-initio* simulations propagate the atomic nuclei positions by computing forces from a suitable quantum mechanical approximation for the electronic degrees of freedom. In previous works, we have gained extensive experience in simulating infrared absorption spectra of water and other fluids in confined geometry [2]. In Figure 1, infrared absorption spectra of a narrow chain of water molecules (panel a) and of a water disk (panel b) are shown. Here, results for a neutral water layer (dashed lines) are compared with results for a water layer with an excess proton (solid lines). The absorption profiles for a radial electric field polarization parallel to the plane (blue) and for an axial electric field polarization perpendicular to the plane (red) are shown. It can be seen that the in-cluster (axial for the chain and radial for the disk) is much stronger than the out-of-cluster absorption, which can be explained by the anisotropic polarization fluctuations. The presence of an excess proton gives rise to a broad continuum band between the OH-stretch peak at around  $3300\text{ cm}^{-1}$  and the OH-bend peak at around  $1600\text{ cm}^{-1}$ . The pronounced

anisotropy of the continuum band was experimentally confirmed by the group of Prof. Heberle (Freie Universität Berlin) [2]. These results show that *ab-initio* simulations allow to calculate infrared spectra in good agreement with experiment and that anisotropy effects, which are important in confinement, can be predicted very well.

In this project, we are simulating water confined between two graphene sheets with different separations spanning the range from ultraconfinement to near-bulk like behavior. We are studying the properties of intercalated water, *i.e.* the density depletion close to the interface, the structure of the hydrogen bond network and the anisotropic IR absorption behavior. Conducting *ab-initio* molecular dynamics simulations of systems of multiple thousand atoms is a very challenging task and is only possible on high performance computing clusters like the systems at the HLRN. We will supplement our work at the HLRN with simulations based on classical force-field models, that we already have conducted. This way we are able to study the absorption spectra of confined water from the MHz to the IR regime. We are applying electric fields of different strength to the intercalated water to calculate the anisotropic dielectric profile, Stark effects in the IR absorption spectra, as well as spontaneous autoprotolysis of water molecules which has been observed under very strong fields [4].



**Figure 2:** Left: Single atom catalytic site: Single iron core immersed in a graphene sheet. Right: Hydroxide ion chemisorbed to catalytic site.

The application of electric fields in nanoconfined environments is not only a theoretical but also a promising experimental tool, where large electric fields, up to several V/nm, can be applied between two planar surfaces, for example by immersing the confining surfaces into an ionic liquid and applying a gating voltage. In this part, we are cooperating with the experimental group of Prof. Bolotin (Freie Universität Berlin). Such large fields can for example be used to control the kinetics and the selectivity of chemical reactions [4]. This effect has been shown both experimentally and theoretically through *ab-initio* calculations and opens the way to finely tune chemical reactions, electric field-mediated catalysis

or suppression of parasitic reactions. The area of electric field-enhanced chemical reactions is thus in great expansion, but faces an important shortcoming: how to create strong electric fields in experiments, and how to control their orientation with respect to the reactant molecules? Experimental setups involve single-molecule scanning tunneling microscopes, exploit electric potential drops at interfaces or use local oriented electric fields within a macromolecule, as they naturally occur in biological molecules. However, these setups cannot easily be scaled to an industrial use yet.

In cooperation with Prof. M.-L. Bocquet (ENS Paris) we are considering water molecules adsorbed at iron cores embedded in graphene sheets (see Figure 2), the active site of a single atom catalyst (SAC). We are studying how the application of oriented electric fields facilitates water protolysis considering different defect geometries and metallic cores. In the future phases of this project we are planning to extend our studies to adsorption of CO<sub>2</sub> on metallic graphene derivatives, to achieve CO<sub>2</sub> reduction, an important process in the context of carbon capture.

## WWW

<https://www.physik.fu-berlin.de>

## More Information

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- [3] J. Cai et. al., *Nat. Commun.* **13**, 5776(2022). doi:<https://doi.org/10.1038/s41467-022-33451-1>
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## Project Partners

Marie-Laure Bocquet (ENS Paris)  
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AG Bolotin (Freie Universität Berlin)

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