Proton transfer reactions are ubiquitous in aqueous media and are essential for numerous chemical, biological and technological systems and applications. While the fundamental principles governing the anomalously efficient proton transport in pure bulk water have been studied in great detail, the most interesting and relevant aqueous proton transport processes that occur in complex, strongly perturbed environments are presently not well understood. These perturbations can be due to co-solutes (such as ions, polar molecules or hydrophobes), or result from geometrical constraints on the systems. Such complex systems have been the target of investigations within the present project.

A key part of the project has been the continued development of the spectroscopic methods within the “Ultrafast Spectroscopy” group at AMOLF. We have especially invested efforts into improving the method of high-frequency broadband dielectric relaxation spectroscopy (DRS) to study aqueous protons under confinement. We now have the capability to measure the dielectric function of liquids from 10 MHz to 2 THz with a combination of complementary approaches. Broadband DRS allows us to separate the conductivity response of free charges as well as the (rotational) dielectric relaxation of all polar species in a sample, yielding information about molecular dipole moments and their associated reorientation dynamics. We have combined this method with femtosecond mid-infrared pump-probe spectroscopy, which is a powerful method to investigate the rotational dynamics of water hydroxyl groups in aqueous solutions. The main results achieved are summarized below. Some results have been published, others have been written up and are submitted to scientific journals, and some projects are still running.

Project 1: Ion-induced perturbations on the structural dynamics of the hydrated proton

It is known that protons exert a strong structuring effect on water, leading to a pronounced decrease of the dielectric response (primarily originating from a reduction in the amplitude of the main Debye relaxation mode at 20 GHz). This decrease partly arises because the proton binds water molecules and partly because water molecules are strongly involved in the (Grotthuss) conduction of the proton. By using dielectric relaxation spectroscopy in the GHz regime we have for the first time observed that the presence of cations leads to a decrease in the number of water molecules that are affected by the proton (seen through the reduced depolarization effects of the ions upon co-solvation, see Fig. 1). The strongest effect is observed when the solution contains divalent cations like Mg$^{2+}$ or Ca$^{2+}$. This non-additive effect is only observed if one of the ions is a proton. We have shown that these findings can only be understood in terms of the soft nature of the excess aqueous proton whose charge is delocalized over several hydrating water molecules. This makes the hydrated proton susceptible to the presence of other strongly hydrating cations (see figure 1) in ways that have hitherto not been discussed in the literature. These results have been written up and submitted for publication. At the time of writing this report the paper was under peer-review.
Project 2: Water mobility nano-porous hydrogen membranes

We have performed an experimental study on the dielectric properties of proton and sodium terminated Nafion membrane at varying degrees of hydration. At low water concentrations, we observe that the orientational mobility of the water molecules in the Nafion membrane channels is strongly slowed down in comparison to bulk water. Only at the highest hydration level does the rotational mobility of the water molecules in the Nafion membranes become similar to that of bulk water. We also observe that the mobilities of protons and sodium ions strongly depend on the degree of hydration of the Nafion membranes. These results provide information on the behaviour of ions, especially protons, in nanoporous aqueous media. This behaviour plays a crucial role in many processes, such as energy transport and acid-base reactions in biological systems, and proton exchange membranes (PEM) in fuel cells. This study was published in J. Phys. Chem. B (W. Ensing et. al, 2013, vol. 117, pp. 12930–12935)

Project 3: Proton conductivity under nano-confinement

Probing the mobility of nano-confined charges is challenging as they do not give rise to any DC conductivity. In this project we have used DRS to probe the polarization response in the GHz regime due to the motions of protons within nanometer-sized reversed micelles (water droplets) in hexane, stabilised by the non-ionic surfactant Igepal-520 – an ideal model system for proton mobility under confinement. We have developed an analytical model which describes the dielectric response as a function of the size of the micelles. Assuming the same diffusion constant of the proton as in bulk solution, the model predicts that the DR resonance monotonously shifts to lower frequencies with increasing size (Fig. 3a). In sharp contrast, the experiments show that the resonance frequency actually increases with size up to r = 3.2 nm (Fig. 3b). We show that this effect can be explained by a dramatically reduced mobility of the proton upon confinement. This project is still ongoing but will soon be written up for publication.

Additional projects

Using DRS and femtosecond mid-infrared spectroscopy we have investigated other related molecular systems. For example, we have been able to separate the dielectric relaxation features originating from the molecular reorientation of the neurotransmitter gamma-aminobutyric acid (GABA) in water, and thereby deduce its preferential molecular conformation, both in neutral and highly acidic solutions. The molecule was found to be non-folded, in contrast to some recent theoretical predictions. This result is of great interest for understanding the biophysical binding mechanism of GABA to its receptors in the mammalian nervous system, where it functions as the primary neuron de-excitatory agent. The study was recently accepted for publication in Phys. Chem. Chem. Phys. (N. Ottosson et. al, 2014, DOI:10.1039/C4CP00671B). Additionally we have performed a DRS study of the hydration dynamics of mixtures of aqueous urea and TMAO. This is of interest to a large biophysical community since the latter molecule is found in many organisms to counteract the denaturating effect of urea, though the mechanism remains elusive. We find evidence of water-mediated interactions between the molecules; results which have been submitted for publication and are currently under review.