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Hydrogen-Bond Dynamics and Proton Transfer in Nanoconfinement

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Engelse samenvatting:

Proton transfer is of fundamental importance to both biology and chemistry. Much is known about proton transfer in large water volumes but often proton transfer reactions take place in very small nanometer sized volumes for example between lipid layers and in proton channels in mitochondria and chloroplasts. Proton transfer in nanoconfinement also plays an important role in industrial applications such as in proton conduction membranes, which are used in the hydrogen fuel cell. In such small water volumes the structure and dynamics of the water molecules is strongly perturbed such that is behaves very differently from bulk water. Therefore it can be expect that proton transfer in these small water volumes can also be very different than in bulk water. However, up to date, there are no experimental studies on aqueous proton transport in nanoconfinement.

In this thesis we use pump-probe and dielectric relaxation spectroscopy to explore the effect of nanoconfinement in reverse micelles. First, we explore the effect of nanoconfinement on water by measuring the reorientation of water molecules in water droplets of different size and shape. Then we insert protons in the reverse micelles and measure the translational diffusion of the protons as function of the of the water droplet. We also explore proton transfer reactions in two different molecular machines: a photo-activated molecular proton crane and a photo-activated molecular H^+/Li^+ ion-exchanger.

We find that nanoconfinement of water slows down the collective water reorientation even beyond the first solvation shell, in the photocycle of a proton crane intramolecular hydrogen-bond breaking precedes the rotation of the crane arm and the return of the proton is about 200 times slower than the arrival, and the translational diffusion of the aqueous proton is strongly effected by nanoconfinement, so that in very small water droplets (1 nanometer diameter) the protons move 200 times slower than in normal water.