



Dynamics of Water and Hydrated Protons in Confinement

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Summary

The proton (H^+) exists in water as a hydrated complex instead of a bare ion, because of its extremely high charge density, as a result of which it strongly binds to surrounding water molecules. Hydration of the proton by one water molecule leads to the formation of a hydronium ion (H_3O^+). In liquid water the hydronium ion is further hydrated to form proton hydration complexes like the Eigen complex $H_9O_5^+$ and the Zundel complex $H_5O_2^+$. In fact there exists a broad distribution of different proton hydration complexes $H \cdot (H_2O)_n^+$ in water, and the Eigen and the Zundel complexes just form two limiting cases. In liquid water the proton hydration complexes are very dynamic, the hydrogen bonds in the hydration shell continuously break and reform. As a result of these structural dynamics the proton charge can get transferred from one water molecule to another.

Protons in water are transferred by the Grotthuss mechanism which involves an ongoing restructuring of the hydrogen-bond network. Thanks to this mechanism, the proton and the hydroxide ion diffuse several times faster than normal ions, that diffuse via ordinary Stokes diffusion: the conductivity of H^+ in water is about seven times higher than that of Na^+ , and the conductivity of OH^- in water is about three times higher than that of Cl^- . Because of its high conductivity and unique transfer mechanism, the proton plays a key role in many chemical and biological processes like atmospheric reactions, photosynthesis, and hydrogen fuel cells. Most of these proton-involved processes take place in confined environments, such as the channels provided by ATP synthetic systems and the nano-channels of Nafion membranes. Understanding the mechanism of proton transfer in confinement is essential for the utilization and control of proton-involved processes.

In order to understand the proton transfer mechanism in confinement on the molecular scale, we investigated the structural and dynamical properties of the O–H vibrations (which strongly absorb light in the infrared region of the spectrum) of the proton hydration complexes, using polarization-resolved femtosecond infrared pump-probe spectroscopy. In this method the O–H vibrational modes of proton hydration complexes are excited by a short and intense infrared pulse. The absorption spectrum of the excited sample is different from

that of the non-excited sample, and this absorption change is monitored by a delayed probe pulse. By varying the delay time of the probe relative to the pump, we obtain the time evolution of the absorption difference spectra, from which we obtain information on several dynamical aspects of the proton hydration complex, like vibrational relaxation, spectral diffusion, molecular reorientation, Förster energy transfer. This information provides us with unprecedented information on the mechanism of proton transfer on the molecular scale.

In Chapter 4, we study the vibrational relaxation and anisotropy dynamics of the hydration shells of OH⁻ ions. We observe that the excited O–H stretch vibration of water molecules that hydrate the OH⁻ ion first relax to a local hot state with a concentration independent time constant of 200 fs. The local hot state then decays to a final state in which the energy is thermally distributed over the focus of the exciting laser pulse. The time constant of the equilibration process rises with increasing concentration, from 1.2 ps for a 0.5 M solution to 4.5 ps for a 10 M solution. The local hot state is observed to be anisotropic, showing that the energy of the excited O–H stretch vibrations is first dissipated within the hydration complex. The anisotropy of the local hot state decays both as a result of the reorientation of the OH⁻ hydration complex and as a result of heat diffusion from the excited complexes to non-excited complexes. Modelling the anisotropy data at different concentrations allows for an accurate determination of the number of water molecules in the hydration shell of the OH⁻ ion, the reorientation dynamics of the OH⁻ hydration complex, and the molecular-scale heat diffusivity.

In Chapter 5, we observe a strong reorganization of the proton hydration structure in hydrated Nafion membranes following single-quantum excitation of a proton vibration with $\sim 4 \mu\text{m}$ light pulses. After excitation by an intense infrared pulse, the O–H vibration in the hydronium core of an Eigen complex evolves to a Zundel proton vibration (O \cdots H $^+$ \cdots O), which is observed as a strong red-shift of the transient bleaching spectrum. Accompanied by the evolution of the O–H vibration to a proton vibration, the other two non-excited O–H modes of the Eigen complex turn into higher-frequency O–H stretch vibrations of water molecules that are flanking the Zundel proton. This evolution is observed as a delayed extra absorption at 3270/3520 cm $^{-1}$. This structural reorganization takes place with a time constant of 170 \pm 20 fs. The higher-frequency O–H stretch vibrations of water molecules flanking the Zundel proton are at a quite large angle with respect to the proton vibration, which agrees with the initial negative value of the anisotropy of the induced water-like O–H stretch absorption bands. The anisotropy values of the excited proton vibration and the induced absorption both relax to a value of ~ 0.1 with a time constant of 120 \pm 30 fs. This final value of the anisotropy indicates that the excitation has randomized in the plane of the central H₃O $^+$ ion of the Eigen hydration structure, meaning that the vibrational excitation is delocalized over the three O–H groups of the central H₃O $^+$ ion.

In Chapter 6, we study the vibrational dynamics of hydrated protons in Nafion membranes at different hydration levels. At low hydration levels we observe that the excitation of the proton vibration of an Eigen-like proton hydra-

tion structure leads to a structural relaxation process in which the Eigen-like structure evolves to a Zundel-like proton hydration structure, as observed in Chapter 5. At high hydration levels the spectral dynamics are dominated by vibrational energy relaxation and subsequent cooling of the proton hydration complex. Using a kinetic analysis of the transient spectral data, we determine the rates of proton transfer, vibrational energy relaxation and cooling as a function of the hydration level. We find that infrared-induced proton transfer occurs at all hydration levels, but becomes less observable at high hydration levels due to the acceleration of the vibrational relaxation and the increasingly dominant influence of the heating effect that results from the vibrational energy relaxation.

In Chapter 8, We studied the vibrational relaxation and thermal relaxation dynamics of proton hydration complexes in acetonitrile at different proton to water ratios ($[H^+]:[H_2O]$ varies from 1:1 to 1:3), following the ultrafast excitation of one of the O-H stretch vibrations of the H_3O^+ ion. We found that there are two relaxation pathways: for most excited vibrations the vibrational energy dissipated in the relaxation (with a time constant <100 fs) is taken up as heat by the aqueous cluster (with a time constant of 320 ± 20 fs). Subsequently, the hot complex cools by transferring its thermal energy to the acetonitrile surroundings (with a time constant of 1.4 ± 0.1 ps). For a small fraction of the complexes the excitation leads to ultrafast predissociation of one of the hydrogen bonds of the proton hydration complex, and thus to the ejection of water monomer fragments. As a result, a long living bleaching signal with high anisotropy is created.

A similar pre-dissociation of proton hydration complexes is observed in *Chapter 7*. In this chapter we investigated the dynamics of the bending mode of the hydronium ion in hydrated Nafion. The excited bending mode relaxes via two relaxation channels. The main fraction of the excited hydronium ions is found to relax to an intermediate (local hot) state with a time constant T_1 of 175 fs, and subsequently to an equilibrated thermal state with a time constant T_{eq} of 1.53 ps. A small fraction of the excited bending modes is observed to relax via predissociation of a hydrogen bond. In this process, one of the hydrogen bonds between the hydronium ion and its first hydration shell is broken, leading to a long-living bleaching of the absorption band of the hydronium bend vibration. Due to the ultrafast character of the predissociation process, this bleaching signal has a high associated anisotropy that decays with a long time constant of 38 ± 4 ps, probably as a result of structural relaxation of the proton hydration complex within the Nafion nano-channel.

In Chapter 9 we use vibrational surface sum-frequency generation (VSFG) spectroscopy to study the vibrational response of the hydration shells of hydrophobic anions like triflate ($CF_3SO_3^-$), ethanesulfonate ($C_2H_5SO_3^-$), and butanesulfonate ($C_4H_9SO_3^-$). The addition of triflate, ethanesulfonate, and butanesulfonate strongly affects the frequency and amplitude of the main band of the VSFG spectrum of H_2O/D_2O . For solutions in H_2O , the addition of these hydrophobic anions leads to a strong blue shift of the main band of the VSFG spectrum but little change in amplitude. In contrast, for solutions in D_2O the addition of these anions hardly changes the frequency of the main band but

leads to a strong increase in amplitude. This observation can be explained by a strong isotope effect in the intra- and intermolecular mixing of the hydroxyl stretch vibrations of the water molecules contained in the hydration shells of the hydrophobic anions. The O–H stretch vibrations of H₂O molecules in the hydration shell are strongly mixed whereas the O–D stretch vibrations of the hydrating D₂O molecules are decoupled. This isotope effect is not observed for other ions like perchlorate (ClO₄[−]), which can be explained from the stronger mixing of the OH vibrations as a result of the smaller difference between the frequencies of the water hydroxyl groups that are hydrogen bonded to anions and the frequencies of the water hydroxyl groups that are hydrogen bonded to other water molecules.