Vibrational Excitation Induced Proton Transfer in Hydrated Nafion Membranes

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Abstract

We study the energy relaxation and structural relaxation dynamics of hydrated protons in Nafion membranes at different hydration levels using femtosecond infrared transient absorption spectroscopy. At low hydration levels we observe that the excitation of the proton vibration of an Eigen-like proton hydration structure leads to a structural relaxation process in which the Eigen-like structure evolves to a Zundel-like proton hydration structure. This reorganization leads to a transfer of the proton charge and closely follows the mechanism of infrared-induced adiabatic proton transfer that has been proposed by S. Hammes-Schiffer, J.T. Hynes and others. At high hydration levels the spectral dynamics are dominated by vibrational energy relaxation and subsequent cooling of the proton hydration structures and the surrounding water molecules. 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 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 increasingly dominant influence of the vibrational energy relaxation.

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Introduction

The mobility of protons in liquid water is a factor of 5 higher than that of other cations like Na^+ and K^+.[?] The high mobility of the proton has been explained from a special transport mechanism that is usually referred to as Grotthuss conduction. In this process the delocalized charge of the proton is transferred to other hydrogen atoms in the hydrogen-bonded network, as a result of a structural reorganization of the water hydrogen-bond network. Ab initio molecular dynamics simulations showed that the proton follows from the structural interconversion between so-called Eigen ($H_9O_4^+$) and Zundel ($H_5O_2^+$) proton hydration structures.[? ? ?] The Eigen structure can be viewed as a central H_3O^+ ion with three surrounding hydrogen-bonded H_2O molecules, the Zundel structure is formed by an H^+ ion between two neighboring H_2O molecules.

When water is confined to the nanometer scale the structure and dynamics of the water network will change, and this will in turn affect the rate and mechanism of proton conduction. For example, Dellago and co-authors calculated that the proton mobility in water-containing carbon nanotubes is accelerated by a factor of 40 in comparison to bulk water.[?] It was also shown that the proton transfer in water-containing carbon nanotubes involves a Zundel-Zundel conversion mechanism rather than the Eigen-Zundel-Eigen mechanism of bulk liquid water.[?] Experimental studies on proton transfer in nanometer size reverse micelles showed that the rate of proton transfer strongly decreases with decreasing size of the reverse micelle.[? ? ? ? ?]

An important nano-confined system for aqueous proton transfer to occur is formed by the nanochannels of Nafion membranes that are widely used as proton exchange membranes (PEM) in hydrogen fuel cells. Nafion is a sulfonated tetrafluoroethylene (Teflon)-based polymer that forms nanometer channels in which the sulfonate ($-SO_3^-$) headgroups bind to water molecules and positive counter ions like Na^+ and protons. It has been found that the proton conductivity of Nafion membranes strongly depends on the hydration level.[? ? ? ?] Only at high hydration levels, i.e. when the nanochannels contain a sufficient amount of water, the Nafion membrane becomes a good conductor of protons. The molecular-scale mechanism of proton conduction in Nafion membranes has been studied with advanced ab initio molecular dynamics simulations.[? ? ? ?] It was found that the proton is predominantly hydrated in an Eigen-like hydration structure, except for the first hydration shell of the sulfonate group where the proton-hydration structure is more Zundel-like.[? ?] It was also shown that proton transfer in hydrated nafion can involve both particle (H_3O^+) diffusion and Grotthuss conduction, the latter process becoming dominant at high hydration levels. An interesting observation is that the two processes are anti-correlated, the particle diffusion takes place dominantly in a direction opposite to the Grotthuss conduction.[? ?]

Recently, we studied the structural dynamics of proton hydration structures in Nafion membranes at low hydration levels with two-color femtosecond mid-infrared spectroscopy. We observed that the excitation of the proton triggers a structural reorganization that involves a partial transfer of the proton charge.[?] Here we study the structural relaxation for Nafion membranes over a wide range of hydration levels. We find that for high hydration levels the structural relaxation is in strong competition with the vibrational energy relaxation of the excited proton vibration.

Experiment

We study the structural relaxation and vibrational energy relaxation of hydrated protons in Nafion membranes with polarization-resolved two-color mid-infrared pump-probe spectroscopy. The infrared pump and probe pulses are generated in two separate parametric nonlinear optical frequency conversion processes that are both pumped with the output of a Ti:sapphire amplified laser system (Coherent Legend Elite). The laser system provides pulses at a wavelength of 800 nm with a pulse energy of 3.5 mJ and a pulse duration of 45 fs at a repetition rate of 1 kHz. The 800 nm beam is split into three parts. The first part of the 800 nm (=12500 cm^{-1}) beam with a pulse energy of $\sim$1 mJ is coupled into a commercial optical parametric amplifier (TOPAS by Light Conversion), in which signal (7500-7700 cm^{-1}) and idler (4800-5000 cm^{-1}) pulses are generated in a BBO (β-barium borate) crystal. The idler is frequency-doubled in a second BBO crystal to a pulse at 9600-10000 cm^{-1}. Subsequently, this pulse is mixed with the second part of the 800 nm beam with a pulse energy of $\sim$1.5 mJ in a KTP (potassium-titanyl-phosphate) crystal to generate pulses at the difference frequency of 2500-2900 cm^{-1}. The generated pulses have a pulse energy of 10 μJ and a pulse duration of 100 fs. The third part of the 800 nm beam with a pulse energy of 0.8 mJ is used to pump a home-built optical parametric amplifier leading to the generation of a tunable signal pulses (7175-8100 cm^{-1}) and idler pulses (4400-5325 cm^{-1}). These signal and idler pulses are mixed in a $AgGaS_2$ (silver-thiogallate) crystal to generate tunable infrared (1850-3700 cm^{-1}) pulses with a pulse energy of 4 μJ and a pulse duration of 75 fs.

The infrared pulse generated by the first two parts of the 800 nm beam is used to excite (pump) the O–H stretch vibrations of proton hydration structures to their first excited $v = 1$ state. This excitation results in a bleaching signal (decreased absorption) at the $v = 0 \rightarrow 1$ frequency of the proton vibration, because of the depletion of the $v = 0$ ground state, and $v = 1 \rightarrow 0$ stimulated emission out of the $v = 1$ state. The excitation also leads to an induced absorption at frequencies corresponding to the transition from the $v = 1$ state to the second excited $v = 2$ state of the proton vibration. For the stretch vibrations of an Eigen proton hydration complex the $v = 1 \rightarrow 2$ transition absorbs at $\sim$1600 cm^{-1}. This transition is redshifted by $\sim$1000 cm^{-1} with respect to the fundamental $v = 0 \rightarrow 1$ transition, due to the extreme anharmonicity of the proton vibrational potential. ? ?

The shape and amplitude of the features of the transient absorption spectrum will change with increasing delay time due to structural relaxation processes and vibrational energy relaxation of the excited $v = 1$ state. The transient absorption changes are measured with the mid-infrared pulse that is generated by the third part of the 800 nm beam. This mid-infrared pulse is sent onto a ZnSe wedged window, and the reflection from the front side is used as the probe pulse in the pump-probe experiment, while the reflection from the rear side serves as a reference to correct the measured signals for pulse to pulse energy fluctuations. The probe pulse is focused to the same spot in the sample as the pump, using the same gold-coated parabolic mirror. The reference pulse is also focused into the sample by this mirror, but not in spatial overlap with the pump and the probe pulses.

After the sample the probe and reference pulses pass through a rotatable polarizer to select the polarization components parallel and perpendicular to the polarization of the pump. Subsequently, the probe and reference pulses are dispersed by a spectrograph, and the intensities of the different frequency components are detected with a Mercury Cadmium Telluride (MCT) detector. The thus obtained transient absorption changes $\Delta\alpha_{\|}(\omega,t)$ and $\Delta\alpha_{\perp}(\omega,t)$ are used to construct the isotropic signal $\Delta\alpha(\omega,t) = \Delta\alpha_{\|}(\omega,t) + 2\Delta\alpha_{\perp}(\omega,t)$. This signal is insensitive to effects caused by reorientation of the molecular vibrations.

The Nafion membranes were purchased from Alpha Aesar. The membranes have a thickness of 180 μm and were cut into circles with a diameter of 9.0 mm. After removing all organic impurities by boiling the samples in 3% H_2O_2 at 50 °C for 24 hours,[? ?] the membranes were put in a 1 M HCl and 1 M NaCl solution for 24 hours, which results in a cation ratio [H^+]:[Na^+]=1:3.[?] We also prepared purely sodiated membranes as reference samples by putting Nafion membranes in a 1 M NaCl solution for 24 hours. As a final preparation step, the membranes were rinsed with deionized water.

Following the preparation the membranes were placed in desiccators containing saturated salt solutions to control the hydration level of the membrane. The hydration level λ defines the number of water molecules per -SO_3^- (sulfonate) group. The attained relative humidity and the hydration level are determined by the nature of the saturated salt solution.[? ?] The membranes are kept in the desiccator for at least one week, as we observed that the water uptake of Nafion can take several days. To perform the experiment, the membranes are transferred to a measurement cuvette. This cuvette is a gastight chamber, ensuring a constant humidity of the Nafion membranes during the experiment. To avoid sample degradation by continuous exposure to the infrared pump pulse, the cuvette was mounted on a rotation stage and was rotated constantly during the experiment in a plane perpendicular to the incoming beams.

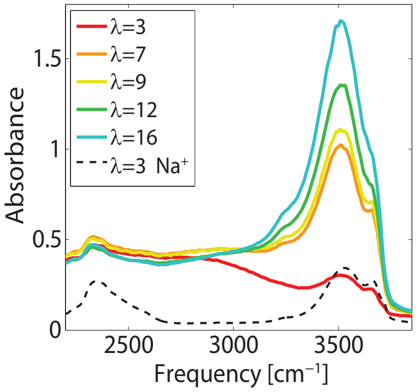

Figure 1: Linear absorption spectrum of hydrated H-Nafion membranes measured at different hydration level λ. For comparison also the spectrum of a Nafion membrane only containing Na^+ at λ=3 is shown.

Results and discussion

Linear spectra

?? shows the linear absorption spectra of protonated Nafion (H-Nafion) membranes at five different hydration levels, λ=3, 7, 9, 12 and 16. These membranes contain 1 cation (H^+ or Na^+, [H^+]:[Na^+]=1:3) and λ water molecules per sulfonate group. For comparison we also show the linear absorption spectrum of a Nafion membrane containing 1 Na^+ ions and λ=3 water molecules per sulfonate group (Na-Nafion). The peaks at 3520 cm^{-1} and 3660 cm^{-1} in the Na-Nafion membrane can be assigned to the hydrogen-bonded and non-hydrogen-bonded O–H stretch vibrations of H_2O molecules hydrating sulfonate groups.

For the H-Nafion membranes the H_2O bands are broadened and smaller in amplitude. In addition to these water peaks, the H-Nafion samples show a broad absorption that extends over the whole spectral range. This broadband absorption is assigned to proton hydration complexes. The absorption in the frequency range 2200-3000 cm^{-1} is assigned to the O–H stretch vibrations of the central H_3O^+ structure of Eigen proton hydration structures.? ? ? ? The absorption at frequencies 3200-3400 cm^{-1} is assigned to the O–H stretch vibrations of H_2O molecules that are hydrogen bonded to the central H_3O^+ ion of the Eigen structure and to the O–H stretch vibrations of H_2O

molecules that flank the proton in the Zundel structure. With increasing hydration level, the water bands at 3520 cm^{-1} and 3660 cm^{-1} grow, because the fraction of water molecules that are not involved in proton hydration structures increases.

Transient absorption spectra

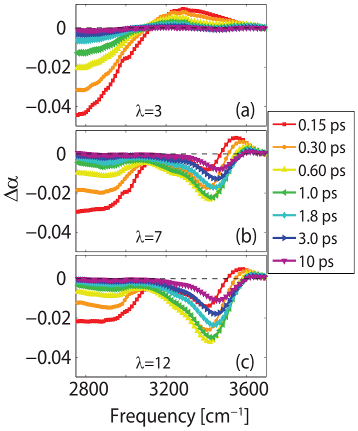

Figure 2: Isotropic transient absorption spectra of H-Nafion measured at different delays after excitation with an intense pump pulse centered at 2800 cm^{-1}, (a) for λ=3, (b) λ=7 and (c) for λ=12.

In **??** transient spectra at different delay times are shown for H-Nafion at three different values of λ. These transient spectra represent the change in isotropic absorption signal $\Delta\alpha$ induced by the excitation of the proton vibrations of an Eigen-like proton hydration structure with a pump pulse centered at 2800 cm^{-1}. The transient spectra thus constitute the difference spectra between the absorption spectra measured at certain pump-probe delays and the room temperature equilibrium spectrum of the sample. The data shown in **??**a for λ=3 are similar to the data presented in Ref. Liu-2014-PRL-112-258301. The data shown here are obtained with an excitation pulse with a different central frequency.

At frequencies <3100 cm^{-1} the transient spectra show a strong bleaching signal (negative $\Delta\alpha$) that rapidly decays with increasing delay time. The bleaching signal decays due to population relaxation of the excited $v = 1$ state and/or structural relaxation. The transient spectrum measured for λ=3 shows an induced absorption at frequencies $>$3100 cm^{-1}. This induced absorption decays on a similar time scale as the bleaching at frequencies $<$3100 cm^{-1}. The transient spectra at λ=7 and 12 show an initial absorption at frequencies $>$3100 cm^{-1} that rapidly evolves to a strong bleaching signal centered at 3400 cm^{-1} and a weak induced absorption signal at $\sim$3550 cm^{-1}. With increasing delay, the strong bleaching signal at 3400 cm^{-1} shows a partial decay and a blue shift to a frequency of 3450 cm^{-1}. Simultaneously, the weak absorption at $\sim$3550 cm^{-1} shows a partial decay and a small blue shift to $\sim$3600 cm^{-1}.

Measurements for long delay times (not shown) reveal that the amplitude and shape of the transient spectrum observed for delays $>$10 ps remain constant on a nanosecond time scale. This transient spectral response can be explained from the increase in temperature of the sample that results from the complete relaxation and equilibration of the energy of the excitation of the proton vibration. Heating leads to a decrease and blue shift of the absorption of the water bands. The difference spectrum between the spectrum at an elevated temperature and the spectrum at room temperature thus shows a bleaching at $\sim$3450 cm^{-1} and a weak induced absorption at $\sim$3600 cm^{-1}, in agreement with the shape of the transient spectrum observed for delays $>$10 ps. This transient spectrum remains constant on a nanosecond time scale because heat diffusion out of the focus is a relatively slow process that occurs on a time scale of microseconds.

In **??**a we present a zoom-in of the high-frequency part of the transient spectra of H-Nafion at λ=7 at early delay times. This figure also contains transient spectra measured at delays of 10 femtoseconds and 100 femtoseconds. The different transient spectra show that the excitation of the proton vibration at 2800 cm^{-1} leads to a rapid rise of an induced absorption at frequencies $>$3300 cm^{-1} that subsequently decays to a strong and relatively slowly decaying bleaching signal. The competition between the induced absorption and the bleaching signal is also illustrated in **??**b. In this figure the normalized absorption change at ν_{det}=3500 cm^{-1} is presented as a function of delay for the three different hydration levels indicated in **??**. It is seen that the excitation leads to the rise of an absorption signal that rapidly decays and evolves to a bleaching signal. The amplitude of the bleaching signal strongly increases with increasing λ. At the high hydration level of λ=12 the

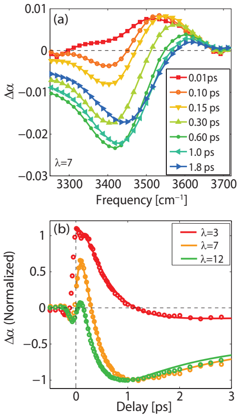

Figure 3: (a) Zoom in of the high-frequency range of the transient spectra of **??**b; (b) Normalized isotropic absorption changes of H-Nafion membranes as a function of delay measured at a probe frequency of ν_{det}=3500 cm^{-1} after excitation with ν_{exc}=2800 cm^{-1}. The absorption changes are shown for protonated Nafion membranes at three different hydration levels. Solid lines are guide for eye.

initial absorption is no longer observable. The bleaching signal shows a partial decay with a time constant of ∼1 ps. This decay becomes slower with increasing hydration level.

In **??** we present transient absorption spectra of H-Nafion with λ=3 over a broad spectral range. Similar data have been presented in Ref. Liu-2014-PRL-112-258301. The data shown here are obtained with an excitation pulse with a different central frequency. The transient spectral response of the Nafion membranes can be measured down to a frequency of ∼1500 cm^{-1}. The Nafion membranes are not transparent below this frequency, as a result of their high concentration of C-F vibrations.[?] In **??**a we present transient spectra in the frequency range 1850-3000 cm^{-1}. The transient spectra show that the bleaching signal initially peaks at ∼2800 cm^{-1} and undergoes a large shift to lower frequencies in the first few hundred femtoseconds after the excitation. As a result, the bleaching signal at <2000 cm^{-1} reaches its maximum at approximately 300 femtoseconds after the excitation.

In **??** the normalized absorption change is presented as a function of delay for four different detection frequencies. The maximum of the bleaching shifts to later delays with decreasing detection frequency, illustrating that the bleaching signal associated with the excitation of the proton vibration of the Eigen-like hydration structure shows a strong red shift directly after the excitation.

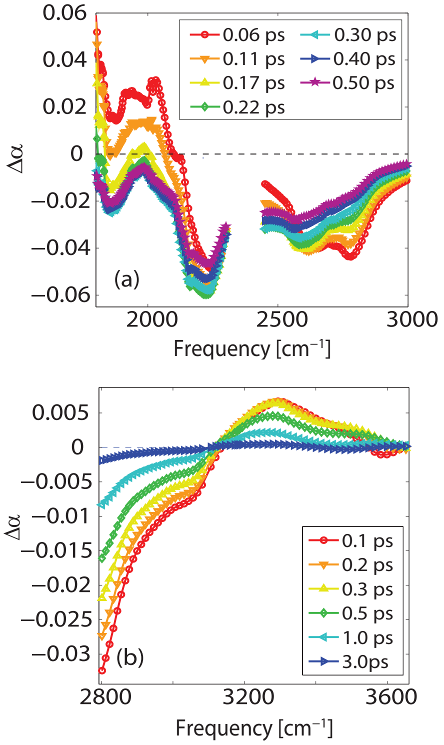

Figure 4: Isotropic transient absorption spectra of H-Nafion at a hydration level of λ=3 measured at different delays after excitation with an intense pump pulse centered at 2800 cm^{-1}. Compared to **??**(a) the spectrum is measured over a much broader frequency range. The frequency range 2300-2450 cm^{-1} is missing because of the too strong background absorption of the Nafion membrane. (a) Frequency range 1850-3000 cm^{-1}; (b) Frequency range 2800-3650 cm^{-1}.

It is also seen that the induced absorption at 3300 cm^{-1} shows a delayed rise with respect to the bleaching signal at 2550 cm^{-1}.

Interpretation

The large red shift of the bleaching signal of **??**a indicates that the excitation of the proton vibration induces a strong structural reorganization of the excited Eigen-like proton hydration structure. As the reorganization leads to a shift of the bleaching signal to frequencies $<$2000 cm^{-1}, this reorganization likely involves the transfer from the Eigen-like proton hydration structure to a Zundel-like proton hydration structure.[? ? ? ?] In this transfer the excited O–H vibration of the central H_3O^+ ion of the $H_9O_4{}^+$ Eigen-like structure evolves to the central O$\cdots$H$\cdots$O vibration of a $H_5O_2{}^+$

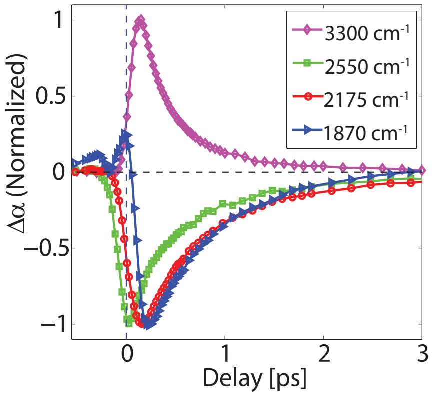

Figure 5: Normalized isotropic absorption changes as a function of delay at four different detection frequencies (ν_{det}=3300, 2550, 2175, and 1870 cm^{-1}) after excitation with ν_{exc}=2500 cm^{-1}. The signals are measured for a H-Nafion sample with λ=3. A positive signal implies an induced absorption, a negative signal a bleaching signal.

Zundel-like structure. This reorganization is illustrated in the top panel of **??**.

The evolution from an Eigen-like proton hydration structure to a Zundel-like structure also accounts for the rise of an induced absorption signal at frequencies >3200 cm^{-1}. The change from Eigen to Zundel affects the character of the two other, non-excited O–H vibrations of the central H_3O^+ ion of the Eigen-like structure. These vibrations evolve to the O–H vibrations of an H_2O molecule flanking the Zundel proton. This evolution is accompanied by a transfer of positive charge from the H atoms of the two non-excited O–H group of the central H_3O^+ ion to the H atom of the excited O–H group. The decrease in positive charge leads to a weakening of the hydrogen bonds of the non-excited O–H groups to H_2O molecules in the second hydration shell and thus to an increase of the frequency of the O–H stretch vibrations. Hence, the transfer from Eigen to Zundel also leads to the evolution of the (non-excited) Eigen-like proton vibrations that absorb at 2200-3000 cm^{-1} to vibrations that absorb at frequencies >3200 cm^{-1}.[? ? ? ?] This explanation agrees with the fact that the observed induced absorption at 3300 cm^{-1} shows a delayed rise with respect to the bleaching signal at 2550 cm^{-1}.

The excitation induced evolution from Eigen to Zundel can be well explained with the model for vibration-excitation induced proton transfer developed by S. Hammes-Schiffer and J.C. Tully,

Figure 6: Upper panel: schematic picture of the evolution from an Eigen proton hydration structure to a Zundel hydration structure and to a final new Eigen proton hydration structure, induced by the excitation of one of the proton vibrations of the Eigen structure. The vibrational frequencies of the different modes of the hydration structures are indicated. Middle and lower panels: two scenarios by which this vibrational excitation induced proton transfer can take place. Scenario I is similar to the scenario depicted in Figure 6.1 of Ref. nobel.

[?] and J.T. Hynes et al.[? ?] In this model excitation of the X–H vibration of an X–H$\cdots$Y hydrogen-bonded system induces a reorganization of the surrounding solvent that adiabatically changes the vibrational potential of the X–H$\cdots$Y system to a much more symmetric potential. This reorganization is driven by the energy reduction associated with the adiabatic evolution of the high energy $v = 1$ state in the tight X–H potential to the much lower energy $v = 1$ state in the broad, near-symmetric X$\cdots$H$\cdots$Y potential.

The evolution to the near-symmetric X$\cdots$H$\cdots$Y potential corresponds to a partial transfer of the proton charge. The proton transfer can be completed with two different scenarios, illustrated in the middle and lower panels of **??**. In scenario (I) vibrational relaxation of the delocalized $v = 1$ state in the X$\cdots$H$\cdots$Y potential will bring the system to a relatively high energy $v = 0$ state within the broad X$\cdots$H$\cdots$Y potential. This $v = 0$ state rapidly evolves either back to the $v = 0$ state of the original tight X–H$\cdots$Y potential or proceeds to the $v = 0$ state of a new tight X$\cdots$H–Y potential. The latter case corresponds to a complete proton transfer from X to Y. Such vibrational excitation induced proton transfer has been proposed for the reaction between HF and H_2O.[?] Scenario (I) is similar to the mechanism of vibrational excitation induced proton transfer shown in Figure 6.1 of

Ref. nobel. In scenario (II), the delocalized $v = 1$ state of the X$\cdots$H$\cdots$Y potential corresponds to the lowest-energy vibrational state in the right well of this potential. This state can adiabatically evolve to the $v = 0$ state of a new tight X$\cdots$H–Y potential, thus completing the proton transfer from X to Y. In scenario (II), the proton transfer is thus directly accompanied by vibrational energy relaxation. Within scenario (II), the delocalized $v = 1$ state of the near-symmetric X$\cdots$H$\cdots$Y potential can also relax back to the $v = 0$ state of this potential, from which the system will evolve back to the $v = 0$ state of the original tight X–H$\cdots$Y potential. The relative importance of the two scenarios will depend on the height of the barrier separating the two wells and the rate at which the vibrational potential changes as a result of the structural evolution of the hydration shell. Scenario II becomes more important if the barrier is low and when the structural evolution is slow.

A prerequisite for both scenarios of excitation-induced proton transfer is that the $v = 1$ state possesses a sufficiently long vibrational lifetime. If the $v = 1$ state would relax very quickly, the system would be back in the vibrational ground state before the adiabatic adaptation of the vibrational potential can take place.

For hydration levels higher than λ =3 we observe that the induced absorption at frequencies >3200 cm^{-1} quickly gives way to a bleaching signal centered at 3400 cm^{-1}. This bleaching signal cannot be due to a transfer of the vibrational excitation from the excited proton vibration to a water O–H vibration, as in this case the resulting signal should not only consist of a $v = 0 \rightarrow 1$ bleaching signal of the water O–H vibrations, but should also contain a clear signature of excited $v = 1 \rightarrow 2$ absorption of these vibrations at a frequency of ~3200 cm^{-1}. This latter absorption is not observed in the transient absorption spectra of **??**. Instead, we observe that the strong bleaching signal at ~3400 cm^{-1} is accompanied by a weak induced absorption at a higher frequency of ~3550 cm^{-1}. This spectral signature can be well explained from the effect of heating on the absorption spectrum of the O–H stretch vibrations of water.[?] Therefore, we assign the strong bleaching signal at ~3400 cm^{-1} and the weak induced absorption at ~3550 cm^{-1} to a local heating effect that results from the vibrational relaxation of the $v = 1$ state of the excited proton vibration. The vibrational relaxation corresponds to the non-adiabatic transition of the $v = 1$ state of the proton vibration to the $v = 0$

state and is enabled by the strong coupling of the proton vibration to the low-energy degrees of freedom of the hydration shell.[?]

The increase in temperature resulting from the vibrational relaxation involves a weakening of the hydrogen bonds between water molecules, and between water molecules and sulfonate groups of Nafion, which in turn leads to a decrease of the absorption cross-section and a blue shift of the O–H stretch vibrations. This explanation is consistent with the observation that the amplitude of the bleaching increases with increasing hydration level. With increasing level of hydration, the proton will be surrounded (hydrated) by a larger number of water molecules and thus the effect of heating on the direct surroundings of the proton will have a more pronounced effect in the absorption region of the O–H stretch vibrations of water.

The bleaching at $\sim$3400 cm^{-1} and induced absorption at $\sim$3550 cm^{-1} show a partial decay and blue shift on a time scale of $\sim$1 ps. As discussed in the previous subsection, the final transient spectrum corresponds very well to the difference spectrum between the absorption of the Nafion sample at an elevated temperature and the spectrum at room temperature. Therefore, we assign the partial decay and blue shift to the cooling of the local hot surroundings of the proton vibration, leading to a full thermalization of the excess energy. In this cooling process, part of the thermal energy will be transferred to the Nafion membrane, thus explaining the decrease in the amplitudes of the bleaching and the induced absorption signal. In the cooling process the thermal energy will also be transferred to water molecules that are further away from the originally excited hydrated proton vibration. For water molecules that are close to a proton the hydrogen bonds will be stronger than for water molecules that are far away from a proton and for water molecules that are close to Na^+ ions. As a consequence, the absorption spectrum of water molecules close to a proton will be red-shifted compared to that of the other water molecules embedded in the Nafion membrane channels. The transfer of thermal energy from the water molecules close to the originally excited proton to water molecules that are further away will thus lead to a small blue shift of the transient spectrum.

Modeling

Following the interpretation of the previous subsection we describe the data of the Nafion membranes with a kinetic model that includes vibration-excitation induced proton transfer, relaxation of the excited proton vibration, and cooling. This model is schematically depicted in **??**.

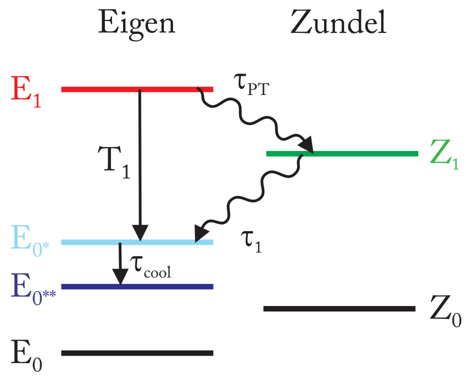

Figure 7: Schematic picture of the kinetic model for excitation-induced proton transfer and vibrational relaxation used to fit the data of **??**.

The levels E_1 and Z_1 correspond to the excited vibrational $v = 1$ states of the Eigen-like and Zundel-like proton hydration structures, and E_0 and Z_0 are the $v = 0$ ground states of these structures. The level E_{0*} corresponds to a locally hot state of the Eigen-like structure, and E_{0**} to the final fully thermalized state of this structure. The excited state E_1 relaxes to Z_1 with a time constant τ_{PT} representing the vibrational-excitation induced proton transfer process. The rate of this transfer is the sum of the proton transfer rates of scenarios (I) and (II), illustrated in **??**, meaning that $(\tau_{\mathrm{PT}})^{-1} = (\tau_{\mathrm{PT,I}})^{-1} + (\tau_{\mathrm{PT,II}})^{-1}$. The description of the proton transfer with two discrete excited vibrational levels E_1 and Z_1 forms a simplified description of the gradual evolution of the Eigen-like proton hydration structure to a Zundel-like structure. This approximation is reasonably valid when τ_{PT} is short. The state E_1 not only evolves to Z_1 with τ_{PT} but also relaxes to E_{0*} with the vibrational relaxation time constant T_1.

The excited proton state Z_1 relaxes with time constant τ_1 to E_{0*}. In scenario (I) and in the case of backward proton transfer within scenario (II), the τ_1 relaxation process consists of vibrational relaxation within the Zundel-like vibrational potential, followed by a structural relaxation as a result of which the potential evolves (back) to an Eigen-like vibrational potential. In the case of forward proton transfer within scenario (II), the τ_1 relaxation process consists of the evolution of the $v = 1$ state of the Zundel-like potential to the $v = 0$ state of a new Eigen-like potential. In all cases the τ_1 relaxation process involves the transfer of the vibrational energy of the excited Zundel-like proton vibration to low-energy (solvent) degrees of freedom. E_{0*} cools with τ_{cool} to the final state E_{0**}. The levels E_1, Z_1, E_{0*}, and E_{0**} are thus coupled by four time constants τ_{PT}, T_1, τ_1 and τ_{cool}. The coupled kinetic equations are:

$$\begin{aligned}
\frac{d}{dt}(n_{E_1}) &= -\frac{n_{E_1}}{\tau_{\text{PT}}} - \frac{n_{E_1}}{T_1} \\
\frac{d}{dt}(n_{Z_1}) &= \frac{n_{E_1}}{\tau_{\text{PT}}} - \frac{n_{Z_1}}{\tau_1} \\
\frac{d}{dt}(n_{E_{0*}}) &= \frac{n_{E_1}}{T_1} + \frac{n_{Z_1}}{\tau_1} - \frac{n_{E_0*}}{\tau_{\text{cool}}} \\
\frac{d}{dt}(n_{E_{0**}}) &= \frac{n_{E_{0*}}}{\tau_{\text{cool}}}
\end{aligned} \tag{1}$$

with n_{E_1}, n_{Z_1}, n_{E_0*}, and n_{E_0**} the populations of the levels denoted in the subscript.

The value of τ_{PT} is determined from a fit of the data obtained at λ=3, the lowest studied hydration level. At higher hydration levels, the signature of the state Z_1 becomes less clear due to the increasing contribution of the vibrational relaxation, making it cumbersome to determine τ_{PT} and τ_1. Therefore we use the value of τ_{PT} obtained at λ=3 in fitting the data at higher hydration levels, and we take τ_1 to be the same as T_1. The values of T_1 and τ_{cool} are fitted to the data at each studied hydration level. Each of the levels of the model has an associated transient spectrum. The amplitude and shape of these transient spectra, form free parameters in fitting the transient spectra of the Nafion sample at each hydration level. The total transient absorption change $\Delta\alpha(\nu,t)$ at detection frequency ν and delay time t is given by:

$$\Delta\alpha(\nu,t) = \sigma_{E_1}(\nu)n_{E_1}(t) + \sigma_{Z_1}(\nu)n_{Z_1}(t) + \sigma_{E_0*}(\nu)n_{E_0*}(t) + \sigma_{E_0**}(\nu)n_{E_0**}(t) \tag{2}$$

In **??** we show the results of the fit for H-Nafion at λ=7 and 12. The fitted transient spectra, represented by the solid lines in **??**a,b, provide an excellent description of the data. **??**c,d show the spectral shapes of σ_{E_1}, σ_{Z_1}, σ_{E_0*}, and σ_{E_0**} and **??**e,f show the population dynamics of these levels.

The spectrum σ_{E_1} consists of a strong bleaching signal around 2800 cm^{-1}, as a result of the excitation of one of the proton vibrations of the Eigen-like hydration structure. This excitation leads to a depletion of the fundamental $v = 0 \rightarrow 1$ absorption from E_0 to E_1 and stimulated emission $v = 1 \rightarrow 0$ from E_1 to E_0. The spectral response σ_{E_1} shows additional small induced absorption changes between 3250 and 3500 cm^{-1}. This latter response can be explained from cross-anharmonic coupling of the excited Eigen proton vibration and the O–H stretch vibrations of nearby water molecules. The cross-anharmonic coupling between an excited vibration and a non-excited vibration leads to a direct shift in frequency of the non-excited vibration, usually to lower frequencies. Hence, excitation of the Eigen proton vibration can lead to a red shift of the O–H stretch vibrations of nearby H_2O molecules, thus explaining the observation of a weak induced absorption in the red wing of the O–H stretch absorption band (near 3350 cm^{-1}) and a decrease in absorption in the blue wing of the O–H stretch absorption band (near 3500 cm^{-1}).

The state E_1 is transferred to Z_1 with a proton transfer time constant τ_{PT} of 170 ± 20 fs. The spectrum of Z_1 shows a smaller bleaching signal in the frequency region around 2800 cm^{-1} than E_1. This change in amplitude is caused by the vanishing of the $v = 1 \rightarrow 0$ stimulated emission contribution to the bleaching signal of the Eigen proton vibration. The residual bleaching around 2800 cm^{-1} is caused by the remaining depletion of the fundamental $v = 0 \rightarrow 1$ absorption from E_0. The spectrum of Z_1 also contains two broad induced absorption peaks at 3250 and 3500 cm^{-1}. This induced absorption signal is present at all studied hydration levels.

As discussed in the previous subsection, the absorption peak centered at 3250 cm^{-1} can be assigned to the O–H stretch vibrations of H_2O molecules flanking the Zundel proton. The absorption peak at 3500 cm^{-1} is assigned to the absorption of water molecules in the second solvation shell of the Zundel proton. The evolution to the Zundel structure turns the water molecules that are hydrogen bonded to the non-excited Eigen proton vibrations to water molecules in the second

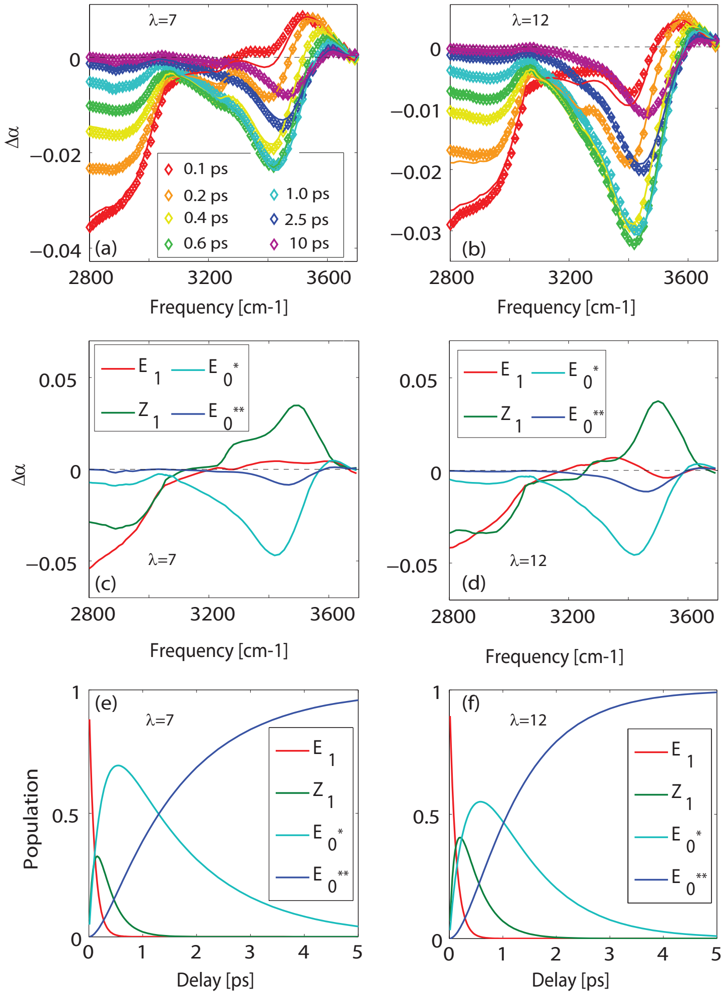

Figure 8: a) and b): Experimental transient spectra (symbols) and fitted results (solid lines) using the kinetic model of **??** and equations **??**, for hydration level λ=7 (a) and λ=12 (b); c) and d): Spectral components of the different levels, corresponding to the fits of a) and b), respectively; e) and f): Population dynamics of the different levels, corresponding to the fits of a) and b), respectively.

hydration shell of the Zundel proton. The increased distance to the proton charge weakens the hydrogen bonds of these water molecules, leading to a shift of their absorption bands to higher frequencies. The resulting absorption will be similar to that of water molecules hydrating a sulfonate group without a nearby (hydrated) proton. These bands absorb at $\sim$3500 cm^{-1}, as can be derived from the absorption spectra of Nafion membranes at high hydration levels.

The blue shift of the absorption of the water molecules that are hydrogen bonded to the non-excited Eigen proton vibrations implies that the original absorption of these molecules, at frequencies of $\sim$3300 cm^{-1}, decreases. This decrease in absorption contributes to the overall amplitude of the σ_{Z_1} spectrum in this frequency region, and thus can explain why the peak at 3250 cm^{-1} of the σ_{Z_1} spectrum is weaker than the absorption peak at 3500 cm^{-1}. This explanation also agrees with the fact that the absorption peak at 3500 cm^{-1} grows with increasing hydration level, as can be seen from the comparison of the σ_{Z_1} spectra of Nafion membranes with λ=7 and 12 in **??**c,d. At higher hydration levels there will be more water molecules hydrating the central H_3O^+ ion of the Eigen-like proton hydration structure, and the shift in absorption of these water molecules from $\sim$3300 cm^{-1} to $\sim$3500 cm^{-1}, following the transfer from Eigen to Zundel, forms a stronger contribution to the overall σ_{Z_1} spectrum.

The states E_1 and Z_1 both relax to the state E_{0*}. The spectrum of E_{0*} consists of a strong bleaching signal centered at 3400 cm^{-1} and a weak absorption around 3550 cm^{-1}. As discussed in the previous subsection, these spectral changes can be well explained from a local heating effect resulting from the relaxation of the proton vibration that changes the absorption spectrum of nearby water molecules. The local hot state E_{0*} cools to the fully thermal state E_{0**} that has a spectrum with a similar shape as the spectrum of E_{0*}, but with a smaller amplitude and shifted to higher frequencies. For the other measured hydration levels (λ=3, 9 and 16) the spectra and population dynamics of the different levels are similar in shape as for the hydration levels shown in **??**. In **??** the fitted values of the time constants T_1 and τ_{cool} are presented as a function of hydration level. It is seen that T_1 becomes shorter with increasing hydration level, and that τ_{cool} becomes longer.

Discussion

The results of **??**, **??** and **??** demonstrate the occurrence of partial transfer of the proton charge in hydrated Nafion membranes following excitation of a molecular vibration to its first excited state. For most systems, the energy of a single vibrational quantum does not suffice to initiate a chemical reaction. An exception is the cis-trans isomerization of nitrous acid (HONO) that can be induced by excitation of the O–H stretch vibration.[? ?] Other examples of vibration-induced

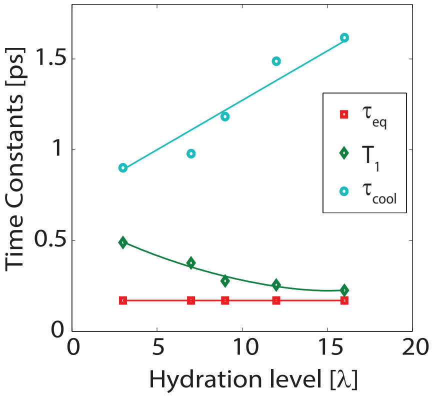

Figure 9: The time constants τ_{PT}, T_1 (T_1=τ_1), and τ_{cool} as a function of hydration level. The time constants are obtained from fits of the data to the kinetic model of **??** and equations (1). In the fit the time constants τ_1 and T_1 are assumed to have the same value. The solid lines are guides to the eye.

reactivity all concern systems that are already in a reactive state, like the bimolecular interactions between radicals and small molecules in the gas phase.[?] [?] For these systems the excitation of a molecular vibration has been observed to increase the rate of particular reaction channels.

It is interesting to compare the presently studied vibration-induced proton transfer in hydrated Nafion with proton transfer by conventional photo-acids. For conventional photo-acids proton transfer is induced by electronic excitation with visible or UV light. This electronic excitation affects the electronic configuration such that a particular O–H or N–H bond of the photo-acid weakens.[?] [?] [?] [?] [?] [?] [?] [?] [?] [?] This is a clear difference with vibration-induced proton transfer in Nafion for which the excitation hardly affects the strength of the O–H bond, as excitation of the proton vibration has a minor direct effect on the electronic configuration. The weakening of the O–H or N–H bond of a conventional photo-acid is usually followed by another electronic reorganization that leads to release of the proton and a stabilization of the conjugate photobase. For the widely studied photo-acid HPTS (8-hydroxy-1,3,6-pyrenetrisulfonic acid) it has been shown that this subsequent reorganization involves a transfer of negative charge from the oxygen atom to which the proton was bound to the aromatic ring system.[?] [?] This redistribution of negative charge is essential for the proton to leave, as it turns the excited photobase into a weak base. Vibration-induced proton transfer in Nafion is probably accompanied by a similar transfer of negative charge from the oxygen atom to which the proton was bound to other atoms in the proton hydration structure, as this transfer is an inherent property of the transfer between Eigen to Zundel proton hydration structures.[? ? ? ? ? ? ?] As in the excited conjugate photobase of HPTS, this redistribution of negative charge aids in the stabilization of the transferred proton state.

For conventional photo-acids the proton release and stabilization of the conjugate photo-base is accompanied by a repositioning of surrounding solvent molecules that lowers the energy of the excited state.[? ? ? ? ?] The lowering of the energy leads to a very strong red shift (Stokes shift) of the fluorescence and the transient absorption.[? ? ? ? ?] In the case of protons in Nafion, the excited proton vibration of the Eigen structure also undergoes a large Stokes shift when it evolves to the much lower energy state of the excited proton vibration of a Zundel structure.

Vibration-induced proton transfer is in strong competition with vibrational relaxation.[?] Relaxation of the excited proton vibration occurs on a time scale <500 fs, and thus the reorganization required for proton transfer has to occur within this short time window. The vibrational relaxation becomes faster with increasing hydration level thus making proton transfer less probable. Nevertheless, the analysis of **??** shows that proton transfer is still possible at higher hydration levels. We find that the state Z_1 which represents the final state of the proton transfer, has a maximum induced absorption of $\sim$0.03 OD in the frequency region $>$3200 cm^{-1}, at all studied hydration levels. The persistence of the amplitude of the absorption of the Z_1 level at $>$3200 cm^{-1} for all studied hydration levels, shows that vibration-excitation induced proton transfer is still possible at high hydation levels. Nevertheless, the fraction of excited Eigen proton hydration structures that reorganizes to a Zundel structure decreases with increasing hydration level because the competing vibrational relaxation becomes faster. We find that the vibrational relaxation time constant T_1 decreases from 490±40 fs at λ=3 to 230±30 fs at λ=16, which means that an increasing fraction of excited Eigen proton vibrational states E_1 relaxes to the local hot ground state E_{0*} and thus no longer proceeds to the first excited Zundel vibrational state Z_1. Due to this competition, Z_1 becomes less populated with increasing hydration level, and vibration-excitation proton transfer is no longer as clearly observed as at low hydration levels. An additional effect is that the amplitude of the bleaching signal associated with the relaxed, local hot state E_{0*} increases with increasing hydration level. This bleaching signal obscures the induced absorption signal in the frequency region >3200 cm^{-1} associated with vibration-induced proton transfer.

The decrease of the vibrational relaxation time constant T_1 with increasing hydration level implies that the density of coupled combination tones that are capable of accepting the energy of the excited proton vibration increases when the number of water molecules close to the proton vibration increases. For pure liquid water the vibrational relaxation time constant T_1 of the Eigen-like proton vibration is observed to be 120±20 femtoseconds.[?] It is to be expected that the value of T_1 of protons in Nafion membranes would approach this value at very high hydration levels. For liquid water, the small value of T_1 of the proton vibration will completely obscure the observation of vibration-excitation induced proton transfer.

We observe that τ_{cool} increases from 0.9±0.05 ps at λ=3 to 1.63±0.05 ps at λ=16, meaning that the cooling of a locally hot cluster of water molecules (surrounding the originally excited proton vibration) becomes slower with increasing hydration level. This increase of the cooling time constant with increasing size of the water cluster is consistent with the results of a study of the cooling of water nanodroplets.[?] In this latter study it was found that the cooling slows down with increasing size of the water nanodroplet. This observation can be explained from the fact that cooling involves the conduction of thermal energy through the surface of the heated volume. As the surface to volume ratio decreases with increasing droplet or water cluster size, the cooling will become slower with increasing level of hydration.

Conclusions

We studied the vibrational relaxation and structural reorganization dynamics of hydrated protons in the nanochannels of Nafion membranes. We excited the proton vibration of Eigen-like ($H_9O_4{}^+$) proton hydration structures with ultrashort mid-infrared light pulses with frequencies in the range

2500-2900 cm^{-1} ($3.4 \sim 4.0$ μm). The subsequent relaxation and structural dynamics are measured with ultrashort mid-infrared detection pulses that are tunable from 1850-3700 cm^{-1} (2.8-5.6 μm). We find that the excitation of the proton vibration leads to a reorganization of the Eigen proton hydration structure to a Zundel-like ($H_5O_2{}^+$) proton hydration structure. This reorganization is driven by the substantial lowering of the energy of the excited $v = 1$ state of the proton vibration when the vibrational potential of the proton adiabatically evolves from the relatively narrow and asymmetric shape associated with the Eigen structure, to the broad and symmetric shape associated with the Zundel structure. The reorganization leads to a transfer of the proton charge from the three hydrogen atoms of the central H_3O^+ ion of the Eigen structure to the central hydrogen atom of the $H_5O_2{}^+$ Zundel-like structure. The time constant τ_{PT} of this transfer is 170±20 fs.

Vibration-excitation induced proton transfer becomes less prominent with increasing hydration level because the vibrational energy relaxation of the proton becomes faster. We observe that the vibrational relaxation time constant T_1 decreases from 490±40 fs at λ=3 to 230±30 fs at λ=16. Vibrational relaxation is observed to lead to a strong local heating effect of nearby water molecules. These hot water molecules cool by transferring their excess energy to the Nafion membrane and to other water molecules that are further away from the initially excited proton vibration. The cooling time constant τ_{cool} increases from 0.90±0.05 ps at λ=3 to 1.63±0.05 ps at λ=16.

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Graphical TOC3

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