

Vibrational and Structural Relaxation of Hydrated Protons in Nafion Membranes

Liyuan Liu, Stephan Lotze, and Huib J. Bakker*

*FOM Institute for Atomic and Molecular Physics,
Science Park 104, 1098 XG Amsterdam, The Netherlands*

Abstract

We study the vibrational dynamics of the bending mode at 1730 cm^{-1} of proton hydration structures in Nafion membranes with polarization-resolved infrared (IR) pump-probe spectroscopy. The bending mode relaxes to an intermediate state with a time constant T_1 of 170 ± 30 fs. Subsequently, the dissipated energy equilibrates with T_{eq} of 1.5 ± 0.2 ps. The transient absorption signals show a long-living anisotropy, which indicates that for part of the excited proton hydration clusters the vibrational energy dissipation results in a local structural change, e.g. the breaking of a local hydrogen bond. This structural relaxation relaxes with a time constant of 38 ± 4 ps.

*Electronic address: bakker@amolf.nl

I. INTRODUCTION

Over the last decades there has been extensive theoretical and experimental research on the nature of excess protons in aqueous systems [1–9]. Protons show an extremely high mobility in aqueous media, which has been explained from special transport mechanisms in which the charge of the proton is transferred between adjacent water molecules. With *ab initio* molecular dynamics simulations it was found that proton transfer in bulk liquid water involves the structural interconversion of proton hydration structures.[10–12]. The two limiting forms of these clusters are the Eigen hydration structure (H_9O_4^+), that is formed by a central hydronium (H_3O^+) ion surrounded by three water molecules accepting hydrogen bonds from the O–H groups of the hydronium ion [13], and the Zundel hydration structure (H_5O_2^+), in which the proton is flanked by two water molecules [14].

Hydrated Nafion membranes constitute a very special medium for protons to be transferred. Nafion is widely used as a proton conducting membrane in hydrogen fuel cells. The chemical structure of Nafion is formed by a hydrophobic Teflon-like backbone containing hydrophilic ionic side groups. The structure of Nafion membranes on the nanometer scale has been intensely studied over the last decades [15–17]. It has been shown that hydrated Nafion likely consists of cylindrical inverted micelles, thus forming parallel water-filled nano-channels with a diameter of ~ 4 nm [17]. The structure of the Nafion membrane is schematically depicted in Fig. 1.

The ability of Nafion to conduct protons strongly depends on the level of hydration of the membrane.[18, 19]. Only above a certain degree of hydration the membranes become proton conducting. The mechanism of proton conduction in Nafion membranes has been studied with advanced *ab initio* molecular dynamics simulations.[20–23] With these simulations it was found that protons in Nafion predominantly form Eigen-like hydration structures, except for the first hydration shell of the Nafion sulfonate groups, where the proton-hydration structure is more Zundel-like.[20, 21] The simulations showed that proton transfer in hydrated nafion can involve both particle diffusion, i.e. Stokes diffusion of charged hydrated structures and Grotthuss conduction, the latter process becoming increasingly important with increasing hydration level.

Recently, we studied the structural dynamics of proton hydration structures in Nafion membranes at low hydration levels with two-color femtosecond mid-infrared spectroscopy of the O–H stretch vibrations of the proton-hydration clusters. We observed that the excitation of the stretch vibration of the proton triggers a structural reorganization that involves a partial transfer of the

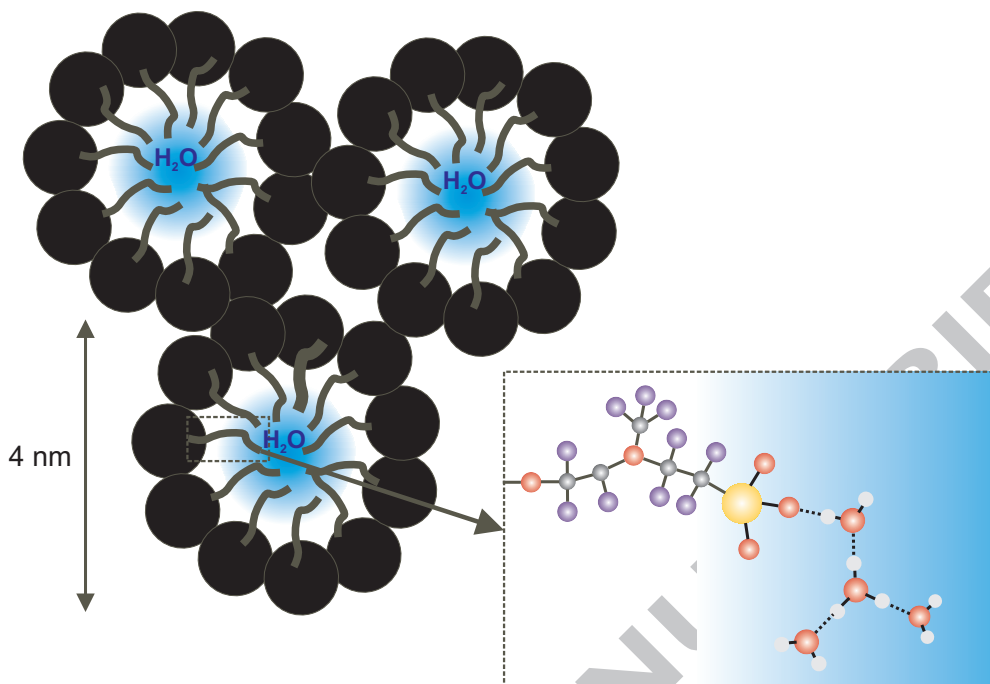


FIG. 1: Schematic picture of Nafion membrane nanochannels in cross-section. Nafion consists of teflon-like polymer backbones (represents as black spheres) with polar headgroups that contain negative SO_3^- (sulfonate) groups and positive counter-ions (H_3O^+ or Na^+). The zoom-in represents the molecular structure of the polar headgroup with H_3O^+ as the counter-ion and three H_2O molecules per sulfonate group. The colors indicate different types of atoms: oxygen is red, carbon is black, fluorine is purple, sulphur is yellow and hydrogen is grey.

proton charge.[24, 25] Here we report on a study of the vibrational and structural relaxation dynamics following excitation of the $\sim 1730\text{ cm}^{-1}$ bending vibrations of proton-hydration clusters in Nafion.

II. EXPERIMENT

We generate mid-infrared pulses near $\sim 1730\text{ cm}^{-1}$ using a white-light seeded high-energy optical parametric amplifier (OPA, Light Conversion HE-TOPAS) that is pumped by the pulses (800 nm, 40 femtoseconds, 4.5 mJ) delivered by a commercial Titanium:Sapphire amplifier (Coherent Legend Elite Duo) at a repetition rate of 1 kHz. The generated mid-infrared pulses have a central wavelength of $5.8\text{ }\mu\text{m}$ (1730 cm^{-1}), a pulse energy of $\sim 20\text{ }\mu\text{J}$, a duration of $\sim 100\text{ fs}$, and a bandwidth of $\sim 300\text{ cm}^{-1}$. The pulses are not bandwidth limited meaning that they possess a sig-

nificant phase modulation. We verified that this phase modulation does not correspond to a linear frequency chirp. We measured the cross-correlation of the excitation and the detection pulse using two-photon absorption in InAs. The width of the cross-correlation trace is ~ 140 fs.

The mid-infrared beam is split into three parts with wedged CaF_2 -windows. The reflections ($\sim 4\%$) of the mid-infrared pulses are used as probe and reference pulses. The transmitted infrared beam is used as the excitation pulse. The probe is sent over a motorized delay-stage and used to monitor the transient absorption changes as a function of time delay between excitation and probe pulses. The excitation beam is modulated at 500 Hz by means of a mechanical chopper, to record the excitation-induced absorption changes $\Delta\alpha$. The reference pulse is used to perform a pulse-to-pulse normalization of the intensity of the probe pulse. A rotatable wire-grid polarizer is placed behind the sample cell to select components of the probe pulses that are polarized either parallel or perpendicular with respect to the polarization of the pump pulses. The probe and reference beams are sent into an imaging spectrograph (Lot Oriel), and imaged on a 2×32 pixel mercury cadmium telluride (MCT) infrared detector (Infrared Associates). The transient absorption changes obtained under parallel ($\Delta\alpha_{\parallel}(\omega, t)$) and perpendicular ($\Delta\alpha_{\perp}(\omega, t)$) polarization of the pump and probe pulses are used to construct the isotropic signal $\Delta\alpha(\omega, t)_{iso}$

$$\Delta\alpha_{iso}(t) = \frac{\Delta\alpha_{\parallel}(t) + 2 \cdot \Delta\alpha_{\perp}(t)}{3} \quad (1)$$

and the anisotropy parameter $R(t)$

$$R(t) = \frac{\Delta\alpha_{\parallel}(t) - \Delta\alpha_{\perp}(t)}{\Delta\alpha_{\parallel}(t) + 2 \cdot \Delta\alpha_{\perp}(t)} \quad (2)$$

The isotropic signal is unaffected by the reorientation of the transition dipole moment of the 1730 cm^{-1} mode and gives information on the decay of the excited vibration states and the subsequent thermalization dynamics. The anisotropy parameter $R(t)$ represents the dynamics of the depolarization of the excitation. To avoid direct excitation of the H_2O bending mode in the sample, we placed a water (H_2O) filter in the optical path of the excitation beam. This water filter is formed by a water layer between two CaF_2 windows separated by a $4 \mu\text{m}$ Teflon spacer. This filter shows an absorption of 1.5 OD at the absorption maximum of the bending mode of H_2O at 1650 cm^{-1} .

We obtained Nafion membranes with a thickness of $50 \mu\text{m}$ thickness from Alpha Aesar. The membranes were boiled for one hour in a 3% H_2O_2 solution to remove organic contamination, for one hour in deionized water, and finally for one hour in a 1 M solution of a mixture of HCl

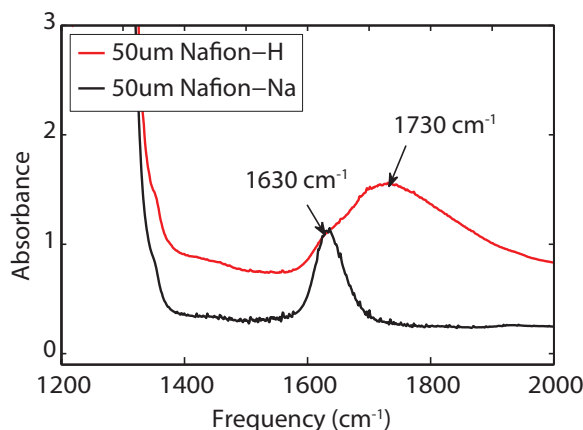


FIG. 2: Linear spectra of proton-terminated (red line) and sodium-terminated (black line) Nafion membranes of 50 μm thickness. The hydration level of both samples corresponds to ~ 4 water molecules per sulfonate group ($\lambda = 4$). The spectrum of sodium-terminated Nafion membrane has been scaled for clarity.

and NaCl where the HCl/NaCl determines the obtained $[\text{H}^+]:[\text{Na}^+]$ cation ratio. Following this treatment, the membranes were rinsed with deionized water [26, 27]. The purified Nafion membranes were subsequently exposed to a saturated aqueous solution of LiBr at room temperature for one week, thus establishing the hydration level of the Nafion membrane with high accuracy. The hydration level of Nafion membrane under the aforementioned conditions corresponds to a ratio λ ($=[\text{H}_2\text{O}]:[-\text{SO}_3^-]$) of approximately four water molecules per sulfonate group.

In the experiments with $[\text{H}^+]:[\text{Na}^+]=1:0$ and $0.75:0.25$ we used a single 50 μm Nafion membrane, and in the experiments with $[\text{H}^+]:[\text{Na}^+]=0.67:0.33$ and $[\text{H}^+]:[\text{Na}^+]=0.5:0.5$ we used two stacked 50 μm Nafion membranes. The sample cell chamber was mounted on a rotating stage to avoid sample degradation during the IR pump-probe experiments.

III. RESULTS AND DISCUSSION

A. Linear Spectra

In Fig. 2 we present the linear infrared absorption spectra of 50 μm -thick proton-terminated ($[\text{H}^+]:[\text{Na}^+] = 1:0$) and sodium-terminated ($[\text{H}^+]:[\text{Na}^+] = 0:1$) Nafion membranes. The absorption spectrum of the sodium-terminated Nafion membrane shows a narrow absorption band with a resonance frequency of $\sim 1630 \text{ cm}^{-1}$. This band can be assigned to the bending mode of water

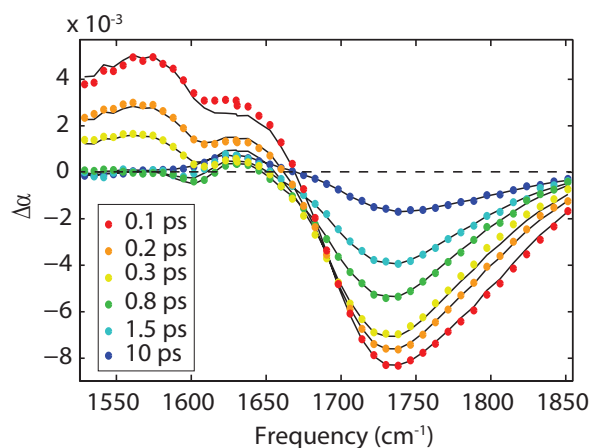


FIG. 3: Transient absorption spectra of proton-terminated Nafion membranes (thickness $50 \mu\text{m}$), hydrated with H_2O ($[\text{H}^+]:[\text{Na}^+] = 1:0$) at different delays after excitation of the bending mode at $\sim 1730 \text{ cm}^{-1}$.

molecules that are hydrogen bonded to other water molecules. The absorption band is red shifted by $\sim 20 \text{ cm}^{-1}$ relative to the H_2O bending mode in bulk water because the hydrogen bonding interactions between water molecules and the sulfonate groups of Nafion, and among water molecules in small water clusters, are weaker than the hydrogen bonding interactions in bulk water. The infrared absorption spectrum of proton-terminated Nafion membranes exhibits a broad and intense absorption band centered at 1730 cm^{-1} . This band has been assigned to the bending modes of Eigen and Zundel proton hydration structures [5, 28–30]. For the Eigen structure this band is associated with the degenerate symmetric and antisymmetric bending modes of the hydronium core of the Eigen structure, for the Zundel structure the 1730 cm^{-1} band results from the bending vibrations of the water molecules flanking the Zundel proton, coupled to the central Zundel proton ($\text{O} \cdots \text{H}^+ \cdots \text{O}$) vibration [4, 5, 28–30]. The red side of the 1730 cm^{-1} band exhibits a small, but significant shoulder at $\sim 1630 \text{ cm}^{-1}$, which we assign to the bending mode of water molecules that are not strongly involved in the hydration of the proton, e.g. to water molecules that are located in the outer hydration shells of the proton, and to water molecules that are located in the hydrophobic pockets of the Nafion membrane.

B. Vibrational Relaxation

Fig. 3 presents isotropic transient absorption changes following excitation of the 1730 cm^{-1} mode in proton-terminated Nafion membranes ($[\text{H}^+]:[\text{Na}^+] = 1:0$) at different delay times. At

short delay times, the transient absorption spectra show a negative (bleaching) signal centered at 1730 cm^{-1} and a positive, induced absorption signal at frequencies below 1680 cm^{-1} . The bleaching signal results from the depletion of the ground state ($\nu=0\rightarrow1$ transition) and stimulated emission from the first excited state ($\nu=1\rightarrow0$). The induced absorption at lower frequencies (1530 cm^{-1} to 1650 cm^{-1}) is due to $\nu=1\rightarrow2$ absorption of the excited proton hydration structures. The absorption changes decay due to vibrational relaxation of the excited $\nu=1$ state. The shape of the transient absorption spectrum hardly changes with delay time, which indicates that the bending modes show little spectral diffusion, in agreement with the results of a recent study of the dynamics of protonated bulk water by the Tokmakoff group [9]. In this study the bending vibrations of the water molecules and the proton hydration structures are observed to show very little spectral diffusion, whereas the O–H stretch vibrations show strong spectral diffusion.

The induced absorption signal shows a dip at $\sim 1620\text{ cm}^{-1}$, indicative of the presence of a weak bleaching signal at this frequency (Fig. 3). The frequency of 1620 cm^{-1} matches well with frequency of the bending mode of H_2O ($\sim 1630\text{ cm}^{-1}$) [31–33]. If the feature at 1620 cm^{-1} would be caused by coupling between the excited bending mode at 1730 cm^{-1} and the bending mode of nearby H_2O molecules, its relaxation dynamics would closely follow the dynamics of the excited 1730 cm^{-1} band. However, the bleaching at 1620 cm^{-1} decays much more slowly than the 1730 cm^{-1} excitation, which means that this feature most likely results from the residual excitation of the bending mode of H_2O molecules present in the sample. This implies that the H_2O filter in the beam of the excitation pulse does not completely prevent the direct excitation of the bending mode of H_2O .

In Fig. 4 we present the isotropic transient absorption change as a function of the delay time between pump and probe for two different probe frequencies. The induced absorption ($\nu=1\rightarrow2$) exhibits a fast decay with a time constant of $\sim 200\text{ fs}$. The dynamics of the bleaching signal are much slower. This difference in the dynamics of the bleaching and induced absorption signals indicates that the excited 1730 cm^{-1} mode relaxes to an intermediate state (leading to a rapid decay of the $\nu=1\rightarrow2$ induced absorption signal). This intermediate state likely corresponds to a local hot state resulting from the local dissipation of energy. The intermediate state relaxes by transferring the excess energy to the surroundings, i.e. the Nafion membrane. This relaxation is much slower and leads to a slow decay of the $\nu=0\rightarrow1$ bleaching signal.

The transient spectrum at delay times $>10\text{ ps}$ mainly results from the increase of the temperature of the sample following the thermalization of the energy of the vibrational excitation. An

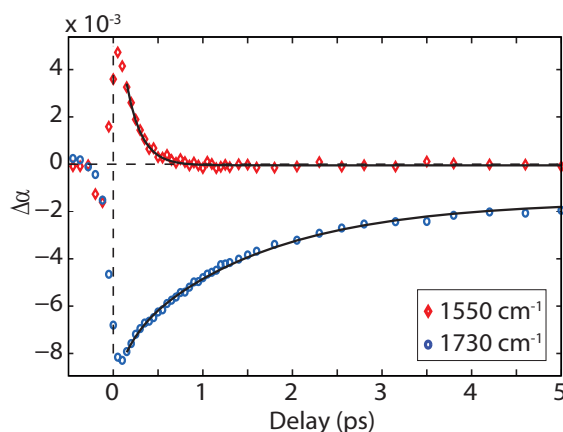


FIG. 4: Transient absorption changes of a proton-terminated Nafion membrane of $50 \mu\text{m}$ -thickness as a function of pump-probe delay time. The blue circles represent the absorption change at the central frequency of the bleaching signal at 1730 cm^{-1} . The red diamonds show the absorption change in the spectral region of the induced absorption at 1550 cm^{-1} . The black curves represent fits to the kinetic model described in the text.

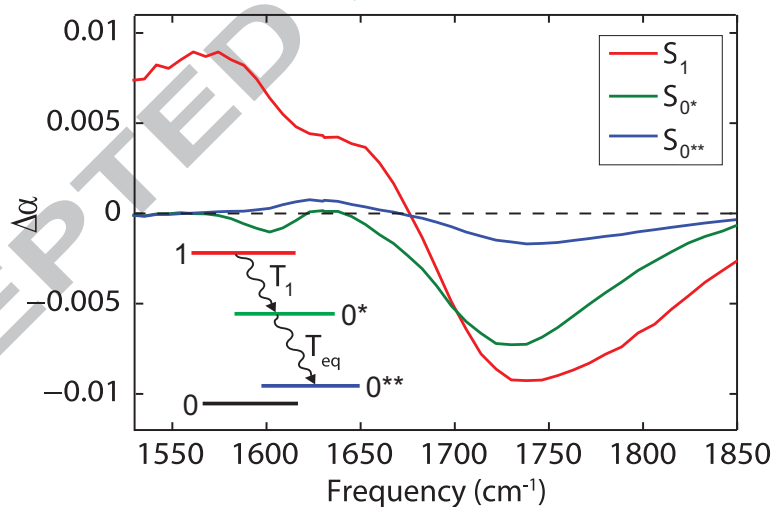


FIG. 5: Spectral components obtained from fitting the kinetic model described in the text to the transient absorption ($\Delta\alpha_{iso}$) data. The kinetic model is schematically depicted in the inset. The red curve indicates the spectrum of the transient absorption change associated with the excitation of the $v=1$ state of the 1730 cm^{-1} bending mode. The green and blue curves represent the transient absorption spectra of the intermediate and the final equilibrated thermal states, respectively.

increase in temperature weakens the hydrogen bonds and leads to a shift of the absorption spectrum of the 1730 cm^{-1} mode to lower frequencies. This shift leads to an increased absorption (positive $\Delta\alpha$) in the lower frequency region $<1670\text{ cm}^{-1}$ and a bleaching signal (negative $\Delta\alpha$) in the higher frequency region $>1670\text{ cm}^{-1}$ [32, 34].

We describe the isotropic transient absorption changes with a kinetic model illustrated in the inset of Fig. 5. The states denoted as 0 and 1 correspond to the vibrational ground state ($v = 0$) and the first excited state ($v = 1$) of the 1730 cm^{-1} mode, respectively. State 1 relaxes to the intermediate state 0^* with time constant T_1 , and the intermediate state 0^* relaxes to the final, thermally equilibrated state 0^{**} with time constant T_{eq} . The coupled rate equations of this kinetic model are:

$$\begin{aligned}\frac{dn_1}{dt} &= -\frac{n_1}{T_1} \\ \frac{dn_{0^*}}{dt} &= \frac{n_1}{T_1} - \frac{n_{0^*}}{T_{eq}} \\ \frac{dn_{0^{**}}}{dt} &= \frac{n_{0^*}}{T_{eq}}\end{aligned}\quad (3)$$

Here, n_1 , n_{0^*} and $n_{0^{**}}$ denote the populations of the states indicated by the subscript. Following the recent study by the Tokmakoff group on the dynamics of protonated bulk water [9], we take the spectral shapes of the states independent of the delay time (no spectral diffusion), meaning that only their amplitudes change with delay time. The total isotropic transient absorption change $\Delta\alpha(\nu)_{iso}$ is thus given by:

$$\Delta\alpha(\nu, t) = S_1(\nu)n_1(t) + S_{0^*}(\nu)n_{0^*}(t) + S_{0^{**}}(\nu)n_{0^{**}}(t), \quad (4)$$

where $S_1 = \sigma_1 - 2\sigma_0$, $S_{0^*} = \sigma_{0^*} - \sigma_0$ and $S_{0^{**}} = \sigma_{0^{**}} - \sigma_0$ denote the difference spectra σ_i of each of the three states indicated by the subscript i , and the ground-state absorption spectrum σ_0 . For the differential spectrum S_1 the ground-state absorption spectrum σ_0 enters with a factor 2, because the population of state 1 with population n_1 leads to a bleaching of the $v = 0 \rightarrow 1$ ground-state absorption (equal to $-n_1\sigma_0$), and to $v = 1 \rightarrow 0$ stimulated emission (also equal to $-n_1\sigma_0$).

We fit the isotropic transient absorption changes by solving the rate-equations (3) in a least-square minimization routine. The transient spectra and delay-time curves resulting from the fit are shown as black solid lines in Fig. 3 and Fig. 4. From the fit we obtain value for T_1 of 170 ± 30 fs,

and for T_{eq} of 1.5 ± 0.2 ps. The T_1 value of 170 ± 30 fs of the 1730 cm^{-1} mode is shorter than the T_1 value of 400 fs of the bending mode of H_2O molecules in a mixture of HDO and D_2O [33], and is similar to the vibrational lifetime of 170 fs that has been measured for the bending mode of H_2O molecules in pure liquid H_2O [37].

The difference spectra S_1 , S_{0^*} and $S_{0^{**}}$ obtained from the fit, are shown in Fig. 5. S_1 shows the bleaching of the $\nu=0 \rightarrow 1$ absorption at $\nu > 1670 \text{ cm}^{-1}$ and the induced $\nu=1 \rightarrow 2$ absorption at $\nu < 1670 \text{ cm}^{-1}$. S_1 also shows a small dip in the induced absorption at $\sim 1620 \text{ cm}^{-1}$ that results from the excitation of the bending vibration of H_2O . In the fitting we did not include this excitation as a separate excited state because it is very weak. The intermediate state with difference spectrum S_{0^*} shows a strong bleaching signal at $\nu > 1650 \text{ cm}^{-1}$, and a weak induced absorption at $\nu < 1650 \text{ cm}^{-1}$. These spectral changes indicate a strong bleaching and a small redshift of the absorption band at $\sim 1730 \text{ cm}^{-1}$, which shows that state 0^+ represents a locally hot state that results from the local dissipation of the energy of the vibrational excitation. The final difference spectrum $S_{0^{**}}$ represents the effect of the thermalization of the excitation energy over the focus of the excitation pulse. $S_{0^{**}}$ has a similar shape as S_{0^*} , but with a smaller amplitude. This smaller amplitude shows that the dissipated energy has been largely transferred to the surrounding Nafion membrane, thus decreasing the effect on the absorption spectrum of the bending vibrations of the proton-hydration clusters.

Recently, two femtosecond mid-infrared studies of the vibrational dynamics of proton-hydration clusters in acetonitrile have been reported [35, 36]. In one of these studies the relaxation following excitation of the bending mode at 1740 cm^{-1} was investigated [36]. Similar to the present results, it was observed that this excitation leads to an induced $\nu=1 \rightarrow 2$ absorption signal near 1600 cm^{-1} that decays much faster than the $\nu=0 \rightarrow 1$ bleaching signal at 1740 cm^{-1} . This observation was also explained from a two-step relaxation process, in which the first step is formed by the rapid relaxation of the excited bending mode leading to a strong local heating effect, and the second step is formed by a much slower thermal equilibration process. The time constant of the vibrational relaxation was found to be < 60 fs, which is significantly shorter than the time constant T_1 of 170 ± 30 fs we observe here for the bending mode of proton-hydration clusters in Nafion. A similar difference in relaxation time constant has been observed for the O–H stretch vibration of proton-hydration clusters in acetonitrile and Nafion. The O–H stretch vibration of proton-hydration clusters in acetonitrile decays with a time constant < 100 fs [35, 36], whereas the O–H stretch vibration of proton-hydration clusters in Nafion decays with a time constant of ~ 400

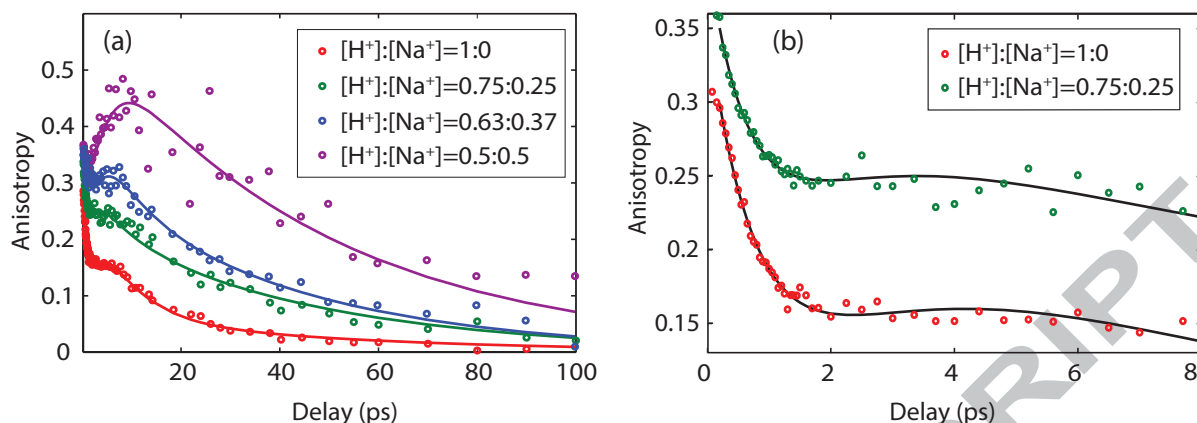


FIG. 6: (a) Anisotropy of the transient absorption signal (averaged from 1700 cm^{-1} to 1750 cm^{-1}) of the 1730 cm^{-1} bending mode as a function of delay time. The cation ratios ($[\text{H}^+]:[\text{Na}^+]$) of the Nafion samples are indicated in the legend. The solid curves are obtained from a bi-exponential fit to the data. (b) Zoom-in of the early component of the anisotropy dynamics shown in panel (a).

fs, depending on the hydration level [24, 25].

C. Anisotropy Dynamics

In Fig. 6 we present the anisotropy decay of the 1730 cm^{-1} mode in a proton-terminated Nafion membrane, averaged over the frequency interval between 1700 cm^{-1} and 1750 cm^{-1} , for four different $\text{H}^+:\text{Na}^+$ ratios. Fig. 6b shows a zoom-in of the data of Fig. 6a measured at the two highest $\text{H}^+:\text{Na}^+$ ratios. The anisotropy exhibits a fast partial decay to a value of 0.15 at ~ 2.5 ps. This partial decay is followed by a re-rise of the anisotropy, which reaches a maximum at a delay time of $\sim 8\text{-}10$ ps (Fig. 6a). After this maximum the anisotropy decays slowly on a time scale of tens of picoseconds.

The decay of the anisotropy has a time constant of 350 ± 30 fs, independent of the $[\text{H}^+]:[\text{Na}^+]$ cation ratio. This time constant is longer than the T_1 time constant of the excited bending mode vibration, which implies that the decay of the anisotropy mainly occurs within the local intermediate state 0^* , and that this state is initially highly anisotropic. This indicates that the vibrational relaxation involves a highly localized dissipation of energy, corresponding to a strong local heating effect that mainly affects the originally excited bending vibration. This heating effect can be associated with a weakening or even a breaking of the hydrogen bonds of the cluster. The decay of the anisotropy can be attributed to a redistribution of the local heat over the low-frequency modes of

the excited proton-hydration cluster. Due to this redistribution, other bending modes that were not directly excited will also be affected in their absorption spectrum. As these other bending modes will have different orientations, the redistribution of heat over the cluster will lead to a partial decay of the anisotropy. This redistribution does not lead to a complete decay of the anisotropy as the hydrated clusters in the channels of the Nafion membrane are small, containing ~ 4 water molecules. Hence these clusters contain only a limited number of O–H stretch and bending vibrations, and the transition dipole moments of these vibrations will not be equally distributed over all spatial directions. For instance, if a cluster consists of a planar Zundel or Eigen structure, the bending mode transition dipole moments will be oriented in the plane of the structure, and there will be no bending-mode transition dipole moment pointing perpendicular to this plane. Hence, the effect of heating on the absorption spectrum of the bending modes will be anisotropic, as long as the heating effect remains restricted to the originally excited proton-hydration cluster.

Fig. 6 shows that for longer delays the anisotropy remains nonzero, and even shows a re-rise. This re-rise occurs with a time constant that is equal to the time constant of ~ 1.5 ps of the relaxation of the local intermediate state 0^* to the final state 0^{**} . This observation indicates that the diffusion of heat from the region of the excited proton-hydration cluster to the surrounding Nafion membrane, leads to a relative increase of an anisotropic signal component. The observation of a re-rise also means that this anisotropic signal component must be long-living. Such a long-living, anisotropic signal component may be due to the breaking of a hydrogen bond of the proton-hydration cluster, for instance the hydrogen bond formed between an $-\text{SO}_3^-$ group of Nafion and an H_2O molecule of the proton hydration structure. Such a structural change leads to a change of the vibrational spectrum of the originally excited proton hydration cluster, and can be long-living as the dissociated fragments will diffuse apart. For hydrogen-bonded clusters such as methanol and ethanol oligomers dissolved in CCl_4 , [38, 39] and for hydrated protons dissolved in acetonitrile, [35] it has been observed that it takes a relatively long time (10-100 ps) for a broken hydrogen bond to reform.

From the above interpretation it follows that the transient spectrum S_{0^*} represents the effect of local heating of the proton-clusters that includes a structural change for part of the clusters (e.g., the breaking of a hydrogen bond), whereas $S_{0^{**}}$ represents the effect of global heating plus the same, persistent local structural change. For a $[\text{H}^+]:[\text{Na}^+]$ cation ratio of 1:0, the anisotropy reaches a maximum intermediate value of ~ 0.2 (red circles), as shown in Fig. 6. This value indicates that $\sim 50\%$ of $S_{0^{**}}$ can be assigned to an isotropic global heating effect and $\sim 50\%$ of

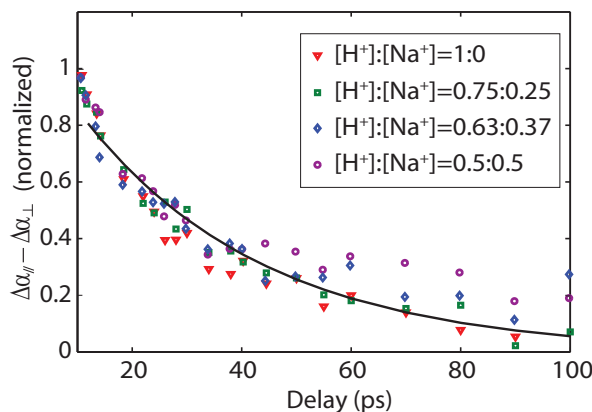


FIG. 7: Normalized difference between the transient absorption changes at 1730 cm^{-1} measured with parallel and perpendicular polarization configurations of the pump and probe pulses ($\Delta\alpha_{||} - \Delta\alpha_{\perp}$), as a function of delay time, for delay times >10 ps.

$S_{0^{**}}$ to an anisotropic signal associated with the local structural change. The amplitude of S_{0^*} is approximately 5 times larger than the amplitude of $S_{0^{**}}$, as shown in Fig. 5. Assuming that the local structural change has the same signal contribution to S_{0^*} and $S_{0^{**}}$, it thus follows that the local structural change would constitute $\sim 10\%$ of the S_{0^*} signal. The branching of the final energy dissipation between heating and structural change (e.g. the breaking of a hydrogen bond) would thus be approximately 10:1.

In Fig. 6 it is seen that the maximum amplitude of the anisotropy depends on the $[\text{H}^+]:[\text{Na}^+]$ cation ratio. For the lowest cation ratio of $[\text{H}^+]:[\text{Na}^+]=0.5:0.5$, the anisotropy exhibits an intermediate rise up to ~ 0.4 . This higher amplitude can be explained from the relative contributions of the global heating and the structural change to the transient absorption spectrum $S_{0^{**}}$, and the dependence of these contributions on the cation ratio. The structural change is a local effect, restricted to the proton-hydration cluster that was originally excited. Hence, the strength of this signal depends on the total number of proton-hydration clusters present, but not on their relative contribution to the total amount of cations. In contrast, the energy dissipation associated with the global heating effect is shared by the whole Nafion membrane sample. Hence, the temperature increase that results from the global heating effect will become smaller with decreasing $[\text{H}^+]:[\text{Na}^+]$ cation ratio. As a result, the anisotropic signal contribution of the local structural change will become relatively more important with decreasing $[\text{H}^+]:[\text{Na}^+]$ cation ratio, thus yielding a larger maximum anisotropy value.

In Fig. 7 the difference of the transient absorption changes at 1730 cm^{-1} measured with par-

allel and perpendicular polarization configurations ($\Delta\alpha_{\parallel}(t) - \Delta\alpha_{\perp}(t)$) is presented as a function of delay time for four different proton concentrations ($[\text{H}^+]:[\text{Na}^+]$ ratios) for delay times >10 ps. In this delay time range, the difference signal $\Delta\alpha_{\parallel}(t) - \Delta\alpha_{\perp}(t)$ shows the same dynamics as the anisotropy parameter, because the isotropic signal is constant for delay times >10 ps. The observed dynamics are quite similar at all concentrations and correspond to a decay with a time constant $\tau_2=38\pm4$ ps that is the same for all proton concentrations, which indicates that the observed relaxation of the anisotropy is a local process occurring within the excited proton hydration cluster. We assign the slow process with a time constant of 38 ± 4 ps to a local restructuring of the proton hydration clusters, leading to a randomization of the transition dipole moments of the bending vibrations of these clusters.

IV. CONCLUSIONS

We investigated the vibrational and structural dynamics of proton hydration clusters in hydrated Nafion membranes following excitation of the bending mode at 1730 cm^{-1} with polarization-resolved mid-infrared pump-probe spectroscopy. We find that a large fraction of the excited bending modes first relaxes to an intermediate state with a time constant of T_1 of 170 ± 30 fs. This intermediate state mainly represents a strong local heating effect of the excited proton hydration cluster. Subsequently the heated proton hydration cluster cools with a time constant T_{eq} of 1.5 ± 0.2 ps by transferring its excess thermal energy to the Nafion membrane and to proton hydration clusters that were not excited.

The transient absorption signals show an anisotropy that decays with a time constant of 350 ± 30 fs followed by a re-rise with a time constant of ~ 1.5 ps, similar to T_{eq} . The decay can be attributed to the redistribution of heat over the excited proton-hydration cluster. The re-rise of the anisotropy indicates the presence of a long-living anisotropic signal component to the transient absorption signal that relatively increases when the proton-hydration clusters cool. The presence of this long-living anisotropy component indicates that for a small fraction ($\sim 10\%$) of the excited bending modes the vibrational relaxation results in a structural change of the proton hydration cluster, e.g. the breaking of a local hydrogen bond. The anisotropy of the absorption signal associated with this structural change relaxes with a time constant τ_2 of 38 ± 4 ps, probably as a result of the structural reorganization of the proton-hydration clusters.

V. ACKNOWLEDGEMENT

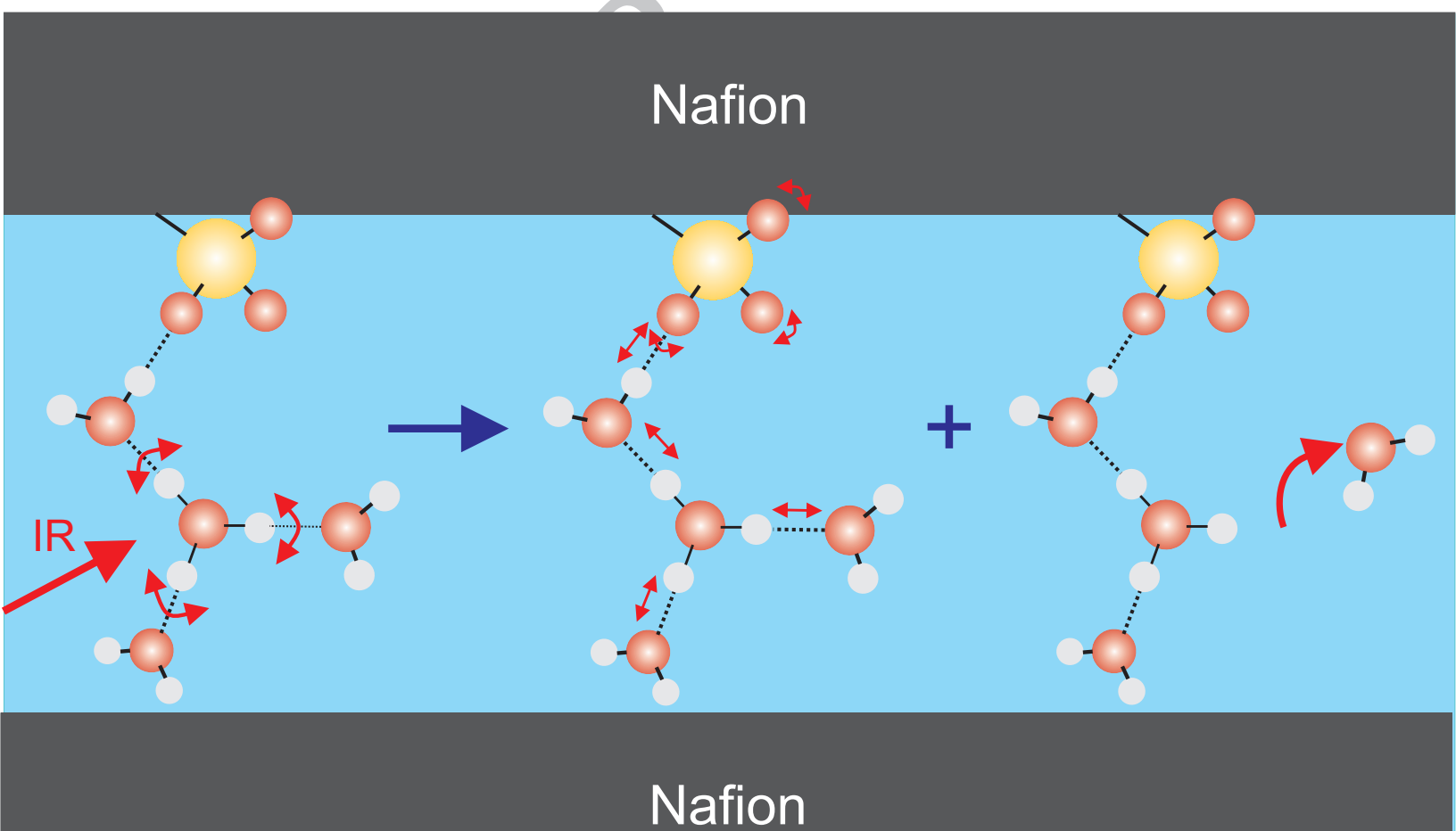
The work is a part of the research program of the “Stichting voor Fundamenteel Onderzoek der Materie (FOM)” which is supported by the “Nederlandse organisatie voor Wetenschappelijk Onderzoek (NWO)”

ACCEPTED MANUSCRIPT

- [1] L. I. Yeh, M. Okumura, J. D. Myers, J. M. Price, Y. T. Lee, Vibrational spectroscopy of the hydrated hydronium cluster ions $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ($n=1, 2, 3$), *J. Chem. Phys.* 91 (12) (1989) 7319–7330.
- [2] N. Agmon, The Grotthuss mechanism, *Chem. Phys. Lett.* 244 (1995) 456–462.
- [3] D. Marx, M. E. Tuckerman, J. Hutter, M. Parrinello, The nature of the hydrated excess proton in water, *Nature* 397 (1999) 601.
- [4] J. Kim, U. W. Schmitt, J. A. Gruetzmacher, G. A. Voth, N. E. Scherer, The vibrational spectrum of the hydrated proton: Comparison of experiment, simulation, and normal mode analysis, *J. Chem. Phys.* 116 (2) (2002) 737–746.
- [5] J. M. Headrick, E. G. Diken, R. S. Walters, N. I. Hammer, R. A. Christie, J. Cui, E. M. Myshakin, M. A. Duncan, M. A. Johnson, K. D. Jordan, Spectral Signatures of Hydrated Proton Vibrations in Water Clusters, *Science* 308 (5729) (2005) 1765–1769.
- [6] S. Woutersen, H. J. Bakker, Ultrafast vibrational and structural dynamics of the proton in liquid water, *Phys. Rev. Lett.* 96 (2015) 138305.
- [7] S. G. Olesen, T. L. Guasco, J. R. Roscioli, M. A. Johnson, Tuning the intermolecular proton bond in the H_5O_2^+ Zundel ion scaffold, *Chem. Phys. Lett.* 509 (2011) 89–95.
- [8] J. Q. Xu, Y. Zhang, G. A. Voth, Infrared Spectrum of the Hydrated Proton in Water, *J. Phys. Chem. Lett.* 2 (2) (2011) 81–86.
- [9] M. Thämer, L. De Marco, K. Ramasesha, A. Mandal, A. Tokmakoff, Ultrafast 2D IR spectroscopy of the excess proton in liquid water, *Science* 350 (2015) 78–82.
- [10] W. Kulig, N. Agmon, A 'clusters-in-liquid' method for calculating infrared spectra identifies the proton-transfer mode in acidic aqueous solutions, *Nat Chem* 5 (1) (2013) 29–35.
- [11] D. Marx, M. E. Tuckerman, M. Parrinello, Solvated excess protons in water: quantum effects on the hydration structure, *J. Phys-Condens. Mat.* 12 (8A) (2000) A153–A159.
- [12] O. Markovitch, H. Chen, S. Izvekov, F. Paesani, G. A. Voth, N. Agmon, Special pair dance and partner selection: Elementary steps in proton transport in liquid water, *J. Phys. Chem. B* 112 (31) (2008) 9456–9466.
- [13] M. Eigen, Proton Transfer, Acid-Base Catalysis, and Enzymatic Hydrolysis. Part I: Elementary Processes, *Angew. Chem. Int. Edit.* 3 (1) (1964) 1–19.
- [14] G. Zundel, Hydrogen Bonds with Large Proton Polarizability and Proton Transfer Processes in Elec-

- trochemistry and Biology, John Wiley & Sons, Inc., 1–217, 2007.
- [15] T. D. Gierke, G. E. Munn, F. C. Wilson, The morphology in Nafion perfluorinated membrane products, as determined by wide- and small-angle X-ray studies, *J. Polym. Sci. Polym. Phys.* 19 (1981) 1687–1704.
- [16] A.-L. Rollet, O. Diat, G. Gebel, A new insight into Nafion structure, *J. Phys. Chem. B* 21 (2002) 3033–3036.
- [17] K. Schmidt-Rohr, Q. Chen, Parallel cylindrical water nanochannels in Nafion fuel-cell membranes, *Nature Mat.* 7 (2008) 75–83.
- [18] A. V. Anantaraman, C. L. Gardner, Studies on ion-exchange membranes. Part 1. Effect of humidity on the conductivity of Nafions, *J. Elec. Chem.* 414 (2) (1996) 115–120.
- [19] D. B. Spry, A. Goun, K. Glusac, D. E. Moilanen, M. D. Fayer, Proton transport and the water environment in nafion fuel cell membranes and AOT reverse micelles, *J. Am. Chem. Soc.* 129 (26) (2007) 8122–8130.
- [20] M. K. Petersen, G. A. Voth, Characterization of the solvation and transport of the hydrated proton in the perfluorosulfonic acid membrane nafion, *J. Phys. Chem. B* 110 (37) (2006) 18594–18600.
- [21] S. L. Feng, J. Savage, G. A. Voth, Effects of Polymer Morphology on Proton Solvation and Transport in Proton-Exchange Membranes, *J. Phys. Chem. C* 116 (36) (2012) 19104–19116.
- [22] S. Feng, G. A. Voth, Proton Solvation and Transport in Hydrated Nafion, *J. Phys. Chem. B* 115 (19) (2011) 5903–5912.
- [23] Y.-L. S. Tse, A. M. Herring, K. Kim, G. A. Voth, Molecular Dynamics Simulations of Proton Transport in 3M and Nafion Perfluorosulfonic Acid Membranes, *J. Phys. Chem. C* 117 (16) (2013) 8079–8091.
- [24] L. Liu, H. J. Bakker, Infrared-Activated Proton Transfer in Aqueous Nafion Proton-Exchange-Membrane Nanochannels, *Phys. Rev. Lett.* 112 (2014) 258301.
- [25] L. Liu, H. J. Bakker, Vibrational Excitation Induced Proton Transfer in Hydrated Nafion Membranes, *J. Phys. Chem. B* 119 (2015) 2628–2637.
- [26] L. M. Onishi, J. M. Prausnitz, J. Newman, Water-Nafion equilibria. Absence of Schroeder's paradox, *J Phys. Chem. B* 111 (34) (2007) 10166–10173.
- [27] T. Okada, S. Moller-Holst, O. Gorseth, S. Kjelstrup, Transport and equilibrium properties of Nafion membranes with H^+ and Na^+ ions, *J Electroanal. Chem.* 442 (12) (1998) 137–145.
- [28] P. A. G. Michael Falk, Infrared Spectrum of the H_3O^+ Ion in Aqueous Solution, *Can. J. Chem.* 35 (1957) 1195–1204.

- [29] N. B. Kalish, E. Shandalov, V. Kharlanov, D. Pines, E. Pines, Apparent Stoichiometry of Water in Proton Hydration and Proton Dehydration Reactions in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ Solutions, *J. Phys. Chem. A* 115 (16) (2011) 4063–4075.
- [30] V. Buch, A. Dubrovskiy, F. Mohamed, M. Parrinello, J. Sadlej, A. D. Hammerich, J. P. Devlin, HCl hydrates as model systems for protonated water, *J. Phys. Chem. A* 112 (11) (2008) 2144–2161.
- [31] D. W. M. Hofmann, L. Kuleshova, B. D' Aguanno, V. Di Noto, E. Negro, F. Conti, M. Vittadello, Investigation of Water Structure in Nafion Membranes by Infrared Spectroscopy and Molecular Dynamics Simulation, *J. Phys. Chem. B* 113 (3) (2008) 632–639.
- [32] M. Falk, Frequencies of H-O-H, H-O-D and D-O-D bending fundamentals in liquid water, *J. Ram. Spec.* 21 (9) (1990) 563–567.
- [33] O. F. A. Larsen, S. Woutersen, Vibrational relaxation of the H_2O bending mode in liquid water, *J. Chem. Phys.* 121 (24) (2004) 12143–12145.
- [34] Y. Maréchal, Infrared spectra of water. I. Effect of temperature and of H/D isotopic dilution, *J. Chem. Phys.* 95 (8) (1991) 5565–5573.
- [35] N. Ottosson, L. Liu, H. J. Bakker, Vibrational Relaxation of the Aqueous Proton in Acetonitrile: Ultrafast Cluster Cooling and Vibrational Predissociation, *J. Phys. Chem. B* 120 (29) (2016) 7154–7163.
- [36] F. Dahms, R. Costard, E. Pines, B. Fingerhut, E. T. J. Nibbering, E. T., The hydrated excess proton in the Zundel cation H_5O_2^+ , *Angew. Chemie Int. Ed.* 55 (2016) 10600–10605.
- [37] N. Huse, S. Ashihara, E. T. J. Nibbering, T. Elsaesser, Ultrafast vibrational relaxation of O-H bending and librational excitations in liquid H_2O , *Chem. Phys. Lett.* 404 (4-6) (2005) 389–393.
- [38] S. Woutersen, U. Emmerichs, H. J. Bakker, A femtosecond midinfrared pump-probe study of hydrogen-bonding in ethanol, *J. Chem. Phys.* 107 (5) (1997) 1483–1490.
- [39] K. Gaffney, P. Davis, I. Piletic, N. Levinger, M. Fayer, Hydrogen Bond Dissociation and Reformation in Methanol Oligomers Following Hydroxyl Stretch Relaxation, *J. Phys. Chem. A* 106 (2002) 12012–12023.



August 30, 2016

Re: Vibrational and Structural Relaxation of Hydrated Protons in Nafion Membranes
By: Liyuan Liu, Stephan Lotze, and Huib J. Bakker

Highlights

- The bending modes of hydrated protons in Nafion membranes are studied with fs mid-IR.
- The vibrational relaxation is ultrafast (170 ± 30 fs) and leads to local heating.
- The dissipated energy thermalizes over Nafion with a time constant of 1.5 ps.
- For $\sim 10\%$ of the excitations the relaxation leads to a long-living structural change.