Structure Dynamics of the Proton in Liquid Water Probed with Terahertz Time-Domain Spectroscopy

K. J. Tielrooij, R. L. A. Timmer, H. J. Bakker, and M. Bonn*

FOM Institute for Atomic and Molecular Physics [AMOLF], Kruislaan 407, 1098 SJ Amsterdam, The Netherlands

(Received 17 December 2008; published 15 May 2009)

We study the hydration of protons in liquid water using terahertz time-domain spectroscopy and polarization-resolved femtosecond midinfrared pump-probe spectroscopy. We observe that the addition of protons leads to a very strong decrease of the dielectric response of liquid water that corresponds to 19 ± 2 water molecules per dissolved proton. This depolarization results from water molecules (∼4) that are irrotationally bound to the proton and from the motion of water (corresponding to the response of ∼15 water molecules) involved in the transfer of the proton charge.

DOI: 10.1103/PhysRevLett.102.198303 PACS numbers: 82.53.Uv, 82.30.Rs, 82.39.Jn

Protons in hydrogen-bonded networks play an important role in many fundamental and technological processes in chemistry, physics, and biology. Examples include acid-base reactions, proton exchange membranes, and transmembrane proton pumps. One of the remarkable properties of protons in aqueous solutions is the anomalously high mobility [1]. This has been attributed to the Grotthuss mechanism, which differs from the typical Stokes mass diffusion for ion transport. The Grotthuss mechanism is based on the efficient interconversion between the Eigen complex H_3O^+ and the Zundel complex $[H_2O\ldots H\ldots H_2O]^+$, which constitutes the proton charge transport [2–7]. Here the proton shuttles to an adjacent water molecule by interconversion of a hydrogen bond and a covalent bond. Hence the charge, rather than the mass, of the proton is transferred, making proton conductivity significantly larger than that of other ions [1]. Molecular dynamics simulations showed that the H_3O^+ complex typically has a coordination number of 3, as opposed to 4 for pure water [2–4]. This means that the presence of the proton causes a structural rearrangement of the hydrogen bond network. Both theory and experiment have found indications that the interaction between protons and the solvating hydrogen bond network has a long range character. Simulations using multistate empirical valence-bond analysis have indicated that proton transfer couples to hydrogen bond dynamics of large water clusters of at least three hydration shells [8].

The hydration of the proton has also been studied with different experimental techniques including infrared and far-infrared spectroscopy [9–16]. These studies have arrived at very different values for the number of water molecules affected by the proton, ranging from ∼6 to ∼100. This wide range of values may be traced to several drawbacks of previous techniques that have been applied to measuring the effect of the proton on water. In the infrared, the aqueous proton gives rise to broad structureless bands, from which it is very difficult to deduce information about the water structure. Microwave spectroscopy is, in principle, very well suited to study the effects of ions on the structural dynamics of water, as has been demonstrated for different salts [9,17–21]. However, for the study of the effect of the proton on water, this technique is not well suited, because the mobility of the proton leads to very strong absorption and loss of signal at microwave frequencies. This problem is much less severe at higher frequencies, because the absorption due to charge mobility is inversely proportional to the probing frequency. Recently, the technique of terahertz time-domain spectroscopy (THz-TDS) [22–24] has been developed, and it was shown that this technique is ideally suited to study water structure and dynamics [25–27]. Here we use this technique in combination with polarization-resolved femtosecond midinfrared pump-probe spectroscopy to study the effects of the proton on the structural dynamics of water.

The THz-TDS setup is based on terahertz generation and detection in ZnTe nonlinear crystals, using 800 nm pulses with a duration of ∼150 fs. The time-dependent electric field strength of the terahertz pulses (∼1 ps) that are transmitted through the sample are measured by means of electro-optic sampling with a variably delayed pulse of 800 nm light with a duration of ∼150 fs in a second ZnTe crystal. THz-TDS provides the frequency-dependent complex dielectric response of a sample $\hat{\epsilon}(\omega)$. We determine the complex dielectric response of water around protons. To isolate specifically the effect of the proton, we measure the difference between the dielectric response of an acid (e.g., HCl) and its accompanying salt (e.g., NaCl) for different acid-salt combinations. This way, we can correct the data for the contribution of the anions on the water solvent. We employ a mechanical device that alternatively positions two samples (a salt and an acid solution in cuvettes that have chambers with an optical path length of 103 ± 0.5 μm) in the terahertz beam. This approach minimizes the effect of fluctuations in terahertz intensity and temperature as noise sources.

The polarization-resolved femtosecond midinfrared pump-probe setup is based on a number of nonlinear conversion steps using femtosecond pulses centered around 800 nm. Pump-probe measurements are performed using a strong pump pulse (~5 μJ) with a duration of ~200 fs that is centered around 2520 cm^{-1}, resonant with the OD-stretch vibration of HDO. We use isotopic dilution (4% D_2O in H_2O) to avoid the measured signals being affected by resonant energy transfer. The pump labels specifically oriented water molecules with a vibrational excitation. The subsequent vibrational and orientational relaxation is monitored using a weak (~20 nJ) probe pulse, also centered at 2520 cm^{-1}. Using this technique, we can readily determine the decay of the anisotropy $R = \frac{\Delta\alpha_\parallel - \Delta\alpha_\perp}{\Delta\alpha_\parallel + 2\Delta\alpha_\perp}$, where $\Delta\alpha_\parallel$ and $\Delta\alpha_\perp$ are the pump-induced change in absorption with the polarization of the pump pulse parallel and perpendicular to the probe pulse, respectively. The exponential decay of the anisotropy gives the (second-order) reorientation time of the excited water molecules. As will be shown below, this parameter is important for the analysis of the dielectric response of protons in water.

We employ THz-TDS in the region between 0.3 and 1.2 THz to examine the hydration of protons in liquid water. Up to a frequency of 1.2 THz, the dielectric response is dominated by dielectric relaxation [28]. The dielectric relaxation response of water $\hat{\epsilon}(\omega)$ contains information on how well the permanent dipoles associated with water molecules can keep up with oscillating fields of angular frequency ω. For pure water at room temperature, $\hat{\epsilon}(\omega)$ can be described with the well-known double Debye relaxation model [22–24,28]:

$$\hat{\epsilon}(\omega) = \frac{S_1}{1 + i\omega\tau_D} + \frac{S_2}{1 + i\omega\tau_2} + \epsilon_\infty. \qquad (1)$$

Here the first (main) term represents the dielectric relaxation process with strength $S_1 = \epsilon_S - \epsilon_1$ and a time constant of $\tau_D \sim 8$ ps (the Debye time) at room temperature. The Debye time describes the cooperative reorganization of water solvent molecules. The second term has been assigned to undercoordinated water molecules [23], and has a much smaller strength $S_2 = \epsilon_1 - \epsilon_\infty$ and a shorter time scale τ_2. Finally, ϵ_∞ represents the dielectric constant in the high frequency limit, and ϵ_S is the static dielectric constant.

When ions are added to water, the dielectric response changes. First of all, the dielectric response includes a contribution from the conductivity of the charged ions. Second, ions may affect both the Debye time τ_D and the strength of the relaxation process S_1 of the water molecules surrounding the ions. The latter occurs when ions form strong bonds with water molecules that, as a result, can no longer participate in the relaxation process. Strong hydration therefore leads to a lowering of the relaxation strength S_1, i.e., to a depolarization effect. We determine how the presence of protons affects the dielectric relaxation parameters by measuring the differential dielectric response for the following acid-salt combinations: HCl-NaCl, HCl-KCl, HCl-CsCl, HCl-LiCl, $HClO_4$-$NaClO_4$, and HI-NaI. The concentrations were varied between 0.25 and 1.0 mol/kg. We use molality (mol/kg) to keep the amount of water in each sample constant.

As a typical measurement, we show the transmitted terahertz pulses through an empty cuvette and through cuvettes filled with a 1 mol/kg solution of HCl and a 1 mol/kg solution of NaCl in pure water; see Fig. 1(a). The acid solution has a somewhat higher absorption and refraction than the salt solution. We analyze the data in the frequency domain using Fresnel equations [29]. Using the independently determined cuvette responses, we extract the dielectric response of the two samples separately.

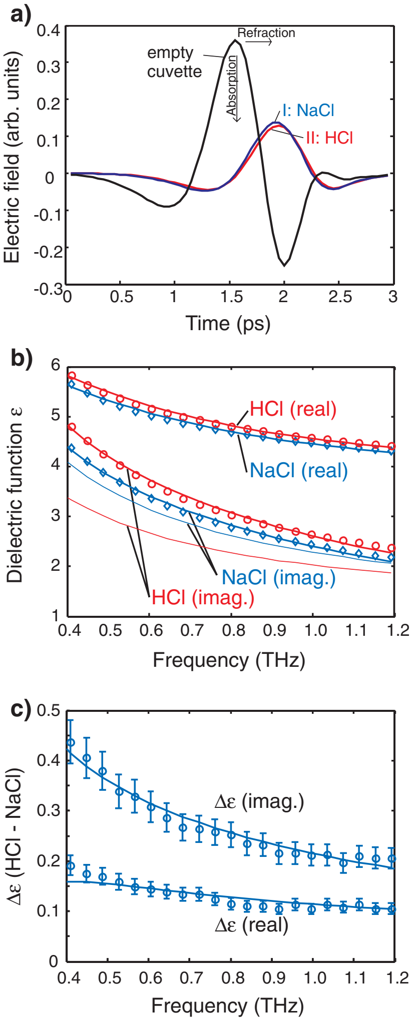

FIG. 1 (color). (a) Terahertz pulses as transmitted through an empty cuvette and through cuvettes filled with a 1 mol/kg solution of NaCl and HCl, respectively. (b) Extracted dielectric function of 1 m HCl and 1 m NaCl. The thick lines that go through the data points are a fit to Eq. (1) with S_1 for the salt fixed to its literature value [17]. The thin lines represent the dielectric response after it has been corrected for the conductivity contribution. (c) Differential dielectric response $\Delta\hat{\epsilon}$ for 1 m HCl-NaCl, with the fit according to Eq. (2). Error bars indicate the 95% confidence interval.

The dielectric responses of the 1 mol/kg HCl-NaCl acid-salt combination and the differential response are shown in Fig. 1(b) and 1(c), respectively. To quantify the effect of the presence of the proton on the water structure and dynamics, we examine the differential dielectric response $\Delta\hat{\epsilon}$ (HY-XY) for each acid-salt (HY-XY) combination. We use the following equation to model the differential dielectric response:

$$\Delta\hat{\epsilon}(\omega) = \frac{\Delta S_{1,H} - \Delta S_{1,X}}{1 + i\omega\tau_D} + \frac{\sigma_{HY} - \sigma_{XY}}{i\omega\epsilon_0} + \Delta(S_2, \epsilon_\infty). \tag{2}$$

In this equation $\Delta S_{1,H}$ and $\Delta S_{1,X}$ represent the proton and the cation effect on the pure water parameter S_1, respectively. The second term, where the vacuum permittivity is given by ϵ_0, is concerned with the difference in conductivity of the acid σ_{HY} and salt σ_{XY} solutions. Following Refs. [17–21], we assume no frequency dependence of the conductivity σ. The last term $\Delta(S_2, \epsilon_\infty)$ comprises the different effects that the proton and the cation have on the relaxation process with strength S_2 and on ϵ_∞. These effects are significantly smaller than the effects on S_1. This is apparent from the spectral shape of the differential response and intuitive given the small (few percent) contribution of the S_2 process to the overall dielectric response.

To arrive at Eq. (2), we have made the assumption that the Debye reorientation time τ_D is the same for acid and salt solutions with the same anion. This assumption is corroborated by (i) microwave measurements of dielectric relaxation that have indeed indicated that τ_D is mainly affected by the presence of anions and not cations [17,18,21] and by (ii) polarization-resolved femtosecond pump-probe measurements in the midinfrared. This measurement technique has proven to be capable of probing the effect of cations and anions on the water reorientation [30]. The results in Fig. 2 show that the reorientation time $\tau_R \sim \frac{1}{3}\tau_D$ is indistinguishable for 0:4, 1:3, and 2:2 aqueous solutions of $HClO_4$:$NaClO_4$ with a constant anion concentration of 4 mol/kg. Since the concentration of anions is kept constant, we isolate the effect of the proton. We do not probe water molecules that are in close proximity of the anion, since these can be resolved spectrally [30]. For these water molecules, τ_D may be different, but this contribution is subtracted in Eq. (2).

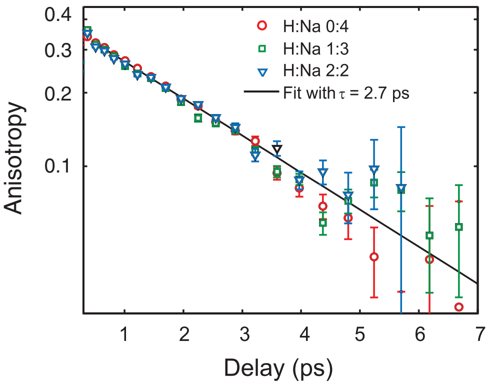

FIG. 2 (color). The decay of the anisotropy R is independent of the proton:cation ratio, corroborating the assumption that τ_D remains the same for protons and cations.

We extract the depolarization effect of the proton $\Delta S_{1,H}$ for each acid-salt combination using Eq. (2). The fit results for the 1 mol/kg solutions of HCl and NaCl are shown in Fig. 1(c). We have first fit the dielectric response of the salt solution to obtain τ_D and use this number to fit the differential dielectric responses to Eq. (2). We use data from the literature for the conductivity of the solutions (σ_{HY} and σ_{XY}) and for the depolarization effect of the cation $\Delta S_{1,X}$. The data for the salt solutions are taken from gigahertz dielectric relaxation measurements by Buchner *et al.* [17–19,21]. We show the results for the depolarization effect of protons $\Delta S_{1,H}$ in Fig. 3. The data are independent of the details of the different cations and anions, showing the validity of our approach to isolate specifically the effect of the proton on the water response.

For all measurements with different acid-salt combinations, the value of $\Delta S_{1,H}$ is negative. This finding is in line with the results of microwave dielectric relaxation measurements [17–19]. In these measurements it was found that cations have a depolarization effect. This is partially due to the excluded volume of the ions and partially due to strong irrotational bonds between water molecules and the cations. Smaller and multivalent cations typically have a stronger hydration and hence larger depolarization effect. Our results show that protons induce an anomalously large depolarization effect. We extract the number of affected water molecules N_H around protons through [31,32]

$$N_H(c) = \left(c_s - \frac{S_1 + \Delta S_{1,H}}{S_1} c_0\right) \Big/ c. \tag{3}$$

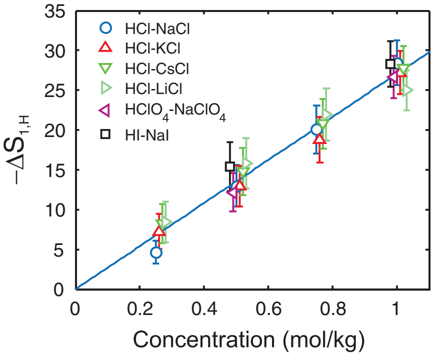

FIG. 3 (color). The depolarization induced by protons for different proton concentrations. Each data point corresponds to a differential measurement for an acid-salt combination and is slightly horizontally offset for clarity. The line is a linear fit to all data points. The slope is a direct measure for the number of water molecules that is affected by the presence of the proton. Above concentrations of 1.5 mol/kg, the relation becomes nonlinear, indicating overlapping hydration layers [26,27].

In this equation c is the concentration of protons, c_s is the concentration of solvent water molecules in the solution, and c_0 represents the concentration of water molecules of pure water. Furthermore, S_1 corresponds to the relaxation strength of pure water and $\Delta S_{1,H}$ to the depolarization effect of protons. Using our results for the depolarization effect of protons, we find that for protons in water $N_H = 19 \pm 2$, where the uncertainty consists of a part due to experimental uncertainty ($\sim 2\%$) and a part due to systematic uncertainty in the assumed literature values for the cation depolarization and the salt and acid conductivities ($\sim 8\%$). Surprisingly, this number of affected water molecules is even larger than for the strongly hydrating cation Mg^{2+}, which has been found to immobilize ~ 10 water molecules [20].

The depolarization effect of the proton likely has a very different origin from that of, for instance, Mg^{2+}. For cations like Mg^{2+}, the depolarization results from the immobilization of nearby water molecules. This effect will also occur for protons, but for the proton an additional effect occurs: The depolarization is also the result of the motion of water molecules associated with the motion of the proton charge. A charge (the proton) that moves in the driving electric field (the terahertz pulse) causes the surrounding water molecules to rotate [33]. The direction of this rotation has an opposite sign compared to the direction of the electric field, hence resulting in a *decrease* in the dielectric relaxation strength. We follow Ref. [17] to calculate the effect of this kinetic depolarization, which is proportional to the solution conductivity with a prefactor that depends only on the dielectric properties of the pure solvent. We find that the kinetic depolarization corresponds to the response of ~ 15 water molecules. The remaining depolarization effect of ~ 4 water molecules is likely due to water molecules that are irrotationally bound by the proton. This number of ~ 4 bound water molecules corresponds well to the so-called Eigen $H_9O_4{}^+$ hydronium complex that is found in MD simulations [2–4]. Our findings experimentally confirm the results of recent simulations, which showed that a small number of very strong hydrogen bonds are present directly around the proton [34] and that the rate-limiting step for proton transport is the collective reorganization of a larger number of water molecules [8].

The observation that a large number of water molecules are involved in aqueous proton transport has important consequences for proton hydration and transport in systems in which the number of water molecules is limited, as is, for instance, the case in confined systems. Examples of these systems are protons confined in micelles and protons in membranes and transmembrane proton pumps. Based on the present observations, we expect that the bulk mechanism of proton transfer is not possible in these systems and that a different, modified mechanism of proton transport is employed.

This work is part of the research program of the ''Stichting voor Fundamenteel Onderzoek der Materie (FOM),'' which is financially supported by the ''Nederlandse organisatie voor Wetenschappelijk Onderzoek (NWO).'' The authors thank H. Schoenmaker for technical support.

---

*bonn@amolf.nl

[1] J. D. Bernal and R. H. Fowler, J. Chem. Phys. **1**, 515 (1933).
[2] M. Tuckerman *et al.*, J. Phys. Chem. **99**, 5749 (1995).
[3] N. Agmon, Chem. Phys. Lett. **244**, 456 (1995).
[4] D. Marx *et al.*, Nature (London) **397**, 601 (1999).
[5] S. Woutersen and H. J. Bakker, Phys. Rev. Lett. **96**, 138305 (2006).
[6] A. Chandra, M. E. Tuckerman, and D. Marx, Phys. Rev. Lett. **99**, 145901 (2007).
[7] O. Markovitch *et al.*, J. Phys. Chem. B **112**, 9456 (2008).
[8] H. Lapid *et al.*, J. Chem. Phys. **122**, 014506 (2005).
[9] J. B. Hasted, D. M. Ritson, and C. H. Collie, J. Chem. Phys. **16**, 1 (1948).
[10] A. S. Lileev, D. V. Loginova, and A. K. Lyashenko, Mendeleev Commun. **17**, 364 (2007).
[11] A. A. Zavitsas, J. Phys. Chem. B **105**, 7805 (2001).
[12] M. Śmiechowski and J. Stangret, J. Chem. Phys. **125**, 204508 (2006).
[13] M. Miyazaki *et al.*, Science **304**, 1134 (2004).
[14] J.-W. Shin *et al.*, Science **304**, 1137 (2004).
[15] K. Mizuse, A. Fujii, and N. Mikami, J. Chem. Phys. **126**, 231101 (2007).
[16] J. Q. Searcy and J. B. Fenn, J. Chem. Phys. **61**, 5282 (1974).
[17] R. Buchner, G. T. Hefter, and P. M. May, J. Phys. Chem. A **103**, 1 (1999).
[18] T. Chen, G. Hefter, and R. Buchner, J. Phys. Chem. A **107**, 4025 (2003).
[19] W. Wachter *et al.*, J. Phys. Chem. B **111**, 9010 (2007).
[20] R. Buchner, T. Chen, and G. Hefter, J. Phys. Chem. B **108**, 2365 (2004).
[21] W. Wachter *et al.*, J. Phys. Chem. A **109**, 8675 (2005).
[22] J. T. Kindt and C. A. Schmuttenmaer, J. Phys. Chem. **100**, 10 373 (1996).
[23] C. Ronne *et al.*, J. Chem. Phys. **107**, 5319 (1997).
[24] C. Ronne, P. O. Astrand, and S. R. Keiding, Phys. Rev. Lett. **82**, 2888 (1999).
[25] J. Knab, J. Y. Chen, and A. Markelz, Biophys. J. **90**, 2576 (2006).
[26] U. Heugen *et al.*, Proc. Natl. Acad. Sci. U.S.A. **103**, 12 301 (2006).
[27] S. Ebbinghaus *et al.*, Proc. Natl. Acad. Sci. U.S.A. **104**, 20 749 (2007).
[28] T. Fukasawa *et al.*, Phys. Rev. Lett. **95**, 197802 (2005).
[29] E. Knoesel *et al.*, J. Chem. Phys. **121**, 394 (2004).
[30] A. W. Omta *et al.*, Science **301**, 347 (2003).
[31] Y. Hayashi *et al.* J. Phys. Chem. B **111**, 1076 (2007).
[32] An alternative method of calculating the number of irrotationally bound molecules, namely, using the solvent-normalized Cavell equation [20], yields $N_H = 20$ instead of 19.
[33] J. B. Hubbard *et al.*, Proc. Natl. Acad. Sci. U.S.A. **74**, 401 (1977).
[34] O. Markovitch and N. Agmon, J. Phys. Chem. A **111**, 2253 (2007).