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Ultrafast Vibrational and Structural Dynamics of the Proton in Liquid Water

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The dynamical behavior of excess protons in liquid water is investigated using femtosecond vibrational pump-probe spectroscopy. By resonantly exciting the O-H$^+$-stretching mode of the $H_9O_4^+$ (Eigen) hydration structure of the proton and probing the subsequent absorption change over a broad frequency range, the dynamics of the proton is observed in real time. The lifetime of the protonic stretching mode is found to be approximately 120 fs, shorter than for any other vibration in liquid water. We also observe the interconversion between the $H_9O_4^+$ (Eigen) and $H_5O_2^+$ (Zundel) hydration structures of the proton. This interconversion, which constitutes an essential step of proton transport in water, is found to occur on an extremely fast (< 100 fs) time scale.

Proton transport in water is of fundamental importance in chemistry and biology, and has been at the focus of extensive experimental [1–7] and theoretical [8–11] work during the last decade. The mobility of the proton is much higher than might be expected based on the size of its solvated structure, indicating that the transport involves a mechanism other than ionic diffusion. The proton in water is believed to occur mainly in two hydration structures, the $H_9O_4^+$ [Eigen [12]] and the $H_5O_2^+$ [Zundel [13]] structures, shown schematically in Fig. 1. Recent *ab initio* molecular dynamics simulations have provided evidence that the transport of protons in water involves a rapid interchange between the Eigen and Zundel forms [9,10]. This interchange takes place by a rearrangement of covalent and hydrogen bonds only, leading to a displacement of the protonic charge without moving the protonic mass [Grotthuss mechanism [14,15]]. Experimental evidence for this mechanism is at present still lacking. Here, we investigate the dynamics of proton transport in water by exciting and probing the Eigen and Zundel structures using ultrafast vibrational spectroscopy.

The Eigen and Zundel structures have O-H-stretching normal modes with distinctly different frequencies [16,17], as indicated in Fig. 1: the O-H$^+$-stretching mode of the HD_2O^+ ion at the center of the Eigen(I) structure absorbs from 2700 to 2950 cm^{-1}, whereas the O-H-stretching mode of the water molecules in the Zundel structure absorbs from 3250 to 3400 cm^{-1}. [16] The OH-stretching mode of water molecules that coordinate the D_3O^+ ion in the Eigen(II) structure also absorbs in this frequency region [17]. Note that in the Eigen(I) and Eigen(II) structures the OH group has a different position with respect to the center of the protonic charge. In our experiment, we excite the O-H$^+$-stretching mode of the Eigen(I) structure using resonant ultrashort infrared pulses, and monitor the subsequent absorption change using weak, delayed probing pulses.

Using an experimental setup which has been described elsewhere [18], we generate midinfrared pump and probe pulses (energies 15 μJ and $\ll 1$ μJ, respectively) which are independently tunable from 2500 to 4000 cm^{-1}. Pump and probe are focused (focal diameter $\sim$200 μm) and overlapped in the sample. The cross correlation of pump and probe (shown in Fig. 2) has a FWHM of 150 fs, which limits our time resolution to about 100 fs. The pump pulse is used to resonantly excite a vibrational mode of the hydrated proton, and the resulting absorption change is measured using the delayed probing pulse. The probe pulse is spectrally dispersed after the sample, and the absorption change is measured as a function of both frequency and delay. We study 5M solutions of HCl:DCl in HDO:D_2O, with a H:D ratio of 1:5 or 1:20 (the main effect of higher H:D ration being a larger effect of heating at long delays). Previous studies have shown that the absorption spectrum of the proton does not change up to a concentration of 1.5M HCl [16]. At the higher concentrations used here, small changes in the spectrum might occur, but these will at most be on the order of 20 cm^{-1} [19]. The isotopic dilution is essential to avoid effects of Förster energy transfer and of
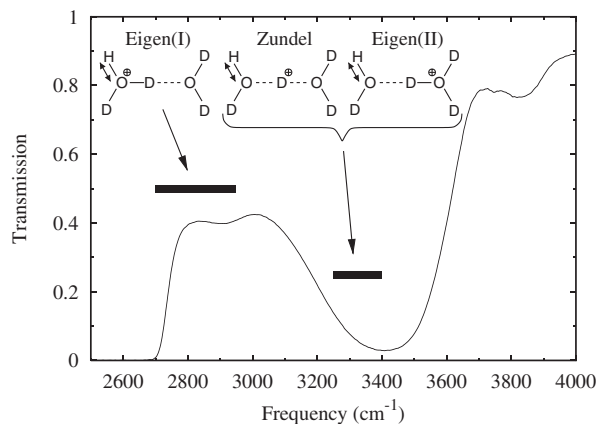

FIG. 1. Infrared spectrum of a 5M solution of HCl:DCl in HDO:D_2O, with a H:D ratio of 1:20. The bars indicate the frequency regions of the O-H-stretching modes of the Eigen(I) and Zundel/Eigen(II) structures.
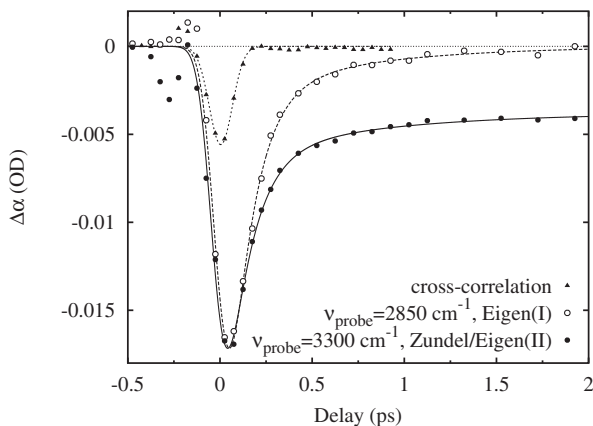
FIG. 2.　Absorption change as function of delay after resonant excitation (at 2935 cm^{-1}) of the O-H$^+$-stretching mode of the Eigen(I) structure. The absorption change is shown for two probing frequencies, one resonant with the Eigen(I) structure, and one resonant with the Zundel and Eigen(II) structures. The curves superimposed on the experimental points are least-squares fits of bi-exponential decays convoluted with the cross correlation of pump and probe. The time constants are 120 fs and 0.7 ps for the dotted curve, and 130 fs and 0.8 ps for the solid curve.

heating. Experiments [20] and calculations [20,21] show that upon partial deuteration, the O-H-stretching frequencies of the Eigen and Zundel structures change no more than ∼50 cm^{-1}, a small shift compared to the linewidths of the O-H-stretching bands. The solutions are prepared by mixing appropriate amounts of concentrated HCl:H$_2$O and DCl:D$_2$O solutions (Sigma Aldrich, purity > 99.9%) with H$_2$O and D$_2$O, and are kept between 2 mm thick CaF$_2$ windows separated by a 25 μm teflon spacer.

Figure 2 shows the absorption change as a function of time delay after excitation of the Eigen(I) structure at 2935 cm^{-1}. The resonant excitation of the Eigen(I) O-H-stretching mode causes bleaching of the $v = 0 \rightarrow 1$ transition and $v = 1 \rightarrow 0$ stimulated emission, resulting in a negative absorption change in the 2700 to 2950 cm^{-1} frequency region. Vibrational relaxation of the $v = 1$ state causes a rapid decay of the negative absorption change, followed by a somewhat slower decay on a time scale of ∼1 ps. In this second, slower relaxation process the energy is equilibrated over all degrees of freedom. This process involves a restructuring of the hydrogen-bond network subsequent to the vibrational relaxation of the O-H$^+$-stretching mode, and has been observed previously for the O-H-stretching mode of pH-neutral HDO:D$_2$O [22,23]. After the second process, the transient spectrum has the form of a thermal difference spectrum. The assignment of vibrational relaxation and subsequent equilibration to the two observed decay processes is confirmed by their different spectral signatures. The different spectral signatures also exclude the possibility that the vibrational relaxation occurs within the pulse duration. From a least-

squares fit to the data we obtain a vibrational lifetime of 120 ± 20 fs for the Eigen(I) O-H$^+$-stretching mode, and an equilibration time of 0.7 ± 0.3 ps [24]. The vibrational lifetime of the Eigen(I) O-H$^+$-stretching mode is thus much shorter than that of the O-H-stretching mode in pH-neutral HDO:D$_2$O (740 fs) [25].

Figure 3 shows the transient-absorption spectrum when exciting the Eigen(I) structure. Interestingly, a negative absorption change is observed not only in the frequency region of the Eigen(I) structure, but also in the frequency region of the Zundel and Eigen(II) structures. To verify that the absorption change in the Zundel/Eigen(II) frequency region is not caused by excitation of the O-H-stretching mode of HDO molecules, we have performed an experiment in which we excite the O-H-stretching band of HDO (at 3400 cm^{-1}) of the same solution. In Figure 4 we compare the resulting absorption change with that observed after excitation of the Eigen structure. Exciting HDO results in absorption changes similar to the ones observed for pH-neutral HDO:D$_2$O: [26] in addition to the negative absorption change at ∼3400 cm^{-1} caused by $v = 0 \rightarrow 1$ bleaching and $v = 1 \rightarrow 0$ stimulated emission, a positive absorption change due to $v = 1 \rightarrow 2$ excited-state absorption is observed at lower frequencies. The absorption change decays with a time constant of 800 ± 40 fs, similar to the lifetime observed in pH-neutral HDO:D$_2$O, [25] and much slower than that observed for the Zundel/Eigen(II) band (see Fig. 2). Hence, exciting water instead of the proton results in absorption changes differing both in frequency and in delay dependence. The negative absorption change observed in Fig. 3 near 3350 cm^{-1} can consequently not be due to the direct excitation of water molecules. A frequency shift of the Eigen(I) OH-stretching mode after its
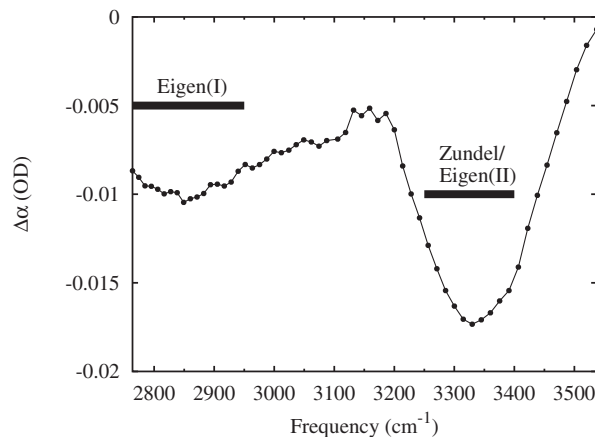

FIG. 3.　Absorption change as function of frequency, 200 fs after resonant excitation (at 2935 cm^{-1}) of the O-H$^+$-stretching mode of the Eigen structure. The spectrum was constructed from spectrally overlapping data sets obtained from samples with H:D ratios of 1:5 and 1:20. Scaling factors were determined by matching the data in the regions of overlap.
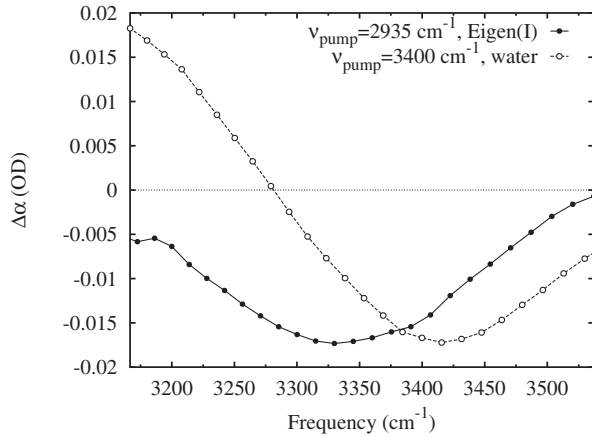
FIG. 4.   Absorption changes at a delay of 200 fs after excitation of the O-H$^+$-stretching mode of the Eigen(I) structure, and after excitation of the O-H-stretching mode of HDO. The data have been scaled for better comparison.

vibrational relaxation can also be excluded as a possible origin of the observed bleaching at 3350 cm^{-1}, since the corresponding signal would have to grow in on a time scale on the order of the observed T_1 of 120 fs, and would involve an increase in absorption at the shifted frequency. We therefore conclude that the decrease in absorption observed in Fig. 3 near 3350 cm^{-1} must be that of the proton in the Zundel or Eigen(II) structure.

In the transient-absorption spectrum, shown in Fig. 3, the absorption changes of the Eigen(I) and Zundel/Eigen(II) structures are observable as broad, but clearly separated bands. Therefore, the population of the Zundel $v = 1$ state when exciting the Eigen(I) structure cannot be due to direct excitation by the pump pulse, since there is no spectral overlap of the pump pulse with the Zundel/Eigen(II) absorption range. Resonant energy transfer between the Eigen(I), Zundel, and Eigen(II) O-H-stretch modes can also be excluded, because of the isotopic dilution [27] and the large difference in vibrational frequency [28]. The exchange between the Eigen(I), Zundel, and Eigen(II) $v = 1$ populations can therefore only result from a structural interconversion between the Eigen(I), Zundel, and Eigen(II) structures, a process in which the vibrational excitation of the O-H-stretch vibration is conserved. The solid curve in Fig. 2 shows the time-dependent response at the O-H-stretching frequency of the Zundel and Eigen(II) structures when exciting the Eigen(I) structure. The instantaneous rise of the signal at the Zundel/Eigen(II) frequency implies that the Eigen-Zundel exchange occurs much faster than the time resolution of our experiment, which is about 100 fs. This is confirmed by the fact that the $v = 1$ population lifetimes observed for the Eigen(I), Zundel, and Eigen(II) structures are identical (120 ± 20 fs and 130 ± 20 fs, respectively): since the exchange between the two structures is faster than the population relaxation, the same effective averaged $v = 1$ decay is

observed for both structures, even though the isolated structures could in principle have different lifetimes. The $v = 1 \rightarrow 2$ excited-state absorption of the Zundel and Eigen(II) structures, which would be expected at a frequency around 3000 cm^{-1}, is probably not visible because it overlaps with the bleaching of the Eigen(I) structure at 2950 cm^{-1}.

The very short T_1 observed for the protonic OH-stretching mode can be explained from several effects. First, the hydrated proton is much more susceptible to local electric field fluctuations than the hydrogen atoms in a water molecule, leading to frequency modulations of the O-H$^+$-stretching mode over a very broad frequency range. The spectral overlap with accepting modes at low frequencies will therefore be larger than for the O-H-stretch mode in pH-neutral HDO:D$_2$O. Second, the stronger hydrogen bonding of O-H$^+$ as compared to O-H gives rise to a larger coupling between the O-H$^+$-stretching and low-frequency modes, leading to a more efficient energy transfer from the former to the latter. Third, it may happen that the proton of the vibrationally excited O-H$^+$ group is transferred to a neighboring oxygen atom through Eigen-Zundel interconversion (note the difference with the Eigen-Zundel interconversion observed in Figs. 2 and 3, in which the excited O-H$^+$ bond acts only as a spectator, see the diagrams in Fig. 1). As the vibrational excitation is probably not conserved during this process, this creates an efficient relaxation channel that does not exist for stretching excitations of neutral O-H groups. An estimate of the relative importance of these three factors is difficult to make, and requires a detailed theoretical description of the vibrational relaxation of the hydrated proton [29,30].

Ab initio molecular dynamics simulations have suggested a mechanism in which the transfer of the protonic charge from an H$_3$O$^+$ ion to a neighboring H$_2$O takes place in two steps [9,10]. In the first step, the hydrogen-bond coordination number of one of the H$_2$O molecules in the first solvation shell is lowered by the breaking of a hydrogen bond to the second solvation shell. Such thermally induced hydrogen-bond breaking also occurs in pH-neutral water, and has been well characterized in previous experiments [23,26,31,32] and simulations [33–35]. In the second step, the protonic charge is transferred from the H$_3$O$^+$ ion to the H$_2$O molecule with the reduced hydrogen-bond coordination number, a process in which the Zundel structure occurs as an intermediate state. Our results show that this second step occurs on an extremely fast time scale. As a consequence, the first step is the rate-limiting one, and the agreement between the solvent reorganization time in water [on the order of 1 ps [23,26,31,32]] with the proton hopping time [estimated to be 1.7 ps from the bulk proton diffusion constant, and 1.3 ps from NMR measurements [36]] confirms this.

We find that the Eigen and Zundel structures interchange within a very short time (<100 fs), which means that the

proton rapidly rattles between the oxygen atoms of two neighboring water molecules. This picture is in agreement with recent theoretical work, in which it has been predicted that the proton transfer along the hydrogen bond should occur essentially barrierless, as the small barrier between the solvation structures is washed out by the zero-point motion of the proton [9]. As a consequence, the proton in water forms a "fluxional complex" with the Eigen and Zundel structures as limiting and intermediate conformations, respectively.

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