

# Dynamics of confined water molecules

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**We present femtosecond midinfrared pump-probe measurements of the molecular motion and energy-transfer dynamics of a water molecule that is enclosed by acetone molecules. These confined water molecules show hydrogen-bond and orientational dynamics that are much slower than in bulk liquid water. This behavior is surprising because the hydrogen bonds to the C=O groups of the acetone molecules are weaker than the hydrogen bonds in bulk water. The energy transfer between the O—H groups of the confined water molecules has a time constant of  $1.3 \pm 0.2$  ps, which is >20 times slower than in bulk water. We find that this energy transfer is governed completely by the rate at which hydrogen bonds are broken and reformed, and we identify the short-lived molecular complex that forms the transition state of this process.**

hydrogen bonding | infrared pump-probe spectroscopy | energy transfer

Water plays an essential role in many chemical and biological processes. Over the last decades, this notion has motivated a lot of work on the dynamical properties of bulk liquid water (1–7). However, the role of water in (bio)chemical processes is often played by a limited number of water molecules in a strongly restricted molecular environment. For example, the stability, structure, and biological function of proteins are largely determined by only a few surrounding layers of water molecules (8). When the water molecules participate directly in a reaction, the number of involved water molecules is even smaller. For example, the proton-pumping function of bacteriorhodopsin involves changes of the hydrogen network that is formed by particular amino acids of the protein and only a few confined water molecules (9–12).

Recently, the dynamics of water in restricted environments was studied by comparing the spectral dynamics of an optically excited probe molecule embedded in a hydrated (bio)molecule with the spectral dynamics of the same probe molecule in bulk water (13). The spectral dynamics reflect the collective rearrangement of the solvating water, and were found to be much slower within the hydrated (bio)molecule than in bulk water. In this article, we present a study of the hydrogen-bond and energy-transfer dynamics of individual H<sub>2</sub>O and <sup>1</sup>H<sup>2</sup>HO molecules in a confined environment. In this study, we probed the dynamics of the water molecules directly with femtosecond midinfrared laser pulses that are resonant with the O—H stretch vibrations.

## Experimental Methods

The system of confined water molecules is prepared by dissolving water (0.4 mol/liter) in a mixture of acetone (4.0 mol/liter) and CCl<sub>4</sub>. The structures that are formed in this mixture have a polar internal part consisting of an enclosed water molecule forming hydrogen bonds to the C=O groups of a few surrounding acetone molecules, and an apolar external part formed by the methyl groups of the acetone molecules. The favorable interaction between the methyl groups and the CCl<sub>4</sub> molecules allows these structures to enter the apolar CCl<sub>4</sub> matrix. The molecular ratio of H<sub>2</sub>O/acetone/CCl<sub>4</sub> is 1:10:40. The system of confined <sup>1</sup>H<sup>2</sup>HO molecules is prepared by using a mixture of H<sub>2</sub>O and D<sub>2</sub>O instead of pure H<sub>2</sub>O. The molecular ratio of the resulting system of <sup>1</sup>H<sup>2</sup>HO/D<sub>2</sub>O/acetone/CCl<sub>4</sub> is 1:4:50:200.

In the pump-probe experiments, an intense femtosecond midinfrared pulse (pump) is used to excite a fraction of the water molecules to the first excited vibrational state of the O—H stretch vibration. The absorption changes that result from this excitation are probed with a second, much weaker pulse (probe). The probe pulse is sent through a variable delay to measure the time-dependence of these absorption changes. In the experiments on vibrational relaxation, the probe polarization is at the magic angle (54.7°) with respect to the polarization of the pump. In the experiments on the orientational relaxation, the probe is polarized at 45° with respect to the direction of polarization of the pump, and it is split after the sample in a parallel and a perpendicular part. The transmitted probe beams are dispersed in a monochromator and detected by a 3 × 32 MCT (mercury-cadmium-telluride) array detector. The frequency resolution is 16 cm<sup>-1</sup> per pixel of the array. The midinfrared pump and probe pulses are generated by means of nonlinear frequency conversion processes that are pumped by the pulses of a commercial system of a Ti:Sapphire oscillator, a regenerative amplifier, and a multipass amplifier. These pulses have a central wavelength of 800 nm, a pulse energy of 2.6 mJ, and a pulse duration of 100 fs. The midinfrared pump pulses are generated by means of parametric generation and amplification in β barium borate (BBO) and KTiOPO<sub>4</sub> (KTP) crystals. The midinfrared probe pulses are generated by means of parametric generation and amplification in a BBO crystal, followed by difference frequency generation in a AgGaS<sub>2</sub> crystal. The pump and probe pulses are independently tunable between 2.6 and 3.3 μm (3,000–3,800 cm<sup>-1</sup>), and they have a pulse duration of 170 fs, spectral widths of 60 and 300 cm<sup>-1</sup> (full width at half maximum), and energies of 10 and 0.1 μJ, respectively. Frequency-resolved cross-correlation measurements show that the large bandwidth of the probe does not result from a linear chirp.

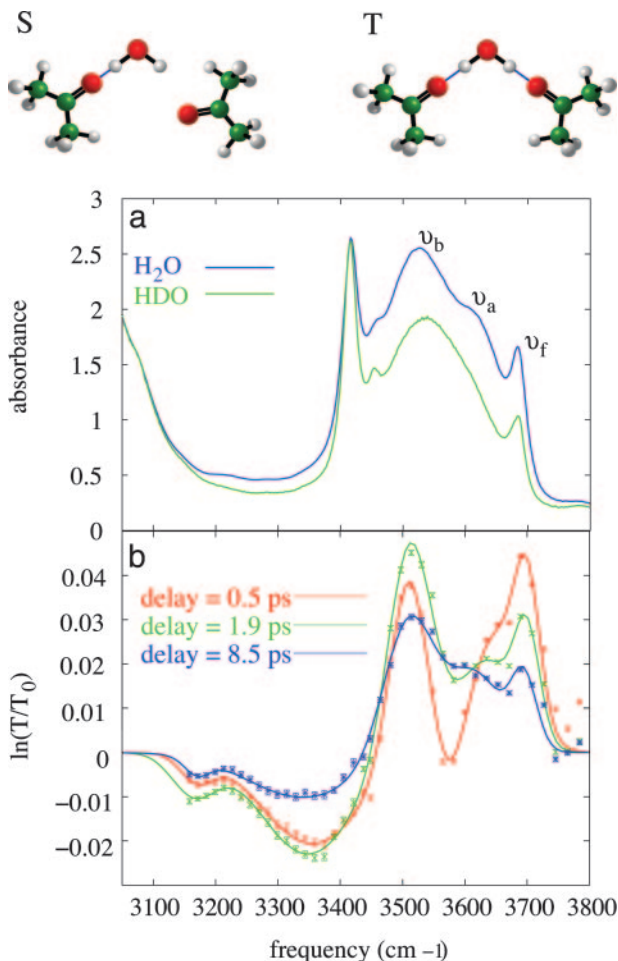
## Results

In Fig. 1a, absorption spectra of the confined water molecules are shown for both H<sub>2</sub>O (solid curve) and <sup>1</sup>H<sup>2</sup>HO (dashed curve). The spectra of H<sub>2</sub>O and <sup>1</sup>H<sup>2</sup>HO show great similarity, both showing a broad band at 3,530 cm<sup>-1</sup> and a narrow band at 3,690 cm<sup>-1</sup>. These frequencies are obtained from a decomposition of the spectrum into Gaussian bands. The bands at 3,530 and 3,690 cm<sup>-1</sup> cannot represent the symmetric and asymmetric O—H stretching modes of H<sub>2</sub>O, because then they would not have been observed for <sup>1</sup>H<sup>2</sup>HO. Instead, these bands represent the vibration of a hydrogen-bonded O—H group ( $\nu_b = 3,530$  cm<sup>-1</sup>) and a non-hydrogen-bonded O—H group ( $\nu_f = 3,690$  cm<sup>-1</sup>) (14, 15). The absorption of the band at  $\nu_b$  is much stronger than the band at  $\nu_f$ , because the cross section of the O—H stretch vibration increases (by a factor of ≈10) upon hydrogen-bond formation. The similarity of the spectra of H<sub>2</sub>O and <sup>1</sup>H<sup>2</sup>HO shows that the two O—H vibrations of H<sub>2</sub>O are decoupled in a similar fashion as the O—H vibration and O—D vibration of <sup>1</sup>H<sup>2</sup>HO. Hence, in the dominant conformation formed by H<sub>2</sub>O/<sup>1</sup>H<sup>2</sup>HO with acetone (structure S in Fig. 1a) only one of the two

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**Fig. 1.** Linear and nonlinear spectral response. (a) Spectra of H<sub>2</sub>O (blue curve) and <sup>1</sup>H<sub>2</sub>HO (green curve) molecules in acetone/CCl<sub>4</sub>. (Inset) The two different structures of the water–acetone complex with the corresponding O—H vibrational modes are shown. The labels  $\nu_b$  and  $\nu_f$  denote the stretch vibrations of the hydrogen-bonded and non-hydrogen-bonded O—H group of structure S, respectively.  $\nu_s$  and  $\nu_a$  denote the symmetric and asymmetric stretch vibrations of the two hydrogen-bonded O—H groups of structure T. The peak at 3,400 cm<sup>-1</sup> represents the absorption of the overtone of the C=O stretch vibration of acetone. (b) Transient spectra of H<sub>2</sub>O molecules confined in acetone/CCl<sub>4</sub> at three different delays after excitation with an intense femtosecond pump pulse with a central frequency of 3,690 cm<sup>-1</sup>.

groups of the H<sub>2</sub>O/<sup>1</sup>H<sub>2</sub>HO molecule is hydrogen bonded to an acetone molecule.

The H<sub>2</sub>O spectrum shows a weak additional band at 3,635 cm<sup>-1</sup> that is not observed for <sup>1</sup>H<sub>2</sub>HO. This band represents the asymmetric O—H stretching mode of the H<sub>2</sub>O molecule. This band indicates the presence of a less abundant second conformation (structure T in Fig. 1a), in which the water molecule forms two hydrogen bonds of approximately equal strength with two acetone molecules. As a result, the O—H stretch vibrations of H<sub>2</sub>O in structure T form delocalized symmetric and anti-symmetric vibrations. The anti-symmetric O—H stretch vibration is observed as a small peak at 3,635 cm<sup>-1</sup> ( $\nu_a$ ). The symmetric O—H stretch vibration has a weaker absorption than the antisymmetric O—H stretch vibration and absorbs at a lower frequency. The absorption of this vibration cannot be distinguished in the spectrum, because it is completely dominated by the strong  $\nu_b$  band of structure S.

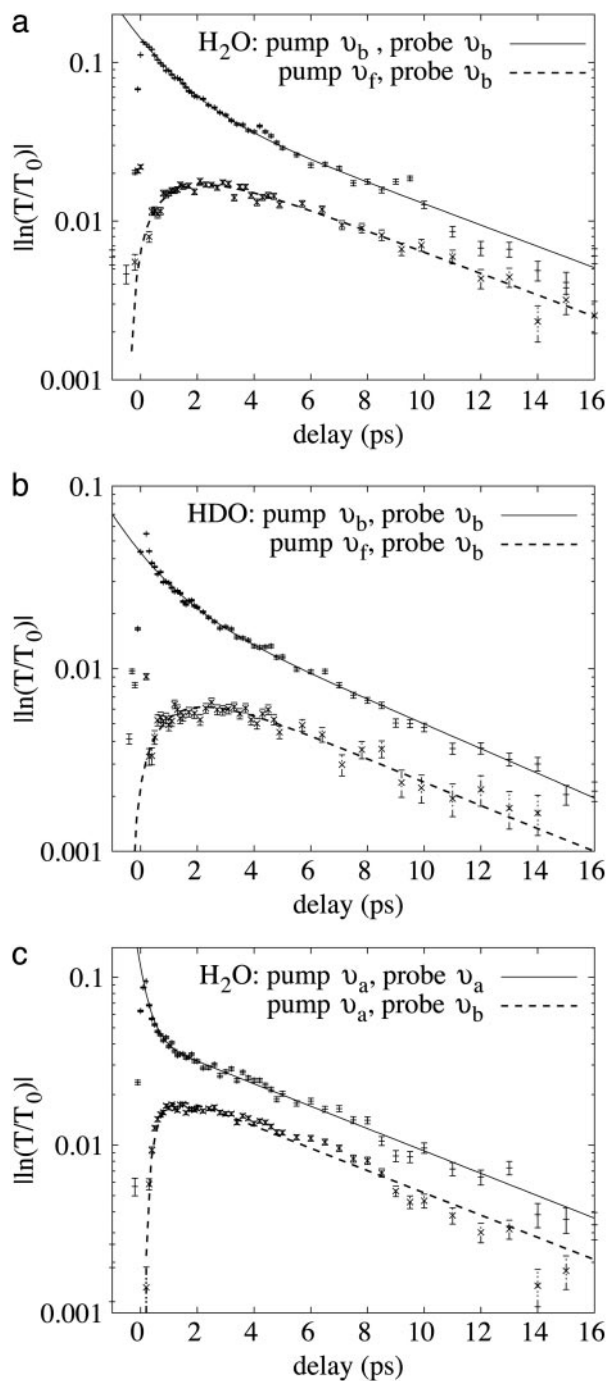
The dominance of the S structure over the T structure can be explained from the steric interactions of the acetone molecules.

The formation of a T structure requires the proximity of two acetone molecules. Because of the repulsion of the methyl groups, the hydrogen bonds of the T structure are relatively long and weak, thus making the T structure less stable than the singly bonded S structure.

In Fig. 1b, the changes in the absorption spectrum of confined H<sub>2</sub>O induced by a strong pump pulse with a central frequency of 3,690 cm<sup>-1</sup> are shown at three different delays after the excitation. This pump pulse is resonant with the 0→1 transition of the  $\nu_f$  band. In all spectra, a decrease in absorption of the three bands  $\nu_b$ ,  $\nu_a$ , and  $\nu_f$  is observed. This absorption decrease results from the bleaching of the fundamental 0→1 transition of the O—H stretch vibrations. In addition, new absorptions are observed at 3,180 and 3,350 cm<sup>-1</sup>. The band at 3,350 cm<sup>-1</sup> mainly represents the 1→2 excited state absorption of  $\nu_b$ , but also contains the 1→2 absorption of  $\nu_a$ . These bands are red shifted compared with the fundamental transitions because of the anharmonicity of the O—H stretch vibrations. The band at 3,180 cm<sup>-1</sup> is not observed for the <sup>1</sup>H<sub>2</sub>HO system, which implies that this band cannot result from acetone or CCl<sub>4</sub>. This band likely results from the transition from the  $\nu = 1$  state of the  $\nu_f$  mode to the  $\nu = 2$  state of the  $\nu_b$  mode of the H<sub>2</sub>O molecule, which is a transition that involves a change of three vibrational quanta. The presence of this transition indicates that the two O—H groups of confined H<sub>2</sub>O are anharmonically coupled. The transient spectra show a strong dependence on delay. The bleaching signal of the  $\nu_b$  band at 3,520 cm<sup>-1</sup> increases in the delay time interval of 0.5–2 ps, which indicates that the original excitation of  $\nu_f$  is partially transferred to  $\nu_b$ . For delays of >3 ps, the shape of the transient spectrum no longer changes, and only the amplitude of the spectrum decreases, because of the relaxation of the  $\nu = 1$  state of the O—H stretch vibrations.

To study the dynamics of the energy transfer between  $\nu_f$  and  $\nu_b$ , we measured delay time scans for both confined H<sub>2</sub>O and <sup>1</sup>H<sub>2</sub>HO (Fig. 2). These curves are measured by using an angle of 54.7° (magic angle) (16) between the pump and the probe polarization. As a result, the measurements only reflect the population relaxation dynamics and the energy transfer between different vibrational bands. All curves shown in Fig. 2 are nonmonoexponential, and they show a strong dependence on the frequencies of pump and are probed for delays of <3 ps. When the  $\nu_b$  band is both pumped and probed (upper curve of Fig. 2a), a fast initial decay with a time constant of 1.3 ± 0.2 ps is observed. If instead  $\nu_f$  is pumped and  $\nu_b$  is probed (lower curve), an ingrowth with the same time constant is observed. These results show that there is an equilibration of the excitation of the  $\nu_b$  and  $\nu_f$  bands with a time constant of 1.3 ± 0.2 ps. As a result of this equilibration, both bands show the same exponential decay at delays of >3 ps. The time constant of this decay is 6.3 ± 0.5 ps and represents the averaged lifetime T<sub>1</sub> of the O—H stretch vibrations. For bulk liquid water, the vibrational lifetime was observed to be 260 fs (17), which implies that the confined water molecules retain the excitation of the O—H stretch vibration >20 times as long. In Fig. 2b, measurements for <sup>1</sup>H<sub>2</sub>HO obtained with the same pump and probe frequencies are shown. Interestingly, the observed dynamics are the same as in Fig. 2a, which implies that the equilibration of the excitation between  $\nu_b$  and  $\nu_f$  cannot result from a direct transfer of vibrational energy between the two O—H groups. The similarity of the data measured for H<sub>2</sub>O and <sup>1</sup>H<sub>2</sub>HO shows that the transfer between the  $\nu_b$  and the  $\nu_f$  bands in the spectrum must result from hydrogen-bond dynamics. When a hydrogen bond is formed at an excited nonbonded O—H group, the frequency of the excitation changes from  $\nu_f$  to  $\nu_b$ . Vice versa, when a hydrogen bond is broken at a hydrogen-bonded, excited O—H group, the frequency changes from  $\nu_b$  to  $\nu_f$ .

The absence of direct energy transfer between the two O—H groups of H<sub>2</sub>O in structure S is surprising, because the presence



**Fig. 2.** Delay time scans of H<sub>2</sub>O molecules confined in acetone/CCl<sub>4</sub> (a and c) and <sup>1</sup>H<sub>2</sub>O molecules confined in acetone/CCl<sub>4</sub> (b) measured with different pump and probe frequencies.

of the relatively strong band at 3,180 cm<sup>-1</sup> shows that the two O—H groups of H<sub>2</sub>O are strongly anharmonically coupled. However, energy transfer requires not only the presence of a strong (anharmonic) coupling, but also that the interacting (combinations of) states are in resonance. Apparently, the energy difference of ≈160 cm<sup>-1</sup> of the  $\nu = 1$  states of the  $\nu_b$  and  $\nu_f$  modes is too large for energy transfer to be possible. Clearly, energy matching is not an issue in exciting the  $\nu = 1$  state of the  $\nu_f$  mode with a 3,180 cm<sup>-1</sup> photon to the  $\nu = 2$  state of the  $\nu_b$  mode, so that anharmonic coupling can be effective in enabling this transition.

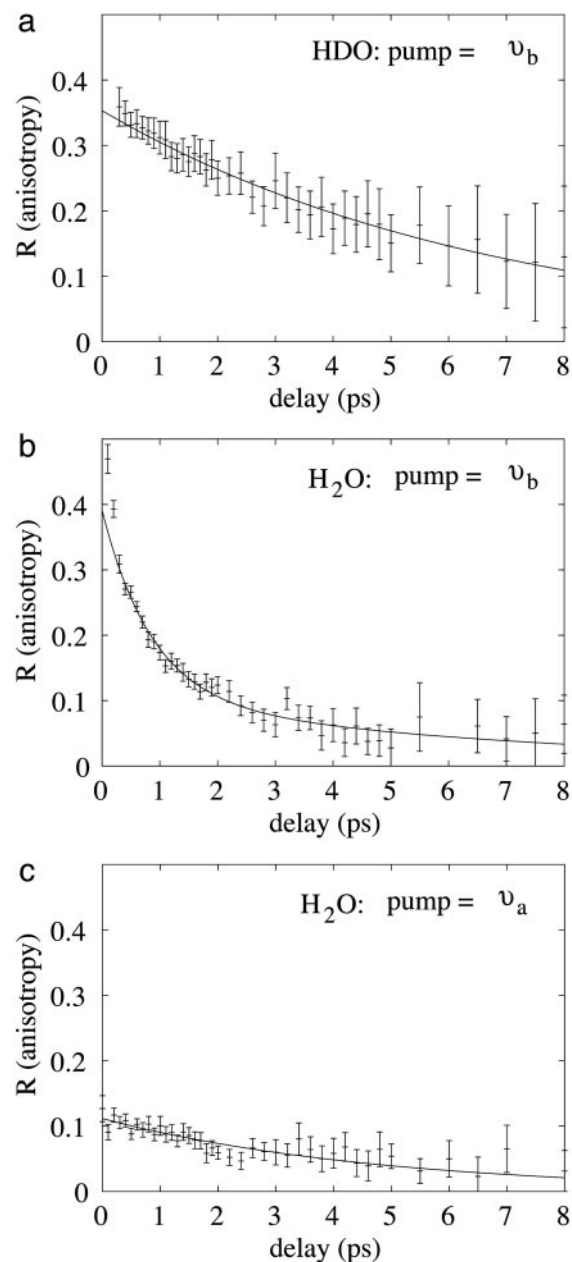
In Fig. 2c, the  $\nu_a$  band of H<sub>2</sub>O is pumped. If the  $\nu_a$  band is also probed (upper curve), the signal contains a rapid decay component with a time constant of  $150 \pm 50$  fs. If the  $\nu_b$  band is probed (lower curve), a rapid ingrowth with the same time constant is observed. These results show that structure T is short-lived and rapidly converted into structure S. At delays of >1 ps, the signal decays with the same time constant of  $6.3 \pm 0.5$  ps that was observed at delays >3 ps (Fig. 2 a and b).

To get additional information on the hydrogen-bond dynamics and the mechanism of energy transfer of the confined water molecules, we measured the dynamics of the anisotropy of the excitation. In our experiments, the excitation is anisotropic, because predominantly O—H groups are excited that are oriented parallel to the pump polarization. The anisotropy is defined as follows:

$$R = \frac{\Delta\alpha_{\parallel} - \Delta\alpha_{\perp}}{\Delta\alpha_{\parallel} + 2\Delta\alpha_{\perp}},$$

where  $\Delta\alpha_{\parallel}$  and  $\Delta\alpha_{\perp}$  are the absorption changes measured with probe pulses that are polarized parallel and perpendicular to the polarization of the pump, respectively. For an ensemble of randomly oriented dipolar oscillators,  $\Delta\alpha_{\parallel} = 3\Delta\alpha_{\perp}$  at zero delay, so that  $R = 0.4$ . At later delays,  $R$  decays because of the reorientation of the water molecule and/or because of resonant energy transfer between the two O—H groups. In Fig. 3a, the  $\nu_b$  band of <sup>1</sup>H<sub>2</sub>O was pumped and probed and  $R$  is observed to show a monoexponential decay with a time constant of  $6 \pm 1$  ps. Clearly, for <sup>1</sup>H<sub>2</sub>O there can be no energy transfer between two differently oriented O—H groups, so that the dynamics of  $R$  represents only the molecular reorientation. In Fig. 3b, the  $\nu_b$  band of H<sub>2</sub>O was pumped and probed. At delays of >3 ps, the signal shows the same decay with a time constant of  $6 \pm 1$  ps that was observed for <sup>1</sup>H<sub>2</sub>O in Fig. 3a. However at shorter delays, the anisotropy shows an additional rapid decay with a time constant of  $1.1 \pm 0.3$  ps to a value of ≈0.1. This time constant is similar to the time constant of the hydrogen-bond dynamics of  $1.3 \pm 0.2$  ps. This similarity and the absence of the fast component for <sup>1</sup>H<sub>2</sub>O indicate that the hydrogen-bond dynamics not only lead to a change of the vibrational frequency of the excited O—H group (Figs. 2 a and b) but also mediate a transfer of energy to the other O—H within the H<sub>2</sub>O molecule. When this process is complete, the two O—H groups of the H<sub>2</sub>O molecule have equal probability of being excited, and the anisotropy should have a value of  $R = \frac{1}{5}(\frac{2}{5} + \frac{2}{5}P_2(\cos \delta))$  (18), where  $P_2$  is the second-order Legendre polynomial and  $\delta$  is the angle between the two transition dipoles. For  $\delta = 104^\circ$ , which is the angle between the two OH-groups of the water molecule, this expression gives  $R(0) = 0.12$ , which is in good agreement with the experimental observation. In Fig. 3c, the  $\nu_a$  band was pumped and the  $\nu_b$  band was probed. In this experiment,  $R$  is observed to have a starting value of 0.12. This result implies that structure T is converted to structure S with equal probability for the two O—H groups to become the hydrogen-bonded O—H group. Note that the dynamics of Fig. 3c do not give information on the dynamics of this conversion, because the anisotropy parameter reflects only the orientation of the probed excitation and not its amplitude.

Based on the findings described above, we can identify the mechanism of energy transfer of the confined water molecules, as shown in Fig. 4. The four structures S<sub>L-IV</sub> differ in which O—H group is hydrogen bonded and in which local O—H vibration ( $\nu_b$  or  $\nu_f$ ) is excited. The mechanism by which energy is transferred from one O—H group the other is as follows. The strong hydrogen bond to one of the O—H groups of an S structure weakens, while simultaneously at the other O—H group, a new hydrogen bond is formed. The time scale of this process is  $1.3 \pm 0.2$  ps. When the hydrogen bonds are approximately equal in strength, the uncoupled O—H stretch vibrations are in near resonance, with the result that the coupling between the two



**Fig. 3.** Anisotropy decay of  $^1\text{H}^2\text{HO}$  molecules confined in acetone/ $\text{CCl}_4$  (a) and  $\text{H}_2\text{O}$  molecules confined in acetone/ $\text{CCl}_4$  (b and c) measured with a probe frequency of  $3,350\text{ cm}^{-1}$  (resonant with the  $1\rightarrow 2$  transition of the  $\nu_b$  mode). The pump frequencies are  $3,520\text{ cm}^{-1}$  (a and b) (resonant with the  $0\rightarrow 1$  transition of the  $\nu_b$  mode), and  $3,620\text{ cm}^{-1}$  (c) (resonant with the  $0\rightarrow 1$  transition of the  $\nu_a$  mode).

O—H groups leads to a strong delocalization of the vibrational excitation over the molecule. This delocalized state constitutes the transition state T. T rapidly evolves with a time constant of  $150 \pm 50\text{ fs}$  to one of the four different structures  $S_{\text{I-IV}}$  by strengthening one of the hydrogen bonds and breaking the other and by transferring the delocalized O—H stretch excitation into a local excitation of one of the O—H groups. Hence, the original excited structure S is equilibrated over all four structures S by going through the T structure. This process leads to an equilibration of the excitation over the  $\nu_b$  and  $\nu_t$  modes and over the two O—H groups. The confined  $^1\text{H}^2\text{HO}$  molecule shows exactly the same hydrogen-bond dynamics and molecular reorientation

as the confined  $\text{H}_2\text{O}$  molecule. However, an important difference is that for  $^1\text{H}^2\text{HO}$  there are only two S structures because the excitation of the O—H stretch vibration can only reside at one side of the molecule. Therefore, for  $^1\text{H}^2\text{HO}$  the S structures are either  $S_{\text{I}}$  and  $S_{\text{II}}$  (O—H at the right side of the molecule), or  $S_{\text{III}}$  and  $S_{\text{IV}}$  (O—H at the left side of the molecule). This notion means that for  $^1\text{H}^2\text{HO}$  the interconversion of the S and T structures will leave the excitation at the same side of the molecule. Hence, for  $^1\text{H}^2\text{HO}$  the interconversion of the S and T structures only leads to an equilibration of the excitation over the  $\nu_b$  and  $\nu_t$  modes.

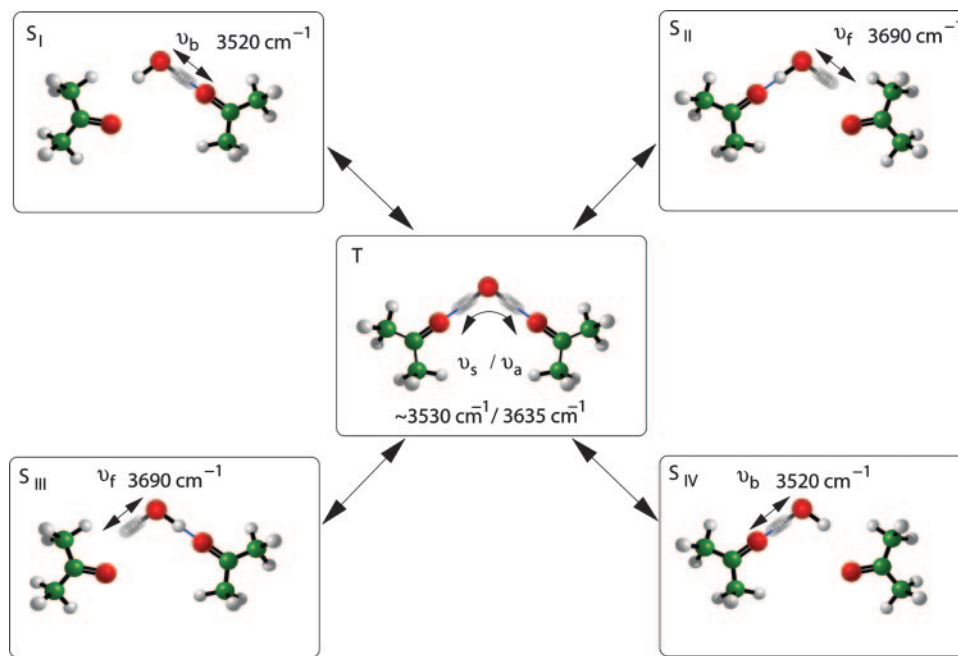
The mechanism of Fig. 4 implies that the  $\nu_a$  band observed in the spectrum constitutes the absorption spectrum of the transition state T for the transition between different S states. For this state, the hydrogen bonds are expected to be weaker than those of the reactant/product structures  $S_{\text{I-IV}}$ . The energy splitting between the delocalized  $\nu_s$  and  $\nu_a$  modes of the  $\text{H}_2\text{O}$  molecule is  $\approx 100\text{ cm}^{-1}$  (19). Hence, the uncoupled O—H vibrations of the T structure are expected to have frequencies of  $\approx 3,580\text{ cm}^{-1}$ , which is less red shifted with respect to the gas phase O—H stretch frequency than the frequency of the  $\nu_b$  band. This smaller red shift shows that the hydrogen bonds of T are indeed weaker.

### Discussion

The observed hydrogen-bond and orientational dynamics of the confined water molecules strongly differ from the corresponding dynamics of bulk liquid water. The hydrogen-bond dynamics of bulk liquid water have been extensively studied with femtosecond midinfrared techniques. In the older studies (1–3), the hydrogen-bond length correlation function was observed to show a single-exponential decay, with a time constant of  $\approx 500\text{ fs}$ . More recently, evidence was found that the decay of this correlation function is nonmonoexponential, with time scales of  $\approx 100\text{ fs}$  and  $\approx 1\text{ ps}$  (5–7). The reorientation of bulk water was observed to have a characteristic time scale of  $2.6\text{ ps}$  (20), which is approximately three times shorter than the reorientation time of  $6 \pm 1\text{ ps}$  observed here for confined water molecules.

Note that the difference between bulk and confined water cannot be explained from the strength of the hydrogen-bond interactions. From the frequencies of the O—H stretch vibrations, it follows that the hydrogen bonds between water and the C=O groups are weaker than those between the molecules in bulk liquid water, from which it could be expected that the dynamics of confined water would be faster instead of slower than the dynamics of bulk water. However, for bulk liquid water, the energy cost of locally breaking a hydrogen bond can be largely compensated by a simultaneous strengthening and/or formation of bonds at nearby molecules, so that the energy barriers in changing the molecular orientation and hydrogen-bond structure can be relatively low.

An interesting finding is the complete absence of direct energy transfer between the two O—H groups of the confined water molecule in structure S, as evidenced by the strong similarity of the spectral dynamics of confined  $\text{H}_2\text{O}$  and confined  $^1\text{H}^2\text{HO}$  (Fig. 2 a and b). Apparently, the energy mismatch of the  $\nu = 1$  states of the  $\nu_b$  mode and the  $\nu_t$  mode of  $\approx 160\text{ cm}^{-1}$  cannot be compensated easily by the participation of a low-frequency intermolecular mode in the energy transfer. This finding may seem surprising, because in the relaxation of the O—H stretch vibration of  $^1\text{H}^2\text{HO}$  dissolved in  $\text{D}_2\text{O}$ , the energy gaps to the accepting modes are much larger than  $160\text{ cm}^{-1}$ , whereas the relaxation time constant  $T_1$  is only  $740\text{ fs}$ . However,  $^1\text{H}^2\text{HO}$  dissolved in  $\text{D}_2\text{O}$  and the present system of confined water molecules strongly differ in their mode density of strongly coupled intermolecular low-frequency modes. For  $^1\text{H}^2\text{HO}$  dissolved in  $\text{D}_2\text{O}$ , there exists a high density of intermolecular



**Fig. 4.** Schematic representation of the mechanism of energy transfer for water molecules confined in acetone/ $\text{CCl}_4$ . Arrows next to O—H groups indicate that the vibration is excited.

hydrogen-bond stretching and bending vibrations that have relatively high frequencies and that are strongly coupled to the O—H stretch vibration. Therefore, an energy mismatch of a few hundred wavenumbers can be compensated easily, leading to relatively fast vibrational relaxation. In the  $\text{H}_2\text{O}/\text{acetone}/\text{CCl}_4$  system, there are not that many high-frequency intermolecular modes as in bulk water, and these fewer modes will only be weakly coupled to the O—H stretch vibrations of the confined  $\text{H}_2\text{O}$  molecule. Therefore, the energy mismatch of  $\approx 160\text{ cm}^{-1}$  between the  $\nu = 1$  states of the  $\nu_b$  and the  $\nu_f$  modes cannot easily be compensated by the solvent, thus making the direct energy transfer between these states very slow. The weak coupling with low-frequency intermolecular modes also explains the relatively long vibrational lifetime  $T_1$  of  $6.3 \pm 0.5\text{ ps}$  of confined  $\text{H}_2\text{O}$  and  $^1\text{H}^2\text{HO}$  in comparison with  $^1\text{H}^2\text{HO}/\text{D}_2\text{O}$  and bulk  $\text{H}_2\text{O}$ .

Because the energy mismatch of the  $\nu_b$  and the  $\nu_f$  modes cannot be compensated, the energy transfer has to wait for the two O—H oscillators to become shifted into resonance. This aspect makes the mechanism of energy transfer of confined water essentially different from that of bulk liquid water. In bulk liquid water, there exists a high concentration of near-resonant O—H oscillators. As a result, these oscillators show a dipolar (Förster) energy-transfer process that is completely independent of the structural (hydrogen-bond) dynamics of the liquid (4). In contrast, for confined water, the energy flow within the molecule is governed completely by the rate at which hydrogen bonds are being broken and reformed, which slows down the energy transfer by a factor  $>20$  in comparison with bulk water.

## Conclusions

We studied the ultrafast dynamics of confined water molecules by using femtosecond midinfrared pump–probe spectroscopy. In

the studied system of a water molecule enclosed by acetone, the hydrogen-bond and orientational dynamics have time constants of  $1.3 \pm 0.2\text{ ps}$  and  $6 \pm 1\text{ ps}$ , respectively, which implies that these processes are much slower than in bulk liquid water. This result is surprising, because the hydrogen bonds of the confined water molecules are weaker than the hydrogen bonds in the bulk liquid. The vibrational relaxation time  $T_1$  of the confined water molecules is  $6.3 \pm 0.5\text{ ps}$ , which means that the O—H stretch vibrations of these molecules retain the excitation energy  $>20$  times as long as the O—H stretch vibrations in bulk liquid water.

The two O—H groups of the confined water molecules show energy transfer with a time constant of  $1.3 \pm 0.2\text{ ps}$ . This energy transfer involves a mechanism that is essentially different from the mechanism of resonant energy transfer in bulk liquid water. For confined water molecules, energy transfer occurs only after the two O—H oscillators are shifted into resonance. As a result, the energy transfer in confined water is governed completely by the breaking and reformation of hydrogen bonds, which slows down the energy transfer by a factor of  $>20$  in comparison with bulk water.

These results show that the dynamics of confined water molecules strongly differ from those of bulk liquid water. This finding means that water molecules participating in (bio)chemical processes cannot be viewed as small amounts of water having bulk water properties. To understand the role of these water molecules in the (bio)chemistry, a specific study of their structure and dynamics would be indispensable.

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