Ultrafast Structural Dynamics of Water Induced by Dissipation of Vibrational Energy

Satoshi Ashihara,[†,‡] Nils Huse,[†] Agathe Espagne,[†] Erik T. J. Nibbering,[†] and Thomas Elsaesser*,[†]

Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie, 12489 Berlin, Germany, and Institute of Industrial Science, University of Tokyo, Tokyo 153-8505, Japan

Received: November 17, 2006; In Final Form: December 22, 2006

In the liquid phase, water molecules form a disordered fluctuating network of intermolecular hydrogen bonds. Using both inter- and intramolecular vibrations as structural probes in ultrafast infrared spectroscopy, we demonstrate a two-stage structural response of this network to energy disposal: vibrational energy from individually excited water molecules is transferred to intermolecular modes, resulting in a sub-100 fs nuclear rearrangement that leaves the local hydrogen bonds weakened but unbroken. Subsequent energy delocalization over many molecules occurs on an ∼1 ps time scale and is connected with the breaking of hydrogen bonds, resulting in a macroscopically heated liquid.

Introduction

The fluctuating equilibrium structure of the hydrogen bond network of liquid water is characterized by multiple molecular rearrangements as well as breaking and reformation of hydrogen bonds.[1] Extensive theoretical work based on molecular dynamics simulations suggests that the fastest of such events occur in the femto- to picosecond time domain and determine fundamental processes such as proton transfer and energy transport which play a key role in (bio)chemical reactions in aqueous envionments.[2−8] Experimental probes of water structure such as neutron diffraction,[9] X-ray scattering,[10] and absorption[11,12] average over these fluctuations in time and space, making an analysis of the elementary structural dynamics difficult. In contrast, nonlinear vibrational spectroscopy with femtosecond time resolution has the potential to monitor nuclear motions and structural dynamics in real time and thus provide a detailed picture of transient structure and molecular interactions.[13−20] In particular, femtosecond excitation of intramolecular water vibrations and their subsequent ultrafast relaxation induce local structure changes which modify the transition frequencies and absorption strength of both intra- and intermolecular vibrations. Such vibrations also allow subsequent structural rearrangements due to energy dissipation and spreading to be followed.

The infrared absorption spectrum of liquid H_2O between 550 and 4000 cm^{-1} (Figure 1) displays the prominent librational L2 band with a maximum at 670 cm^{-1}, broad librational absorption extending up to 1750 cm^{-1}, the fundamental transition of the intramolecular OH bending mode with a maximum at 1650 cm^{-1}, and the OH stretching band between 2900 and 3700 cm^{-1}. A schematic of the vibrational states is shown in the inset of Figure 1, including the measured decay times (τ) of the $\nu = 1$ OH stretching and bending states.[14,16,17]
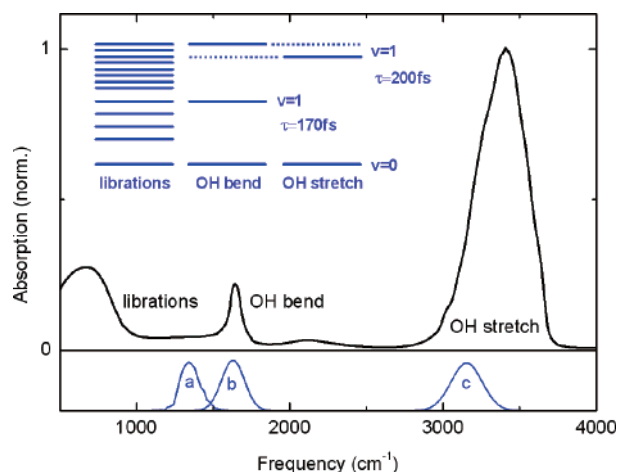

Figure 1. Steady-state vibrational spectrum of liquid H_2O at $T = 298$ K (black solid line). Lower panel: spectra of the femtosecond pump pulses exciting (a) high-frequency librations (center frequency $E_{ex} = 1350$ cm^{-1}), (b) the OH bending mode ($E_{ex} = 1650$ cm^{-1}), and (c) the OH stretching mode ($E_{ex} = 3150$ cm^{-1}). Inset: vibrational level scheme of the OH stretching, OH bending, and librational degrees of freedom including the population lifetimes (τ) of the OH stretching and bending modes. A Fermi resonance exists between the $\nu = 1$ state of the symmetric OH stretching mode and the $\nu = 2$ state of the OH bending mode.

Both the librations that give rise to the L2 band and the OH bending mode are highly sensitive probes of water structure. L2 librations are rotational motions of water molecules hindered by hydrogen bonds.[21−24] Their potential energy surface and, in particular, their force constants are determined by intermolecular geometries and interactions. As a result of fluctuating motions in the hydrogen bond network, the microscopic mode character, that is, the molecular elongations of librations contributing to the L2 absorption display fluctuations and the steady-state L2 band reflects such behavior averaged both in space and in time.[4−6] Nevertheless, a reduction of hydrogen bond strength

* To whom correspondence should be addressed. Phone: +49 30 6392 1400. Fax: +49 30 6392 1409. E-mail: elsasser@mbi-berlin.de.
† Max Born Institut für Nichtlineare Optik und Kurzzeitspektroskopie.
‡ University of Tokyo.

results in a shift of the L2 band to lower frequencies, as is evident from vibrational spectra and molecular dynamics simulations for a wide range of temperatures and pressures.[4,24] The line shape of librational absorption is determined by the collective dipole−dipole correlation function to which interferences between permanent and induced dipoles contribute significantly.[25,26]

The OH bending absorption displays an asymmetric spectral envelope with an extended wing toward small frequencies.[27] It has been decomposed into two components reflecting different hydrogen-bonded structures: (i) Water molecules forming four intermolecular hydrogen bonds give rise to a $250-300$ cm^{-1} broad component which is similar to the weak OH bending absorption of tetrahedral ice.[28] (ii) Water molecules in a distorted local environment with less than four hydrogen bonds cause a sharper (100 cm^{-1} broad) absorption feature. This component increases with an increasing fraction of broken hydrogen bonds (induced, e.g., by a temperature rise), causing a narrowing and a shift of OH bending absorption to lower frequency.

In our study, femtosecond changes of librational and OH bending absorption serve as probes of structural dynamics induced by ultrafast energy deposition. We demonstrate for the first time the two-stage and ultrafast nature of the structural response of water upon energy dissipation, namely, a sub-100 fs weakening of hydrogen bonds around excited water molecules and a slower 1 ps delocalization of energy into the liquid connected with hydrogen bond breaking.

Experimental Methods

Water layers of $3-7$ μm thickness were held between the 0.8 μm thick Si$_3$N$_4$ windows of a nanofluidic cell or prepared as a free-standing water film flowing between two stainless steel wires of 1 cm separation. To ensure film stability at a few micrometer thickness for several hours, 0.9 wt % sulfo-amber acid-bi-(2′ethylexylester) sodium salt (hereafter called soap) was added. The addition of soap had no measurable effect on the experimental results, as was checked by comparing stationary and transient spectra measured with the two types of samples.

In order to monitor the ultrafast librational response, we extended the spectral range of femtosecond vibrational spectroscopy down to 560 cm^{-1}. Transient spectra of the librational and OH bending absorption were measured in spectrally and temporally resolved pump−probe experiments with excitation of (a) high-frequency librational modes, (b) the OH bending vibration, and (c) the OH stretching vibration. The lower panel of Figure 1 gives the spectral profiles of the 100 fs pump pulses of $1-2$ μJ energy that excite a fraction of $0.5-1$% of the water molecules. In this way, local excitations surrounded by a much larger volume of unexcited liquid are generated. The resulting change of vibrational absorption is measured by independently tunable $100-170$ fs probe pulses that are spectrally dispersed after interaction with the sample and detected by a HgCdTe array detector. Measurements with parallel and perpendicular linear polarizations of pump and probe pulses give the same transient behavior.

Results and Discussion

In Figure 2, we present transient vibrational spectra of H$_2$O between 560 and 1750 cm^{-1} measured at different delay times after excitation of (b) high-frequency librational modes, (c) the OH bending vibration, and (d) the OH stretching vibration. The change of vibrational absorbance (ΔA) is plotted as a function of probe frequency for different delay times between pump and probe. For comparison, the steady-state spectrum in this
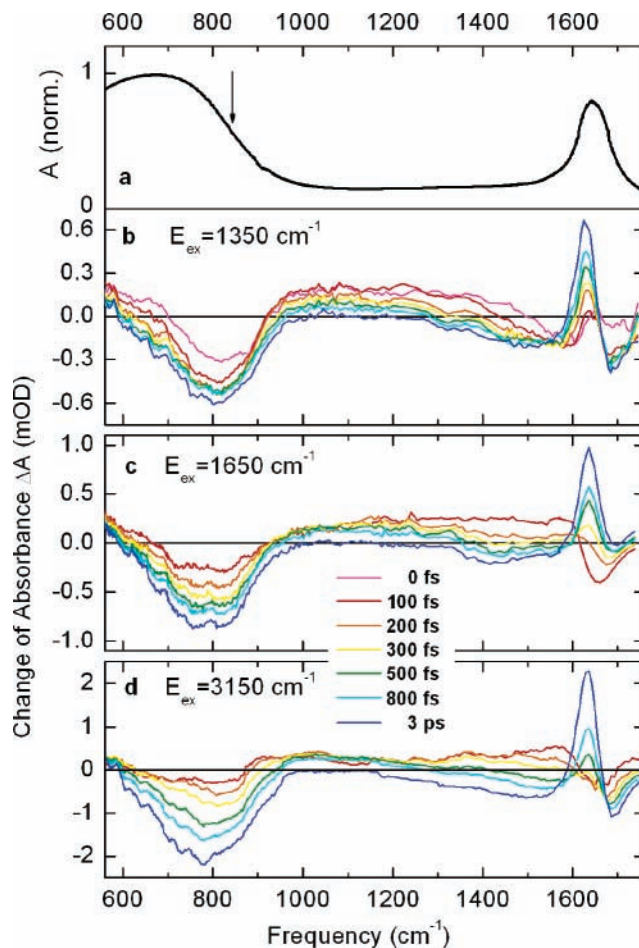

Figure 2. (a) Linear absorption spectrum of H$_2$O between 560 and 1750 cm^{-1} normalized to the peak absorbance of the librational L2 band at 670 cm^{-1}. Arrow: spectral position at which the transients in Figure 3 were measured. (b−d) Transient vibrational spectra after femtosecond excitation of (b) high-frequency librations, (c) the OH bending mode, and (d) the OH stretching mode (E_{ex}: center frequency of the respective pump pulse, cf. Figure 1). The change of absorbance, $\Delta A = -\log(T/T_0)$ (T, T_0: sample transmission with and without excitation), is plotted for delay times of 0 fs (magenta), 100 fs (red), 200 fs (orange), 300 fs (yellow), 500 fs (green), 800 fs (cyan), and 3 ps (blue). The data display a pronounced shift of the L2 band to lower frequencies and a reshaping of the OH bending absorption around 1650 cm^{-1}.

frequency range is shown in Figure 2a. Upon librational excitation (Figure 2b), a broadband enhancement of librational absorption is observed from 950 up to 1500 cm^{-1}. In the spectral range of the pump pulse (cf. spectrum a in Figure 1), such absorption change decays within the 100 fs time resolution of our experiments, showing the very fast relaxation of directly excited librational states. The decrease of absorption between 600 and 950 cm^{-1} corresponds to a pronounced shift of the librational L2 band to lower frequency and increases with time. Librational excitation also leads to a narrowing and a slight shift of the OH bending absorption from 1650 cm^{-1} to lower frequency with the OH bending oscillator remaining in its $v = 0$ ground state.

A similar shift of the librational L2 band to lower frequency occurs after OH bending and OH stretching excitation (Figure 2c,d), displaying, however, a different time evolution. For such excitation conditions, the changes of OH bending absorption observed at early delay times are governed by the population kinetics of the $v = 0$, $v = 1$, and $v = 2$ states of the OH bending oscillator.[17,18] After the decay of the $v = 2$ and $v = 1$

Letters

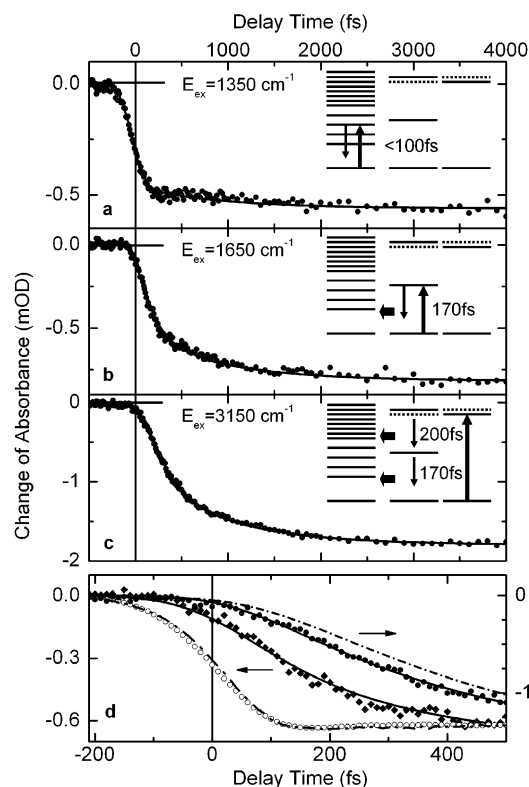*J. Phys. Chem. A, Vol. 111, No. 5, 2007* **745**

Figure 3. Change of librational absorbance at 840 cm^{-1} as a function of pump−probe delay after excitation of (a) high-frequency librations, (b) the OH bending mode, and (c) the OH stretching mode (solid circles). The kinetics of the initially excited modes determine the rise of ΔA as illustrated by the level schemes (insets) and reproduced by numerical calculations (solid lines) with the lifetimes of the OH stretching mode (200 fs), OH bending mode (170 fs), high-frequency librations (<100 fs), and a 0.9 ps energy delocalization kinetics. (d) Initial rise after OH bending excitation [data (diamonds), time-integrated cross-correlation of pump and probe pulses (open circles)] and after OH stretching excitation [data (solid circles), cross-correlation (dash−dotted line)]. Solid lines: numerical fits (Figure 3b,c). Short dash−dotted line: kinetics calculated for a decay of the OH stretching mode into two OH bend quanta followed by OH bend relaxation.

Figure 4. (a) Transient OH bending absorption after excitation of high-frequency librations by pulses centered at $E_{ex} = 1350$ cm^{-1}. The change of absorbance is plotted versus the pump−probe delay for a probe energy of $E_{pr} = 1630$ cm^{-1}, that is, in the range of the frequency shifted OH bending absorption (cf. Figure 2b). The kinetics (solid line: monoexponential rise with a 0.7 ps time constant) reflects the fast energy delocalization in the molecular network and the concomitant breaking of hydrogen bonds. (b−d) Schematic of local water configurations (b) before excitation, (c) after local rearrangement around an excited molecule, and (d) after breaking a hydrogen bond somewhere in the hydrogen bond network.

populations, the OH bending absorption shifts in frequency and its spectral envelope narrows, similar to Figure 2b.

In Figure 3, we summarize kinetic data on the transient L2 absorption measured at 840 cm^{-1} (cf. arrow in Figure 2a) after (a) librational, (b) OH bending, and (c) OH stretching excitation (solid circles). Figure 3d shows the initial rise of the signals after OH bending (diamonds) and OH stretching excitation (solid circles) together with the time-integrated cross-correlation of pump and probe pulses (open circles and dash−dotted line).[29] The transients were analyzed by a rate-equation model considering the particular excitation condition and fitting a sequence of monoexponential kinetics (solid lines) to the data. For this, the measured lifetimes of 200 fs of the OH stretching mode, 170 fs of the OH bending mode, and sub-100 fs of high-frequency librations were used.[16,17] The time-resolved absorption decrease at 840 cm^{-1} is caused by the shift of the L2 absorption tail to lower frequency with the kinetics changing markedly with the excitation conditions: Librational excitation (Figure 3a) results in a decrease of absorption within less than 100 fs, followed by a weak 0.9 ps component. For OH bending excitation, time constants of 170 fs and 0.9 ps are found (Figure 3b). Upon OH stretching excitation (Figure 3c), the absorption decrease displays kinetic components with time constants of 200 and 170 fs and identical amplitudes, followed by the 0.9 ps component. For each excitation condition, identical kinetics are found for
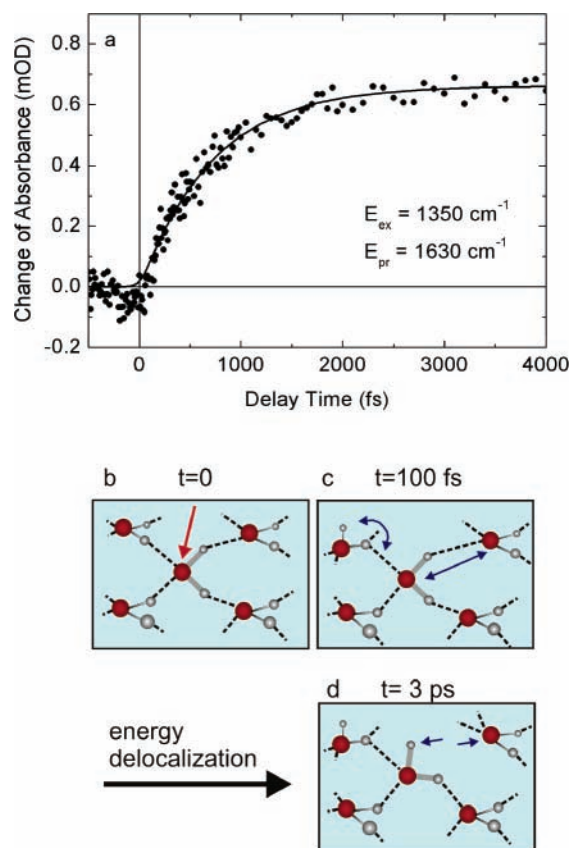
all probe frequencies between 800 and 900 cm^{-1}; that is, the high-energy tail of the L2 band shifts in frequency without significant reshaping. In all cases, the decrease of absorption remains practically constant for delay times from ∼5 up to 500 ps. Upon librational excitation, the $v = 0-1$ absorption of the OH bending oscillator at 1630 cm^{-1} (Figure 4a) rises with a time constant of ∼0.7 ps, whereas a fast rise comparable to the L2 frequency shift (Figure 3a) is absent.

We now discuss our findings in terms of vibrational and structural dynamics. Upon librational excitation (Figures 2b and 3a), one finds the sub-100 fs decay of enhanced librational absorption at high frequencies and a simultaneous shift of the L2 band to lower frequency. A decrease of librational absorption due to ground-state bleaching and stimulated emission from excited states as well as changes of the L2 envelope other than the frequency shift are absent. This demonstrates a sub-100 fs decay of any excited librational state in this frequency range and may be rationalized by considering librations a broad manifold of strongly coupled and fluctuating quantum states in which population and excess energy are redistributed.

The shift of the L2 band (and of the high-frequency librational absorption[17]) to lower frequencies corresponds to a decrease of the $v = 0-1$ transition frequencies which originates from the ultrafast energy transfer from the initially excited vibrations into degrees of freedom of the hydrogen bond network. The shift to

lower frequencies gives evidence for a weakening of intermolecular hydrogen bonds, connected with a softening of the intermolecular librational potential and a corresponding decrease of the librational force constants. The weakening of intermolecular hydrogen bonds is equivalent to increasing their length and/or bond angles (Figure 4b,c). The time scale of this sub-100 fs response is set by librational periods and occurs well within the average lifetime of hydrogen bonds of ∼1 ps, the latter being determined by a concerted rotational reorientation and change of hydrogen bond length.[8] Thus, the sub-100 fs structural response leaves the local hydrogen bond environment around the initially excited molecule(s) weakened but intact.[30]

After the molecular rearrangement within a few librational periods, there is a slower response with rise times close to the hydrogen bond lifetime, contributing to librational kinetics (Figure 3a) and dominating the shift of the OH bending absorption to lower frequency (Figure 4a). After 3−5 ps, both librational and OH bending absorption reach values that are constant for hundreds of picoseconds. The small shift to lower frequency and the spectral narrowing of the OH bending absorption are close to the behavior of thermally heated water samples.[27] Therefore, we attribute the slower kinetics to intermolecular energy transfer into the hydrogen bond network. The rise time of ∼1 ps and the characteristic changes of OH bending absorption demonstrate that formation of such a macroscopically heated ground state implies breaking of intermolecular hydrogen bonds (Figure 4d), in this way enhancing the fraction of water molecules with less than four hydrogen bonds.[31] Due to energy delocalization, the change of OH bending absorption originates from molecules anywhere in the heated hydrogen bond network rather than from the initially excited local environment.

This two-stage scenario of structural response is confirmed by our measurements with (intramolecular) OH bending and OH stretching excitation (Figures 2c,d and 3b−d). Here, the rate of energy disposal into the network is determined by the—essentially monoexponential—decay of the initially populated vibrational states.[14,16,17] Upon intramolecular OH bending excitation, one finds an initial rise of the librational frequency shift with the OH bending lifetime of 170 fs, followed by the 0.9 ps kinetics (Figure 3b,d). After excitation of the OH stretching mode, the rise of the librational frequency shift exhibits 200 and 170 fs components of identical amplitude (Figure 3c,d), due to a two-step energy transfer: first, the $v = 1$ OH stretching state of 200 fs lifetime decays to the $v = 1$ OH bending state with the energy difference transferred to the hydrogen bond network. The second step originates from the $v = 1$ to $v = 0$ relaxation of the OH bending oscillator occurring with a 170 fs time constant and providing roughly the same amount of excess energy.[32] In all cases, the librational states involved in vibrational relaxation do not cause any additional delay in the response, underlining their sub-100 fs lifetime.

In conclusion, our work using L2 librations and the intramolecular OH bending oscillator as structural probes establishes a two-stage structural response of liquid water upon local vibrational excitation, a sub-100 fs weakening of hydrogen bonds around the excited molecules, and a slower ∼1 ps

spreading of energy over many molecules connected with breaking of hydrogen bonds. Our findings emphasize the key role of librational motions for both ultrafast energy dissipation and the loss of local structural correlations. The scenario of structural response found here should be highly relevant for local energy disposal during and after (bio)chemical reactions and structural changes in aqeous environments.

References and Notes

(1) Eisenberg, D.; Kauzmann, W. *The structure and properties of water*; Oxford University Press: New York, 1969.
(2) Stillinger, F. H. *Science* **1980**, *209*, 451.
(3) Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. *Nature* **1999**, *397*, 601.
(4) Martí, J. *J. Chem. Phys.* **1999**, *110*, 6876.
(5) Ohmine, I.; Saito, S. *Acc. Chem. Res.* **1999**, *32*, 741.
(6) Cho, M.; Fleming, G. R.; Saito, S.; Ohmine, I.; Stratt, R. M. *J. Chem. Phys.* **1994**, *100*, 6672.
(7) Lawrence, C. P.; Skinner, J. L. *J. Chem. Phys.* **2003**, *118*, 264.
(8) Laage, D.; Hynes, J. T. *Science* **2006**, *311*, 832.
(9) Soper, A. K. *Chem. Phys.* **2000**, *258*, 121.
(10) Head-Gordon, T.; Hura, G. *Chem. Rev.* **2002**, *102*, 2651.
(11) Wernet, P.; et al. *Science* **2004**, *304*, 995.
(12) Smith, J. D.; Cappa, C. D.; Wilson, K. R.; Messer, B. M.; Cohen, R. C.; Saykally, R. J. *Science* **2004**, *306*, 851.
(13) Nibbering, E. T. J.; Elsaesser, T. *Chem. Rev.* **2004**, *104*, 1887.
(14) Lock, A. J.; Bakker, H. J. *J. Chem. Phys.* **2002**, *117*, 1708.
(15) Pakoulev, A.; Wang, Z.; Dlott, D. *Chem. Phys. Lett.* **2003**, *371*, 594.
(16) Cowan, M. L.; Bruner, B. D.; Huse, N.; Dwyer, J. R.; Chugh, B.; Nibbering, E. T. J.; Elsaesser, T.; Miller, R. J. D. *Nature* **2005**, *434*, 199.
(17) Ashihara, S.; Huse. N.; Espagne, A.; Nibbering, E. T. J.; Elsaesser, T. *Chem. Phys. Lett.* **2006**, *424*, 66.
(18) Larsen, O. F. A.; Woutersen, S. *J. Chem. Phys.* **2004**, *121*, 12143.
(19) Rey, R.; Møller, K. B.; Hynes, J. T. *Chem. Rev.* **2004**, *104*, 1915.
(20) Lawrence, C. P.; Skinner, J. L. *J. Chem. Phys.* **2003**, *119*, 1623.
(21) Walrafen, G. E. *J. Chem. Phys.* **1967**, *47*, 114.
(22) Zelsmann, H. R. *J. Mol. Struct.* **1995**, *350*, 95.
(23) Castner, E. W., Jr.; Chang, Y. J.; Chu, Y. C.; Walrafen, G. E. *J. Chem. Phys.* **1995**, *102*, 653.
(24) Tassaing, T.; Danten, Y.; Besnard, M. *J. Mol. Liq.* **2002**, *101*, 149.
(25) Guillot, B. *J. Chem. Phys.* **1991**, *95*, 1543.
(26) Sharma, M.; Resta, R.; Car, R. *Phys. Rev. Lett.* **2005**, *95*, 187401.
(27) Walrafen, G. E.; Hokmabadi, M. S.; Yang, W. H. *J. Phys. Chem.* **1988**, *92*, 2433.
(28) Devlin, J. P.; Sadlej, J.; Buch, V. *J. Phys. Chem. A* **2001**, *105*, 974.
(29) The width of the cross-correlation measured with a thin semiconductor layer is mainly determined by the 840 cm^{-1} probe pulses and the same for the three excitation conditions.
(30) Changes of OH bending absorption upon weakening of hydrogen bonds are minor (cf. Bertie, J. E.; Ahmed, M. K.; Eysel, H. H. *J. Phys. Chem.* **1989**, *93*, 2210). Thus, sub-100 fs kinetics are absent in the ultrafast OH bending response (Figure 4a).
(31) The final temperature rise is proportional to the pump energy deposited in the sample and reaches values of 1−5 K for our excitation conditions. The absence of local overheating is evident from the monotonous increase of the frequency shifts.
(32) The sequential energy transfer to librations rules out other schemes proposed for OH stretching relaxation, in particular the generation of two OH bending quanta on different molecules (Lindner, J.; et al. *Chem. Phys. Lett.* **2006**, *421*, 329). An L2 kinetics calculated for the latter case (Figure 3d) is in clear disagreement with the data.