Ultrafast structural dynamics of hydrogen bonds in the liquid phase

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Résumé **Dynamique structurale ultra-rapide des liaisons hydrogène en phase liquide**

La liaison hydrogène joue un rôle fondamental dans la structure et les propriétés chimiques des liquides tels que l'eau, ainsi que dans des structures macromoléculaires comme les protéines. À l'échelle moléculaire, les mouvements des groupes liés par des liaisons hydrogène, la dissipation d'énergie en leur sein, la délocalisation ainsi que les fluctuations de leur structure ont lieu dans des temps inférieurs à une picoseconde. Au cours des dernières années, la spectroscopie vibrationnelle subpicoseconde est devenue l'une des méthodes les plus directes pour sonder la dynamique des liaisons hydrogène et des structures transitoires. Cet article fournit une introduction à ce nouveau domaine passionnant et décrit les résultats récents sur deux types de structures liées par liaison hydrogène : les dimères d'acide carboxylique dans un liquide aprotique et le réseau désordonné et fluctuant des liaisons hydrogène dans l'eau liquide.

Mots-clés **Dynamique des liaisons hydrogène, spectroscopie vibrationnelle femtoseconde, dimères d'acide carboxylique, eau liquide.**

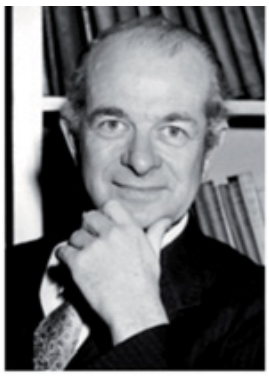
Abstract Hydrogen bonding plays a fundamental role for the structure and chemical properties of liquids such as water and macromolecular structures such as proteins. On a molecular level, motions of hydrogen-bonded groups, energy dissipation and delocalization as well as fluctuations of hydrogen bonded structure occur in the time domain below 1 picosecond. In recent years, vibrational spectroscopy in this time domain has become one of the most direct probes of hydrogen bond dynamics and transient structure. This article provides an introduction to this exciting new field and describes recent results on two different types of hydrogen-bonded structure: carboxylic acid dimers in an aprotic liquid environment and the disordered fluctuating hydrogen bond network of liquid water.

Keywords **Hydrogen bond dynamics, femtosecond vibrational spectroscopy, carboxylic acid dimers, liquid water.**

Hydrogen bonds: a key element of molecular structure and function

Hydrogen bonding represents a fundamental local interaction determining the structural, physical and chemical properties of molecular systems. This type of bond has been discovered around 1920 [1-2] and the term "hydrogen bond" was coined by the early Linus Pauling (*figure 1*) [3]. A hydrogen bond X-H···Y is mediated through the attractive interaction between a hydrogen donor group X-H (X = O, N, F) and a neighbouring electronegative acceptor atom Y (Y = O, N, F, Cl). The binding energy of 4 to 40 kJ/mol is only a fraction of that of covalent bonds and depends on the particular molecular geometries and interaction strengths. Relevant are the attractive Coulomb interaction between the hydrogen and the acceptor atom, van der Waals and dispersion forces and – in strong hydrogen bonds – covalent contributions [4]. The binding energy is high enough to define molecular structure such as intramolecular hydrogen bonds, hydrogen bonded dimers and biological macromolecules like DNA. The limited bond strength, on the other hand, allows for structural changes by a "making and breaking" of hydrogen bonds, leading for instance to structural fluctuations in extended disordered hydrogen bond networks such as liquid water and alcohols.

Molecular vibrations represent one of the most direct probes of hydrogen-bonded structures and their dynamics. Steady-state infrared and Raman spectroscopy is a major tool to grasp the occurrence of new vibrational bands and characteristic changes of frequency position and line shape



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THE NATURE OF THE CHEMICAL BOND. APPLICATION OF RESULTS OBTAINED FROM THE QUANTUM MECHANICS AND FROM A THEORY OF PARAMAGNETIC SUSCEPTIBILITY TO THE STRUCTURE OF MOLECULES

BY LINUS PAULING

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Figure 1 - Linus Pauling and the title of ref. [3] in which he introduced the term "hydrogen bond".

of existing bands upon hydrogen bond formation [4]. Time-resolved vibrational spectroscopy allows for inducing and probing vibrational excitations on time scales well below 1 picosecond [1 ps = 10^{-12} s = 1 millionth of a millionth of a second, 1 ps = 1 000 femtoseconds (fs)]. In this way, the real-time dynamics and the underlying molecular interactions are revealed [5]. Changes of steady-state vibrational absorption upon hydrogen bonding are illustrated in *figure 2* where the O-H stretching absorption bands of (a) the free O-H group of phenol dissolved in CCl_4, of (b) water and of (c) the cyclic dimer of acetic acid are presented. With increasing hydrogen bond strength, the spectral position is (red-)shifted to lower frequencies and the absorption bands are broadened with a strongly altered spectral envelope. The red-shift is due to a reduction of the vibrational force constant by the attractive interaction with the acceptor atom Y. The broadening and occurrence of substructure in the spectra reflect – to a large extent – hydrogen bond dynamics in a time-integrated way. They are caused by a combination of mechanisms including spectral diffusion and/or vibrational dephasing, anharmonic couplings to modes at lower frequency and others. A separation of such mechanisms and an understanding of the underlying microscopic dynamics require highly sophisticated techniques of nonlinear spectroscopy, some of which are discussed in the following.

Motions of the hydrogen-bonded groups on atomic length and time scales determine the dynamics of hydrogen bonds and, thus, the structural dynamics of hydrogen-bonded structure. There are characteristic molecular vibrations setting the time scales:

- The X-H stretching vibration – in a classical picture modulating the X-H bond length (*figure 3a*, left panel) – displays a very short oscillation period of the order of 0.01 ps = 10 fs, corresponding to oscillation frequencies in the range of 3 000 cm^{-1} = 9 x 10^{13} s^{-1} = 90 THz.

- Hydrogen bond vibrations change the hydrogen bond geometry directly, e.g., by affecting the X····Y distance (*figure 3a*, middle panel) and/or the spatial arrangement of the hydrogen bonded groups. They occur on a substantially slower time scale of up to several hundreds of femtoseconds, corresponding to frequencies between 100 and 300 cm^{-1}. Such low frequencies originate from the much smaller force constant of the X····Y oscillator which is determined by the hydrogen bond strength, and the much larger mass of the heavy atoms X and Y compared to the light hydrogen. In most cases, the X-H stretching mode and hydrogen bond modes are coupled *via* anharmonic interactions, i.e., excitation of the stretching mode results in elongations of low-frequency modes.

- In intermolecular hydrogen bonds, there are additional librational modes which represent molecular rotations hindered by hydrogen bonding and translational motions of low frequency. Librations and translations play a key role for the breaking and reformation of hydrogen bonds, processes that occur on a subpicosecond to picosecond time scale and are induced by structural fluctuations.

This article is devoted to recent progress in understanding structural dynamics of hydrogen-bonded systems. Such progress is mainly based on novel methods of time-resolved vibrational spectroscopy in the femtosecond time domain and in-depth theoretical calculations. After a brief description of the experimental techniques, ultrafast hydrogen bond dynamics are discussed for two prototype systems: the cyclic acetic acid dimer representing a comparably small time-independent hydrogen-bonded structure, and liquid water, an extended hydrogen-bonded network undergoing structural fluctuations on a multitude of time scales.

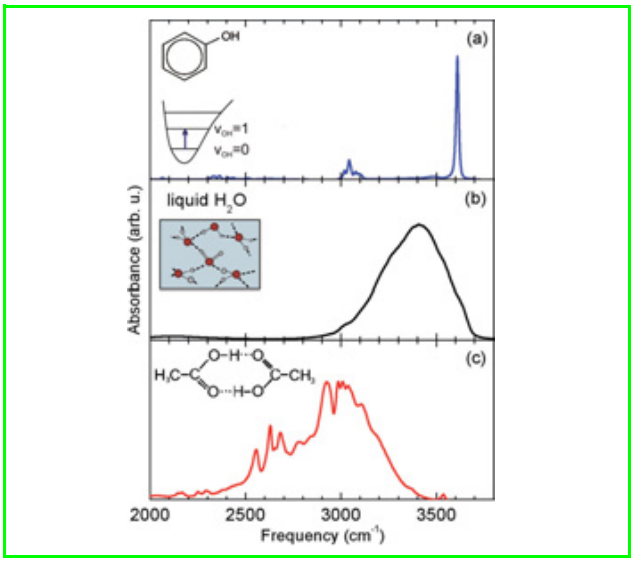

Figure 2 - Vibrational OH stretching absorption bands of (a) phenol monomers in CCl_4 with a free OH group (inset: molecular structure and vibrational potential with quantum states ν_{OH} = 0 and 1), (b) liquid water (inset: schematic of hydrogen bond network), and (c) cyclic dimers of acetic acid (inset: dimer structure).
With increasing hydrogen bond strength, the absorption maximum shifts to smaller energies and the absorption bands broaden.

Probing hydrogen bond dynamics in real-time: femtosecond vibrational spectroscopy

Femtosecond vibrational spectroscopy of hydrogen bonds allows for the observation of structural dynamics in real-time and for the measurement of couplings between different oscillators or between oscillators and their molecular environment [5]. Femtosecond infrared spectroscopy is based on the resonant interaction of femtosecond light pulses with vibrational dipole transitions. Infrared pulses of ~ 100 fs duration are available in the wavelength range from 2.5 to 20 µm (frequency range 4 000 to 500 cm^{-1}), covering a major part of the vibrational spectrum of hydrogen bonds. Though direct infrared excitation of hydrogen-bond vibrations at even lower frequency has not been possible so far, anharmonic coupling of such modes to high-frequency vibrations allows for studying their transient behavior as well.

The results presented in the following are based on the pump-probe technique and on two-dimensional vibrational spectroscopy, both exploiting the third order nonlinear response of the molecular system. In general, femtosecond resonant excitation of a transition between two quantum states of an oscillator (*figure 3a*) generates both a coherent polarization, i.e., a dipole-mediated superposition of the quantum-mechanical wavefunctions of the two states, and a population change by promoting molecules from the lower to the upper state. In a pump-probe experiment, such excitation is probed by a second pulse monitoring changes of vibrational absorption as a function of pump-probe delay. The simplest case is illustrated in *figure 3a* where the pump pulse (blue arrow, left panel) excites the ν_{OH} = 0 to 1 transition of an OH stretching oscillator and transient vibrational

populations are probed *via* changes of the $\nu_{OH} = 0$ to 1 and $\nu_{OH} = 1$ to 2 absorption (red arrows). The reduced population of the $\nu_{OH} = 0$ state and the excess population of the $\nu_{OH} = 1$ state lead to a change of absorption $\Delta A < 0$ on the $\nu_{OH} = 0$ to 1 transition due to bleaching and stimulated emission (blue profile in the right panel of *figure 3a*). Simultaneously, the $\nu_{OH} = 1$ excess population results in an enhanced absorption $\Delta A > 0$ on the $\nu_{OH} = 1$ to 2 transition (red profile) which occurs at lower frequency because of the anharmonicity of the vibrational potential. Measuring ΔA as a function of pump-probe delay gives insight into the population kinetics and the related redistribution of energy.

In two-dimensional (2D) spectroscopy, a sequence of 3 femtosecond infrared pulses interacts with the molecular sample and induces a coherent vibrational response which is read-out by generating a so-called photon-echo signal [6-7]. This signal is detected in a phase-resolved way. From the photon echo signal, one derives 2D spectra in which the Fourier transform of the third order polarization of the sample is plotted as a function of two frequencies, the excitation frequency ν_1 and the detection frequency ν_3. The real part of this quantity gives the absorptive, the imaginary part the dispersive response of the sample.

In *figure 3b*, the case of spectral diffusion is illustrated schematically [8]. In a disordered hydrogen-bond network like water, the $\nu_{OH} = 0$ to 1 transition frequency of the OH stretching mode depends on the local environment, resulting in a (inhomogeneous) frequency distribution within the OH stretching absorption band (left panel). As the structure of hydrogen bond network and – thus – the local molecular environments fluctuate, the frequency position of a particular oscillator changes with time, undergoing statistical frequency shifts within the spectral envelope, i.e., spectral diffusion. In the steady-state vibrational absorption band, spectral diffusion shows up as a broadening giving no information on the underlying time scale of structural dynamics. In contrast, 2D absorption spectra (right panel of *figure 3b*) reveal such phenomena; 2D spectra for T = 0 when the second and third pulse interact simultaneously with the sample, reflect the distribution of transition frequencies: for each excitation frequency ν_1, there is a signal at the corresponding detection frequency ν_3, resulting in a spectrum elongated along the diagonal $\nu_1 = \nu_3$ of the 2D plot. During a finite time interval T between the second and the third "read-out" pulse, the molecular system undergoes spectral diffusion destroying the correlation of excitation and detection frequencies. As a result, the 2D spectrum measured for T > 0 shows an essentially round shape reflecting the randomization of transition frequencies. In other words, the system has lost its frequency and underlying structural "memory".

Two-dimensional spectroscopy also allows for a measurement of couplings between different vibrational transitions [6-7] as illustrated in *figure 3c* with the help of the OH stretching band of cyclic acetic acid dimers [9]. The steady-state OH stretching absorption (left panel) consists of a large number of lines, resulting in the highly complex spectral envelope. In the 2D absorption spectra, couplings between the different components show up directly (right panel): whenever a particular transition is excited (blue or red profile), it gives rise to a signal at the same frequency, i.e., on the diagonal of the 2D spectrum (blue and red symbols), and – more important – to an off-diagonal peak at the frequency position of the other coupled transition (black symbols). In this way, complex coupling schemes are readily deciphered with the strength of the off-diagonal peaks reflecting the strength of the couplings. In fact, the OH stretching absorption of cyclic acetic acid dimers has been analyzed in a quantitative way by combining 2D spectroscopy with a thorough theoretical analysis [9-10].

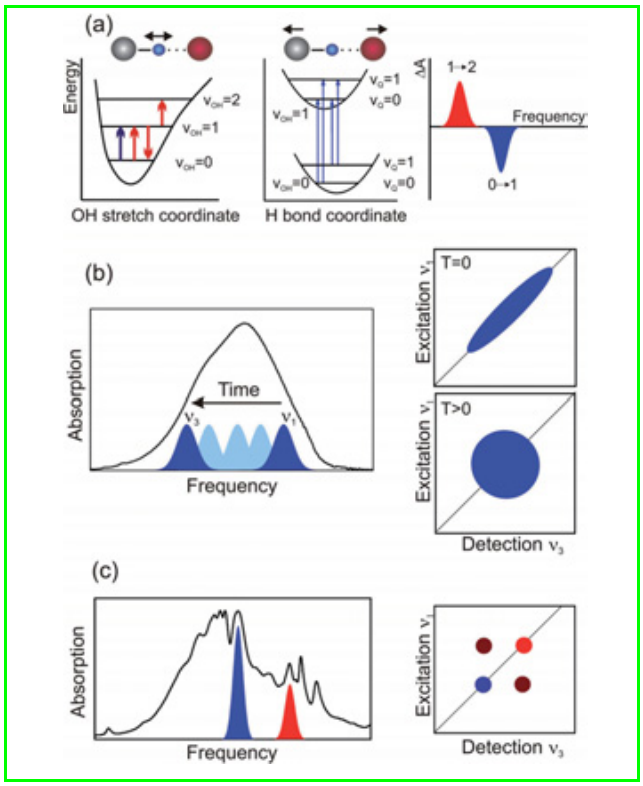

Figure 3 - (a) Vibrational potential energy diagrams of a hydrogen bond consisting of an O-H donor group (grey/blue spheres) and an acceptor atom (red sphere).
Left panel: schematic potential of the OH stretching oscillator with the ν_{OH} = 0, 1 and 2 quantum states. In a femtosecond pump probe experiment, a pump pulse (blue arrow) excites molecules from the $\nu_{OH} = 0$ to the $\nu_{OH} = 1$ state. The resulting change of infrared absorption is measured with a probe pulse interacting either the $\nu_{OH} = 0 \rightarrow 1$ or the $\nu_{OH} = 1 \rightarrow 2$ transition (red arrows). Middle panel: potentials of the hydrogen bond mode with quantum states $\nu_Q = 0.1$. Anharmonic coupling to the OH stretching mode results in different potentials of this mode for the $\nu_{OH} = 0$ and $\nu_{OH} = 1$ states of the stretching oscillator. The OH stretching transition breaks up in a number of transition lines (blue vertical arrows). Right panel: Schematic absorption changes ΔA observed in a pump-probe experiment: decrease of absorption on the $\nu_{OH} = 0 \rightarrow 1$ transition (blue line) and an increase of absorption on the red-shifted $\nu_{OH} = 1 \rightarrow 2$ transition (red line).
(b) Schematic of spectral diffusion in water.
Left panel: the overall OH stretching absorption band of water (black solid line) consists of a distribution of absorption lines from water molecules in different environments (blue profiles). Structural fluctuations in the liquid lead to an ultrafast shift of the transition of a particular molecule from its initial frequency ν_1 to a new frequency ν_3. This process is called spectral diffusion and can be made visible in two-dimensional vibrational spectra (right panel, explanation in the text).
(c) Anharmonically coupled transitions in the OH stretching absorption (solid line) of acetic acid dimers.
The absorption band consists of a number of transitions coupled *via* so-called Fermi resonances. The couplings are derived from the strength of the off-diagonal peaks in the two-dimensional spectrum (black circles in the right panel, explanation in the text).

Hydrogen bonds in swinging motion: the acetic acid dimer

Cyclic dimers of carboxylic acids are held together by two intermolecular O-H····O hydrogen bonds and represent a prototype structural motif present in biomolecules. The planar geometry of cyclic acetic acid dimer is shown in the inset of *figure 2c*. In the pump-probe experiments, the O-H stret-

ching vibration of dimers dissolved in CCl_4 is excited by a 100 fs infrared pulse and the resulting change of vibrational absorption is measured by a delayed probe pulse [11-13]. In *figure 4a*, transient vibrational spectra (blue lines) are shown together with the steady-state absorption band (red line). The blue lines represent the change of vibrational absorption plotted as a function of probe frequency for different pump-probe delays. The pump-induced transient population of the $v_{OH} = 1$ state gives rise to an enhanced absorption $\Delta A > 0$ on the $v_{OH} = 1$ to 2 transition around 2 500 cm^{-1}. The strong absorption decrease ($\Delta A < 0$) at higher frequencies originates from the $v_{OH} = 0$ to 1 transition which splits into several lines due to anharmonic coupling to other vibrational states in the same energy range (so-called Fermi resonances). With increasing pump-probe delay, the $v_{OH} = 1$ to 2 absorption decays with a time constant of 200 fs, the lifetime of the $v_{OH} = 1$ state (not shown). Concomitantly, the amplitude of the absorption decrease becomes smaller with the peak positions remaining unchanged. This demonstrates the absence of spectral diffusion, i.e., the hydrogen bonded dimer structure remains unchanged. On the same time scale, enhanced absorption $\Delta A > 0$ builds up at frequencies above 3 150 cm^{-1}. This transient band is due to dimers in which the $v_{OH} = 1$ state has decayed, i.e., the OH stretching oscillator is in the $v_{OH} = 0$ state but its energy has been transferred to other intra-dimer vibrations, in this way creating a vibrationally "hot" ground state. In the hot dimers, the hydrogen bonds are weakened and thus, the OH stretching absorption occurs at higher frequencies. The hot dimers cool down to the temperature of the surrounding liquid within several tens of picoseconds, resulting in a complete decay of all absorption changes.

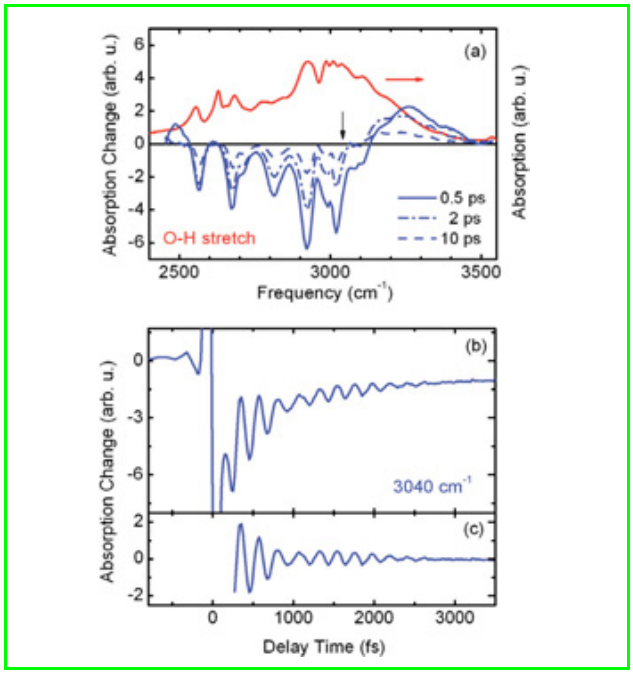

Figure 4 - (a) Transient OH stretching absorption spectra of acetic acid dimers as measured in femtosecond pump-probe experiments. The blue lines represent the absorption change in the measured 0.5, 2 and 10 ps after excitation. Red line: steady-state OH stretching absorption. (b) Time evolution of the absorption change at 3 040 cm^{-1}. The pronounced oscillatory component is due to coherent low-frequency vibrations of the dimer. (c) Oscillatory component after subtraction of other contributions to the absorption change.

In *figure 4b*, the absorption change at a frequency of 3 040 cm^{-1} (arrow in *figure 4a*) is shown as a function of pump-probe delay. The decrease of vibrational absorption displays a fast partial recovery within the first 3 ps originating from population relaxation, followed by the slower complete recovery due to vibrational cooling. The fast recovery is superimposed by strong oscillations which are plotted separately in *figure 4c*. The oscillatory absorption changes display a period of approximately 200 fs that is much longer than the OH stretching period of 10 fs. The frequency spectrum of the oscillations as determined by Fourier analysis is shown in *figure 5a* and consists of two major frequency components at 145 and 170 cm^{-1}.

The oscillations are due to low-frequency vibrations of the dimer. Such vibrations are – anharmonically – coupled to the much faster O-H stretching mode. As illustrated in the middle panel of *figure 3a*, this coupling can be visualized as a potential of the low-frequency oscillator that depends on the excitation and thus, quantum number v_{OH} of the OH stretching mode [14]. Upon excitation of the OH stretching mode from its $v_{OH} = 0$ to $v_{OH} = 1$ state (cf. left panel), a simultaneous change of the quantum number v_Q can be induced, resulting in several transition lines, a so-called progression (blue vertical arrows in the middle panel). The femtosecond pump pulse excites several progression lines simultaneously, in this way creating a superposition of low-frequency levels with different v_Q in the $v_{OH} = 1$ state. Simultaneously, a Raman-type excitation process creates a similar superposition in the $v_{OH} = 0$ state [11-13]. Such superpositions are quantum mechanical wavepackets and represent non-stationary excitations oscillating in the respective potential with their intrinsic frequency. As such motions are coupled to the OH stretching mode, the OH stretching absorption is periodically modulated, resulting in the oscillatory absorption changes shown in *figure 4b-c*. A theoretical analysis of the vibrational spectra and anharmonic couplings of

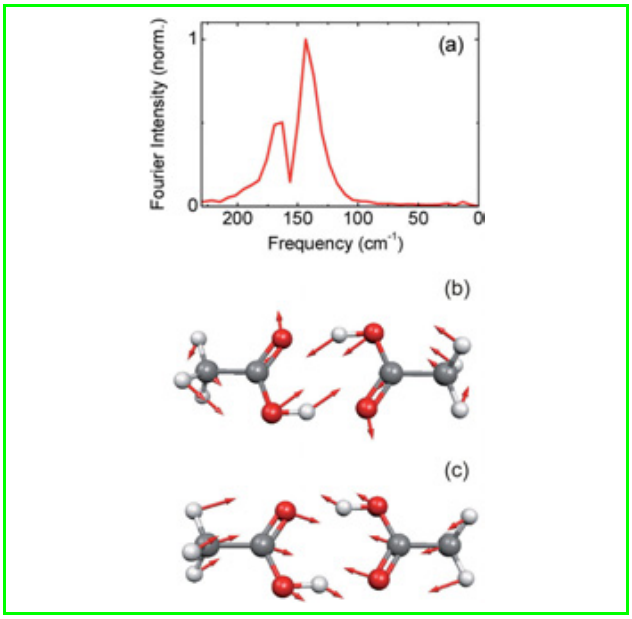

Figure 5 - (a) Frequency spectrum of the oscillations shown in *figure 4*.
The two frequency components at 145 and 170 cm^{-1} represent the in-plane bending and in-plane stretching modes of the dimer, both modulating the hydrogen bond geometry. The atomic elongations connected with such motions are shown for (b) the in-plane bending and (c) the in-plane stretching mode.

acetic acid dimers shows that the underlying low-frequency modes are the in-plane dimer bending and stretching modes with the microscopic elongations shown in *figure 5b-c* [12].

The coupling of the high-frequency OH stretching vibration and the low-frequency hydrogen bond modes in the dimer allows for inducing and observing in real-time changes of the dimer geometry. It is interesting to note that such motions persist for several picoseconds due to the underdamped character of the low-frequency modes even in the liquid phase. Exciting the OH stretching oscillator with a sequence of pulses instead of a single pulse generates tailored superpositions of low-frequency states and, in this way, influences coherent hydrogen-bond motions. This may pave the way for inducing and steering chemical processes such as hydrogen transfer in a controlled way.

Ultrafast structural dynamics and memory loss of water

Water forms an extended fluctuating network of intermolecular hydrogen bonds in which molecules undergo multiple rearrangements and hydrogen bonds are broken and reformed. Such events occur in the femto- to picosecond time domain. Water structure has been probed experimentally by neutron diffraction, x-ray scattering and x-ray absorption, all averaging over such fluctutations in time and space and thus providing limited insight into the elementary structural dynamics. In contrast, femtosecond infrared spectroscopy allows for resolving molecular motions and transient structure in time. In the following, the first femtosecond experiments on structural dynamics in neat H_2O are discussed [8, 15-16].

Spectral diffusion of OH stretching excitations, the shift of vibrational transition frequencies due to structural fluctuations of the hydrogen bond network, is a direct probe of structural dynamics. It can be made visible by 2D infrared spectroscopy as explained in *figure 3b*. In *figure 6*, 2D spectra of the OH stretching mode are shown for two different delays T between the second and the third pulse interacting with the sample, a 500 nm thick film of H_2O [8]. The yellow-red signal is due to the $\nu_{OH} = 0$ to 1 transition of the OH stretching oscillator whereas the blue feature in the T = 0 fs spectrum originates from the $\nu = 1$ to 2 transition. For T = 0 fs, the $\nu_{OH} = 0$ to 1 spectrum is stretched along the diagonal $\nu_1 = \nu_3$ (straight solid line) reflecting the initial inhomogeneous broadening due to a distribution of molecular sites in the hydrogen bond network. At T = 50 fs, spectral diffusion has completely destroyed this correlation between excitation and detection frequencies, resulting in a round shape of the 2D spectrum. In other words, the molecular configuration around an excited OH stretching oscillator changes within 50 fs to an extent that a major part of correlation between the initial and the final configuration is lost. This behavior gives evidence of an ultrafast loss of structural memory in the liquid.

Such loss of structural memory requires intermolecular motions on a 50 fs time scale. The hydrogen bond mode of water changing the O···O distance between neighboring water molecules has a vibrational period of 170 fs which is too long to play a dominant role in this process. Instead, high-frequency hindered rotations of water molecules, so-called librations, change the relative orientation of neighboring water molecules, in this way inducing spectral diffusion. Liquid water displays a broad librational spectrum extending up to frequencies of 1 700 cm^{-1} (*figure 7a*). The observed 50 fs time scale suggests that librations with a frequency

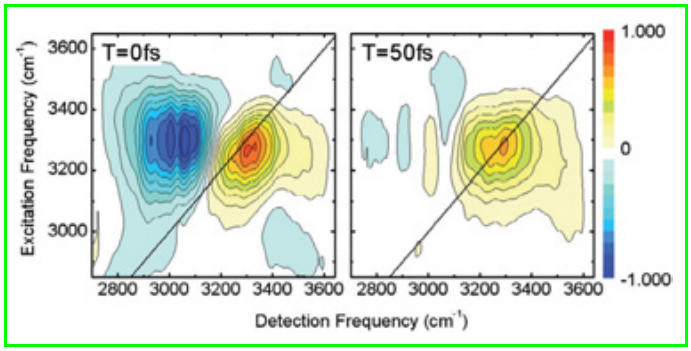

Figure 6 - Two-dimensional OH stretching infrared spectra of water taken during excitation (T = 0) and at a delay of T = 50 fs.
At T = 0, the $\nu_{OH} = 0 \rightarrow 1$ spectrum (yellow to red contour) is elongated along the diagonal, giving evidence of the initial distribution of transition frequencies. After T = 50 fs, the spectrum has a circular shape due to ultrafast spectral diffusion. The blue feature in the T = 0 spectra is due to the $\nu_{OH} = 1 \rightarrow 2$ transition of the OH stretching oscillator.

around 1 000 cm^{-1} cause the fastest structural rearrangements that are observed in the 2D spectra.

Resonant transfer of OH stretching excitations between neighboring water molecules represents a second mechanism contributing to spectral diffusion. In a neighborhood of water molecules with slightly different OH stretching frequencies, coupling of their transition dipoles leads to a hopping of the excitation from one molecule to the other, in this way slightly changing the transition frequency. In neat H_2O, typical excitation transfer times are between 50 and 100 fs [8].

So far, we have concentrated on using OH stretching excitations as probes of the ultrafast structural dynamics of water and have found that the fastest structural rearrangements are connected with intermolecular motions. Such motions play a key role also for the decay of vibrational excitations on individual water molecules and the dissipation of energy into the bulk of the liquid [15-17]. The $\nu_{OH} = 1$ state of the OH stretching vibration of a water molecule has a lifetime of 200 fs. It decays *via* the OH bending mode and, eventually, the excess energy ends up in intermolecular modes of the network. This process is connected with structural changes that have been characterized in recent femtosecond pump-probe experiments [17].

Figure 7a shows the steady-state absorption of water between 550 and 1 750 cm^{-1} displaying a strong librational band called L2 with maximum at 670 cm^{-1}, a weak absorption of high-frequency librations extending up to approximately 1 700 cm^{-1} and the OH bending absorption with maximum at 1 650 cm^{-1}. To study the structural response induced by the dissipation of excess energy, transient infrared spectra throughout this range were measured after femtosecond excitation of high-frequency librations around 1 350 cm^{-1}. Such spectra are presented in *figure 7b*. They exhibit a strong decrease of absorption below 1 000 cm^{-1} corresponding to a red-shift of the L2 band, a short-lived enhancement of librational absorption at higher frequencies and a red-shift of the OH bending absorption.

In *figure 7c-d*, the time evolution of the librational red-shift (probe frequency 833 cm^{-1}) and of the red-shift of bending absorption (1 630 cm^{-1}) are shown. At 833 cm^{-1}, the absorption decreases within the time resolution of the experiment of 100 fs, followed by a weak 1 ps component. The absorption decrease, i.e., red-shift of the L2 band reached after 4 ps persists for hundreds of picoseconds (not shown). The absorption increase found at 1 630 cm^{-1} (*figure 7d*) is

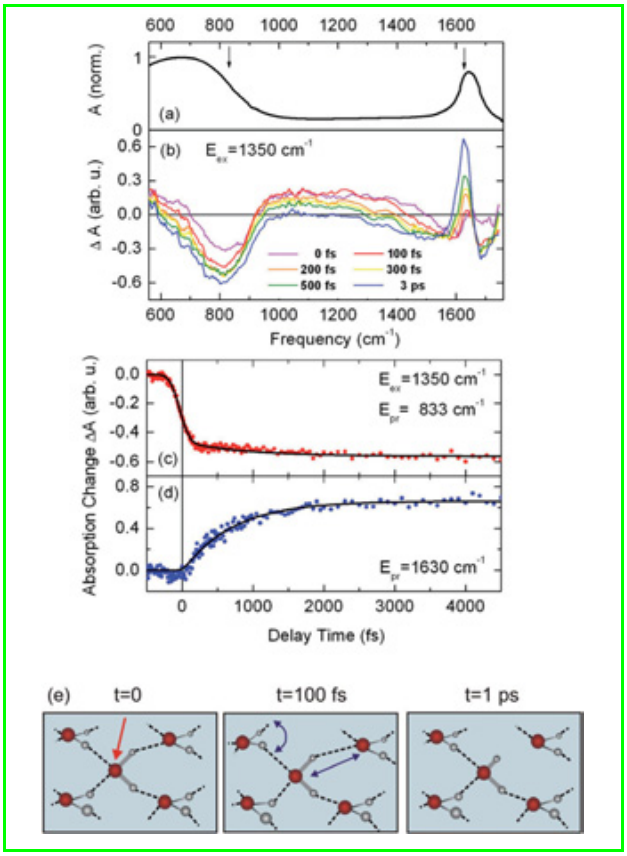

Figure 7 - (a) Infrared absorption of liquid water consisting of the librational L2 band with maximum at 670 cm^{-1}, a background absorption of high-frequency librations extending up to ~ 1 700 cm^{-1} and the OH bending absorption with maximum at 1 650 cm^{-1}. (b) Transient vibrational spectra after excitation of high-frequency librations at E_{ex} = 1 350 cm^{-1}. The change of absorption ΔA is plotted versus frequency for different time delays after excitation. (c-d) Time evolution of the absorption changes at (c) E_{pr} = 833 cm^{-1} in the L2 band and (d) E_{pr} = 1 630 cm^{-1} on the OH bending absorption. The bottom panel illustrates structural changes of the hydrogen bond network induced by vibrational energy dissipation.

due to the red-shift of the OH bending absorption and rises with a time constant of approximately 1 ps, much slower than the initial rise of the librational response in *figure 7c*.

The data of *figure 7* reveal the structural changes induced by the decay of the initial librational excitation within 100 fs. The red-shift of the L2 band is equivalent to a decrease of librational frequency which originates from a weakening of the local hydrogen bonds by an increase of the O···O distance of neighboring water molecules and/or a change of the angular configuration of the molecules (middle panel in *figure 7e*). This process occurring within the first 100 fs after excitation is driven by the local disposal of excess energy and leaves the local hydrogen bonds weakened but unbroken. On a slower time scale, excess energy is spread throughout the molecular network, resulting in a rise of the average molecular temperature by a few degrees Kelvin. The temperature rise is connected with breaking a small fraction of hydrogen bonds somewhere in the network, a process resulting in the slower 1 ps change of librational absorption and the much more pronounced red-shift of the OH bending absorption occurring with the same slow kinetics. Water molecules with a red-shifted OH bending absorption are located at sites with broken hydrogen bonds (right panel, *figure 7e*), as has been concluded from extensive steady-state spectroscopy on heated water samples [18]. Moreover, recent molecular dynamics calculations of hydrogen bonds breaking in water suggest an average lifetime of hydrogen bonds of approximately 1 ps, in very good agreement with the kinetics discussed here. Eventually, cooling of the liquid back to the initial temperature, a microsecond process, increases the number of hydrogen bond again and the changes of vibrational absorption disappear.

In conclusion, librational motions in water play a central role for the loss of structural memory on a 50 fs time scale and for the dissipation and delocalization of excess energy in the hydrogen bond network. The latter processes result in a two-stage structural response with a local weakening of hydrogen bonds on a 100 fs time scale and a 1 ps breaking of hydrogen bonds due to the subsequent increase of temperature in the bulk of the liquid. Such results underline the potential of ultrafast vibrational spectroscopy for unraveling the microscopic couplings and structural dynamics of hydrogen bonds in a wide variety of systems, most recently also including biologically relevant macromolecular structures.

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