Water jump reorientation and ultrafast vibrational spectroscopy

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ABSTRACT

The reorganization of water's hydrogen-bond (HB) network by breaking and making HBs lies at the heart of many of the pure liquid's special features and many aqueous media phenomena, including chemical reactions, ion transport and protein activity. An essential role in this reorganization is played by water molecule reorientation, long described by very small angular displacement Debye rotational diffusion. A markedly contrasting picture has been recently proposed, based on simulation and analytic modeling: a sudden, large amplitude jump mechanism, in which the reorienting water molecule rapidly exchanges HB partners in an activated process which has all the hallmarks of a chemical reaction. In this contribution, we offer a brief review of the jump mechanism together with a discussion of its application to, and probing by, modern ultrafast infrared spectroscopy experiments. Special emphasis is given to the direct characterization of the jumps via pioneering two-dimensional infrared spectroscopic measurements.

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1. Introduction

Liquid water's numerous remarkable features include the great lability of its hydrogen-bond (HB) network. This network constantly rearranges by breaking and forming HBs on a picosecond timescale [1–5]. Further, water's reorganization dynamics plays a key role in a host of fundamental processes, such as S_N2 [6] and proton transfer reactions [7,8], proton transport [9], and protein activity [10]. The HB network rearrangements involve the reorientation of individual water molecules, which has been traditionally viewed as very small step angular Brownian motion of the molecule [10].

In stark contrast with this Debye rotational diffusion picture, two of us recently proposed a very different molecular mechanism, in which water reorientation mainly proceeds through sudden, large amplitude angular jumps [4,11]. In this new picture, which has a robustness vis-à-vis changes in the water force field [11], large jumps occur when a water hydroxyl (OH) group trades HB acceptors, providing the elementary mechanism of HB network rearrangement. Subsequent simulation work depicted these angular jumps as a universal feature of liquid water; they occurred not only in neat water, but also in a broad gamut of aqueous environments, including aqueous solutions of ions [12] and amphiphilic solutes [13,14], confining geometries [15–18] and biomolecular hydration layers [10,19–21].

In this contribution, we initially recount some key aspects of the new picture and its detailed description via molecular dynamics simulation and analytic modeling. We then turn to a focus on experimental probing of the validity of this novel jump picture via ultrafast infrared (IR) spectroscopic measurements, including rotational anisotropy experiments [22] and two-dimensional infrared (2D-IR) spectroscopic experiments [3,23,24]. As will be seen, it is often important to also refer to nuclear magnetic resonance (NMR) spectroscopic experiments [25,26] for a useful comparison for the IR measurements. We will conclude that the jump model provides a predictive theoretical framework to understand not only pure water dynamics but also how a solute alters the surrounding water's dynamics, as illustrated by recent ionic and amphiphilic aqueous solution examples [27]. We do not aim for a complete discussion here, and refer the interested reader to other reviews [10,28] for further details and references.

2. The jump reorientation mechanism: bulk water

As related in Section 1, molecular dynamics (MD) simulations of water indicate the occurrence of large angular jumps when a water OH group trades HB acceptors [4,11]. Fig. 1 depicts this exchange process, which has the essential character of a chemical reaction involving the reactant HB and the final HB. The first step in this mechanism is the initial HB's elongation while a new water oxygen acceptor approaches, in most cases from the second hydration shell of the reorienting water molecule. Once the initial and final oxygen acceptors are equidistant from the rotating water's oxygen, the water OH can suddenly execute a large-amplitude angular jump from one acceptor to another. At the transition state for this HB

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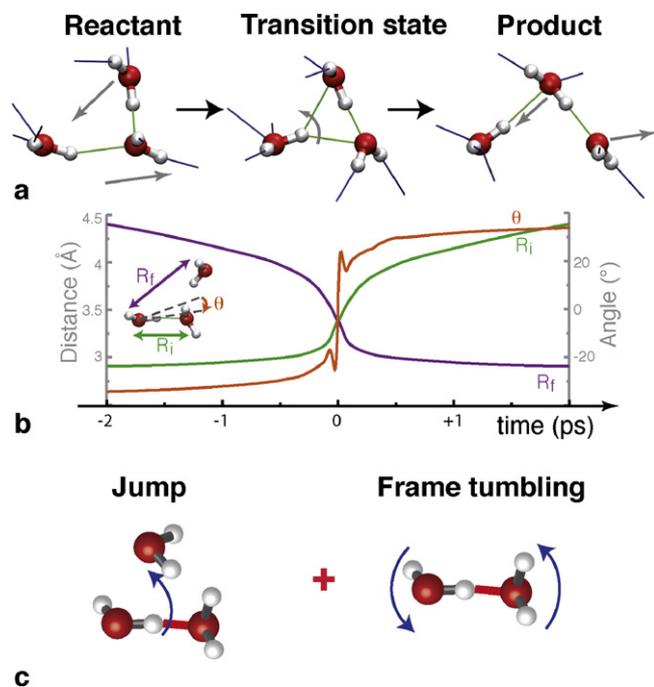
Fig. 1. (a) Schematic representation of typical reactant, transition state and product configurations for the jump mechanism, (b) Average time evolution of three key quantities during a jump: distance R_i to the initial HB acceptor, distance R_f to the final HB acceptor and (signed) angle θ between the reorienting OH and the bisector plane of the angle between the initial HB axis and the final HB axis. The origin of the time axis is set to the crossing of the transition state. (c) Schematic representation of the dominant jump motion and of the slower diffusive tumbling of the HB axis leading to a reorientation of the local frame.

exchange reaction, the rotating water forms a symmetric bifurcated HB with its initial and final water acceptors [4,11]; this concerted feature of the reaction avoids the cost of completely breaking the initial HB to form a "dangling" OH, since the new HB is partially formed while the original one is being broken [11]. The HB with the new partner eventually stabilizes, while the initial partner leaves. As is implied by the concerted character just noted, the jump mechanism's free energy barrier originates not only from the initial HB's elongation, but also from the new partner's penetration into the first shell (additional smaller contributions arise from HB fluctuations and from the OH angular motion) [11,29,30].

The mechanism displayed in Fig. 1 should clearly be understood as an average, simplified, but nonetheless representative mechanism. The actual exchange paths are distributed around this typical mechanism, an aspect illustrated by the wide jump angle distribution found around the average amplitude of 68° [11].

Since the jumps discussed above result in the reorientation of water molecules, their signature can be sought in the time-correlation function (tcf) of the molecular orientation. These dynamics can be probed by ultrafast IR spectroscopy [22], as well as more traditional NMR methods [25,26]. For a given body-fixed vector such as the water OH bond, this function reveals the rate of the loss of the memory of the initial orientation. Its definition is

$$C_n(t) = \langle P_n[\mathbf{u}(0) \cdot \mathbf{u}(t)] \rangle,$$

with P_n the nth order Legendre polynomial and $\mathbf{u}(t)$ the molecular orientation at time t. Ultrafast polarized pump-probe infrared spectroscopy experiments measure the anisotropy decay, which is approximately proportional to $C_2(t)$ [22,31]. Beyond an initial time interval (<200 fs) where water molecules partially reorient via fast librational motions, i.e. rotations hindered by the HB network-imposed restoring torques, $C_2(t)$ decays exponentially with a characteristic time τ_2.

The characteristic reorientation time resulting from a reorientation through large jumps can be determined through the jump model developed by Ivanov [32], which generalizes the diffusive angular Brownian motion picture to finite amplitude jumps [4,11]. With the assumptions that the jumps have a constant amplitude $\Delta\theta$, are uncorrelated, and occur with a frequency of $1/\tau_{jump}$ around axes distributed isotropically, the (second-order) reorientation time is

$$\tau_2 = \tau_{jump} \left\{ 1 - \frac{1}{5} \frac{\sin(5\Delta\theta/2)}{\sin(\Delta\theta/2)} \right\}^{-1}$$

Simulations can provide the two features of the jumps, their amplitude $\Delta\theta$ and their frequency $1/\tau_{jump}$ (from SPC/E water simulations at 300 K, $\Delta\theta = 68°$ and $\tau_{jump} = 3.3$ ps [11]). A key point is that the jump frequency $1/\tau_{jump}$ is now identified as the forward rate constant for the reaction which breaks an initial stable HB to form a new different stable HB [4,11].

However, this simple model incorrectly assumes fixed molecular orientation between jumps, and thus requires extension. In particular, this assumption implies that while a water OH bond retains the same HB acceptor, the OH direction remains frozen. But this is not the case, due to the intact HB axis reorientation through a tumbling motion of the local molecular frame of the hydrogen-bonded pair, which needs to be included (see Fig. 1c). The jump contribution can be combined with the frame component to produce the extended jump model (EJM) [4,11], which gives an overall EJM reorientation time

$$\frac{1}{\tau_2^{EJM}} = \frac{1}{\tau_2^{jump}} + \frac{1}{\tau_2^{frame}}$$

The structure of this result indicates that the faster of the two contributions will dominate the overall time; this will typically be the jump time, although on occasion the frame time can become important [19,33,34].

The EJM provides an excellent description of the τ_2 reorientation times measured by both pump-probe IR anisotropy and NMR spectroscopies and calculated from simulations [4,11]. However, a diffusive model could still give rise to the experimental data. The measured smooth exponential decay of $C_2(t)$ could either result from sharp large amplitude jumps averaged over a great number of water molecules jumping at different times, or rather from infinitesimal reorientations for each water molecule. The ratio of the second-order time τ_2 with the first- or third-order times would be needed to furnish the distinction between pictures [4,11], but these latter times are currently not experimentally accessible. We note here that while the Debye dielectric relaxation time is a first-order reorientation time, it pertains to the *collective* reorientation of the total dipole, and due to strong correlations between individual water molecules, it is significantly longer than the first-order single-molecule reorientation time of interest here [11]. Other direct and incisive experimental evidence is thus necessary to determine unambiguously the reorientation mechanism.

Some first experimental support of the jump model came from the analysis of quasi-elastic neutron scattering spectra (QENS), discussed elsewhere [35]. But among the many experimental techniques probing water HB dynamics, including QENS [35], NMR spectroscopy [26] and ultrafast pump-probe IR spectroscopy [22], the most recent – and arguably most powerful – has been 2D-IR spectroscopy, which accounts for its special emphasis here. Numerous discussions of 2D-IR are available [23,36–38]; our present discussion addresses only the key relevant aspects necessary for water HB dynamics [3,36,39–41]. This technique follows the time-fluctuations of vibrational frequencies and yields the correlation between the frequencies at two instants separated by a given time delay. Its application to water [31] provides

detailed HB dynamical information, since the water OH stretch vibration is a sensitive hydrogen-bonding interaction probe. An OH engaged in a strong HB vibrates at a lower frequency: the OH bond is weakened by stabilizing interaction with the HB acceptor, inducing an average OH frequency red-shift; conversely, a weakly hydrogen-bonded OH exhibits a blue-shifted frequency. 2D-IR probing of the OH frequency time-evolution accordingly reports on HB network fluctuations and HB breaking and forming events. It has already been successfully exploited for water HB dynamics in a broad gamut of contexts, from the bulk case [3,5,29,39,40] to e.g. ionic aqueous solutions [41–43], confining environments [44] and biomolecular hydration [39].

That 2D-IR has the potential to provide insight on the presence of angular jumps can be readily understood. The jump transition state (TS) determined from MD simulations is a bifurcated HB structure in which the reorienting water OH donates two weak HBs to two acceptors, resulting in an OH stretch vibrational frequency blue-shift [3,4,11,40]. OH frequency changes during the jump thus make 2D-IR spectroscopy a promising tool for enquiry upon the presence of angular jumps in water, exploiting its ability to selectively follow systems with given initial and final vibrational frequencies. As we will see, however, the situation is not completely straightforward for liquid water itself. In general, to characterize angular jumps, 2D-IR often requires supplementary experimental information (e.g. polarization-resolved measurements) and its interpretation can be greatly aided by theory.

A first somewhat indirect support of the jump picture can be found in a 2D-IR study [3] performed prior to the theoretical proposal of jumps [4]. Focusing on the spectral relaxation of blue-shifted OH frequencies corresponding to very weak or broken HBs, this study first evidenced the transient and unstable character of non-HB states, which very quickly (<200 fs) relax to form a HB [3]. While not itself suggesting or establishing a mechanism for HB exchange dynamics, this result is at least fully consistent with the jump mechanism in which HB acceptor exchanges occur through the concerted breaking and forming of HBs [4], in contrast with a sequential mechanism involving a long-lived broken HB state ruled out by the experiment.

In fact, most blue-shifted OHs do not even lie at the jump mechanism TS, since most do not execute a jump between HB acceptors. Simulations indicate that most blue-shifted water OHs (~80%) only experience a transient HB break and quickly return to their initial HB acceptor and orientation without any jump and resulting formation of a HB with a new acceptor; the OHs jumping from one acceptor to another only represent a minor (~20%) part [11].

This implies, unfortunately, that water molecules close to the jump TS cannot be selectively excited using blue-shifted infrared excitation. Further, the 2D-IR measured frequency dynamics cannot distinguish the jump and libration contributions. This is because the OH frequency dynamics is similar for a successful jump forming a new HB with a different water acceptor and for an unsuccessful jump (i.e. a large amplitude libration) reforming an HB with the initial acceptor. This important feature was recently confirmed by the great similarity of the calculated 2D IR spectra of water with and without the jumps [14] (see Fig. 2 and Ref. [14]).

Indeed, fast transient HB breaking/reforming and slower HB jump exchanges provide very *different* contributions to the frequency dynamics (measured in 2D-IR) and to the reorientation dynamics (monitored by the pump-probe IR anisotropy decay). Although fast transient HB breaks do not lead to a stable reorientation, they cause most of the frequency dephasing [1,31,45]. In contrast, slower HB jump exchanges (their rate constant is approximately four times smaller than that of the transient breakings at room temperature [11]) are the key reorientation pathway; they also lead to frequency decorrelation, but by the time a jump occurs, most of the memory of the initial frequency has already been lost
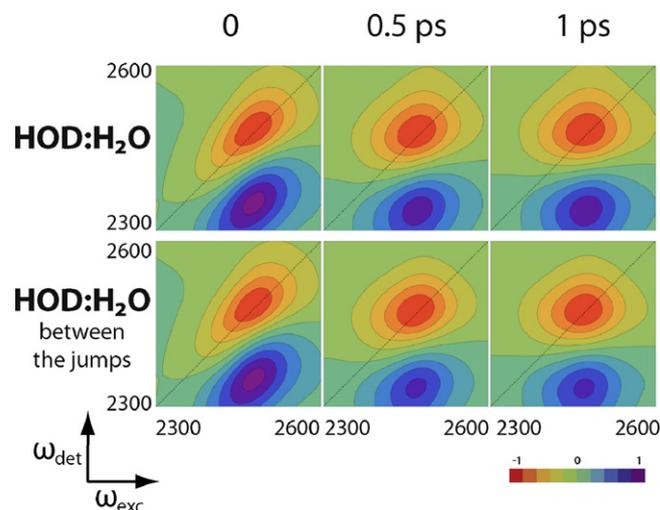

Fig. 2. Bulk water 2D-IR spectra [31] calculated for different population delays from a regular simulation (top panel) and from the same simulation during the time intervals between the jumps (bottom panel). Horizontal and vertical axes correspond to excitation and detection frequencies.

due to transient HB breaks [1]. Further, for HB exchanges from one water acceptor to another, the product HB's frequency is just the same as the reactant HB, so the former's production will not contribute to the frequency dephasing. These considerations will later prove to be crucial when we consider 2D-IR spectroscopy for aqueous solutions of amphiphilic solutes.

For discrimination between successful jumps and failed jump attempts, the key criterion is that only the former lead to a stable, long-time reorientation, i.e. the formation of a stable, product HB. Accordingly, specific evidence for angular jumps can only ensue from the combined study of spectral dynamics and orientation dynamics. This is achievable through polarization-resolved 2D-IR spectroscopy [29], as will be discussed in the next section. Such experiments provide a frequency-resolved extension of the conventional anisotropy decay $C_2(t)$: for each delay t, with the reorientation now given as a function of the initial and final water OH vibration frequencies. Accordingly, this allows e.g. specifically following the reorientation rate of water OHs which start and end in weakly bonded configurations, i.e. with blue-shifted frequencies. Experimentally, such 2D anisotropy maps can be obtained either by polarization-resolved pump-probe [46] or 2D-IR methods [29,42].

A frequency-dependent version of the EJM (FD-EJM) can be used to interpret such 2D anisotropy diagrams and identify spectral features which unambiguously show the presence of angular jumps [29]. This extension describes the jump probability's moderate dependence on the initial HB strength, and thus on the OH vibrational frequency. The free energy barrier to reach the jump TS was shown to be mostly due to the concerted elongation of the initial HB and penetration of the new partner within the rotating water's first shell [11]. The respective free energy costs of the elongation and of the new partner's approach were found to be similar [29]. An initially blue-shifted frequency corresponds to a water OH which has already weakened its initial HB, but does not imply that a new HB partner is available to effect a jump. This provides the explanation of the observations that the jump probability increases with vibrational frequency blue-shift, but that this increase is very moderate [11,29].

The FD-EJM predicts that angular jumps should result in a faster anisotropy decrease for blue-shifted frequencies, provided that memory of the initial frequency is retained [29]. Such accelerated reorientation has already been observed in frequency-resolved pump-probe spectroscopic studies [46] and it can be rigorously

connected to the presence of jumps through the FD-EJM. Future polarization-resolved 2D-IR measurements should give a more detailed picture. For the moment, however, a more telling investigation of the water angular jumps is provided by studies of water dynamics in the hydration shells of solutes, discussed next.

3. Aqueous salt solutions

We now commence the discussion of the jump picture and associated IR spectroscopic experiments for water dynamics in the hydration shells of solutes. Pioneering pump-probe ultrafast IR experiments on water dynamics in the hydration shells of anions [47,48] have provided a new time-dependent spectroscopic window in this important area for transport and reactivity, complementing traditional NMR spectroscopic results [25]. An early MD study of the iodide anion hydration dynamics [49] identified an important contribution to the time dependence inferred from these experiments arising from exchange of a water molecule between the anion hydration shell and the water bulk, a phenomenon we will meet again. A subsequent study of water reorientation dynamics in Cl$^-$ hydration shells showed [12] that due to the different vibrational population lifetimes of water in the bulk and in the anionic shell, the experimental ultrafast anisotropy decay [50] actually measures the slower frame diffusive reorientation of the intact anion–water HB complex and is essentially insensitive to the faster jump reorientation. The jump mechanism for the hydration shell water was found to be the major mechanism for the reorientation as determined e.g. via NMR spectroscopy [25], and Cl$^-$ was dynamically characterized as a weak structure-breaker (i.e. it slightly accelerates water dynamics in its hydration layer), in accord with earlier NMR descriptions. It is interesting to note that a recent simulation/EJM examination of the small, high charge density F$^-$ case indicates that, due to the exceptionally strong anion–water HB, the jump and frame contributions to the reorientation time are in fact comparable, representing an anomaly among the halides [33].

But ionic solutions also have a central, direct role to play in the experimental probing *per se* of the validity of the jump model. As discussed in Section 2, in neat water, the main difficulty in distinguishing an actual jump from a large amplitude libration arises from the symmetry between initial and final HB acceptors, which are both water oxygens. Ions have thus been used to break this symmetry and provide a direct characterization of the angular jumps through 2D-IR experiments [41–43]. As indicated at the beginning of this section, in the presence of a salt, simulations show that some jumps occur from an initial state where a HB is donated to an anion to a final state with a HB to a water molecule [12,33]. If the anion accepts very weak HBs [41–43], the vibrational frequency of the water OH bonded to the anion is sufficiently blue-shifted to become separate from the broad distribution of vibrational frequencies observed for OH groups bonded to a water. In the linear IR spectrum, this results in the tell-tale signature of two distinct OH stretch bands (Fig. 3).

The great strengths of 2D-IR spectroscopy are to extract dynamical information, and to reveal and measure the kinetics of the chemical exchange between these two states, respectively hydrogen-bonded to an anion and to a water oxygen. Chemical exchange between two states usually manifests itself in 2D-IR spectra through the presence of two distinct diagonal peaks and the growth of off-diagonal peaks [36,41,43,51]. The latter correspond to OH groups with the same type of HB acceptor when the system is first excited and after a delay *T* when the correlation is measured (Fig. 3). As *T* is increased, exchange between the two populations causes these two diagonal peaks to decrease, while off-diagonal peaks progressively grow. These off-diagonal peaks correspond to OH groups which have different initial and final frequencies,
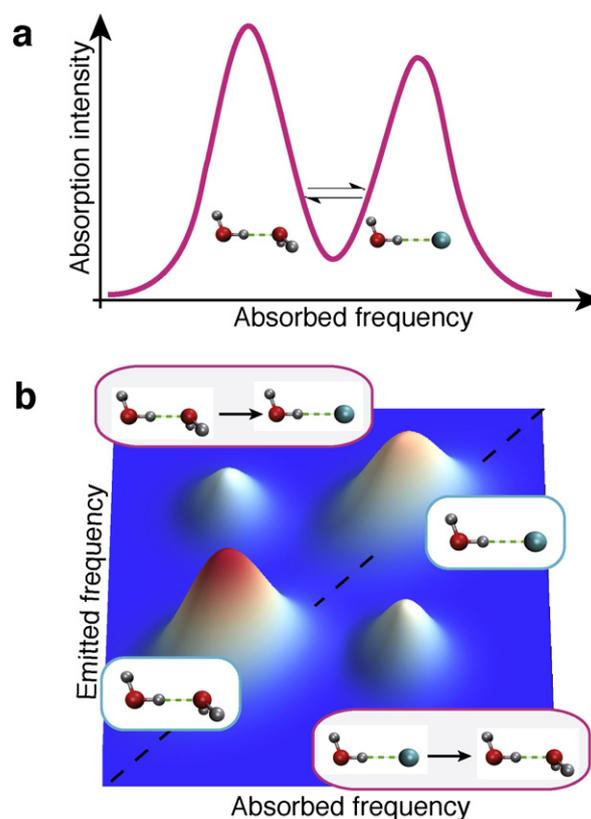

Fig. 3. Schematic representation, for a concentrated ionic aqueous solution, of (a) the linear infrared spectrum and (b) a 2D-IR spectrum after a few picoseconds, with growing off-diagonal peaks due to exchanges.

which implies that they have undergone exchange between the two states (Fig. 3). 2D-IR experiments on concentrated salt solutions (respectively 5.5 M NaBF$_4$ [41] and 6 M NaClO$_4$ [43]) measured the exchange time for a water OH to go from an anion acceptor to a water acceptor [31], which corresponds to the jump time in the EJM terminology. The experimental values (respectively 7 ps [41] and 6 ps [43]) are consistent with the time determined from a simulation study of a different salt solution (3.6 ps in a 3 M NaCl solution), considering the different nature of the salt and more importantly the strong concentration dependence of the jump time, which dramatically increases for increasing salt concentrations [12].

These pioneering 2D-IR experiments provided the first time-resolved measurement of water exchange kinetics between different HB acceptors, but could not yet establish unambiguously that exchanges occur through large angular jumps, since they do not contain any information on the exchange mechanism. Subsequent polarization-resolved 2D-IR experiments have very recently provided a quantitative measure of the reorientation associated with HB exchange [42]. Following the same approach as pump-probe IR anisotropy measurements, comparison of spectra acquired with parallel and perpendicular polarizations evidenced that systems which exchange between the two states (off-diagonal peaks) experience a much larger reorientation than those which remain in the same state (diagonal peaks). Analysis of the spectra via a kinetic model leads to an average jump angle of $49 \pm 4°$ [42], in qualitative agreement with the distributions of jump angles determined from MD simulations of various aqueous solutions, whose averages lie between 60° and 70° [4,12,13,16,19,33].

2D-IR spectroscopy thus appears as an exquisite technique to follow water HB exchange kinetics, and unambiguously supports the existence of angular jumps. One could therefore hope to extend these measurements to other aqueous environments in order to

assess how the jump mechanism is altered, and compare with theoretical predictions. However, a broad applicability of 2D-IR is still limited by several factors. Perhaps most importantly, a large fraction of the water hydroxyls bonded to solute acceptors is necessary to obtain a detectable spectral peak. Experiments on very dilute solutions (<1 M) available for instance in NMR measurements [26] are thus still inaccessible. It is all the more unfortunate that water HB dynamics is extremely sensitive to the solute concentration, so that dilute solution behavior cannot be easily inferred from concentrated solution measurement. In addition, these 2D-IR studies require the existence of spectrally distinct populations, i.e. the vibrational frequency shift between the two states should exceed the frequency fluctuations within each state. This condition is unfortunately not met for most singly charged anions, e.g. halides, for which 2D-IR cannot be used to directly follow HB exchanges, although information on spectral diffusion is still provided [52]. Nonetheless, one can anticipate further aqueous solution 2D-IR experiments on ions satisfying the frequency shift requirement.

4. Water next to amphiphilic solutes

Many, if not most, solutes of interest are amphiphilic, with both hydrophobic and hydrophilic portions. In this section, we will consider water dynamics about such solutes. Our discussion will begin with a fairly extended consideration of the hydrophobic limit.

In addition to the neat water and salt solution cases, simulations indicate that water also reorients through large angular jumps next to hydrophobic groups [13]. The jump mechanism and amplitude are almost identical to those found in bulk water, but the jump rate constant $1/\tau_{jump}$ is smaller. This was explained through a Transition State Excluded Volume (TSEV) effect for HB exchange (Fig. 4a), which provided the first quantitative treatment of a hydrophobic group's influence on the surrounding water HB and reorientation dynamics. This model determines how the approach of a new water partner necessary for the HB exchange is hindered by the hydrophobe's presence. For hydrophobic hydration shell water molecules, the TSEV slowdown factor in the jump time (relative to bulk) is directly related to the local fraction of space occupied by the solute [13]. For usual convex hydrophobic groups (e.g. methyl, dimethyl and trimethyl groups, whose radii range between 3 and 5 Å), the TSEV slowdown factor is close to 1.4, thus showing that a single hydrophobic group has a very limited effect on water HB dynamics. Such a moderate slowdown quantitatively agrees with dilute solution studies using a broad range of techniques, including NMR [26], dielectric relaxation [53], Kerr effect spectroscopy [54], light scattering [55] and MD simulations (both with classical force fields [13] and first principles dynamics [56]).

We now examine to what extent 2D-IR spectroscopy can provide an experimental characterization of these jumps next to hydrophobic groups. Recent experiments [57–59] and calculations [14] have been performed on a series of small (amphiphilic) solutes containing hydrophobic methyl groups. The computed spectra [14] (Fig. 5a) compare very well with experiment [57–59]. In dilute (1 mol/kg) solution, the 2D spectra are very similar to those of bulk water, due to the dominant bulk water population in the collected signal. But in the concentrated (8 mol/kg) case, the spectral relaxation becomes much slower, and the frequency correlation persists over several picoseconds [14,31,57]. This very slow spectral relaxation was interpreted by some authors as revealing a dramatic intrinsic effect of hydrophobic groups on water dynamics. These groups would suppress HB acceptor jumps and "immobilize" the orientation of a fraction of the water molecules within their hydration layer, in line with previous controversial conclusions reached by IR pump-probe anisotropy experiments [60] on these solutes. But such a picture is in stark contrast with the moderate retardation
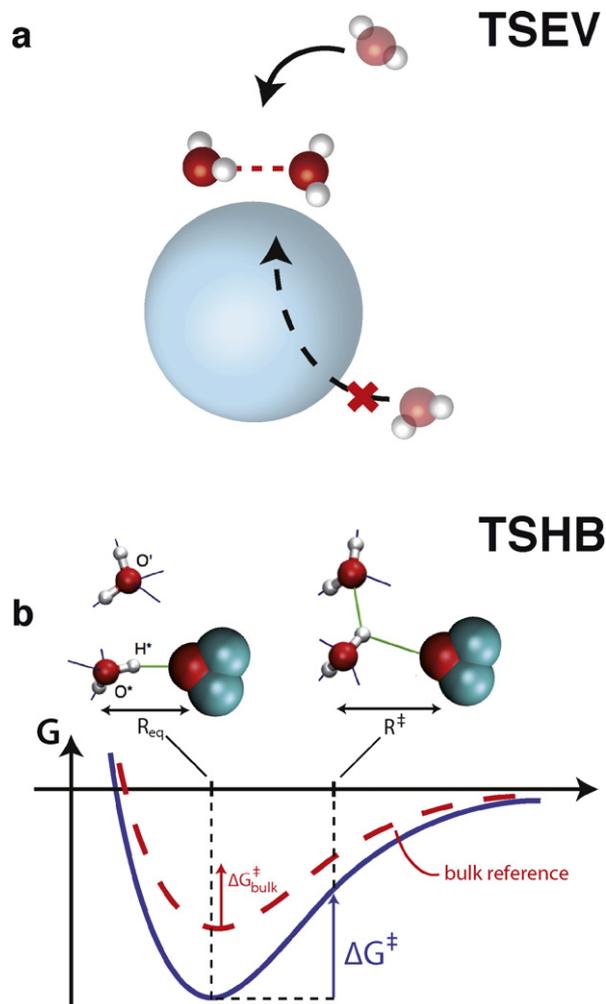

Fig. 4. Schematic representations of the (a) TSEV and (b) TSHB effects of a solute on the water jump rate constant. The TSEV model describes the jump slowdown due to the solute which blocks the approach of some new HB acceptors. The TSHB model connects the free energy cost $\Delta G^{\ddagger}$ to stretch the initial HB from its equilibrium length R_{eq} to its transition state length $R^{\ddagger}$ to the acceleration or slowdown factor induced by the HB acceptor on the water jump dynamics.

measured by simulations and other experiments, and rationalized by the EJM/TSEV models. We now show that the 2D-IR spectra are very ambiguous in such non-homogeneous cases and that this disagreement can be resolved through a careful interpretation of 2D-IR spectra, leading to a picture fully consistent with the moderate hydrophobic effect predicted by the EJM/TSEV model.

The hydrophobic portion of these amphiphilic solutes can neither donate nor receive HBs, and water molecules in their vicinity form HBs with other water molecules. In the hydration layer of hydrophobic groups, jumps therefore occur from one water oxygen to another. This is the same type of symmetric jump discussed in Section 2 for the neat water case, where it was shown that 2D-IR could not discriminate spectral dynamics due to transient HB breaking/reforming with a single HB acceptor and to actual jumps between two different HB acceptors. An indication that the slowdown in the spectral decay is not due to suppressed jumps comes from the 2D-IR spectra computed in the total absence of jumps (Fig. 2), which are found to be very similar to the regular spectra including jumps. This similarity is a consequence of the dominant contribution made by transient HB breaks (unsuccessful jumps) to spectral dephasing [14]. The conclusion is that very retarded 2D-IR spectral decay for aqueous solutions of amphiphilic solutes is
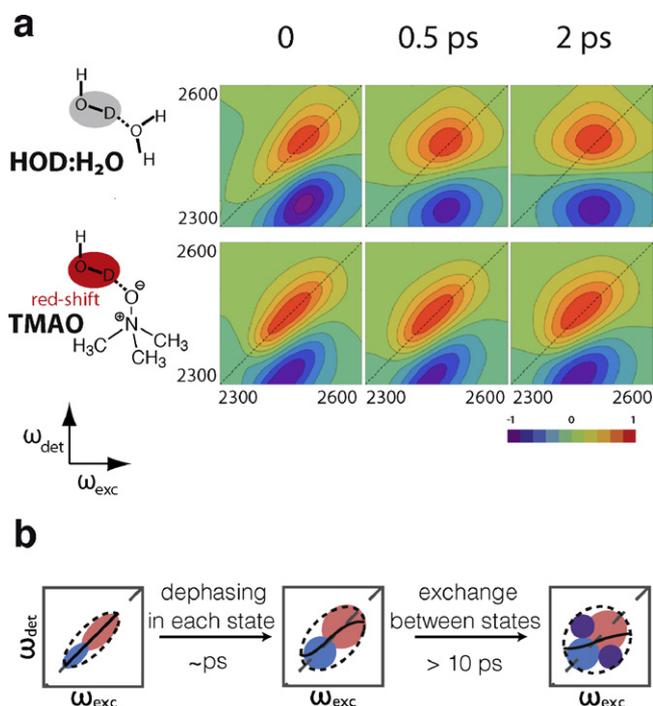
Fig. 5. (a) Simulated 2D-IR spectra at several delays for HOD:H$_2$O [31] and for a concentrated (8 mol/kg) aqueous solutions of TMAO in HOD:H$_2$O. (b) Schematic representation of the 2D-IR spectral decays (omitting the negative 1–2 transition peak), first due to dephasing within each HB state and then due to exchange between HB acceptors.

thus very unlikely to originate from suppressed jumps and water immobilization by hydrophobic groups.

As to be detailed presently, this slow spectral decay actually has a different origin: it arises from the slow exchange of water molecules donating a HB to the other moiety of these solute molecules, which are amphiphilic [10,13,26,29,57,60] and contain an HB accepting hydrophilic group. This implies that, just as for the ionic solutions discussed in Section 3, two states are possible for each water OH, corresponding to two different HB acceptors: either a water oxygen or a hydrophilic headgroup (whose respective fractions are 76% and 24% at 8 mol/kg [14]). Depending on the HB strength with the hydrophilic head, these two populations may have distinct vibrational frequency dynamics.

Because these hydrophilic heads are not so different from a water oxygen, the frequency shift between the OH populations respectively hydrogen-bonded to water and to the solute is limited (at most 30 cm^{-1}), leading to a single broad band in the linear IR spectrum [14,59]. In the 2D-IR spectra, the two frequency distributions are also too close to be resolved separately, and the characteristic signatures of exchange discussed above for ionic solutions, including the presence of off-diagonal peaks, are not visible. Nonetheless, exchange between these two populations has an important dynamical consequence: it can significantly slow down the spectral relaxation, as now discussed.

In these two-component systems, spectral relaxation proceeds via two mechanisms [31]. The first, faster contribution arises from transient HB breaking and making events [1,45], similar to the mechanism in neat water discussed above. These HB breaks occur without any change in the HB acceptor identity and thus do not lead to an exchange between the two populations. The resulting spectral relaxation time only moderately depends on the HB strength, and is thus similar in the two states. After ∼ 1 ps, the 2D-IR spectra have decayed from the sum of two diagonally elongated bands to the sum of two round peaks (see the schematic

representation in Fig. 5b, supported by quantitative frequency time-correlation functions [14]). When these two peaks are offset slightly, the resulting 2D-IR spectra remain diagonally elongated [14,36], which explains the observed incomplete spectral relaxation. Full spectral relaxation then requires a second, slower contribution coming from exchanges between the two peaks, i.e. HB jumps between water oxygens and solute hydrophilic heads. The magnitude of this second component is proportional to the frequency shift between the peaks. For trimethylamine-N-oxide (TMAO), the very polar oxygen headgroup is a strong HB acceptor and induces a large red-shift relative to the bulk. The appearance of this additional contribution due to the slow exchange between the two types of HB acceptors causes the marked slowdown in the spectral relaxation compared to the bulk. In neat water this contribution is absent because there is a single type of HB acceptor.

In concluding this section, it is useful to stress the subtle effects induced by amphiphilic solutes in 2D-IR spectra: the same chemical group can have radically different impacts on the water reorientation dynamics and on the water spectral dynamics. While a hydrophobic group slows down the surrounding water molecules' reorientation by a factor less than 2 (cf Section 4), it has a very limited effect on water spectral relaxation, since a new HB population is not produced; spectral relaxation remains almost bulk-like, resulting from transient HB breaks largely unaffected by the hydrophobic group. Hydrophilic HB acceptor groups can also have very different impacts on the water HB exchange and thus reorientation dynamics. A hydrophilic group accepting an HB stronger than a water–water HB leads to a reorientation dynamics slowdown (potentially much more pronounced than that induced by hydrophobic groups [19]); conversely, weak HB acceptors lead to an accelerated water reorientation; both of these effects are described via a Transition State Hydrogen-Bond model [19] (Fig. 4b). This model provides a quantitative connection between the free energy cost to stretch the initial HB to its transition state length and the acceleration or slowdown factor induced by the hydrophilic group on the reorientation dynamics of the HB donating water [61]. In contrast with this considerable span of possible effects on water reorientation, all hydrophilic HB acceptors lead to a new HB type, and therefore—except when the two populations have superimposable frequency distributions—results in an additional slow component in the water spectral relaxation associated with chemical exchanges between HB acceptors. This can have some striking consequences: some weak HB acceptors can accelerate the water reorientation dynamics while retarding the spectral relaxation [62].

5. Concluding remarks

Theory and ultrafast IR spectroscopic experiments have led to considerable new insights for our understanding of water and aqueous solution hydrogen bond dynamics. In our discussion, we have shown that the presence of large angular jumps in water, initially suggested through simulations and analytic models [4], has subsequently received clear support from pioneering 2D-IR spectroscopy measurements [41,42]. These jumps appear to be a universal feature of liquid water and have been found in a wide span of environments, including e.g. the bulk, the interface with small hydrophilic groups (e.g. ions), hydrophobic and amphiphilic solutes, the interface with extended surfaces [16,17], and the hydration layer of biomolecules [19,20]. Predictive analytic models describe how different chemical groups affect the jump kinetics, and MD simulations and analytic modeling coupled with 2D-IR spectra calculations greatly assist in providing a molecular picture for complex and sometimes ambiguous 2D-IR spectral patterns [14]. Novel theoretical advances and experimental developments, especially in polarization-resolved 2D-IR [29,42], surface-sensitive

2D-IR [63] and 3D-IR [64] spectroscopies, should provide additional insight into the water's fascinating dynamics in its various regimes and habitats. Among those currently under theoretical investigation are supercooled water, water (and aqueous solutes) next to electrodes and in the grooves of DNA.

Acknowledgements

References

[1] K.B. Moller, R. Rey, J.T. Hynes, Hydrogen bond dynamics in water and ultrafast infrared spectroscopy: a theoretical study, J. Phys. Chem. A 108 (2004) 1275–1289.

[2] R. Rey, K.B. Moller, J.T. Hynes, Hydrogen bond dynamics in water and ultrafast infrared spectroscopy, J. Phys. Chem. A 106 (2002) 11993–11996.

[3] J.D. Eaves, J.J. Loparo, C.J. Fecko, S.T. Roberts, A. Tokmakoff, P.L. Geissler, Hydrogen bonds in liquid water are broken only fleetingly, Proc. Natl. Acad. Sci. U.S.A. 102 (2005) 13019–13022.

[4] D. Laage, J.T. Hynes, A molecular jump mechanism of water reorientation, Science 311 (2006) 832–835.

[5] J.B. Asbury, T. Steinel, K. Kwak, S.A. Corcelli, C.P. Lawrence, J.L. Skinner, M.D. Fayer, Dynamics of water probed with vibrational echo correlation spectroscopy, J. Chem. Phys. 121 (2004) 12431–12446.

[6] B.J. Gertner, R.M. Whitnell, K.R. Wilson, J.T. Hynes, Activation to the transition-state - reactant and solvent energy-flow for a model S_N2 reaction in water, J. Am. Chem. Soc. 113 (1991) 74–87.

[7] K. Ando, J.T. Hynes, HCl acid ionization in water – a theoretical molecular modeling, J. Mol. Liq. 64 (1995) 25–37.

[8] K. Ando, J.T. Hynes, Molecular mechanism of HCl acid ionization in water: Ab initio potential energy surfaces and Monte Carlo simulations, J. Phys. Chem. B 101 (1997) 10464–10478.

[9] D. Marx, M.E. Tuckerman, J. Hutter, M. Parrinello, The nature of the hydrated excess proton in water, Nature 397 (1999) 601–604.

[10] D. Laage, G. Stirnemann, F. Sterpone, R. Rey, J.T. Hynes, Reorientation and allied dynamics in water and aqueous solutions, Annu. Rev. Phys. Chem. 62 (2011) 395–416.

[11] D. Laage, J.T. Hynes, On the molecular mechanism of water reorientation, J. Phys. Chem. B 112 (2008) 14230–14242.

[12] D. Laage, J.T. Hynes, Reorientional dynamics of water molecules in anionic hydration shells, Proc. Natl. Acad. Sci. U.S.A. 104 (2007) 11167–11172.

[13] D. Laage, G. Stirnemann, J.T. Hynes, Why water reorientation slows without iceberg formation around hydrophobic solutes, J. Phys. Chem. B 113 (2009) 2428–2435.

[14] G. Stirnemann, J.T. Hynes, D. Laage, Water hydrogen bond dynamics in aqueous solutions of amphiphiles, J. Phys. Chem. B 114 (2010) 3052–3059.

[15] J. Chowdhary, B.M. Ladanyi, Hydrogen bond dynamics at the water/hydrocarbon interface, J. Phys. Chem. B 113 (2009) 4045–4053.

[16] G. Stirnemann, P.J. Rossky, J.T. Hynes, D. Laage, Water reorientation, hydrogen-bond dynamics and 2D-IR spectroscopy next to an extended hydrophobic surface, Faraday Discuss. 146 (2010) 263–281.

[17] G. Stirnemann, S.R.V. Castrillon, J.T. Hynes, P.J. Rossky, P.G. Debenedetti, D. Laage, Non-monotonic dependence of water reorientation dynamics on surface hydrophilicity: competing effects of the hydration structure and hydrogen-bond strength, Phys. Chem. Chem. Phys. 13 (2011) 19911–19917.

[18] D.E. Rosenfeld, C.A. Schmuttenmaer, Dynamics of the water hydrogen bond network at ionic, nonionic, and hydrophobic interfaces in nanopores and reverse micelles, J. Phys. Chem. B 1 (15) (2011) 1021–1031.

[19] F. Sterpone, G. Stirnemann, J.T. Hynes, D. Laage, Water hydrogen-bond dynamics around amino acids: the key role of hydrophilic hydrogen-bond acceptor groups, J. Phys. Chem. B 114 (2010) 2083–2089.

[20] Z.C. Zhang, M.L. Berkowitz, Orientational dynamics of water in phospholipid bilayers with different hydration levels, J. Phys. Chem. B 113 (2009) 7676–7680.

[21] A.V. Verde, R.K. Campen, Disaccharide topology induces slowdown in local water dynamics, J. Phys. Chem. B 115 (2011) 7069–7084.

[22] H.J. Bakker, J.L. Skinner, Vibrational, Spectroscopy as a probe of structure and dynamics in liquid water, Chem. Rev. 110 (2010) 1498–1517.

[23] M.D. Fayer, D.E. Moilanen, D. Wong, D.E. Rosenfeld, E.E. Fenn, S. Park, Water dynamics in salt solutions studied with ultrafast two-dimensional infrared (2D IR) vibrational echo spectroscopy, Acc. Chem. Res. 42 (2009) 1210–1219.

[24] K.J. Gaffney, M. Ji, M. Odelius, S. Park, Z. Sun, H-bond switching and ligand exchange dynamics in aqueous ionic solution, Chem. Phys. Lett. 504 (2011) 044516.

[25] L. Endom, H.G. Hertz, B. Thul, M.D. Zeidler, A microdynamic model of electrolyte solutions as derived from nuclear magnetic relaxation and self-diffusion data, Berich Bunsen Gesell 71 (1967) 1008–1031.

[26] J. Qvist, B. Halle, Thermal signature of hydrophobic hydration dynamics, J. Am. Chem. Soc. 130 (2008) 10345–10353.

[27] Analysis ignores certain features present in ultrafast IR spectroscopy, including e.g. local heating and reorientation and dephasing in vibrationally excited states. These features are not relevant for comparison with NMR experiments.

[28] D. Laage, G. Stirnemann, F. Sterpone, J.T. Hynes, Water Jump Reorientation: from theoretical prediction to experimental observation, Acc. Chem. Res. 45 (2012) 53–62.

[29] G. Stirnemann, D. Laage, Direct evidence of angular jumps during water reorientation through two-dimensional infrared anisotropy, J. Phys. Chem. Lett. 1 (2010) 1511–1516.

[30] D. Laage, J.T. Hynes, Do more strongly hydrogen-bonded water molecules reorient more slowly? Chem. Phys. Lett. 433 (2006) 80–85.

[31] Dilute HOD in H_2O or D_2O is used to avoid fast resonant intermolecular vibrational energy transfer which in neat H_2O causes both a fast anisotropy decay (S. Woutersen, H.J. Bakker, Resonant Intermolecular Transfer of Vibrational Energy in Liquid Water. Nature 1999, 402, 507–509) and a fast frequency dephasing (M. L. Cowan, B.D. Bruner, N. Huse, J.R. Dwyer, B. Chugh, E.T.J. Nibbering, T. Elsaesser, R.J.D. Miller, Ultrafast memory loss and energy redistribution in the hydrogen bond network of liquid H_2O. Nature 2005, 434, 199–202).

[32] E.N. Ivanov, Theory of rotational brownian motion, Sov. Phys. JETP 18 (1964) 1041–1045.

[33] J. Boisson, G. Stirnemann, D. Laage, J.T. Hynes, Water reorientation dynamics in the first hydration shells of F^- and I^-, Phys. Chem. Chem. Phys. 13 (2011) 19895–19901.

[34] A.A. Vartia, K.R. Mitchell-Koch, G. Stirnemann, D. Laage, W.H. Thompson, On the reorientation and hydrogen-bond dynamics of alcohols, J. Phys. Chem. B 115 (2011) 12173–12178.

[35] D. Laage, Reinterpretation of the liquid water quasi-elastic neutron scattering spectra based on a nondiffusive jump reorientation mechanism, J. Phys. Chem. B 113 (2009) 2684–2687.

[36] Y.S. Kim, R.M. Hochstrasser, Applications of 2D IR spectroscopy to peptides, proteins, and hydrogen-bond dynamics, J. Phys. Chem. B 113 (2009) 8231–8251.

[37] P. Hamm, M.T. Zanni, Concepts, Methods of 2D Infrared Spectroscopy, Cambridge UK, Cambridge University Press, 2011.

[38] M.D. Fayer, Dynamics of liquids, molecules, and proteins measured with ultrafast 2d IR vibrational echo chemical exchange spectroscopy, Annu. Rev. Phys. Chem. 60 (2009) 21–38.

[39] T. Elsaesser, Two-dimensional infrared spectroscopy of intermolecular hydrogen bonds in the condensed phase, Acc. Chem. Res. 42 (2009) 1220–1228.

[40] S.T. Roberts, K. Ramasesha, A. Tokmakoff, Structural rearrangements in water viewed through two-dimensional infrared spectroscopy, Acc. Chem. Res. 42 (2009) 1239–1249.

[41] D.E. Moilanen, D. Wong, D.E. Rosenfeld, E.E. Fenn, M.D. Fayer, Ion-water hydrogen-bond switching observed with 2D IR vibrational echo chemical exchange spectroscopy, Proc. Natl. Acad. Sci. U.S.A. 106 (2009) 375–380.

[42] M.B. Ji, M. Odelius, K.J. Gaffney, Large angular jump mechanism observed for hydrogen bond exchange in aqueous perchlorate solution, Science 328 (2010) 1003–1005.

[43] S. Park, M. Odelius, K.J. Gaffney, Ultrafast dynamics of hydrogen bond exchange in aqueous ionic solutions, J. Phys. Chem. B 113 (2009) 7825–7835.

[44] E.E. Fenn, D.B. Wong, M.D. Fayer, Water dynamics at neutral and ionic interfaces, Proc. Natl. Acad. Sci. U.S.A. 106 (2009) 15243–15248.

[45] C.P. Lawrence, J.L. Skinner, Vibrational spectroscopy of HOD in liquid D2O. III. Spectral diffusion, and hydrogen-bonding and rotational dynamics, J. Chem. Phys. 118 (2003) 264–272.

[46] H.J. Bakker, Y.L.A. Rezus, R.L.A. Timmer, Molecular reorientation of liquid water studied with femtosecond midinfrared spectroscopy, J. Phys. Chem. A 112 (2008) 11523–11534.

[47] A.W. Omta, M.F. Kropman, S. Woutersen, H.J. Bakker, Negligible effect of ions on the hydrogen-bond structure in liquid water, Science 301 (2003) 347–349.

[48] M.F. Kropman, H.J. Bakker, Dynamics of water molecules in aqueous solvation shells, Science 291 (2001) 2118–2120.

[49] B. Nigro, S. Re, D. Laage, R. Rey, J.T. Hynes, On the ultrafast infrared spectroscopy of anion hydration shell hydrogen bond dynamics, J. Phys. Chem. A 110 (2006) 11237–11243.

[50] M.F. Kropman, H.K. Nienhuys, H.J. Bakker, Real-time measurement of the orientational dynamics of aqueous solvation shells in bulk liquid water, Phys. Rev. Lett. 88 (2002) 77601.

[51] D.D. Dlott, Ultrafast chemical exchange seen with 2D vibrational echoes, Science 309 (2005) 1333–1334.

[52] S. Park, M.D. Fayer, Hydrogen bond dynamics in aqueous NaBr solutions, Proc. Natl. Acad. Sci. U.S.A. 104 (2007) 16731–16738.

[53] K. Hallenga, J.R. Grigera, H.J.C. Berendsen, Influence of hydrophobic solutes on the dynamic behavior of water, J. Phys. Chem. 84 (1980) 2381–2390.

[54] K. Mazur, I.A. Heisler, S.R. Meech, THz spectra dynamics of aqueous solutions studied by the ultrafast optical Kerr effect, J. Phys. Chem. B 115 (2011) 2563–2573.

[55] L. Lupi, L. Comez, C. Masciovecchio, A. Morresi, M. Paolantoni, P. Sassi, F. Scarponi, D. Fioretto, Hydrophobic hydration of tert-butyl alcohol studied by Brillouin light and inelastic ultraviolet scattering, J. Chem. Phys. 134 (2011) 055104.

[56] P.L. Silvestrelli, are there immobilized water molecules around hydrophobic groups? Aqueous solvation of methanol from first principles, J. Phys. Chem. B 113 (2009) 10728–10731.

[57] A.A. Bakulin, C. Liang, T.L. Jansen, D.A. Wiersma, H.J. Bakker, M.S. Pshenich-nikov, Hydrophobic Solvation: A 2D IR spectroscopic inquest, Acc. Chem. Res. 42 (2009) 1229–1238.

[58] C. Petersen, A.A. Bakulin, V.G. Pavelyev, M.S. Pshenichnikov, H.J. Bakker, Fem-tosecond midinfrared study of aggregation behavior in aqueous solutions of amphiphilic molecules, J. Chem. Phys. 133 (2010) 164514.

[59] A.A. Bakulin, M.S. Pshenichnikov, H.J. Bakker, C. Petersen, Hydrophobic molecules slow down the hydrogen-bond dynamics of water, J. Phys. Chem. A 115 (2011) 1821–1829.

[60] Y.L.A. Rezus, H.J. Bakker, Observation of immobilized water molecules around hydrophobic groups, Phys. Rev. Lett. 99 (2007) 148301.

[61] The net effect of a solute on the surrounding water dynamics is the product of the TSEV slowdown and of the TSHB slowdown or acceleration. Therefore, strong HB acceptors always slow down water dynamics, but for weak HB accep-tors the net effect depends on the competition between the TSEV slowdown and the TSHB acceleration. At high solute concentration, increased excluded volume effects lead to a slowdown, even for solutes which lead to an acceleration in dilute solutions.

[62] A possible example may be dilute $ClO_4{}^-$ ions, depending on the result of the competition between TSEV and TSHB effects (see Ref. [61]).

[63] Z. Zhang, L. Piatkowski, H.J. Bakker, M. Bonn, Interfacial water structure revealed by ultrafast two-dimensional surface vibrational spectroscopy, J. Chem. Phys. 135 (2011) 021101.

[64] S. Garrett-Roe, P. Hamm, What can we learn from three-dimensional infrared spectroscopy? Acc. Chem. Res. 42 (2009) 1412–1422.