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Non-linear infrared spectroscopy of the water bending mode: Direct experimental evidence of hydration shell reorganization?

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Abstract

The structure and dynamics of liquid water are further studied by investigating the bend vibrational mode of HDO/D₂O and pure H₂O via two-dimensional infrared spectroscopy (2D-IR) and linear absorption. The experimental findings and theoretical calculations support a picture in which the HDO bend is localized and the H₂O bend is delocalized. The HDO and H₂O bends present a loss of the frequency-frequency correlation in subpicosecond time scale. While the loss of correlation for the H₂O bend is likely to be associated with the vibrational dynamics of a delocalized transition, the loss of the correlation in the localized HDO bend appears to arise from the fluctuations/rearrangements of the local environment. Interestingly, analysis of the HDO 2D-IR spectra shows the presence of multiple overlapping inhomogeneous distributions of frequencies that interchange in a few picoseconds. Theoretical calculations allow us to propose an atomistic model of the observed vibrational dynamics in which the different inhomogeneous distributions and their interchange are assigned to water molecules with different hydrogen-bond states undergoing chemical exchange. The frequency shifts as well as the concentration of the water molecules with single and double hydrogen-bonds as donors derived from the theory are in good agreement with our experimental findings.

1 Introduction

Water is one of the most important and studied liquids to date.^{1,2} The structure and dynamics of water have been investigated thoroughly by experiments and theory.³⁻⁵ From the different studies of water, a unified molecular picture of the ultrafast dynamical processes occurring in the liquid has been developed.³⁻⁵ Liquid water consists of an extended and disordered network of hydrogen-bonded molecules that undergoes fluctuations and rearrangements.³⁻⁶ While the water fluctuations involve small atomic motions and the dynamics is on a fem to second time scale, the water rearrangements comprise the making and breaking of hydrogen-bonds and has a characteristic time of a few picoseconds.⁷⁻¹⁴ Evidence of the network fluctuation has been obtained indisputably by two-dimensional infrared (2D-IR) experiments^{11,12,14-17}, but a direct experimental observation of the water

hydrogen-bond exchange, namely transitions between different hydrogen-bond states, has remained elusive. One of the reasons is that most studies have focused on the OH/OD stretch vibrational mode.^{11,12,14-17} While the water stretch mode is very sensitive to its environment¹⁸ and has a large transition dipole magnitude¹⁹, the delocalization of the OH/OD stretch in isotopically pure samples, the ultrafast time scale of the water motions, and the OH/OD stretch sensitivity produce a very broad distribution of stretch frequencies which obscure the observation of network rearrangement.^{11,12,14-17} Moreover, even in isotopically dilute samples where the OH/OD stretches are isolated, no direct experimental evidence of the hydrogen bond exchange has been observed.^{9,11,12,14,17,20,21} The different hydrogen bonded states show large frequency fluctuations, due to the environment, in OH/OD stretch as compared to the mean values for each type of hydrogen bonded state. This large distribution of frequencies could mask the spectral signature of chemical exchange.¹³

Another vibrational mode that has been used to investigate the ultrafast processes of water is the bend mode. The bending mode is the vibrational mode of water with the lowest frequency. In the gas phase, the water bend is located at $\sim 1594\text{ cm}^{-1}$ and it shifts to higher frequencies either in liquid, $\sim 1645\text{ cm}^{-1}$, or in ice $\sim 1670\text{ cm}^{-1}$.²²⁻²⁴ The frequency shift of the water bend towards higher frequencies in stronger hydrogen bond networks²⁵ makes the water bending mode a suitable vibrational probe for studying the hydration structure and dynamics of water. The susceptibility of the water bend to its environment was first presented by Falk in 1984.²² However, few experimental studies involving the vibrational spectroscopy of the water bend have been performed since then²⁶⁻³⁶, mainly due to the smaller transition dipole magnitude and local environment susceptibility of the bend compared to the OH/OD stretch. Although the small sensitivity is in principle a drawback for using the water bend as a vibrational probe, it might provide an opportunity to directly observe and characterize the hydrogen-bond rearrangements in water.

In this study, the ultrafast processes governing the dynamics of the water bend in HDO/D₂O and pure H₂O are investigated by linear absorption and non-linear infrared spectroscopy, namely 2D-IR spectroscopy. Isotopically dilute solutions are used to avoid the creation of vibrational delocalized states^{3,37}, while pure water samples allow us to observe the vibrational dynamics of the H₂O bend when the delocalization of the vibrational transition is possible.

2 Experimental and theoretical methodologies

A Experimental methods

The 2% HDO in D₂O samples were prepared by mixing 5 mg of pure H₂O (18 M Ω resistance) with 0.5g of D₂O (100.0% atom D Across organics). Samples were held between two CaF₂ windows with a 25 μm spacer for the HDO solution and no spacer for pure H₂O.

Linear FTIR spectra were obtained with a Thermo Nicolet 6700 FTIR spectrometer having 0.5 cm^{-1} resolution. All the measurements were done at room temperature.

The 2D-IR photon echo experiment used in these experiments has been previously described in Ref. 38. Briefly, a Ti:Sapphire amplifier coupled to a homemade OPA with a difference frequency generator is used to produce the Fourier transform limited infrared pulses. This IR source delivers 80 fs duration pulses centered at 1470 cm^{-1} with 400 nJ energy. The IR pulses are split into three replicas and their polarization is carefully set by polarizers before the sample. The photon echo signal in the phase matching direction ($-k_1 + k_2 + k_3$) is measured using the box configuration geometry. The signal is heterodyned with a fourth IR pulse (LO) and detected by liquid nitrogen cooled 64 element MCT array detector after dispersion in a monochromator (50 grooves/mm). In all the experiments LO preceded the signal field by ~ 1 ps. The two-dimensional spectra was produced by combining the rephasing (non-rephasing) echo signal which is obtained for the pulses with the wave vector $k_1(k_2)$ arriving at the sample before those with wave vector $k_2(k_1)$. The time parameters for the coherence were a total time interval of 1 ps with a 2 fs step. The waiting time was acquired with 50 fs steps for the first 300 fs, 100 fs from 300 fs to 1 ps, 250 fs from 1 ps to 2.5 ps and 1 ps from 3 ps to 5 ps. To accurately phase the rephasing and non-rephasing parts of the spectrum, the projection of the 2D-IR spectrum was matched by using the projection on ω_t .

B Theoretical methods

The molecular dynamics (MD) simulations were performed using AMBER 11 program package. The extended simple point charge model (SPC/E) force-field was used to model water. The system consists of a water box of ~ 1000 waters. The system temperature was then raised from 0 K to 298 K during a constant volume MD simulation (NVT) of 20 ps with a Langevin thermostat. The NVT step was followed by a 1 ns run at constant pressure (NPT) using a Berendsen barostat ($\tau_{\text{bar}} = 2.0$ ps) to maintain the constant pressure. During this NPT step, the system was checked to achieve constant density. The next run involved a 100 ps constant volume MD (NVT) trajectory after which the temperature control was switched off and a final run of 10 ns under NVE conditions was performed. The production runs were obtained after the latest NVE run by running a 1 ns trajectory at NVE conditions in which each snapshot was recorded every 2 fs. The simulations were performed under periodic boundary conditions using a time step of 1 fs with the SHAKE algorithm to constrain the intramolecular bonds and angles. The long-range electrostatic interactions were treated using the particle-mesh Ewald summation method with a cut-off of 8 Å.

The methodology used here is the same as the one developed and used by Skinner and co-workers in their study of the azide ion.³⁹ To calculate the vibrational frequencies of the water molecules 100 different clusters of water molecules were selected from the MD simulation. The clusters were picked every 10 ps to avoid any possible correlation. The selection criterion for the water in the cluster was defined as all the water molecules with their oxygen atom within the 4.5 Å of the selected water. The SPC/E model treats the water as a rigid body and the geometry does not match the gas phased optimized geometry of water. Thus, the central SPC/E water molecule in the clusters, on which the frequency calculation was performed, was replaced by the optimized structure. The bend coordinate of the geometrically optimized molecule was then moved according to the normalized atomic displacement of the bending mode in a step-wise manner (from -Q to Q in 0.25Q steps,

where Q is the characteristic length of the bending mode displacement $\sqrt{\hbar/(\mu\omega)}=0.1394$ Å), while keeping the center of mass of the water molecule fixed. Finally, for every cluster a series of single point energy calculations were performed, corresponding to the displacements in the bending mode coordinate, at the density functional level of theory with the B3LYP functional and the 6-311++G** basis set (Gaussian 09 software package). This methodology allows us to determine the potential energy of the water bend in a cluster as a function of the bending mode coordinate Q .

To determine the frequency of the bending mode vibration, the single point energies as function of the normal mode coordinate were fit to a harmonic oscillator function of the form: $V(Q) = k(Q - Q_0)^2$, and the harmonic frequency was found by $\omega = \sqrt{2k/\mu}$.

3 Results

The IR absorption spectrum of HDO in the bending mode region with background subtracted shows a broad absorption band (full width at half maximum of ~ 80 cm^{-1}) centered at 1458 cm^{-1} that is slightly asymmetric at the low frequency side (Figure 1, top panel) and cannot be modeled with any single peak function (see Electronic Supplementary Information, ESI[†]). The band is well modeled with two Gaussian functions with maxima located at 1437 cm^{-1} and 1469 cm^{-1} and an area ratio of $\sim 1:2$, respectively. Note that the full width at half maximum of the two fitted bands (1437 cm^{-1} and 1469 cm^{-1}) differs less than 2 cm^{-1} . The FTIR spectra of the H_2O bending mode (Figure 1, bottom panel) shows an absorption band located at 1644 cm^{-1} with a full width at half maximum of ~ 85 cm^{-1} . In contrast with the HDO bend, the H_2O bend is slightly asymmetric towards the high frequency side of the spectrum. This absorption band is well described with a pair of Lorentzian functions centered at 1641 cm^{-1} and 1675 cm^{-1} and a ratio of areas of $\sim 1:6$ (see ESI[†]). While the bend absorption band for H_2O can be modeled in terms of the different component of the total dipole moment³⁷, the unsymmetrical shape of the HDO bend band is most likely caused by the presence of different and slowly exchanging inhomogeneous distributions of water bend states (see below).

The 2D-IR spectra of the water bending for HDO and H_2O with pulses having parallel polarization ($\langle \text{XXXX} \rangle$) as a function of the waiting time (T_w) are presented in Figure 2. Due to its small anharmonicity, at $T_w = 0$ ps the 2D-IR spectrum of the water bending mode of both samples is composed of two overlapping peaks. The negative peak (blue in Figure 2) corresponds to the excited state absorption signal ($v=1 \rightarrow v=2$) and the positive peak (red in Figure 2) to the ground state bleach ($v=0 \rightarrow v=1$) and the stimulated emission ($v=1 \rightarrow v=0$) signals. Also, at zero waiting time the 2D-IR spectrum of either HDO or H_2O shows the positive and negative peaks elongated along the diagonal ($\omega_t = \omega_r$, dashed line in Figure 2) and each having the same asymmetric shape as the linear absorption spectrum (Figure 1), i.e., an asymmetry at the low(high) frequency side of the 2D-IR spectrum for HDO(H_2O).

[†]Electronic Supplementary Information (ESI) available: procedures for the computation of the peak-shift, cross-peak signals, and diagonal traces; background subtraction for the computation of the linear IR absorption; anisotropy of the transient grating signal of H_2O ; vibrational modes of a water dimer; simulation of the 2D-IR spectrum for two overlapping transitions; the histogram of the H_2O bend frequencies as a function of the number of hydrogen-bonds; and the effect of water grating signal in the 2D-IR spectrum.

Moreover, at $T_w = 0$ ps both samples have positive peaks that spread over approximately the same frequency range in ω_t (i.e., $\sim 100 \text{ cm}^{-1}$), but the anti-diagonal width of their positive peaks is clearly broader for H_2O than for HDO.

As T_w increases, the two water samples show completely different spectral shape evolutions. During $T_w < 0.5$ ps, the 2D-IR spectra of HDO do not present a significant change in the tilt and shape of the diagonal peaks, while the diagonal peaks of H_2O acquire a full upright shape. Moreover, in this time interval the 2D-IR spectrum of HDO shows a change in the apparent “separation” between the positive and negative peaks very noticeable at the high frequency side of the transition ($\omega_t \sim 1480 \text{ cm}^{-1}$), which is not observed in the 2D-IR spectrum of H_2O . In addition, the maximum of the 2D-IR spectra positive peak in H_2O shifts by $\sim 12 \text{ cm}^{-1}$ from its initial position at $T_w = 0$ ps, but the maximum of the HDO positive peak does not exhibit any significant variation in its frequency position. The shift in the peak maximum or its lack of can be easily observed in the diagonal traces obtained from the 2D-IR spectra (see Figure 4).

At longer waiting times ($T_w > 0.5$ ps), the peaks of HDO suffer severe spectral changes which leave the positive peak with a square-like shape and a negative peak down-shifted by $\sim 50 \text{ cm}^{-1}$ in ω_t whereas no significant changes in the diagonal peaks of H_2O are observed. However, the 2D-IR spectra of H_2O at $T_w > 0.5$ ps displays a new pair of positive and negative peaks downshifted by more than 100 cm^{-1} in ω_t from the diagonal peaks. This set of new peaks has an invariant shape and a constant relative intensity with respect to the diagonal peak after the first picosecond of waiting time. Note that no significant change in the positions of the 2D-IR positive peak is observed for $T_w > 0.5$ ps in either of the samples.

In addition to the time evolution of the 2D-IR spectral features, the spectral amplitudes of the 2D-IR diagonal peaks also present notoriously different dynamics for both samples (Figure 3). The signal strength of the positive diagonal peak for both samples does not have the simple exponential decay dynamics as expected from the vibrational lifetime. As is presented in the next section, the complex dynamics of the signal's amplitude arise from the decay of the vibrational population and the growth of the water thermal grating.

4 Discussion

A Population relaxation dynamics

Analysis of the positive peak spectral amplitudes shows two different population dynamics for the samples: a biexponential decay for the HDO bend and a decay and a rise for the H_2O bend. While the HDO peak maximum of the first 0.4 ps can be well modeled with a single exponential function having 0.41 ± 0.08 ps characteristic times (dashed blue line of Figure 3), the H_2O transient signal can be modeled with a single exponential decay with a time constant of 0.20 ± 0.04 (blue line of Figure 3). These fast exponential decays have been previously assigned to the vibrational relaxation of the population of the first excited state and they are in agreement with previous experimental values.^{30-32,36} For either sample, the overall transient population is well modeled with the sum of an exponential decay and an exponential rise of the form $f(t) = A(1 - \exp(-kt)) + B \exp(-kt)$ (red lines of Figure 3). The single rate constant, k , required to model the data is found to be 0.35 ± 0.08 for HDO and

0.20 ± 0.10 for H_2O . While the decay component of the signal can be directly assigned to the vibrational lifetime of the bend first excited state, the component giving rise to the positive signal can be assigned to various photo-induced processes.

Unlike the transient signal observed by IR pump-probe spectroscopy where changes in the index of refraction of the combination (librations plus bends) band of D_2O for HDO and libration overtone band for H_2O produce changes in the signal, the non-linear signal observed in the 2D-IR spectrum can only arise from those processes that fulfill the phase matching direction condition.⁴⁰ Two processes that can give rise to a signal in the non-linear spectrum are the water thermal grating⁴¹ and the generation of a hot vibrational ground state^{27,30,31}. However, the spectral signatures of these two processes are expected to be significantly different.

The water thermal grating is a signal generated by the background absorption of the pump pulses (k_1 and k_2) with a spatial periodicity of $k_2 - k_1$.⁴¹ The spatial modulation created by the pump pulses (k_1 and k_2) diffracts the k_3 pulse in the phase matching direction $-k_1 + k_2 + k_3$. The water thermal grating grows when the time difference between the pump and the probe pulses (T_w) is increased because the absorbed energy by the background (the combination band of D_2O for HDO and libration overtone band for pure H_2O) is redistributed to all molecular states resembling those of the thermal distribution.⁴¹ Moreover, the response of the solvent is impulsive giving to the water thermal signal a bandwidth equal to that of the excitation pulse, i.e., spread over the whole 2D-IR spectrum. In contrast, the creation of a hot vibrational ground state is produced when the excited molecules do not have the possibility to redistribute the excitation energy with the surroundings in the short time period after the light interaction. Thus, the spectral signature of a “hot” vibrational ground state is expected to be the same as that observed by heating the samples, i.e., a shift of the frequency of the transition. In the case of the bending mode, the frequency shift due to a “hot” ground state yields a red-shift of the transition frequency.^{27,30,31} The creation of water molecules with a “hot” vibrational ground state is directly observed in the 2D-IR spectra of H_2O where a set of off-diagonal peaks located between 1500 and 1575 cm^{-1} appear for waiting times longer than 1 ps (Figure 2). No clear and direct indication of the presence of “hot” HDO molecules is deduced from the 2D-IR spectra. Although the spectral signature of the “hot” vibrational state in HDO is not directly observed either due to an overlap with other spectral features or because it appears in a different region of the 2D-IR spectrum, it is clear from the 2D-IR spectra of H_2O (Figure 2) that its contribution is not significant. Thus, the decay and rise dynamics of these samples is most likely due to the vibrational lifetime and transient grating signals, respectively. Moreover, the rate constants for the population relaxation times and the water thermal grating dynamics are in good agreement with previously published experimental values of pure and isotopically dilute water.^{30,41-43} Note that the energy of the IR pulses cannot increase the temperature of the sample by more than $\sim 0.6\text{ K}$ under the experimental conditions used for this study. Thus the central frequency of the water bend, of either HDO or H_2O , will not be significantly affected by the heat imposed by the IR pulses.¹⁹

B Nature of the bend transitions

Due to the small transition dipole, it has been theorized that the water bending mode should be a localized transition.³⁴ Although the localized vibrational transition describes correctly the non-linear response of HDO bend, it appears that the vibrational experimental data of H₂O is not well characterized by a localized vibrational transition. Firstly, the anisotropy of the transient grating signal⁴⁴ of the H₂O bend shows a fast decay (see ESI[†]). Secondly, there is a significant change in the central frequency of the positive peak in the 2D-IR spectrum (red peak of Figure 2) during the first 0.5 ps of waiting time in H₂O. Thirdly, it appears that at $T_w = 0.2$ ps the 2D-IR spectrum of water contains a cross-peak (dash circle in Figure 2). Finally, the linear absorption spectrum of HDO and H₂O present an opposite asymmetry. Although one could explain the anisotropy decay and the observed changes in the 2D-IR spectra of H₂O by a simple energy transfer model, it is very hard to reconcile the position and asymmetry of the positive peak in the 2D-IR for $T_w < 0.25$ ps and the linear absorption line shape with the energy transfer picture.

If the H₂O bend vibrational modes were localized, one would expect that the diagonal trace of the 2D-IR spectrum at $T_w = 0$ ps will show the same distribution of frequencies as the concentration of hydrogen bonded water molecules; i.e., a band with an asymmetry towards its low frequency part and with its maximum at the high frequency side (see molecular mechanism section and ESI[†]). This type of asymmetric distribution is observed for HDO in the linear and non-linear spectra. In contrast, neither the linear spectrum nor the 2D-IR spectra of H₂O show an asymmetry towards the high frequency side, except for waiting times longer than 0.2 ps.

The change in the central frequencies of the 2D-IR spectra can be simply observed in the diagonal slices of the non-linear spectra for $T_w < 0.25$ ps (Figure 4 and see ESI[†]).

Figure 4 shows that the H₂O bands do not maintain the same frequency positions of $T_w = 0$ ps, while the HDO bands do. This experimental data indicates that another underlying vibrational process, such as localization, might be taking place in H₂O. Note that during this waiting time interval, the effect of “heating” is not significant.

The initial low frequency position of positive peak maxima in the 2D-IR spectra of H₂O at $T_w < 0.25$ ps compared to $T_w = 2$ ps implies that if the different H₂O bending modes are coupled, their coupling constant must be negative and on the order of ~ 10 cm⁻¹. To corroborate the sign and value of the coupling constant, a DFT calculation on a water dimer was performed. The calculations show that the water dimer has two delocalized vibrational transitions at 1611 cm⁻¹ and 1630 cm⁻¹ in which the low frequency transition has twice the intensity of the high frequency transition (see ESI[†]). This theoretical calculation predicts that the coupling constant is indeed negative and close to 10 cm⁻¹ as observed experimentally, and provides further support to the delocalization of the H₂O bend in pure water.

Here, the experimental data suggests that the bend mode of H₂O is delocalized and that changes of the 2D-IR spectra at early waiting times arise from the localization of the initially delocalized vibrational states. Although previous reports also contradict the possible

delocalization^{27,45}, a recent theoretical study of the H₂O bend mode concluded that the bend mode is delocalized³⁷. To reconcile our experimental findings with previous studies, a detailed theoretical study of H₂O bend is needed and this is beyond the scope of this study.

C Spectral diffusion

Since the 2D-IR spectrum represents the correlation between the pumped (ω_p) and the probed (ω_r) bend frequencies, the peak elongation along the diagonal at $T_w = 0$ ps for the HDO and H₂O bending peaks in the 2D-IR spectra confirms that the pump and probe frequencies are correlated when no time is given for their evolution.⁴⁰ As T_w increases, the strong variations of the environment causes fluctuations in the initially excited bending frequencies producing a loss of the correlation between the pump and probe frequencies. For overlapping positive and negative peaks like the bending mode, the loss of correlation is usually observed as the 2D-IR peaks acquiring an upright shape, i.e., more elongated along ω_r .⁴⁶⁻⁴⁹ Although the time evolution of the H₂O 2D-IR spectra clearly shows that the positive and negative peaks acquire a vertical elongation within 0.5 ps of waiting time (Figure 2), the tilt of the HDO 2D-IR spectra remains almost unchanged in the same time window.

The loss of correlation, or equivalently the decay of the frequency-frequency correlation function (FFCF), can be quantified by measuring different spectral properties of the 2D-IR spectrum, such as the slope of the zeroth contour plot⁵⁰, the central line slope⁵¹, etc. Here, the center line slope (CLS) of the positive peak is used to characterize the FFCF correlation times because it has been shown that it can be used in the presence of multiple transitions.⁵² As previously stated, the 2D-IR spectrum of HDO does not show any fast time-evolution of the peaks tilt for $T_w = 0.5$ ps while the diagonal peaks of the spectrum of H₂O does (Figure 2). This difference in the time evolution of the 2D-IR spectral shape is corroborated by measuring the CLS dynamics at the frequencies within ± 10 cm⁻¹ of the absorption band maximum of the water bend (Figure 5). The time evolution of the CLS shows that the dynamics of the FFCF for HDO is slower than H₂O. The characteristic times measured by modeling the CLS with exponential decay functions are 1.2 ± 0.2 ps for HDO and 0.15 ± 0.03 ps for H₂O.

The fast dynamics of the FFCF (CLS) of the H₂O bend can correspond to that of a vibrational delocalized transition (see previous section) and not to a single localized vibrational transition. In fact, in recent theoretical work, Saito and co-workers have assigned the observed dynamics to a strong intramolecular coupling combined with intermolecular hydrogen bond dynamics.⁵³ In contrast, the slow time evolution of HDO's CLS is clearly unexpected given that the ultrafast fluctuations and rearrangements of the hydrogen-bond network should produce a fast loss of the correlation of the initially pumped frequencies. In this case, the slow dynamics of the CLS is not attributed to a slow correlation decay, but to the presence of multiple and slowly exchanging distributions of frequencies produced by the different inhomogeneous distributions of water bends.⁴⁸

To demonstrate that the lack of time evolution of the slope is most likely arising from the presence of multiple distributions of frequencies, the dynamics of the integrated photon-echo peak-shift is characterized (Figure 5 and see ESI[†] for details). Similar to the slope, the

time-evolution of the peak-shift quantifies the correlation time of the FFCF.^{54,55} The peak-shift dynamics determined from the 2D-IR spectra show that both samples have similar dynamics (Figure 5) with a very fast time evolution that is well modeled with a sum of exponential functions of the form: $(A_1 \exp(-t/\tau_{1c}) + A_2(-t/\tau_{2c}))$. The decay times are $\tau_{1c} = 0.30 \pm 0.05$ ps ($A_1 = 76 \pm 6$) and $\tau_{2c} = 7 \pm 7$ ps ($A_2 = 6 \pm 4$) for HDO and $\tau_{1c} = 0.24 \pm 0.08$ ps ($A_1 = 50 \pm 10$) and $\tau_{2c} = \infty$ ps ($A_2 = 3 \pm 3$) for H₂O. Note that the peak-shift for either sample also exhibits a damped oscillation that has not been considered in the fit. The peak-shift ultrafast dynamics in both samples indicates and corroborates that the HDO as well as H₂O molecules are strongly perturbed by the fluctuations and rearrangements of the solvation shell. In the case of H₂O, the correlation time predicted by the CLS and the peak-shift show good agreement suggesting that the difference between these two observables in HDO is caused by other factors, such as the presence of multiple and overlapping inhomogeneous transitions. Moreover, a very recent theoretical work predicts two FFCF correlations times of 70 and 120 fs for the peak-shift and slope dynamics of H₂O, which agree well with the experimental values of this work.⁵³ Although no experimental or theoretical measurement of the FFCF times of HDO in D₂O is available, the measured characteristic times of the peak-shift are on the same time scale as those observed for the OD or OH stretch.^{11,12,14-17} Overall, the fast and slow frequency correlation times observed from the peak-shift dynamics and the slow evolution of the CLS strongly suggest that the HDO bend band is composed of a set of slowly exchanging inhomogeneous distributions in which the slow dynamical component of the peak-shift corresponds to the exchange between the different distributions. Moreover, the simulation of the 2D-IR with a set of two vibrational transitions having fast correlation times corroborates that the peak-shift will show a fast correlation time while the CLS will present a decay with a much slower characteristic time irrespective of the range of frequencies used in the determination (see ESI[†]). This provides further support to the present interpretation of the experimental data.

D Heating and chemical exchange

To evaluate whether the time changes in the 2D-IR spectra, observed for HDO at waiting times longer than 1 ps, correspond to a heating effect or a chemical exchange, the difference between the absolute value of the spectra at $T_w = 2$ ps and $T_w = 0.5$ ps and $T_w = 2$ ps and $T_w = 1$ ps are analyzed. In Figure 6, the difference of absolute value of the 2D-IR spectra, $|S(\omega_r, T = 2 \text{ ps}, \omega_d)| - |S(\omega_r, T = X \text{ ps}, \omega_d)|$ of HDO and H₂O show two types of features: positive (red) and negative (blue). While the red features correspond to parts of the spectrum that increase their intensity with waiting time, the blue represent those regions that decrease with T_w . In the sets of difference spectra, the observed positive and negative features change their amplitude, but not their location (Figure 6). For the H₂O sample, a region with positive amplitude is seen in the central part of the spectrum and two negatives on its left and right sides. While the positive feature is produced by an increase in the peak intensity with waiting time as seen in the diagonal peak amplitude (Figure 3), the negative features are a consequence of the change in the spectral shape of the 2D-IR spectra probably caused by spectral diffusion and/or heating. Moreover, it is the change of the spectrum, which is broad in ω_r and towards the low frequency side of the diagonal that strongly suggests a thermal signal.

In the case of the HDO spectra, the difference spectra show the opposite behavior, i.e., a region with negative amplitude in the center of the spectrum and section with positive on both sides. It is straightforward to assign the negative feature of the difference spectrum to the change in the diagonal peaks due to the lifetime. However, the positive features of these two difference spectra, such as that located at $\omega_{\tau} \sim 1450 \text{ cm}^{-1}$ and $\omega_{\tau} = 1350 \text{ cm}^{-1}$, increase with waiting times and can be assigned to processes like the growth of the water thermal signal. The peak intensity dynamics shows that the thermal spectral signal is fairly constant after $\sim 1 \text{ ps}$ (Figure 3), but the positive features are still observed in the difference spectrum computed between $T_w = 2 \text{ ps}$ and $T_w = 1 \text{ ps}$ (Figure 6B). Thus, the regions with positive amplitude cannot be simply assigned to a heating effect. Moreover, these two signals are localized in small areas of the spectrum, which is unexpected for a signal arising from water thermal grating where the spectral response should cover the bandwidth of the pulse.⁴¹ In addition, a previous pump-probe study of HDO in D_2O showed that the signal at long waiting times is exclusively composed of HDO bend; i.e., the spectral signatures of the D_2O librations are not observed.³⁰ Finally, the presence of hot vibrational states cannot explain the positive feature observed in the right side of the difference spectra since its shift is to high frequencies which is opposite to what has been observed experimentally in this and previous works. All these results suggest that the features observed in the 2D-IR spectra at $T_w > 1 \text{ ps}$ are cross-peaks arising from chemical exchange.

The presence of slowly exchanging distributions of water molecules is also supported by the linear and non-linear spectra of HDO. In the FTIR, the HDO bend band is asymmetric (Figure 1). Even though the asymmetry of the linear absorption band of the water bend in HDO can also be produced by a frequency-dependent cross section of the bend transition similar to what is observed in the OH/OD stretch⁵⁶, early studies on the temperature dependence of the bend linear absorption have demonstrated that the oscillator strength of the bending mode in pure and isotopically dilute samples is virtually unaffected by changes in temperature and/or hydrogen bond strength.^{57,58} Thus, it is unlikely that the asymmetric shape of the band is due to a frequency dependence of the oscillator strength. In the non-linear spectrum, the presence of multiple inhomogeneous distributions of frequencies that exchange with waiting time in the HDO bend is also supported by the appearance and growth of cross-peaks in the 2D-IR spectra with T_w . The cross-peaks, product of the chemical exchange between vibrations in the different inhomogeneous distributions, produce not only a significant change in the apparent “separation” between the positive and negative peaks (most evident at $\omega_{\tau} = 1490 \text{ cm}^{-1}$), but they also create a protuberance at the high(low) frequency side of the negative(positive) peak which is evident in the HDO 2D-IR spectra at $T_w = 0.5 \text{ ps}$ (Figure 2). The growth of cross-peaks also causes the positive peak to acquire a square-like shape at $T_w > 1 \text{ ps}$. The square-like spectral signature has been seen in many systems undergoing chemical exchange and corresponds to the cross-peaks generated by the back and forward chemical exchange processes.^{40,59,60} Moreover, the 2D-IR spectral features that give the square-like shape to the positive peak of the HDO bend at $T_w = 2 \text{ ps}$ cannot be removed by cutting the 2D-IR signal in the first 100 fs of τ time where bulk of the water thermal grating signal is located (see ESI[†]).⁴¹

The occurrence of the cross-peaks is also observed by computing the difference between the normalized real absorptive spectra at $T_w = 0.5 \text{ ps}$ and $T_w = 2 \text{ ps}$ (Figure 7). The difference

spectrum shows that the two positive features seen in the difference of the absolute value spectra (Figure 6) correspond to two positive cross-peaks each with its an harmonically shifted negative peak located at $\omega_t = 1457 \text{ cm}^{-1}$, $\omega_t = 1402 \text{ cm}^{-1}$ and $\omega_t = 1441 \text{ cm}^{-1}$, $\omega_t = 1507 \text{ cm}^{-1}$. The two cross-peaks are assigned to the frequency exchange between the frequencies close to the peak maximum at $T_w = 0 \text{ ps}$ and low and high frequency vibrational transitions of the bend absorption band. Moreover, the difference spectrum of Figure 7 shows that not only do these cross-peaks arise from two different subsets of frequencies within the central part of the diagonal peak, but they also have different intensities giving a strong indication that the cross-peaks are due to the exchange between two different inhomogeneous distributions of bend frequencies that have different concentrations. In addition, the dynamics of these two cross-peaks evaluated at $\omega_t = 1420 \text{ cm}^{-1}$, $\omega_t = 1520 \text{ cm}^{-1}$ and at $\omega_t = 1480 \text{ cm}^{-1}$, $\omega_t = 1320 \text{ cm}^{-1}$ (Figure 7 and see ESI[†] for details), shows that both cross-peaks grow with T_w and their dynamics is well modeled with an exponential rise of the form: $S_{\text{cross}} = A(1 - \exp(-T_w/\tau))$. The characteristic times and amplitudes for the left and the right cross-peaks are $1.5 \pm 0.3 \text{ ps}$ and $2.2 \pm 0.9 \text{ ps}$, and 1.9 ± 0.1 and 0.7 ± 0.1 , respectively. Note that if the cross-peaks were contributions from the water thermal grating they would have a characteristic time of $\sim 0.3 \text{ ps}$ as shown in the previous sections. In addition, the characteristic times determined from the dynamics of the cross-peak show good agreement with the experimental and theoretical values of the time scales associated with hydrogen bond making and breaking.^{11,17,21,61,62}

E Molecular mechanism

The bend mode has the opposite frequency shift when compared with the OH/OD stretch where high(low) frequency side of the stretch band corresponds to those configurations with weak/less (strong/more) hydrogen-bond interactions.^{22,34} The assignment of the low and high frequency sides of the bend absorption band in HDO to the different hydrogen-bonded states of the water molecules provides a reasonable explanation for the HDO 2D-IR spectra since the cross-peak at the right(left) side of the spectrum corresponds to water molecules that at a later time, T_w , will gain(lose) hydrogen-bond partners. Also the mechanism explains the difference in cross-peak intensity given that the cross-peaks arising from the different water hydrogen-bonded states will depend on the probability of water being in those states.⁵⁹ Moreover, the rise times of the cross-peaks are in good agreement with the time scale of the hydrogen-bond reorganization.^{11,62} Thus, the molecular mechanism that could explain the cross-peaks is the chemical exchange between different HDO molecules with different hydrogen-bond environments. Although two HDO molecules at hydrogen-bond distance can produce cross-peaks in the 2D-IR spectrum by exciton formation and energy transfer, the probability of having one or more HDO molecules in the hydration shell is only ~ 8 percent (assuming an average of 4 water molecules at the hydrogen-bond distance⁶³) making the spectral signatures of the exciton very small. Therefore, it is very unlikely that the HDO cross-peaks are due to the interaction between two HDO bend modes and they are most likely caused by other mechanism, such as the chemical exchange between water with different number of hydrogen-bond partners.

To investigate whether the chemical exchange observed in the 2D-IR is produced by the different hydrogen-bond states of HDO, the bend frequency of water molecules in different

solvation shell arrangements is studied theoretically. The bend frequencies, computed for a water molecule with 100 different solvation shells, show a distribution with an average frequency of 1647 cm^{-1} and a standard deviation of 17 cm^{-1} that is slightly asymmetric on the low frequency side (see Figure S7 of ESI[†]). The calculated frequencies predict that the water bend has an average blue shift of $\sim 45\text{ cm}^{-1}$ due to solvation and is in good agreement with the experimental value of $\sim 49\text{ cm}^{-1}$.²² When the individual bend frequencies are plotted as a function of the total number of hydrogen-bonds, defined by $r\text{-}\beta$ of Ref. ⁶³, weak and positive correlations of $R = 0.40$ and $R = 0.15$ are observed (Figure 8) for the donated and accepted hydrogen-bonds, respectively. This small correlation is expected since the bend frequency distributions for the different number of hydrogen-bonds are broad and show significant spectral overlap for either hydrogen-bond case (see Figure S8 of ESI[†]). In addition, the mean frequency of the distributions as a function of the number of hydrogen-bonds predicts an increase of 15 cm^{-1} and 4 cm^{-1} in the average frequency per added hydrogen-bond (Figure 8) for the donor and acceptor cases, respectively. The small sensitivity of the average bend frequency as a function of the accepted hydrogen-bonds and the small correlation between frequencies and number of accepted hydrogen-bonds indicate that the bend vibrational frequency is most affected when the water molecule acts as a donor. These computed parameters agree with the water bend motion being mainly defined by the two hydrogen atom displacements.⁶⁴ Also, the simulations show that the probability of having a water molecule with two, one, and zero hydrogen-bond partners through its hydrogen atoms (donor) is 0.61, 0.34, and 0.05, respectively.

The theory predicts that if the chemical exchange observed in the 2D-IR spectra is due to a change in the number of hydrogen-bond partners, the cross-peaks for both the water molecule going from two hydrogen-bonds to one ($2\text{HB} \rightarrow 1\text{HB}$) should be very close to the maximum of the transition in ω_{p} , but the $1\text{HB} \rightarrow 2\text{HB}$ and $0\text{HB} \rightarrow 1\text{HB}$ cross-peaks should be red shifted by 15 cm^{-1} and 30 cm^{-1} , respectively. Furthermore, the difference in the probability of having the different hydrogen bond partners should produce a difference in intensity of the cross-peaks since the cross-peak intensity directly depends on the probability (concentration) of species that are exchanging.⁵⁹ The experimental data agrees with this theoretical model as the cross-peak corresponding to $1\text{HB} \rightarrow 2\text{HB}$ ($\omega_{\text{t}} = 1441\text{ cm}^{-1}$, $\omega_{\text{t}} = 1507\text{ cm}^{-1}$) is red shifted by 16 cm^{-1} in ω_{t} with respect to the diagonal peak, 2HB , ($\omega_{\text{t}} = 1457\text{ cm}^{-1}$, $\omega_{\text{t}} = 1402\text{ cm}^{-1}$) and the $2\text{HB} \rightarrow 1\text{HB}$ cross-peak ($\omega_{\text{t}} = 1457\text{ cm}^{-1}$, $\omega_{\text{t}} = 1402\text{ cm}^{-1}$). Moreover, the experimental amplitude of the cross-peaks derived from their dynamics (Figure 7) shows a ratio of $[1\text{HB} \rightarrow 2\text{HB}]/[2\text{HB} \rightarrow 1\text{HB}] = 0.7/1.9 = 1/2.7$ which is in excellent agreement with the theoretical value of 1:1.8. In addition, if the bend linear absorption is fitted with two Gaussian functions centered at the locations of the two cross-peaks (1437 cm^{-1} and 1469 cm^{-1}), a ratio of 1:1.7 is observed for the area of the low frequency to the high frequency Gaussian (Figure 1 and ESI[†]). Thus, the match between experiment and theory suggests that the molecular mechanism responsible for the 2D-IR cross-peaks is the chemical exchange between water molecules with different number of donated hydrogen-bonds.

Summary

To summarize, the analysis of the two dimensional infrared spectra of the HDO in D₂O and pure H₂O shows that the water bend is sensitive to the fluctuations due to rearrangements of the water environment. The loss of the FFCF measured from the photon-echo signals shows two ultrafast characteristic indicating that the fluctuations as well as reorganization of the hydration shell are on that time scale. The fast FFCF correlation time of H₂O are not easily assigned to the fluctuations of the environment because they most likely arise from vibrational processes related to delocalized transitions, such as localization. In contrast, HDO in D₂O, where the resonant energy transfer is minimized, also shows very fast FFCF correlation times which are associated with the hydrogen bonded network fluctuation and reorganization. Moreover, the network reorganization of the solvation shell is observed directly as cross-peaks in the 2D-IR spectrum which grow with characteristic times of a few picoseconds in agreement with the time scale of making and breaking of hydrogen bonds. A ratio of the concentration of species with a single and double donor hydrogen-bond of 1:2.7 is deduced from the experimental data. Molecular dynamics simulations and calculations of the bend frequency of water clusters support the proposed mechanism.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

FTIR spectra of HDO in D₂O and H₂O in the bend region. Top panel and bottom panels show the HDO and H₂O bend, respectively. The black open squares represent the bend absorption spectrum, with solvent background subtracted for HDO, whereas the blue line represents a model fit with a two peak functions (red dotted line and green dashed lines) as described in the text. Inset on the upper panel shows the absorption spectrum in the region of the HDO bend (see ESI[†]). The black line in the H₂O linear absorption spectrum corresponds to the “background” (see ESI[†]).

Figure 2.

Real part absorptive 2D-IR spectra of in the bending region of HDO in D₂O and pure H₂O. 2D-IR spectra for the <XXXX> pulse polarizations at different waiting times: 0, 0.1, 0.2, 0.5, 1, and 2 ps. Black dashed line corresponds to the diagonal ($\omega_t = \omega_\tau$). The dashed circle marks a possible cross-peak.

Figure 3.

Peak amplitude of the 2D-IR spectra as a function of waiting time. Top and bottom panels show the time evolution of the diagonal signal with waiting time, T_w , for HDO and H₂O, respectively. The black open circles squares correspond to the signal of the maximum of the positive peak normalized to zero waiting time, whereas the solid red and the dashed blue lines are the fit with exponential functions as described in the text.

Figure 4.

Diagonal slices passing through the maximum of the 2D-IR spectrum. Top and bottom panel shows the diagonal slices of H₂O and HDO for the $T_w = 0.25$ ps, respectively. The depicted waiting times are 0 ps, 0.05 ps, 0.1 ps, 0.15 ps, 0.2 ps, and 0.25 ps from top to bottom, respectively.

Figure 5.

Time evolution of the spectral diffusion metrics for the HDO and H₂O samples. Top and bottom panel exhibits the CLS and integrated photon echo peak-shift extracted from 2D-IR data as a function of waiting time. The solid squares and open circles correspond to the HDO and H₂O samples, respectively. The red lines correspond to the fits with exponential functions as described in the text.

Figure 6.

Difference between the absolute value spectra at different waiting times. The left and right columns correspond to the HDO and H₂O samples, respectively. Top panels (A and C) and bottom panels (B and D) correspond to the difference absolute value spectra between $T_w = 2$ ps and $T_w = 0.5$ ps and $T_w = 2$ ps and $T_w = 1$ ps.

Figure 7.

2D-IR spectrum time evolution of the cross peaks. The 2D-IR spectrum of the cross-peaks is calculated as the difference between the normalized absorptive 2D-IR spectrum at $T_w=0.5$ and $T_w=2$ ps. The dashed circles correspond to the positions used to characterize the cross-peaks dynamics as indicated in the text. The two bottom panels show the relative magnitudes of the cross-to-diagonal peak ratio ($|S_{\text{xpeak}}|/|S_{\text{dpeak}}|$) versus waiting time T_w in the bleach and stimulated emission region (middle panel) and in the new absorption region (bottom panel). The black squares are the experimental values and the red lines correspond to their fits with an exponential rise as described in the text.

Figure 8.

The individual and mean water bending frequencies as function of the number of hydrogen-bonds. Top panel and bottom panels represent the frequencies for the H₂O as an acceptor and donor, respectively. The black squares and the red circles represent the individual vibrational frequencies and their average, respectively. The dashed line shows the linear fit of the mean frequencies for those distributions with more than 10% probability of occurring.