

Water dynamics: dependence on local structure probed with vibrational echo correlation spectroscopy

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Abstract

Ultrafast infrared vibrational echo correlation spectroscopy with full phase information of the entire O–D stretching band of HOD in H₂O and molecular dynamics simulations are employed to investigate water dynamics. The wavelength dependence of the measured dynamics demonstrates that different hydrogen bonded water species are subject to distinct ultrafast (~100 fs) local fluctuations and essentially identical slower (0.4 ps to ~2 ps) structural rearrangements. Simulations provide insights into the nature of the very fast and slower dynamics. The results also show that the theoretical methods that are widely used in the description of nonlinear optical experiments need to be advanced to adequately describe water dynamics.

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1. Introduction

Water is ubiquitous in nature. It has profound effects on diverse fields of science from astronomy to zoology. The properties of liquid water are dominated by the hydrogen bonds that form among water molecules. The hydrogen bonds produce structured networks of water molecules that are responsible for water's unique properties. The networks are dynamic. Long (weak) hydrogen bonds become short (strong) bonds and vice versa. A water molecule can make zero to four hydrogen bonds that are constantly being formed and broken. The weakening and strengthening, breaking and forming of hydrogen bonds occur over a range of time scales. The constantly changing local structures of water hydrogen bond networks permit water to accommodate an incredibly wide array of chemical processes, making water the most important liquid on Earth.

The measurement of hydrogen bond network dynamics is the gateway to understanding water. The knowledge of the full dynamics of the hydrogen bond

networks is essential to construct meaningful water models that can be applied *inter alia* for simulations of protein folding [1,2], ion hydration [3] and technically important polymerization reactions [4].

Here we present ultrafast infrared vibrational echo correlation spectroscopy (VECS) experiments [5,6] combined with water simulations [7–9] to examine water hydrogen bond network dynamics. We find frequency dependent dynamic linewidths due to fast local fluctuations of the hydrogen bond network. The experiments and simulations look at the time evolution of the hydroxyl stretching frequency (the OD stretch of HOD in H₂O), which acts as a local probe of the structural evolution of the water network. The frequency of the hydroxyl stretch is lowered (red shifted) when water makes a hydrogen bond [10,11]. Stronger hydrogen bonds cause a greater red shift of the hydroxyl oscillator frequency than weaker hydrogen bonds [12]. More hydrogen bonds to a water molecule cause a larger red shift than fewer hydrogen bonds [10,11]. As the hydrogen bond network structure evolves in time, the strength and number of hydrogen bonds change, which in turn causes the water oscillators' frequencies to change.

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VECS measures the time evolution of the oscillators' frequencies, and therefore, the time evolution of the hydrogen bond network structure. To understand how this is done, consider a single water molecule hydroxyl oscillator. At $t = 0$, it will have a particular frequency, $\omega(0)$. As the local H-bond structure changes (bonds strengthen and weaken, form and break), the frequency will change. At long time, independent of its starting frequency the oscillator can have any frequency in the entire broad hydroxyl stretch absorption spectrum, because it has lost memory of its starting frequency (structure). A measure of the frequency evolution, and therefore the structural evolution, is the frequency–frequency correlation function (FFCF). The FFCF is related to the probability that an oscillator with initial frequency $\omega(0)$ still has the same frequency at time t later, averaged over all starting frequencies. Vibrational echo experiments make the FFCF an experimentally observable quantity [13]. The FFCF is the basic input into time dependent diagrammatic perturbation theory that is used to calculate non-linear optical experimental observables in general [13] and vibrational echo signals in particular [7].

In an ultrafast one-dimensional vibrational echo decay experiment [14–16] or in a one dimensional vibrational echo peak shift experiment [17,18], all wavelengths contribute to the observables. The importance of VECS is that it is a multidimensional method that provides an extra frequency dimension in a manner akin to multidimensional NMR [19]. The two dimensional nature of the correlation spectra makes it possible to examine whether different regions of the hydroxyl stretching band (different water structures) have different dynamics, and if so, to determine on what time scales the differences occur. The two-dimensional correlation spectra also make it possible to test the validity of water simulations by simulating the FFCF and then calculating the dynamical spectra.

While the dynamics of hydrogen bond networks can be studied using a variety of methods, including dielectric relaxation [20], ultrafast infrared spectroscopic methods are particularly useful because of their high time resolution and the sensitivity of the hydroxyl stretch to hydrogen bond dynamics [9]. Infrared experiments performed to date have measured orientational relaxation [21,22] or aspects of the time dependence of the hydroxyl stretch (spectral diffusion) [15–18,23,24] within the hydrogen bonded network. In contrast to previous measurements, the VECS experiments presented here probe, in two dimensions with full phase information, the entire $\sim 400\text{ cm}^{-1}$ hydroxyl stretch band simultaneously using the shortest IR pulses produced to date (45 fs) to provide a new and unique view of water dynamics. Previously [7], the experimental data were compared to widely used molecular dynamics (MD) simulations of water, [10,11,25–28] TIP4P and

SPC/E, [29,30] using frequency independent nonlinear response theory [7]. The comparison provides a very sensitive test of the MD simulations, which have been used extensively to study the structure and evolution of hydrogen bonding networks [10,11,25–28]. Building on the previous study [7], we investigate the evolution of different hydrogen bonded species in water observed through frequency dependent dephasing dynamics within the hydroxyl stretch band. In addition, the analysis of the frequency dependent data sheds light on the applicability of the commonly used frequency independent nonlinear response theory.

2. Experimental considerations

Forty-five femtoseconds transform-limited IR pulses at $4\text{ }\mu\text{m}$ (2500 cm^{-1}) are generated using a Ti:Sapphire regeneratively amplified laser system with an optical parametric amplifier. The ultrashort pulses provide the bandwidth ($>400\text{ cm}^{-1}$) necessary to examine the full range of structures and dynamics in water.

Two thousand five hundred cm^{-1} is the center of the OD stretch band of HOD in H_2O . HOD in water was studied for two important reasons. First, in contrast to the vast majority of previous studies, here we examined the dynamics of water rather than deuterium oxide (D_2O). Second, water and other hydrogen bonding liquids are known to break hydrogen bonds following vibrational relaxation of the hydroxyl stretch [31–33]. Hydrogen bond breaking following vibrational relaxation can interfere with determination of the equilibrium thermal fluctuations of the network. The vibrational lifetime of the OD stretch of HOD in H_2O is $\sim 1.8\text{ ps}$, rather than the $\sim 0.7\text{ ps}$ lifetime of the OH stretch in D_2O [21], more than doubling the time window in which we can extract the dynamics of the hydrogen bonded network unperturbed by photoproducts. We have performed detailed spectrally resolved IR pump–probe experiments and find that broken hydrogen bond photoproducts do not make a measurable contribution for times $< 2\text{ ps}$. Consequently, we only consider correlation spectra measured at times $< 2\text{ ps}$. As shown below, important dynamics occur for times $> 1\text{ ps}$. Therefore the distinction between studying water with an OD probe vs. studying deuterium oxide with an OH probe is very important. The sample, 5% HOD in H_2O , was held in a sample cell of CaF_2 flats with a spacing of $6\text{ }\mu\text{m}$.

Three IR pulses impinge on the sample and stimulate the emission of the vibrational echo. A fourth pulse, the local oscillator, is overlapped with the vibrational echo pulse to phase resolve the signal. The frequency and phase-resolved, stimulated vibrational echo was measured as a function of one frequency variable, ω_m , and two time variables, τ and T_w , the time between the first

and second and the second and third IR pulses, respectively. The vibrational echo signal is frequency resolved by a monochromator, providing the frequency axis ω_m [6]. By numerical Fourier transformation, the τ scan data are converted into the frequency variable ω_τ , providing the ω_τ axis of the 2D vibrational echo correlation spectrum. Correlation spectra are recorded for different T_w delays. During the T_w time period, the hydrogen bond network evolves and structural relaxation and rearrangement processes take place that cause spectral diffusion. The evolution of the network causes the hydroxyl stretch frequencies to change, and, therefore, the FFCF to decay. The changes in the vibrational echo correlation spectrum as T_w is increased provide a measure of spectral diffusion. Experimental details are discussed elsewhere [6].

3. Results and discussion

Vibrational echo correlation spectra were taken for T_w delays between 100 fs and 1.6 ps. Fig. 1 displays correlation spectra for four of the T_w delays, 100, 400, 800 fs, and 1.6 ps. Two peaks are observed along the ω_m axis corresponding to the 0–1 and the 1–2 hydroxyl stretch vibrational transitions. The positive going peak, which comes from the vibrational echo emitted at the 0–1 transition frequency, appears on the diagonal (represented by the line $\omega_m = \omega_\tau$). The negative going peak, from the 1–2 transition, is red shifted along the ω_m axis by the vibrational anharmonicity [7]. From a fit, we have determined that the anharmonicity of the OD stretch vibration is $140 \pm 20 \text{ cm}^{-1}$.

Looking in particular at the 0–1 band, it is clear that the correlation spectra undergo a dramatic change in shape from $T_w = 100 \text{ fs}$ to 1.6 ps. A good way to visualize and analyze the change is to select a particular ω_m value (e.g., 2500 cm^{-1} , the center of the 0–1 transition) and project the line shape along this single value of ω_m onto the ω_τ axis. The projection on the ω_τ axis (horizontal axis) is the dynamical line shape of the 0–1 transition for a given T_w and ω_m , and the width of the projection is the dynamical line width. The width is caused by the very fast fluctuations of the hydrogen-bonded network. As T_w is increased, additional fluctuations come into play that cause the dynamical line to broaden further. Changes in the dynamical line width reflect the spectral diffusion dynamics [9,34]. Therefore, the change in the shape of the correlation spectrum provides information on the hydrogen bond dynamics over a range of time scales.

As discussed qualitatively above, the key quantity that connects the vibrational echo correlation spectra and theoretical descriptions of the data and of water dynamics is the frequency–frequency correlation function of the hydroxyl stretch frequency. The FFCF is

written as $C(t) = \langle \delta\omega(t)\delta\omega(0) \rangle$, where $\delta\omega$ is the change in the hydroxyl stretch frequency from its average value. Structural change will lead to the change of the frequency of a given hydroxyl oscillator and decay of $C(t)$. Therefore the FFCF monitors any structural change experienced by a hydroxyl oscillator.

The FFCF describes the loss of correlation of the frequency of the ensemble of OD stretch oscillators as time progresses. The FFCF can be extracted from the experiment using non-linear response theory [13]. The FFCF can also be calculated from MD simulations by coupling a quantum oscillator to the time dependent structure from the simulations [7–9,27]. The FFCFs

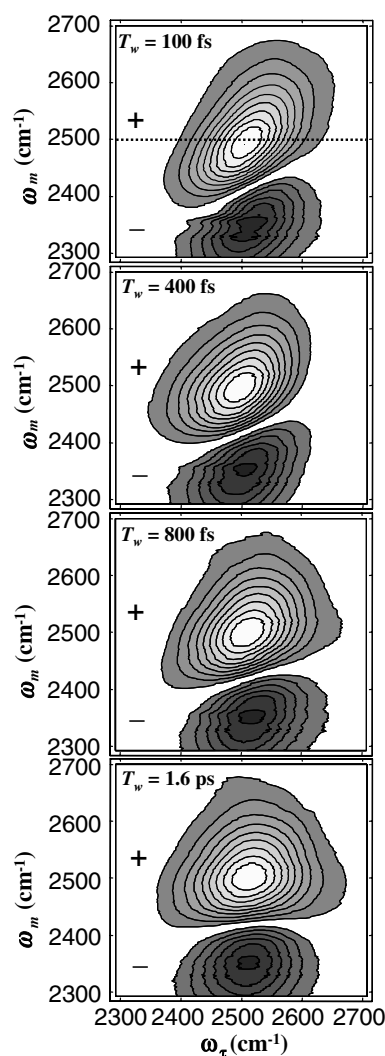


Fig. 1. The experimental vibrational echo correlation spectra of the OD stretch of HOD in H_2O as a function of time T_w . As time progresses the shape of the peaks change because of evolution of the hydrogen bond network structure. The contours represent 10% steps. The diagonal peak (0–1 transition) is positive going (+), while the off-diagonal peak (1–2 transition) is negative going (-). The dashed line in the top panel ($\omega_m = 2500 \text{ cm}^{-1}$) is the center of the 0–1 band of the correlation spectrum. Projection of this cut onto the ω_τ axis is the dynamic linewidth for that ω_m .

obtained from the MD simulation are exceedingly well described by a sum of three exponential functions, although a small oscillatory feature at early times, which does not change the observables, is not captured. We will henceforth refer to the tri-exponential analytical representation as the FFCF. It has the form

$$C(t) = A_0^2 \exp(-t/\tau_0) + A_1^2 \exp(-t/\tau_1) + A_2^2 \times \exp(-t/\tau_2). \quad (1)$$

The A_i refers to the bandwidth of frequencies that the oscillator samples at a rate constant τ_i^{-1} . The overall amplitude of Eq. (1) was adjusted so that the calculation of the linear absorption line shape was able to reproduce the full width at half maximum of the experimentally measured absorption spectrum [7].

Experimental data and the results of calculations are shown in Fig. 2. The figure plots the dynamical line widths (defined above) for $\omega_m = 2500 \text{ cm}^{-1}$ extracted from the data and from the calculations. The dynamical line widths are compared at the center of the 0–1 band ($\omega_m = 2500 \text{ cm}^{-1}$) to construct a simple plot and, more importantly, to exclude ω_m dependence of the hydrogen bond network dynamics due to different water conformers (see below). The experimental data appear as diamonds with error bars. The horizontal line at 147 cm^{-1} is the long time asymptotic line width, that is, the line width that would be observed in the limit of infinite T_w . The solid line through the data is obtained through fitting by varying the phenomenological FFCF of form given in Eq. (1) [7]. In the fitting procedure, the linear absorption linewidth was always matched and the resulting linear line shape is close to the experimental one. Full details of the fitting are given in [7]. Also shown in the figure are two calculations based on standard water simulations, TIP4P and SPC/E [7]. The top curve (dots) is from the TIP4P model and the next lowest curve (dashes) is from the SPC/E model. Details of the simulation methods and com-

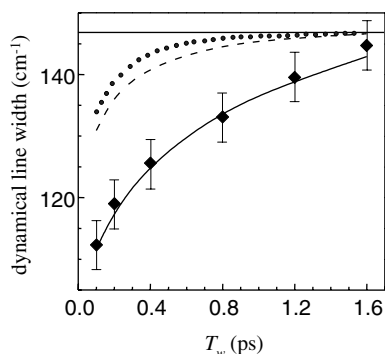


Fig. 2. Dynamical line widths for $\omega_m = 2500 \text{ cm}^{-1}$ from the experimental correlation spectra (diamonds with error bars), the TIP4P (dots) and SPC/E (dashes) water models, and the FFCF obtained from fitting the data (solid line through the data) [7]. See [7] for parameters.

parisons of the simulation results to the data and the phenomenological fit to the data are discussed extensively in [7]. For the purposes of this letter, the important observations are that the fit to the data and the simulations all have FFCFs that divide into roughly two time scales, a very fast component ($\sim 30 \text{ fs}$), and slower components. The simulations overestimate the magnitude of the fast component and have too little amplitude in the slow components. Furthermore, the slow components in the simulations' FFCFs are too fast, that is $< 1 \text{ ps}$, compared to the phenomenological FFCF from the data fit that has a slowest component with significant amplitude of $\sim 2 \text{ ps}$ [7]. While the simulations do not reproduce the data, they do give qualitative insights into the nature of the structural fluctuations that occur on different time scales. The description of the structural fluctuations obtained from the simulations will be used below to provide qualitative insights into the nature of the frequency dependence of water's ultrafast dynamics.

VECS can be used to examine the timescales of local hydrogen bond network structural fluctuations of different water conformers. Water molecules with different numbers of hydrogen bonds have different transition frequencies, although they are not resolvable within the broad hydroxyl stretch absorption band [9,26]. Furthermore, the strength of a hydrogen bond determines the hydroxyl stretch transition frequency to a great extent [12]. We can investigate if distinct dynamics are associated with structural differences by analyzing the VECS dynamic linewidths for various ω_m slices, thereby selecting out particular hydrogen bonded subsets of water.

Dynamical line widths were determined from the full correlation spectra at a number of frequencies, ω_m , and T_w delays. Some of the results are shown in Fig. 3. The

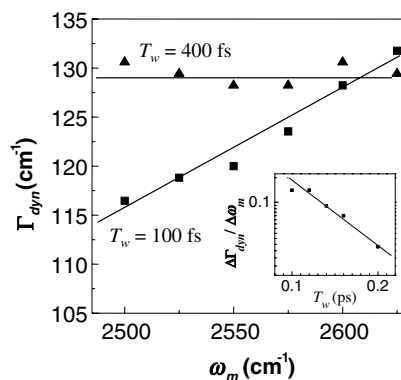


Fig. 3. Dependence of the dynamical line width Γ_{dyn} on ω_m (structure) for two T_w s, 100 and 400 fs. For 100 fs there is a distinct dependence of the width on ω_m . By 400 fs there is no dependence. Inset: the decay ($\sim 100 \text{ fs}$) of the differences in dynamics associated with different structures vs. T_w .

main body of the plot shows the dynamical line widths, Γ_{dyn} , as a function of frequency for two of the times studied, 100 and 400 fs. The 100 fs data demonstrate very clearly that Γ_{dyn} varies significantly with wavelength. As the frequency increases, the dynamical line width increases. The change in Γ_{dyn} with ω_m demonstrates that the hydrogen bond dynamics vary with frequency, and, therefore depend on the local hydrogen bond network structure. The frequency dependence of the width can be seen in the 100 fs correlation spectrum shown in Fig. 1. The spectrum is clearly broader for higher ω_m . However, the 400 fs data (Fig. 1) and line in Fig. 3 show that by 400 fs, within experimental error, there is no longer a frequency dependence to Γ_{dyn} . The inset in Fig. 3 displays the change in the dynamical line width with ω_m as a function of T_w . The points are the slopes of lines like the 100 fs line in the body of Fig. 3. The line through the data yields the time scale for the decay of the variation in the dynamics with local structure. The dynamical differences among structures decay with a time constant of ~ 100 fs.

The results show that hydrogen bond dynamics observed through their effect on the hydroxyl stretch frequency depend on the hydroxyl stretch frequency examined. The amount of spectral diffusion is smaller at lower frequencies at short times. Recent MD simulations demonstrate that the hydroxyl stretch band is composed of differently hydrogen-bonded species [11,27]. The red side of the line is composed primarily of water molecules with more hydrogen bonds than the blue side of the line. In addition, stronger hydrogen bonds red shift the frequency relative to weaker hydrogen bonds for a given number of hydrogen bonds. However, the bands for different numbers of hydrogen bonds, inhomogeneously broadened by the strengths of the hydrogen bonds, overlap substantially, and are not spectroscopically resolvable. Nonetheless, it is safe to say that the blue side of the line corresponds to fewer and weaker hydrogen bonds relative to the red side of the line.

Analysis of simulations indicates that the short time spectral diffusion (structural evolution) arises mainly from hindered translational motion of the hydrogen bond under observation (stretching of the hydrogen bond length coordinate) although angular variations play some role [9,11,26,27]. The slower spectral diffusion is assigned to the influence of hydrogen bond equilibration (formation and breaking) [9,11,27]. Any given water molecule, over time, will experience all hydrogen bonding configurations. There is an average number of hydrogen bonds for water molecules. A particular water molecule at $t = 0$ will have a certain number of hydrogen bonds. Over time it will regress toward the average. For some molecules the regression will require a net formation of hydrogen bonds, while for others it will require a net breaking of hydrogen bonds. This equilibration process will result in hydroxyl

stretch frequency shifts and is less local than the very fast fluctuations.

The wavelength dependence of the dynamic linewidths displayed in Fig. 3 provides qualitative insight into the different nature of spectral diffusion due to fast local fluctuations and slower hydrogen bond equilibration. With fewer hydrogen bonds, the blue side local networks will not be as constrained, and fluctuations about the local structure that give rise to spectral diffusion will be greater. This is born out by the simulations when wavelength dependent conditional probabilities are examined [35]. The second moment of these conditional probability distributions (see Fig. 8.2 of [35], which is closely related to the dynamical linewidth, shows that spectral diffusion at 100 fs is greater on the blue side of the line than in the center. For times longer than ~ 400 fs, the lack of a wavelength dependence in the data suggests that the dynamics and associated spectral diffusion are dominated by more substantial network structural evolution (hydrogen bond equilibration) that does not depend on the details of the local structure. Thus 400 fs may be a rough boundary between very local fast fluctuations about relatively fixed structures and the randomization of the local structures. While the fast fluctuations make important contributions to the vibrational echo correlation spectra, it is the equilibration time scale that may be of greater importance in chemical and biological processes that require significant local structural changes in the water solvent.

The calculations presented in Fig. 2, and the detailed comparisons between the data and simulations presented previously, were performed with the diagrammatic perturbation theory treatment of non-linear optical experiments [13]. Because of the Gaussian approximation that is at the core of the treatment, a single FFCF describes an entire absorption line. The data presented here show that an advance in theory is required to describe complex systems such as water on all timescales. A new theory needs to be able to describe wavelength dependent differences at short times in a natural manner and then go over to the current calculated results at longer time.

The fundamentally important observations on the differences in dynamics for different water structures at short times do not change the basic conclusions drawn from comparisons of data and simulations (see Fig. 2) about the efficacy of the water simulation models reported previously [7]. The major deviations between FFCFs obtained from the simulations and from the data mainly occur for times >400 fs, times for which there is no wavelength dependence. Independent of the wavelength selected for comparison, the simulated results do not agree with the data. The ability of a new theory to relate different wavelength dependent dynamics displayed in Fig. 3 to different local network structures will be significant.

4. Concluding remarks

Ultrafast infrared vibrational echo correlation spectroscopy was employed to study the influence of different hydrogen bonded structures on dynamics in water. By examining the time evolution of dynamic line widths for different wavelengths in the OD hydroxyl stretch band of HOD in water, it was found that dynamics depend on the local hydrogen bonding structure at very short times, but by ~ 400 fs, the dynamics are structure (wavelength) independent. Simulations, which display structure (wavelength) dependent dynamics on very short time scales [27,35], support the observations. The wavelength dependence of the dynamic linewidth demonstrates that the correlation spectra cannot be rigorously analyzed using standard diagrammatic perturbation theory methods [13]. Advances in theory are necessary to thoroughly analyze the relation between the observations and the details of water structural evolution.

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