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*Original*

Pressure Dependence of Hydrogen-Bond Dynamics in Liquid Water Probed by Ultrafast Infrared Spectroscopy / Lapini, Andrea; Pagliai, Marco; Fanetti, Samuele; Citroni, Margherita; Scandolo, Sandro; Bini, Roberto; Righini, Roberto. - In: THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS. - ISSN 1948-7185. - 7:18(2016), pp. 3579-84-3584. [10.1021/acs.jpcllett.6b01375]

*Availability:*

This version is available at: 11696/58669 since: 2018-10-04T17:02:11Z

*Publisher:*

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DOI:10.1021/acs.jpcllett.6b01375

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*J. Phys. Chem. Lett.*, **Just Accepted Manuscript** • DOI: 10.1021/acs.jpclett.6b01375 • Publication Date (Web): 25 Aug 2016

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# Pressure Dependence of Hydrogen Bond Dynamics in Liquid Water Probed by Ultrafast Infrared Spectroscopy

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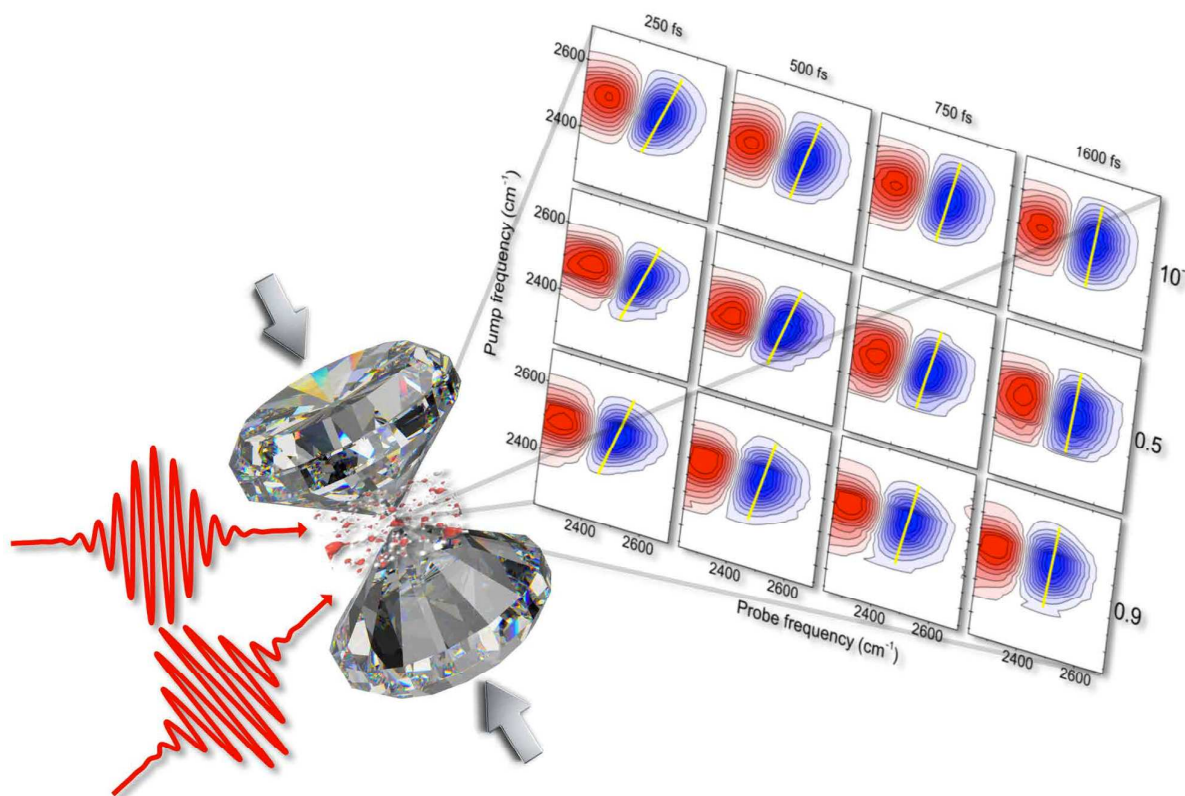
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## Abstract

Clarifying the structure/dynamics relation of water hydrogen bond network has been the aim of an extensive research over many decades. By joining anvil cell high-pressure technology, femtosecond two-dimensional infrared spectroscopy and molecular dynamics simulations, we studied, for the first time, the spectral diffusion of the stretching frequency of an HOD impurity in liquid water as a function of pressure. Our experimental and simulation results concordantly demonstrate that the rate of spectral diffusion is almost insensitive to the applied pressure. This behavior is in contrast with the previously reported pressure induced speed up of the orientational dynamics, which can be rationalized in terms of large angular jumps involving sudden switching between two hydrogen-bonded configurations. The different trend of the spectral diffusion can be, instead, inferred considering that the first solvation shell preserves the tetrahedral structure with pressure and the OD stretching frequency is only slight perturbed.

## TOC



Liquid water has a primary role in many biological, chemical, physical, geological and environmental processes.<sup>1</sup> Despite the enormous amount of experimental and theoretical studies performed in the last century, a full understanding of its dynamical and structural properties is still lacking. The molecular self-association through hydrogen bonds is the characterizing feature: H-bonding determines the tetrahedral arrangement of the first shell molecules and characterizes the three-dimensional extended network in liquid and solid water.<sup>2</sup> This characteristic property is the origin of most of the water anomalous properties, like heat capacity, enthalpy of vaporization and melting, interfacial tension, density, compressibility and solvency.<sup>3</sup> Clarifying the structure/dynamics relation of the hydrogen bond network, and its dependence on the applied external conditions, is the key step to understand the nature of water. While temperature dependence of water structural and dynamical properties, both in stable and metastable phases, has

been widely investigated with a number of different techniques, far fewer studies have been concerned with the pressure dependence, mostly because of the experimental difficulties. In recent years,<sup>4</sup> time resolved nonlinear infrared spectroscopy provided a very effective tool for the experimental investigation in this field. In particular, the O-D vibration of isolated HOD dissolved in H<sub>2</sub>O represents the ideal system to this purpose: O-D is an almost perfect one-dimensional oscillator, dynamically decoupled from the O-H vibration of the HOD molecule. At the same time, the O-D oscillator is hydrogen bonded to the neighboring molecules, and is a very sensitive probe of the local intermolecular structure and of the H-bond dynamics. We recently combined anvil cell high-pressure technology and ultrafast transient infrared absorption spectroscopy to investigate the pressure/temperature behavior of water in a large region of the P-T phase diagram.<sup>5-6</sup> We identified and characterized two coexisting dynamic regimes, connected to two different local structures of different densities; in particular, we pointed out the different pressure dependence of the orientational dynamics in the two forms. Here, we turn our attention to the hydrogen bond dynamics. It is well known that the stretching vibrational frequencies of water are strongly affected by hydrogen bonding,<sup>7-10</sup> and that the fluctuations of the hydrogen bond strength lead to frequency modulations that result in the so-called spectral diffusion,<sup>11</sup> directly measurable in two-dimensional time resolved infrared (2D-IR) experiments.<sup>12-13</sup> In this study we characterize for the first time the spectral diffusion of the OD stretching as a function of pressure, combining 2D-IR spectroscopy with classical molecular dynamics simulations (MD) and *wavelet analysis*.<sup>14-16</sup> The measurements were carried out on a 3.5% m/m D<sub>2</sub>O in H<sub>2</sub>O mixture in a high-pressure membrane cell, equipped with z-cut sapphire anvils.<sup>5-6</sup> We obtained the 2D spectra using the two beam dynamic hole burning technique.<sup>17</sup> In fact, for anvil cell measurements, this scheme guarantees a much easier and effective suppression of scattered light, in comparison to interferometric techniques. In this method, a narrow-band (45 cm<sup>-1</sup>, 600 fs) pulse is used to excite the sample; after a given delay time  $T_w$ , a broadband pulse probes the induced transient spectrum. By recording a series of transient spectra at different excitation frequencies, we reconstruct the 2D map for each pump-probe delay time. Some

representative 2D maps are collected in Figure 1; a detailed description of the experimental apparatus is reported in the Experiment section of Supporting Information. The characteristic feature of the 2D spectra is the change of the peak shape as a function of the delay  $T_w$  between pump and probe. At short delay the peak is tilted towards the diagonal, as the OD oscillators keep memory of the excitation frequency. With increasing waiting time, they visit more and more sites in the configuration space: correspondently, the 2D peak alignment approaches the vertical direction. We used the central line slope (CLS, yellow lines in Figure 1) method<sup>18</sup> to extract the spectral diffusion from 2D spectra, because it is less sensitive to experimental artefacts caused by the low signal to noise ratio.<sup>19,20</sup> The time evolution of the CLS at different pressures is shown in Figure 2a. Three distinct temporal components have been reported for the room pressure ( $10^{-4}$  GPa) spectral diffusion of OD stretching:<sup>21-22</sup> an ultrafast decay (60-80 fs), an intermediate one (ca. 400 fs), and a third one in the picosecond range.

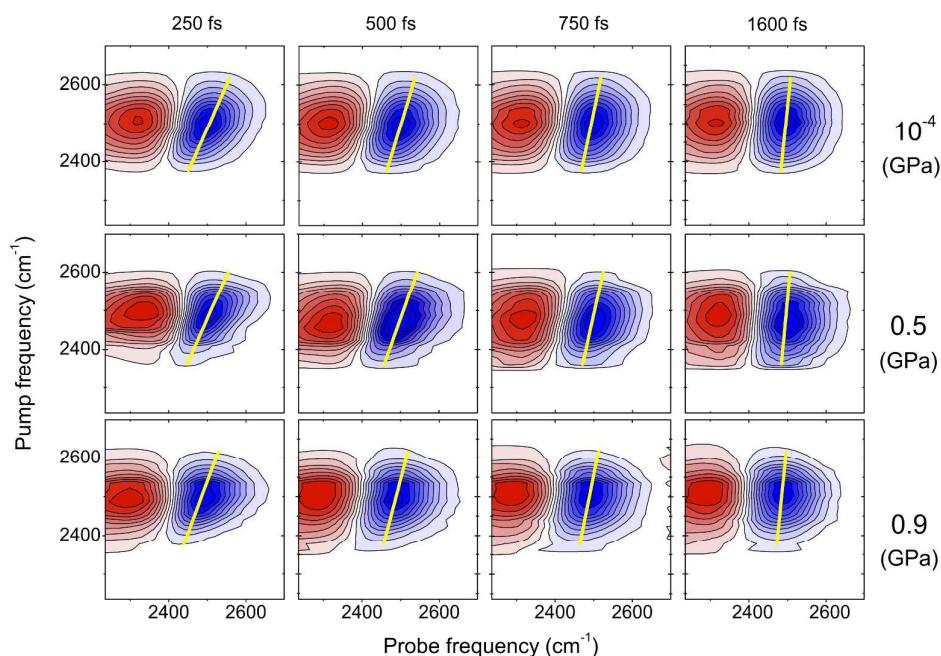


Figure 1. Selected 2D-IR spectra of the 3.5% D<sub>2</sub>O/H<sub>2</sub>O mixture measured at  $10^{-4}$  (room pressure), 0.5 and 0.9 GPa. The 2D maps are composed by a negative peak (blue) related to bleaching and stimulated emission, and a positive peak (red) which represents the excited state absorption. In yellow we report the central line, which is the line that connects the minima of the negative peak in a series of slices of the 2D spectrum parallel to the probe frequency axis.



The ultrafast decay reflects the fast fluctuations of the O-D distance (due to the hydrogen bond stretching) and of the O-D...O angles (due to librational motion) between the water molecule and the hydrogen-bonded nearest neighbors; the intermediate and picosecond components are commonly attributed to collective rearrangements of molecules in the hydrogen bond network.<sup>21-23</sup> However, using a three exponential function to fit the data can lead to some degree of uncertainty in the values of the decay constants. Hence, we limited the number of fitting parameters by adopting a two-exponential decay function, keeping the first temporal component fixed at 250 fs (see Decay Fitting Function section of Supporting Information) and neglecting the ultrafast component, which is definitely below the temporal resolution (500 fs) of our experiment. The best fit of the CLS at 298 K and room pressure gives a time constant of  $1.45 \pm 0.2$  ps for the slower component. This lower value, compared to that (1.8 ps) of ref.<sup>22</sup>, is a consequence of the two-exponential fit adopted here. At 0.5 GPa the time constant becomes  $1.35 \pm 0.2$  ps; it does not change when pressure increases up to 0.9 GPa ( $1.3 \pm 0.2$  ps).

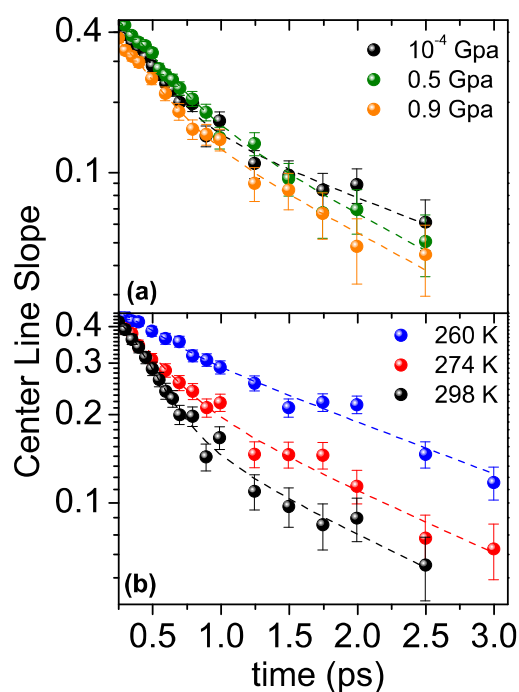


Figure 2. Temporal evolution of the CLS (dots) and the corresponding bi-exponential fit (dashed line) for: (a) Room temperature, pressure:  $10^{-4}$  (black dots), 0.5 GPa (green dots) and 9 GPa (orange dots); (b) Room pressure, temperature: 260 K (blue dots), 273 K (red dots) and 298 K (black dots).

The picosecond time constants for spectral diffusion measured at different pressure are collected in Figure 3a. The high pressure time constants are slightly lower than at room pressure, although their error bars overlap. The observation that the CLS values at 400 fs in Figure 2a are similar ( $\sim 0.4$ ) at all pressures, suggests that also the ultrafast component of the decay is not very sensitive to pressure. The very weak dependence of the spectral diffusion picosecond time constant on the applied pressure shows a different behavior respect to the decay time constants of the spectral anisotropy (from ref.<sup>5</sup>) shown in Figure 3b. This result appears, at first sight, surprising and is worth of specific consideration. In our previous work<sup>5</sup> we showed that pressure and temperature act in the same direction on the rotational dynamics of water molecules: increasing T and P cause a substantial speed-up of the molecular reorientation rate. Because temperature induces a sensible variation of spectral diffusion decay time, a careful analysis of the pressure effect is required.

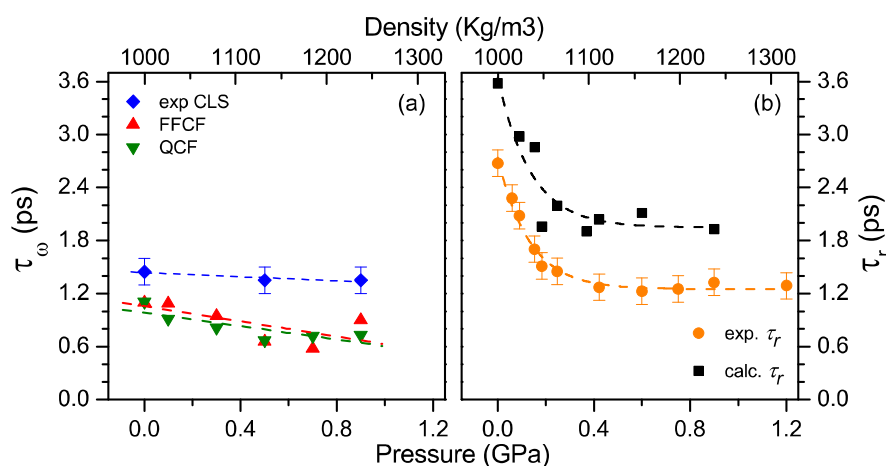


Figure 3. Comparison of the pressure dependence of the spectral diffusion and of the reorientational dynamics. (a) Picosecond decay component obtained from the exponential fitting of: experimental CLS (*blue* diamonds); calculated frequency-frequency correlation function FFCF (*red* triangles); correlation function of the tetrahedral order parameter (QCF) (*green* triangles) calculated with the O...H distance criteria; (b) *Black* squares and *orange* dots are, respectively, the calculated and experimental anisotropy decay times (from ref.<sup>5</sup>). The dashed lines are just guidelines for the eyes.

To dispel any doubt that the weak dependence of the spectral diffusion on the applied pressure may depend on an inadequate sensitivity of our experimental method, we repeated 2D-IR



measurements as a function of temperature at room pressure and compared our results with the three-pulse photon-echo experiments reported in refs.<sup>18,22</sup>. That technique is indeed characterized by higher temporal and spectral resolution in comparison to the dynamic hole burning method used in this work. We measured the spectra at three different temperatures: 260 K, 274 K and 298 K. The CLS data and bi-exponential fitting curves are shown in figure 2. A clear trend is evident for the picosecond time constant: it goes from 1.45 ps at 298 K to 1.8 ps at 274 K and 2.45 ps 260K. At the same time, we observe a gradual decrease of the relative weight of the faster temporal component, which goes from 80 % at 298 K to 40 % at 260 K. The temperature dependence of the picosecond component of spectral diffusion is reported in Figure 4, together with the results of the molecular dynamics simulations and the data from refs.<sup>18,22</sup>.

To elucidate the effects of pressure on the orientational dynamics and on the decay of frequency correlation, we performed a series of classical molecular dynamics (MD) simulations in the NVE ensemble at different pressures and temperatures (Computational details on the simulations are reported in the Molecular Dynamics Simulations section of Supporting Information): We employed the ASAP polarizable force field with flexible molecules.<sup>24</sup> This model proved particularly effective in the description of structural and dynamic properties of water at different temperature and pressure conditions.<sup>5-6</sup> The flexible model allows to calculate the oscillation of the OD bond length during the simulation. Differently from calculations with rigid models,<sup>12,25</sup> in this approach a time-frequency analysis is required to extract the time evolution of the stretching frequency. We obtained the frequency-frequency correlation function (FFCF) by taking advantage of the simultaneous localization in frequency and time domains provided by the wavelet transform<sup>14-15</sup> (details in the Wavelet Analysis of Supporting Information). The reliability of the computational method is confirmed by the comparison to the experimental data of this work and of previous studies<sup>18, 22</sup> shown in Figure 4. To be consistent with the results of *Perakis et al.*<sup>18</sup> and *Nicodemuset al.*,<sup>22</sup> we used for the fitting of our data (experiment and simulation) both a single-exponential (Figure 4a) and a bi-exponential function (Figure 4b), excluding the data points at very

short delay times ( $< 250$  fs), thus omitting the ultrafast decay component. The time constants in Figure 4b are those of the slower component of the two-exponential function. It is evident that the simulations show a substantial decrease of the FFCF decay time as the temperature increases, in accordance with the temperature dependence observed in the experiments. The results of the simulations performed at room temperature and different pressure values are shown in Figure 3a; here we report the time constants of the slower component of the FFCF, obtained from a two-exponential fit (red triangles), together with the experimental values (blue diamonds). The decrease of the calculated values on going from room pressure to 0.9 GPa is analogous to that of the experimental data, although slightly faster. This confirms that the applied pressure has limited effect on the decay time of the FFCF, mainly if compared to that of the orientational time constant (Figure 3b). Even from the quantitative point of view, the overall agreement between experiment and calculation is extremely good, especially if we consider the purely classical approach used for the simulations.

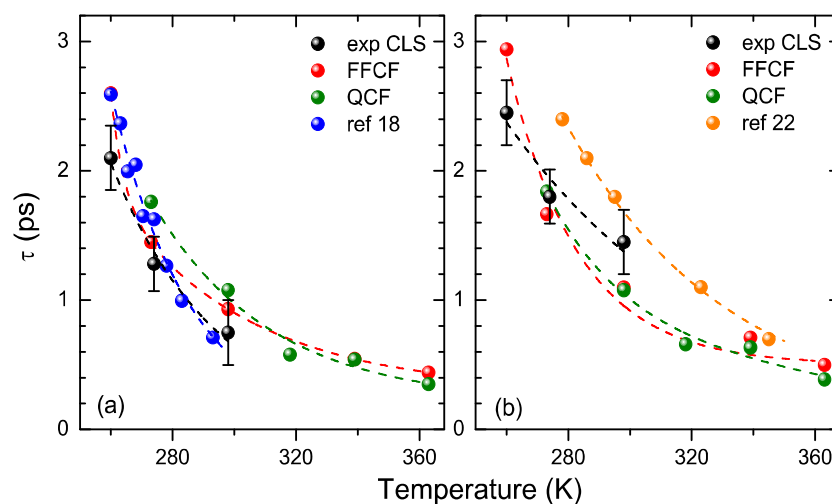


Figure 4. Temperature dependence of the picosecond decay time of: Experimental central line slope (CLS, black); calculated frequency-frequency correlation function (FFCF, red); calculated tetrahedral order parameter correlation function (QCF, green). The values in panel (a) were obtained with a single exponential fitting function; those in panel (b) with a double exponential function. The values reported in refs. <sup>18</sup> and ref. <sup>22</sup> are also shown. The dashed lines have to be considered as guidelines for the eyes.

The crucial role that hydrogen bond plays in determining both the vibrational properties of water and its liquid structure, suggests a connection between the frequency fluctuations of the OD stretching ( $\omega_{OD}$ ) measured in 2D-IR experiments and the structure of the liquid. We analyzed the structure of the nearest neighbor hydrogen bonded water molecules by means of the tetrahedral order parameter  $Q$  based on the O...H distance criteria (as defined in the Supporting Information).<sup>26-28</sup> The autocorrelation function of the tetrahedral order parameter,<sup>27</sup> QCF, is a measure of the stability of the water molecules in the first solvation shell. The decay of the QCFs resembles very closely that of the FFCFs (see Correlation Functions section in Supporting Information), with a femtosecond fast decay and a picosecond component. We fitted the different decays using the same model employed for the experimental FFCFs; the results for the slow component are given in Figure 3a (pressure dependence) and Figure 4 (temperature dependence). It is clear that, in both cases, the picosecond decay constants of FFCF and QCF show a very similar trend.

The different behaviors of the spectral diffusion with pressure and temperature can be rationalized considering the structural variations described by the pair radial distribution functions ( $g(r)$ ) for O...H and O...O interactions. The changes in  $g(r)$  induced by temperature have been explained in terms of hydrogen bond weakening and of faster interchange between first shell and second shell molecules, with a consequent loss of tetrahedrity of the cage.<sup>5</sup> In contrast, the variations in position and shape of the second peak of the  $g(r)$  for O...O upon isothermal compression,<sup>29</sup> correspond to the progressive collapse of the second solvation shell onto the first one. This structural change results in a higher rate of hydrogen bond breaking and making, but it substantially preserves the structure of the hydrogen bonded tetrahedral first solvation shell.

Our experimental 2D-IR data and computer simulation results collected in Figure 3a, concordantly demonstrate that this process has very little effect on the spectral diffusion, while it largely affects the orientational dynamics of the water molecules. The wavelet analysis of the simulated trajectories provide clear evidence of the diverging effects that the structural

modifications induced by pressure and by temperature have on the OD vibrational frequency. Figures 5A and 5B show that pressure induces only slight variations on the OD frequency distribution in dependence of the first neighbor hydrogen bond distance, whereas large changes due to temperature can be appreciated in Figures 5C and 5D.

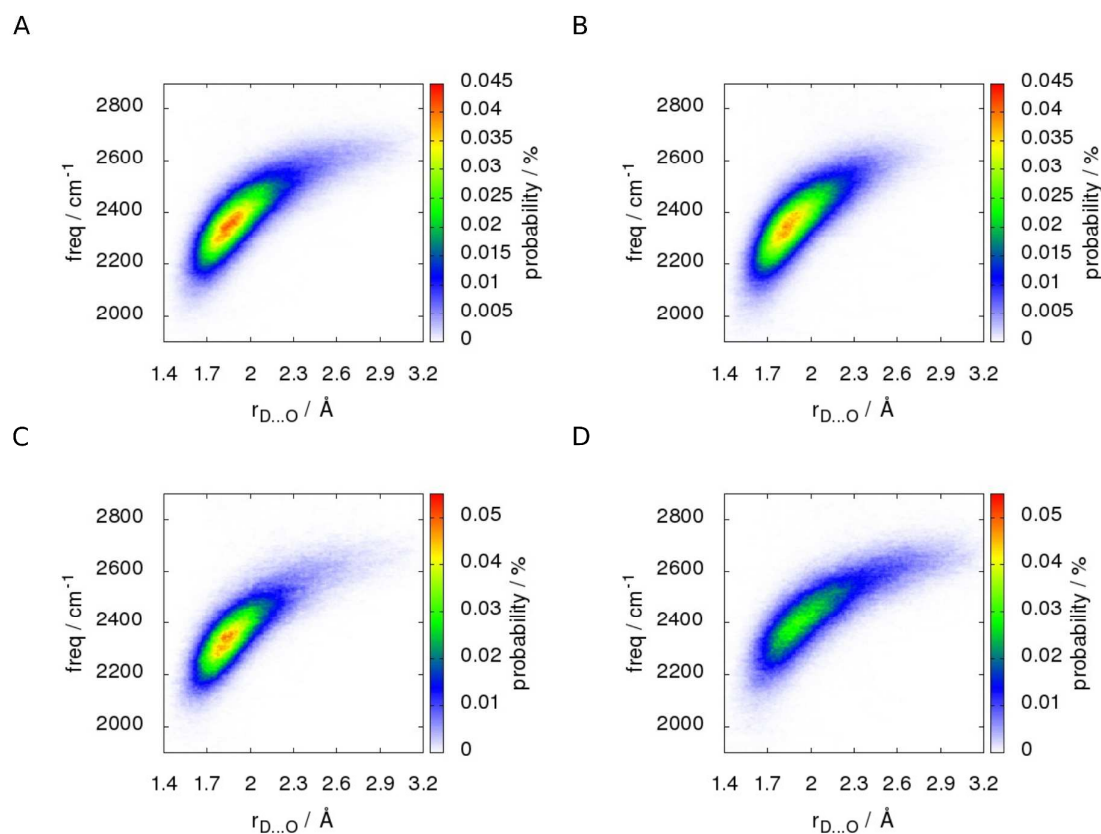


Figure 5. Spectrograms for the OD stretching frequency in dependence of the first neighbor hydrogen bond distance obtained from wavelet analysis. Panels A (10<sup>-4</sup> GPa) and B (0.9 GPa) show that the effect of pressure is negligible at room temperature. In contrast, panels C (273 K) and panel D (363 K) indicate a large effect of temperature at room pressure. No scaling factor has been used for the calculated frequencies.

We believe that this finding provides an important new piece of information about the role of hydrogen bonding in determining different dynamical properties of water. The emerging picture can be rationalized in the light the model developed by Laage and Hynes for the molecular rotation in

liquid water.<sup>30-31</sup> A large angle sudden rotation (jump) of the tagged water molecule is driven by one of the OH bonds switching its hydrogen-bond partner from molecule a to molecule b. The H-bond breaking (with molecule a) and making (with molecule b) are almost simultaneous and lead to the rotational jump. In the transition state (TS) of these sparse jump events the OD frequency undergoes a sudden increase (ref.<sup>22</sup>); however, the very short lifetime of TS ( $\sim 200$  fs, ref.<sup>32</sup>) reduces substantially the contribution of the process to the spectral diffusion. MD simulations and wavelet analysis support this interpretation: pressure increase preserves the tetrahedral structure of the first solvation shell and, in average, induces small perturbations of the OD stretching frequencies.

In this scenario, the sparse rotational jump events are interspersed within thermal fluctuations of the intermolecular O-H $\cdots$ O angles and distances. Isothermal compression, while leaving the thermal fluctuations essentially unchanged, leads to an increase of the rate of large rotational jumps. This speeds up the molecular reorientation, but has only marginal effect on the spectral diffusion.

**Supporting Information Available:** Description of the material included.

Experiment  
Molecular Dynamics Simulations  
Tetrahedral Order Parameter  
Wavelet Analysis  
Decay Fitting Function  
Correlation Functions

Acknowledgements

Supported Deep Carbon Observatory initiative (grant “Extreme Physics and Chemistry of Carbon, Transformation and movements in Planetary Interiors” from the Alfred P. Sloan Foundation), and by MIUR (grants FIRB - Futuro in Ricerca 2010 RBFR109ZHQ and RBFR10Y5VW).

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