



UNICA

UNIVERSITÀ
DEGLI STUDI
DI CAGLIARI



Università di Cagliari

UNICA IRIS Institutional Research Information System

This is the Author's preprint manuscript version of the following contribution:

Jie Yang, Riccardo Dettori, J. Pedro F. Nunes, Nanna H. List, Elisa Biasin, Martin Centurion, Zhijiang Chen, Amy A. Cordones, Daniel P. Deponte, Tony F. Heinz, Michael E. Kozina, Kathryn Ledbetter, Ming-Fu Lin, Aaron M. Lindenberg, Mianzhen Mo, Anders Nilsson, Xiaozhe Shen, Thomas J. A. Wolf, Davide Donadio, Kelly J. Gaffney, Todd J. Martinez & Xijie Wang, "Direct observation of ultrafast hydrogen bond strengthening in liquid water", *Nature* **596**, 531-535, 2021

The publisher's version is available at:

<https://doi.org/10.1038/s41586-021-03793-9>

When citing, please refer to the published version.

This full text was downloaded from UNICA IRIS <https://iris.unica.it/>

Direct Observation of Ultrafast Hydrogen Bond Strengthening in Liquid Water

Jie Yang^{1,2,11*}, Riccardo Dettori³, J. Pedro F. Nunes⁴, Nanna H. List^{1,2,5}, Elisa Biasin^{1,2}, Martin Centurion⁴, Zhijiang Chen¹, Amy A. Cordones², Daniel P. Deponete¹, Tony F. Heinz^{2,6}, Michael E. Kozina^{1,2}, Kathryn Ledbetter^{2,7}, Ming-Fu Lin¹, Aaron M. Lindenberg^{2,8,9}, Mianzhen Mo¹, Anders Nilsson¹⁰, Xiaozhe Shen¹, Thomas J. A. Wolf^{1,2}, Davide Donadio^{3*}, Kelly J. Gaffney^{2*}, Todd J. Martinez^{1,2,5*}, Xijie Wang^{1*}

¹SLAC National Accelerator Laboratory, Menlo Park, CA, USA.

²Stanford PULSE Institute, SLAC National Accelerator Laboratory, Menlo Park, CA, USA.

³Department of Chemistry, University of California-Davis, Davis, CA, USA.

⁴Department of Physics, University of Nebraska-Lincoln, Lincoln, NE, USA.

⁵Department of Chemistry, Stanford University, Stanford, CA, USA.

⁶Department of Applied Physics, Stanford University, Stanford, CA, USA.

⁷Department of Physics, Stanford University, Stanford, CA, USA.

⁸Department of Materials Science and Engineering, Stanford University, Stanford, CA, USA.

⁹Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory, Menlo Park, CA, USA.

¹⁰Department of Physics, AlbaNova University Center, Stockholm University, Stockholm, Sweden.

¹¹Present address: Center of Basic Molecular Science, Department of Chemistry, Tsinghua University, Beijing, China

*email: jieyang1@tsinghua.edu.cn; ddonadio@ucdavis.edu; kgaffney@slac.stanford.edu; todd.martinez@stanford.edu; wangxj@slac.stanford.edu.

Water is one of the most important, yet least understood, liquids in nature. Many anomalous properties of liquid water originate from its well-connected hydrogen bond network¹, including unusually efficient vibrational energy redistribution and relaxation². An accurate description of the ultrafast vibrational motion of water molecules is essential for understanding the nature of hydrogen bonds and many solution-phase chemical reactions. Most existing knowledge of vibrational relaxation in water is built upon ultrafast spectroscopy experiments²⁻⁷. However, these experiments cannot directly resolve the motion of the atomic positions and require difficult translation of spectral dynamics into hydrogen bond dynamics. Here we measured the ultrafast structural response to the excitation of the OH stretching vibration in liquid water with femtosecond temporal and atomic spatial resolution using liquid ultrafast electron scattering. We observed a transient hydrogen bond contraction of roughly 0.04 Å on a timescale of 80 femtoseconds, followed by a thermalization on a timescale of ~1 picosecond. Molecular dynamics simulations reveal the need to treat the distribution of the shared proton in the hydrogen bond quantum mechanically to capture the structural dynamics on the femtosecond timescales. Our experiment and simulations unveiled the intermolecular character of the water vibration preceding the relaxation of the OH stretch.

The vibrational spectroscopy of water has critically contributed to our understanding of the

dynamics of hydrogen bond (HB) reorganization and energy redistribution in liquid water. It is established that the vibrational spectrum of water has both intra- and intermolecular character⁴ and needs to be described in terms of collective excitations⁸, but the spectrum-to-structure interpretation has proven challenging due to many complications, including the strong anharmonic coupling among intra- and intermolecular vibrational modes⁸. A complete unveiling of the intermolecular dynamics of water requires direct time- and structure-resolved measurements. Neutron and X-ray scattering are routinely used to measure the equilibrium atomic structure of liquid water in different environments^{9,10}, femtosecond (fs) X-ray pulses generated from X-ray free-electron-lasers (XFELs) have been used to study ultrafast heating^{11,12} and cage effects¹³ in water, and inelastic neutron scattering has provided great insights on both intra- and intermolecular vibrational dynamics in water⁹. In addition, XFELs have allowed the study of femtosecond structural dynamics of molecules in solution^{14,15}. Nevertheless, neither X-ray nor neutron scattering has been exploited to study the ultrafast vibrational relaxation of water in a pump-probe scheme.

Recently, liquid ultrafast electron scattering (LUES) was enabled by the combination of an ultrathin liquid sheet jet with a mega-electron-volt (MeV) electron beam¹⁶. The experimental setup is schematically shown in Fig. 1a. The sample is delivered through a gas-accelerated liquid sheet jet¹⁷ with a thickness of ~ 100 nm. We used a ~ 3315 cm^{-1} IR pulse to excite the OH stretching vibration in the sample and probed it with a 3.7 MeV electron pulse. The scattering pattern in the range of $0.2 < Q < 11.8$ \AA^{-1} was recorded on an electron detector. Approximately 5% of the probed molecules were excited. The instrument response function (IRF) of the system was roughly 200 fs full-width-at-half-maximum (FWHM) (Methods). The static scattering intensity $I^{exp}(Q)$ is shown in Fig. 1b along with a simulated $I^{sim}(Q)$ and its elastic and inelastic component (Methods), where Q is the momentum transfer between the scattered and the incident MeV electrons. The inelastic component is a smooth curve that dominates over small Q , and the structure in the elastic component encodes the atomic structure of water.

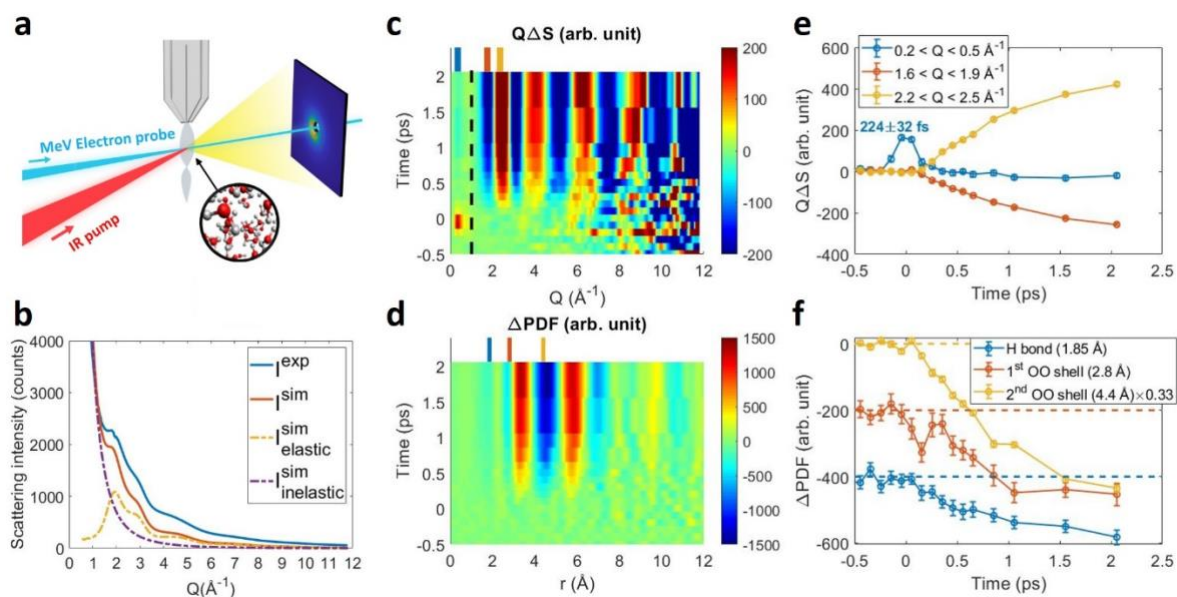


Fig. 1 | Experiment overview. **a**, A schematic of the experimental setup. The pump IR laser (red) and probe electron pulse (blue) are introduced to the interaction point with a 30-degree angle. The ~ 100 nm water sample is delivered through a gas-accelerated sheet jet. The scattering patterns are recorded on a phosphor screen-based detector. **b**, Experimental static scattering (blue solid) plotted together with simulated static scattering (red solid) and its elastic (yellow dashed) and inelastic (purple dashed) components. **c**, Experimental difference scattering curve $Q\Delta S$ displayed in false color map. The black dashed line represents $Q = 1 \text{ \AA}^{-1}$, which roughly separates the inelastic ($Q < 1 \text{ \AA}^{-1}$) and elastic ($Q > 1 \text{ \AA}^{-1}$) contributions. The three colored bands on top show the Q ranges over which the data in part **e** are integrated. **d**, Experimental ΔPDF displayed in false color map, calculated using $1 < Q < 11.8 \text{ \AA}^{-1}$. The three colored bands on top show the r ranges over which the data in part **f** are integrated. **e**, $Q\Delta S$ at three different Q ranges shown in the legend. **f**, ΔPDF at three important distances shown in the figure legend. Dashed lines show the baseline for each curve. The blue and orange curves are shifted vertically for visibility. Error bars in parts **e** and **f** represent standard error of the mean (SEM) of 60 independent measurements.

Similar to previous time-resolved X-ray scattering studies¹⁴, we use difference scattering curves $Q\Delta S$ (Methods) to show the change in the scattering pattern as a function of pump-probe delay, as depicted in Fig. 1c. The time evolution of three transient features is plotted in Fig. 1e. Most features at $Q > 1 \text{ \AA}^{-1}$ have a slow picosecond (ps) turn on, but the low- Q ($0.2 < Q < 0.5 \text{ \AA}^{-1}$) feature is short-lived with a time constant of 224 ± 32 fs (mean ± 1 SE from Gaussian fit). We attribute the appearance and disappearance of this feature to the change in inelastic scattering amplitude upon excitation and relaxation of the OH stretching mode. This interpretation is supported by an *ab initio* electron scattering simulation shown in Extended Data Fig. 1. In this work, time zero is determined by the peak of this transient signal (Fig. 1e).

The difference pair distribution function (ΔPDF), calculated through a Fourier-sine transform of the $Q\Delta S$ curve¹⁸ (see Methods), is shown in Fig. 1d. The strongest features in the ΔPDF are the broadening of the 2nd OO coordination shell, indicated by a bleaching band of the original 2nd OO shell location ($\sim 4.4 \text{ \AA}$) and the emergence of two strong positive bands next to it. These features agree well with the ΔPDF of equilibrium water under different temperatures measured in a previous X-ray scattering experiment.¹⁹ The time evolution of the ΔPDF intensity at three major short-range distances—the initial HB OH at $\sim 1.85 \text{ \AA}$, the 1st OO shell at $\sim 2.8 \text{ \AA}$ and the 2nd OO shell at $\sim 4.4 \text{ \AA}$ —are shown in Fig. 1f. At all three distances, the ΔPDF intensity becomes negative after time zero, indicating the loss of the intermolecular order present prior to vibrational excitation. The ~ 1 ps relaxation timescale was observed in many previous ultrafast spectroscopy experiments in pure water and was ascribed to the overall thermalization of the sample.²⁻⁶ This thermalization has also been routinely observed in the case of photoexcited solutes in aqueous solution²⁰. However, the ΔPDF intensity assigned to the 1st OO shell shows a non-monotonic time dependence in the first ~ 500 fs, which resembles the underdamped oscillation observed in a previous vibrational echo measurement⁶. This feature is a result of the initial structural response before the vibrational energy relaxation. In the rest of the manuscript, we will first focus on the 1st shell

HB dynamics in Fig. 2, then present the dynamics of hydrogen atoms in the 1st coordination shell in Fig. 3, and finally examine the thermalization dynamics in Fig. 4.

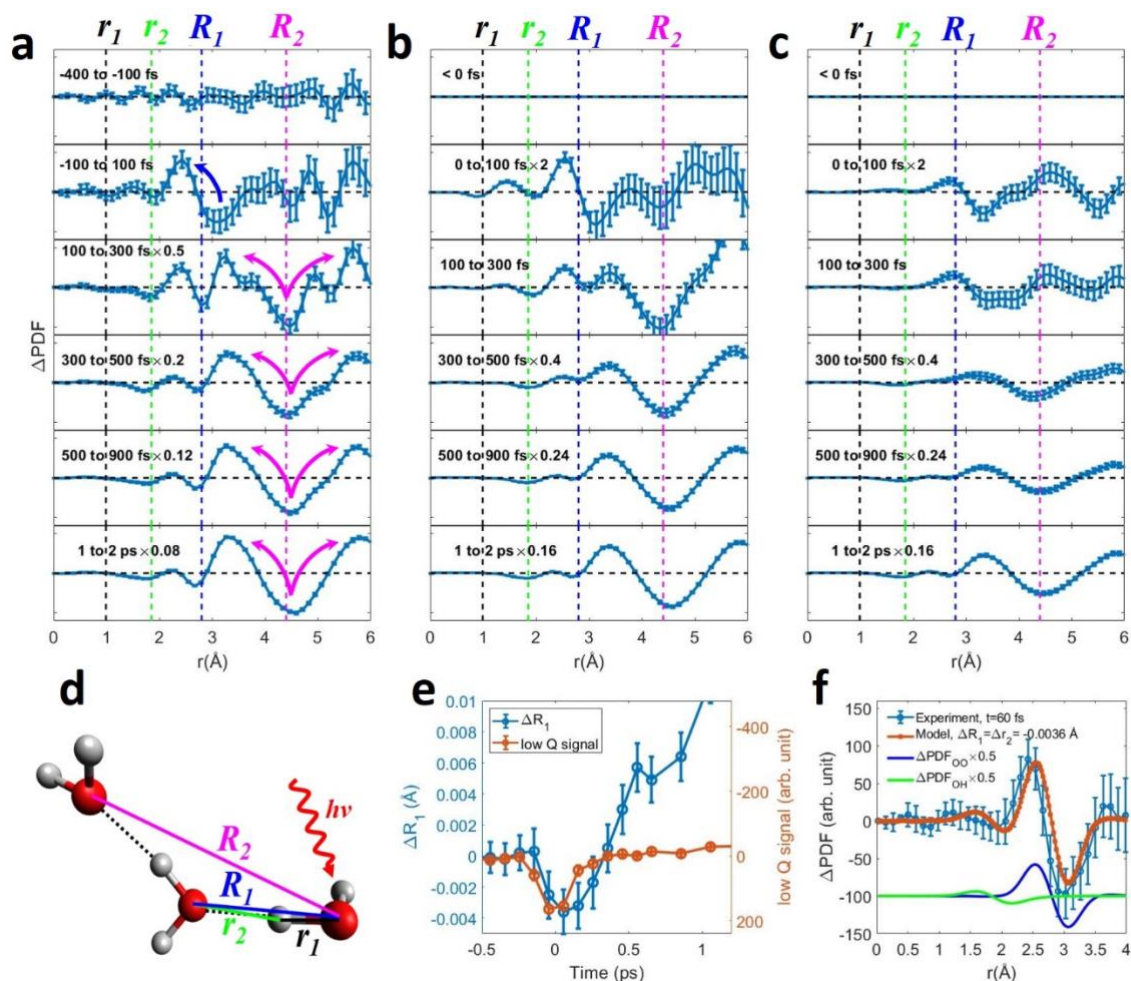


Fig. 2 | Transient HB strengthening. **a-c**, Experimental (**a**), simulated with quantum excitation (**b**), and simulated with classical excitation (**c**) Δ PDF for six selected time windows. Vertical dashed lines indicate the initial position of four distances (color code see part **d**). The vertical scale is the same for all sub-panels. Horizontal dashed lines are the baseline for each curve. The rows 2-6 in part **a** are scaled by 1, 0.5, 0.2, 0.12 and 0.08, and in part **b-c** are scaled by 2, 1, 0.4, 0.24 and 0.16, respectively. Colored arrows denote important atomic motions (see text). **d**, A ball-and-stick model showing four important distances. The color codes of the four important atom pairs are: black for covalent OH bonded r_1 , green for hydrogen bonded r_2 , blue for 1st OO shell R_1 , and magenta for 2nd OO shell R_2 . The wavy arrow represents the photoexcitation. **e**, The fitted 1st OO contraction from experimental data (blue symbols, left axis) and the low- Q signal (orange symbols, right axis). **f**, The experimental Δ PDF at 60 fs and its best fit (see text). The underlying Δ PDF for OO and OH pairs are plotted with a vertical shift for visibility. Symbols represent measurement and lines represent a Gaussian fitting. Error bars representing the SEM of 60 independent measurements (**a**, blue curve in **f**, orange curve in **e**), the SEM of 200 independent simulations (**b**, **c**), or the standard error from the fit (blue curve in **e**).

The experimental Δ PDFs over six selected time windows are displayed in Fig. 2a. In this manuscript, we use lower case letter “ r ” to represent OH distances and upper case letter “ R ” to represent OO distances, see Fig. 2d. Starting at 100-300 fs, the broadening of R_2 becomes the strongest signal (magenta arrows), marking the beginning of the ~ 1 ps heating process. For -100 to 100 fs, when the R_2 signal is still nearly absent, a strong contraction of R_1 is observed (blue arrow), indicating a transient strengthening of the HB. We extract the HB length change as a function of delay time using a simple single-parameter model: we assume that all of the R_1 and r_2 pairs expand or contract by the same amount ΔR_1 as a result of the motion of the 1st shell oxygen atom, with no change in any other atom pair distances (Methods). The fitting is applied for the Δ PDF signal between 1.5 and 3 Å to focus on the first coordination shell dynamics. The fitting results (blue curve in Fig. 2e) show a fast mean R_1 contraction of all OO distances with a maximum value of 0.0036 ± 0.0014 Å (mean ± 1 SE from fit), that disappears as the $\nu_{\text{OH}}=1$ population decays. This decay initiates a slower (~ 1 ps) R_1 expansion. Figure 2f shows the experimental and fitted Δ PDF at the maximum contraction (i.e. at 60 fs). Most features in the Δ PDF are captured by this simple 1-parameter model, except a deviation around the zero-crossing at 2.7 Å that will be discussed in Fig. 3. The time delay between the photoexcitation and the R_1 contraction is 81 ± 51 fs (SE from Gaussian fit), a value roughly equal to the half period of the HB stretching coordinate, as expected for the underdamped contraction of the HB.

The early R_1 contraction reflects the dynamics in the excited-unexcited OO pairs (one oxygen atom in the pair is from an excited molecule, and the other is from a neighboring unexcited molecule), which only accounts for 10% of atom pair population when the excitation fraction is 5%. Using 10% as a scaling factor, we obtain the averaged R_1 contraction to be 0.036 ± 0.014 Å for excited-unexcited pairs.

We performed extensive nonequilibrium molecular dynamics (MD) simulations using a neural network potential trained on *ab initio* MD simulations²¹ (Methods). The excitation process was modeled in two different ways: classical excitation with a hot-spot thermostat based on the generalized Langevin equation^{22,23} for 100 fs; instantaneous quantum excitation using the pure state $\nu_{\text{OH}}=1$ Wigner phase-space sampling based on the refined Lippincott–Schroeder model⁵, thereby accounting for the phase-space configurations of the excited quantum OH stretch vibrational state in a hydrogen bonded system (Extended Data Fig. 7 and Supplementary Information). The two simulated Δ PDFs are shown in Fig. 2b-c (details in Methods). The simulation with quantum excitation (Fig. 2b) is able to reproduce the shape of the experimental Δ PDF, including the early 1st shell OO contraction and the subsequent 2nd shell broadening. The simulation with classical excitation (Fig. 2c), on the other hand, predicts smaller changes in the structure and a delayed disordering of the 2nd shell compared to experiment and the quantum excitation. This comparison proves that accounting for the quantum distribution of the shared proton upon vibrational excitation is critical for correctly modeling the sub-picosecond dynamics of liquid water vibrational energy relaxation and redistribution. From here on, we focus on the quantum excitation simulation. In spite of the good match in shape between Fig.2a and b, the Δ PDF amplitude in the simulation is roughly

a factor of two lower than that in the experiment. This mismatch could originate from uncertainty in the experimental excitation fraction, or from limitations in the MD simulations, such as the neglect of potential coherent vibrational excitation involving multiple O-H bonds or quantum effects in the relaxation dynamics. In fact, our approach assumes that the decoherence time of the collective vibrational excitation to be faster than the excitation pulse.

The seemingly counterintuitive contraction-expansion behavior of the hydrogen bond is the result of both individual HB properties and the collective behavior of the HB network in water. In hydrogen bonded O-H...O systems, the O...O distance (R_1 here) decreases sharply as the O-H distance (r_1 here) increases. This behavior is observed experimentally²⁴ and explained by a number of theoretical models with various levels of complexity, such as the Lippincott-Schroeder model^{5,25,26}, simple proton donor-acceptor models²⁷, and an increase in the covalency of HB using bond order arguments^{24,28}. Ultimately, it is a result of the coupling between the OH stretching and the HB motions. By exciting the system from the $\nu_{\text{OH}}=0$ to the $\nu_{\text{OH}}=1$ state, the expected value for the O-H distance is increased by 0.024 Å for the quantum Wigner distribution, twice as much as its classical counterpart (Extended Data Fig. 8). Based on these models, the r_1 expansion in the excited OH stretching quantum state will lead to a strong R_1 contraction. Therefore, the early HB contraction is a fundamental quantum-mechanical property of hydrogen-bonded systems during the excitation of the OH stretch that appears locally around the excited molecules. This motion also can be understood as the “intermolecular character” of the water vibration because of its appearance on the vibrationally excited $\nu_{\text{OH}}=1$ state. In addition, this contraction-expansion is responsible for the underdamped oscillatory behavior shown in the orange curve in Fig. 1f. On a longer timescale, energy is efficiently funneled from the stretching modes into all the degrees of freedom in water, leading to an increased temperature, HB weakening, and global R_1 expansion.

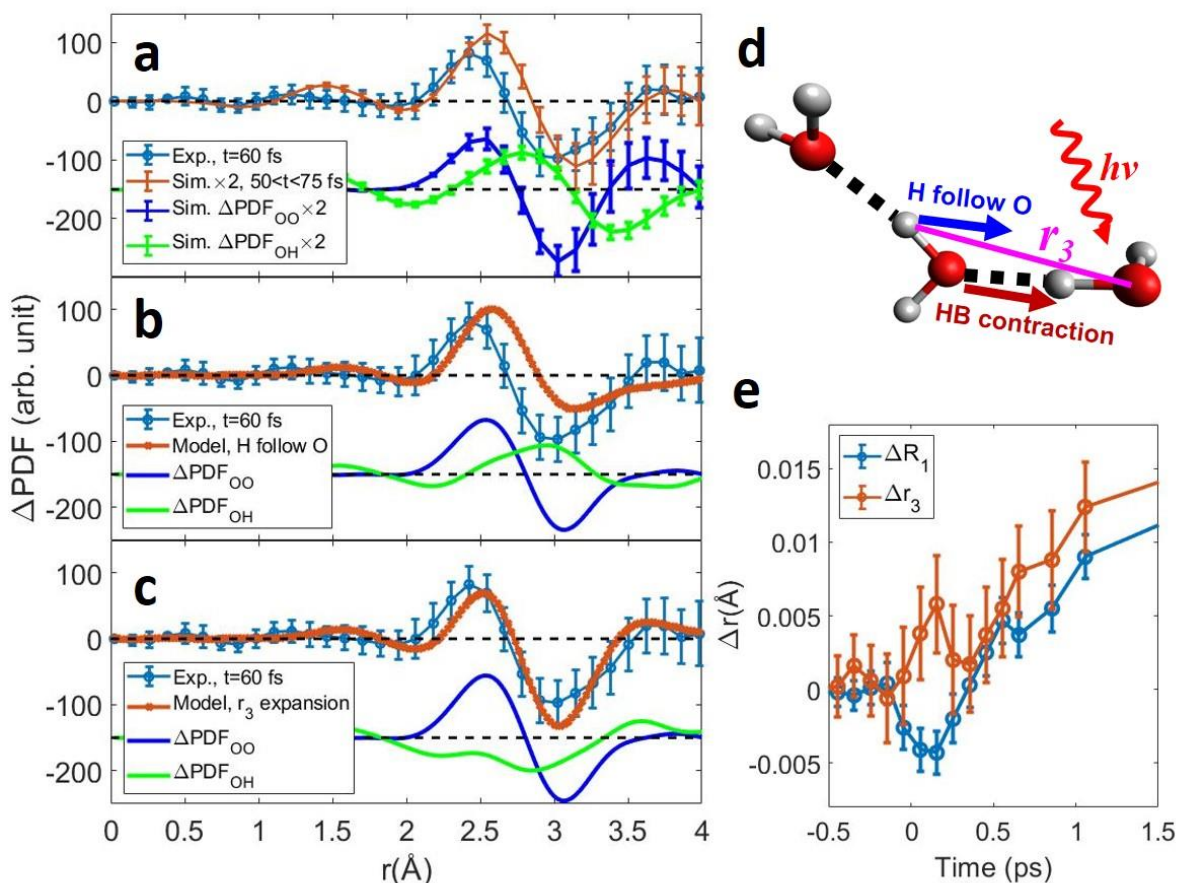


Fig. 3 | First shell hydrogen atom dynamics. **a**, The ΔPDF for experiment ($t=60$ fs) and simulation with quantum excitation ($50 < t < 75$ fs) with the simulation results amplified by a factor of two. **b-c**, The ΔPDF for two different models for the 1st shell hydrogen motion: **b**, hydrogen atoms follow parent oxygen atom ($\Delta R_1 = \Delta R_2 = \Delta R_3 = -0.0036$ \AA); **c**, r_3 expansion ($\Delta R_1 = \Delta R_2 = -0.0041$ \AA , $\Delta R_3 = 0.0038$ \AA). These values are obtained from the 1-parameter and 2-parameter χ^2 fittings (Fig. 2e and Fig. 3e). **d**, The ball-and-stick diagram for the H follow O model, corresponding to parts **a-b**. **e**, The fitted ΔR_l and Δr_3 from experimental data. In parts **a-c**, the OO and OH components are plotted separately with a vertical shift, and the dashed lines represent the baselines. Exp., experiment, Sim., simulation. Error bars representing SEM of 60 independent measurements (Exp. in **a-c**), SEM of 200 independent simulations (Sim. in **a**), or the standard error from the fit (**e**).

Electron scattering is capable of resolving hydrogen atoms in water molecules²⁹. Fig. 3a shows the experimental and simulated ΔPDF at around 60 fs, in which the simulation is able to reproduce all the major features of the experimental curve except the zero-crossing around 2.7 \AA . In the previous analysis (Fig. 2e-f), we have used a minimalistic model that does not account for the motion of the 1st shell hydrogen atoms. Here we consider the hydrogen atom dynamics by additionally shifting r_3 , the distance between the two 1st shell hydrogen atoms and the photoexcited oxygen atom (marked in Fig. 3d). In Fig. 3b we assume that the 1st shell hydrogen atoms follow the parent oxygen atom ($\Delta r_3 = \Delta R_1$), as shown by the ball-and-stick

model in Fig. 3d. The Δ PDF predicted with this model somewhat matches with simulation but disagrees with the experiment considerably, indicating that the 1st shell hydrogen atoms are not passively following their parent oxygen atom. Fig. 3c shows that the experimental Δ PDF can be better reproduced by an r_3 expansion model. To capture the r_3 as a function of time, we performed a two-parameter fitting, where ΔR_1 and Δr_3 are the two fitting parameters, Δr_2 is set to be equal to ΔR_1 , and all other atom pair distances are unchanged (Methods). While this two-parameter model (Fig. 3e) more accurately reproduces the experimental findings during the first ~ 200 fs, to do so requires an unphysical expansion of the OH bond length in the central HB accepting molecules in Fig. 3d. This indicates the origin of the discrepancy between experiment and MD simulation results for more subtle intermolecular interactions. Potential origins of the discrepancy between theory and simulation include the lack of quantum effects in the Newtonian relaxation dynamics in simulation, the assumption of localized vibrational excitation in the present simulation, or the breakdown of the rudimentary pair distance-shifting model used for analyze the experimental data.

At later delay times, thermalization becomes the dominant source of the Δ PDF signal. In scattering experiments, the temperature of water can be characterized by g_2 , the peak height of the 2nd OO shell in the radial distribution function¹⁰. Figure 4a shows the experimental g_2 and the corresponding temperature, using the calibration provided by Sellberg et al.¹⁰ (Methods). The temperature starts to rise at ~ 300 fs and increases by 37.5 ± 3.5 K over the 2.2-ps observation window. The time constant for the temperature rise is roughly 1 ps. The experimental Δ PDF at 2.2 ps is plotted in Fig. 4b, matching well with a simulated Δ PDF from two equilibrated water boxes with a temperature difference of 37 K. We have also measured the scattering signal and temperature evolution up to 100 ps, presented in Extended Data Fig. 2 (Methods).

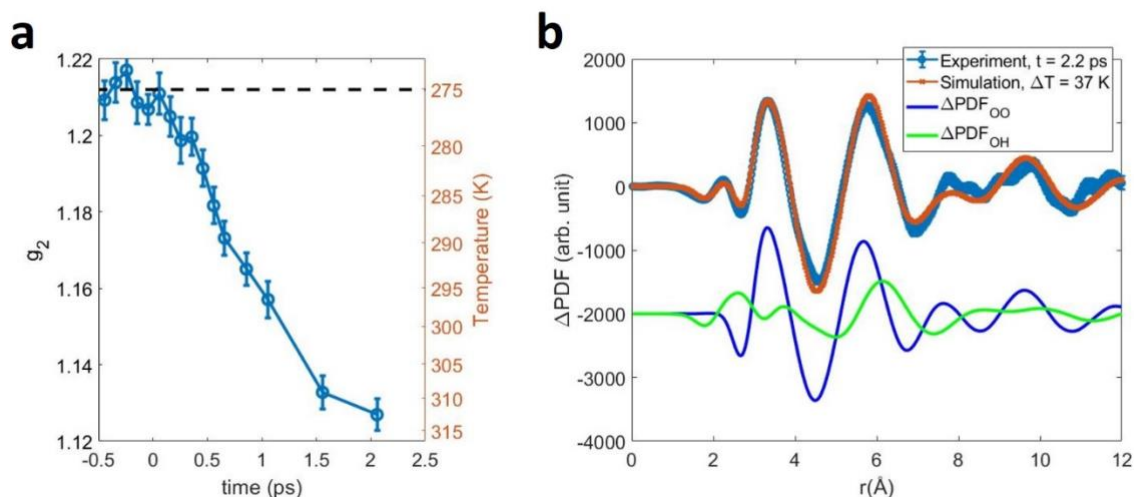


Fig. 4 | Thermalization. **a**, Experimental g_2 , the peak height of the 2nd OO shell in the radial distribution function and corresponding temperature of water. **b**, The experimental Δ PDF at 2.2 ps and simulated Δ PDF from two equilibrated water boxes at 275 and 312 K. The Δ PDF_{OO} and Δ PDF_{OH} from simulation are plotted with a vertical shift for visibility. Error bars representing SEM of 60 independent measurements.

Our observations shed new light on the coupling between intra- and intermolecular vibrations in water. Early studies have been primarily focusing on the relaxation pathway of the water vibration, which showed that the strong Fermi resonance coupling between the stretching modes and the first overtone of the bending mode is a key step in OH stretch relaxation^{3,7}. Recently, using ultrafast broadband 2D infrared spectroscopy, Ramasesha et al. have measured a unique spectral feature in the first ~ 50 fs⁴, confirming the existence of intermolecular motions preceding vibrational relaxation, but the structural dynamics during this time remains unclear. In this experiment, we have identified the very first intermolecular structural response to be an OO contraction in the 1st coordination shell. Given OH stretching strengthens HB while both bending and libration weakens HB³⁰, the observed OO contraction suggests, counterintuitively, that the intermolecular structural reorganization (which involves the translational motion of the heavy oxygen atoms) occurs before the Fermi resonance coupling into the bending overtone (which only involves the motion of light hydrogen atoms). Our observation confirms that the strong coupling between intra- and intermolecular modes is a defining characteristic of water vibrational structure⁴, and, in addition, provides a direct atomic resolution visualization of the intermolecular character of water vibration.

Data availability

Experimental data were generated at the MeV-UED facility at the SLAC National Accelerator Laboratory. Data behind each figure are available in Zenodo with the identifier DOI: 10.5281/zenodo.4050593. Raw datasets are available from the corresponding authors on reasonable request.

Code availability

The non-commercial codes used for the simulation and analysis here are available from the corresponding authors on reasonable request.

Acknowledgements We thank the helpful discussion with Thomas E. Markland. We thank Gregory M. Stewart for the help of making Fig. 1a. The experiment was performed at SLAC MeV-UED facility, which is supported in part by the DOE BES SUF Division Accelerator & Detector R&D program, the LCLS Facility, and SLAC under contract Nos. DE-AC02-05-CH11231 and DE-AC02-76SF00515. J. P. F. N., and M. C. are supported by the U.S. Department of Energy Office of Science, Basic Energy Sciences under Award No. DE-SC0014170. K. L. is supported by a Melvin and Joan Lane Stanford Graduate Fellowship and a Stanford Physics Department fellowship. J. Y. T. F. H., A. C., T. J. A. W., E. B., N. H. L., T. J. M., and K. J. G. were supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division. A.M.L. acknowledges support from the DOE BES Materials Science and Engineering Division under contract DE-AC02-76SF00515. Z. C. and M. M. are supported by the DOE Fusion Energy Sciences under FWP No. 100182.

Author Contributions

J. Y., K. J. G., A. M. L. and X. W. proposed the study. J. P. F. N., K. L., E. B., M. C., D. P. D.,

M. L., M. M., X. S., T. J. A. W. J. Y., A. A. C., and X. W. developed the experimental setup. M. E. K. developed the pump laser setup. J. Y., J. P. F. N., E. B., Z. C., A. A. C., T. F. H., K. L., M. L., M. M., X. S., T. J. A. W and X. W. performed the experiment. J. Y. analyzed the experimental data and performed the χ^2 fitting. J. Y., A. N., T. J. M., and K. J. G. interpreted the experimental data. R. D. and D. D. performed the pump-probe MD simulation. J. P. F. N. performed the equilibrium water simulation. N. H. L. and T. J. M. performed the 1D and 2D quantum simulations and the *ab-initio* electron scattering simulation. J. Y., R. D., N. H. L., D. D., T. J. M., K. J. G. and X. W. wrote the manuscript with inputs from all authors.

Competing interests The authors declare no competing interests.

Correspondence and requests for materials should be addressed to J. Y., D. D., K. J. G., T. J. M. and X. W.

Methods

LUES data collection

The experimental data was collected at the SLAC MeV-UED facility. The experimental setup was described in detail in a previous publication¹⁶. The neat water was delivered through a gas-accelerated liquid jet¹⁷, under a flow rate of 0.20 mL/min and a helium carrier gas pressure of 72 psi. The sample thickness at the interaction point was measured to be ~ 100 nm using an optical interferometer. The electron beam was accelerated to a kinetic energy of 3.7 MeV using an rf-type photoinjector³¹. Each electron pulse contained roughly 60,000 electrons per pulse at the photocathode, and roughly 3,000 electrons per pulse at the sample location. The electron beam size was 88 (horizontal) \times 37 (vertical) μm FWHM, measured by a knife-edge scan. The transmission of the electron beam after the liquid sheet was measured to be $\sim 90\%$. The scattering patterns were recorded on a phosphor screen-based detector. In this experiment, the accessible Q range is 0.2 to 11.8 \AA^{-1} . A 2.9 mm diameter hole was drilled in the center of the phosphor screen to transmit the unscattered electron beam. The small angle scattering signal was obtained by intentionally off-center the scattering pattern on the phosphor screen.

The 3.018 μm pump laser pulse was generated by pumping a commercial optical parametric amplifier with a 800 nm pulse generated from a Ti:Sapphire laser system. The energy on the sample was roughly 22 μJ , the spot size was 360 (horizontal) \times 430 (vertical) μm FWHM, measured by a knife-edge scan. The spectrum of the pump laser was not directly measured due to the equipment limitation, but the spectra of the 2nd and the 3rd harmonic were measured after a BBO crystal. The 2nd harmonic was centered at 1.509 μm with a bandwidth of 25 nm FWHM, and the 3rd harmonic at 1.003 μm with a bandwidth of 17 nm FWHM, as shown in Extended Data Fig. 3. The pulse duration was not measured but estimated to be between 100 and 150 fs FWHM. The pump fluence was estimated to be around 18 mJ/cm^2 . The initial temperature, 275 ± 10 K, was determined through a fitting of static scattering pattern to a classical force-field simulation, detailed in a previous publication¹⁶. The electron pulse and the pump laser pulse were operated at a repetition rate of 360 Hz. The IRF is between 209 ± 4 fs (previous measurement¹⁶) and 224 ± 32 fs (fastest signal in the current

dataset).

We have also measured experimental data up to a delay time of 100 ps using a step size of 10 ps in a separate dataset under similar experimental conditions. For this dataset, the electron gun is operated under a “high charge mode”, where the charge per electron pulse is a factor of 2-3 higher but the overall temporal resolution is degraded to > 500 fs. From this dataset we extracted the temporal evolution of g_2 and temperature using the same method as in Fig. 4a in the main text, shown in Extended Data Fig. 2. The measurement shows that temperature rapidly increases in the first 10 ps and slowly recovered in the rest of the observation window. The temperature increased ~ 25 K at 100 ps.

The excitation ratio was estimated using three methods

1. 4.7%, from Beer-Lambert law using the pump fluence and the peak molar absorption coefficient measured by Bertie and Lan³².
2. 4.7%, using the 25K temperature increase measured in scattering signal at 100 ps delay. Detailed in the Supplementary Information.
3. 7.1%, using the 37K temperature increase measured in scattering signal at 2 ps delay. Detailed in the Supplementary Information.

Since the first two methods agree with each other, and 2 ps is likely to be too short for reaching a complete thermal equilibrium, we use 5% as an estimated excitation ratio in the main text. However, each of the three methods above is subject to experimental uncertainties, which might partially contribute to the factor-of-two disagreement in amplitude between experiment and simulation shown in Fig. 2a-b in the main text. The uncertainty in excitation ratio does not alter the main conclusion of this work. If the excitation fraction is 7% instead of 5%, the amplitude of the initial HB contraction will be ~ 0.03 Å rather than ~ 0.04 Å.

Scattering pattern processing

The scattering intensity $I(t; Q)$ is generated through a standard processing procedure of baseline subtraction, center finding, normalization and radial average.

The difference scattering curve $Q\Delta S(t; Q)$ is calculated using the following equation

$$Q\Delta S(t; Q) = Q \frac{I(t; Q) - I_{ref}(t < 0; Q)}{[\sum_{\alpha=1}^3 f_{\alpha}(Q)]^2} \quad (1)$$

where $I_{ref}(t < 0; Q)$ is a reference pattern that is taken before time zero, the sum over α is performed over the three atoms in a water molecule and $f_{\alpha}(Q)$ is the modified atomic scattering factor^{10,33}. Here the modified atomic scattering factors are computed using a similar method as Sorenson et al.³³, but adapted for electron scattering using the Mott-Bethe formula³⁴:

$$f_{\alpha}(Q) = \frac{Z - [1 + (a_{\alpha} - 1) \exp(-Q^2/2\delta^2)] f_{\alpha}^X(Q)}{Q^2} \quad (2)$$

where Z is atomic number (8 for oxygen, 1 for hydrogen), a_{α} is partial charge scaling factor (1.11 for oxygen, 0.56 for hydrogen), $\delta = 2.2 \text{ \AA}^{-1}$, and f_{α}^X is the atomic form factor under the

independent atom model for X-ray scattering, taken from Hubbell et al.³⁵.

The time zero in the experimental data is determined by the peak location of a Gaussian fitting to the low- Q signal shown in Fig. 1e in the main text.

Fourier-sine transform to calculate ΔPDF

The ΔPDF can be calculated through a Fourier-sine transform of $Q\Delta S(t; Q)$, as explained by Ihee et al.^{14,18}:

$$\Delta PDF(t; r) = r \int_{Q=1}^{Q_{max}} Q\Delta S(t; Q) \sin(Qr) e^{-0.03Q^2} dQ \quad (3)$$

where $e^{-0.03Q^2}$ is a damping term to avoid edge effects in the transform and is equivalent to a Gaussian smoothing in the real space. Only $Q > 1 \text{ \AA}^{-1}$ is used in equation (3) to avoid the contribution from the inelastic component at low Q . Q_{max} in this experiment is 11.8 \AA^{-1} . The experimental damped $Q\Delta S$ is plotted in Extended Data Fig. 4, which shows the high- Q noises in Fig. 1c are mitigated. The $PDF(r)$ and $\Delta PDF(t; r)$ used in the main text represent the probability of finding an atom pair at any distance r . The radial distribution function (RDF) $g(r)$, widely used in the literature and used in this work to make Fig. 4a in the main text, represents the probability of finding an atom pair in a unit volume at any distance r . The relation between the two representations, up to a scaling factor, is given by:

$$PDF(r) = 4\pi r^2 [g(r) - 1] \quad (4)$$

One-parameter and two-parameter χ^2 fitting

In the main text, we used a one-parameter (Fig. 2e) and a two-parameter (Fig. 3c) standard χ^2 fitting to extract bond distance changes. In the one-parameter fitting, a simple shift ΔR_l is introduced to the $g(r)$ for both the 1st OO shell (R_l) and the hydrogen bonded OH pairs (r_2), and the $g(r)$ for all other atom pairs are unchanged. From this modified $g(r)$, a scattering pattern is simulated (see **Equilibrium water simulation** section below), and then a ΔPDF is calculated from the simulated scattering pattern using equation (3) above. Several examples of the shifted $g(r)$ and ΔPDF are shown in Extended Data Fig. 5. The simulated ΔPDF is compared to the experimental ΔPDF and the result corresponding to minimum χ^2 value is returned as the fitting output. To exclude contributions from the covalent bond OH, the 2nd OO shell and other atom pairs, only distances between 1.5 and 3 \AA are used for the fit. The two-parameter fitting includes an additional parameter Δr_3 that additionally shifts $g_{OH}(r)$ for $r > 2.5 \text{ \AA}$, representing the change of the 1st shell OH distance, with all other conditions identical to the one-parameter fitting. The χ^2 is calculated through:

$$\chi^2 = \int_{r_{min}}^{r_{max}} \frac{(c_s \Delta PDF_{sim}(r,t) - \Delta PDF_{exp}(r,t))^2}{\sigma(r,t)^2} dr \quad (5)$$

where $r_{min}=1.5 \text{ \AA}$, $r_{max}=3 \text{ \AA}$, ΔPDF_{sim} and ΔPDF_{exp} are the simulated and experimental ΔPDF . c_s is a global scaling factor between experimental and simulation that is obtained by matching the 1st OO shell peak in charge-pair-distribution-function (next section in Methods, Extended

Data Fig. 6a). σ is the standard deviation of experimental data.

g_2 and temperature extraction

In Fig. 4 in the main text, we used g_2 , i.e., the peak height of the 2nd OO shell in the RDF, to extract the temperature for each delay time. To extract g_2 , we need to directly analyze the raw scattering patterns rather than the difference scattering patterns. This requires proper treatment of both the inelastic and structureless atomic scattering background.

In a recent paper, we have proposed a charge-pair-distribution-function (CPDF) that can be obtained directly from the raw patterns with neither atomic form factors nor background removal³⁶.

$$CPDF(t; r) = r \int_{Q=0}^{Q_{max}} Q^5 I(t; Q) \sin(Qr) e^{-kQ^2} dQ \quad (6)$$

The advantage of this method is that the contribution from inelastic and other forms of background are concentrated at $r < \sim 2$ Å, and thus does not affect the peak height of the 2nd shell at ~ 4.4 Å. The disadvantage is that each peak has two negative shoulders on each side. This disadvantage is not an issue for extracting the height of a single peak. A comparison of the static water data and simulation is given in Extended Data Fig. 6a, showing that experimental CPDF captures the 1st to the 4th OO shells. Extended Data Fig. 6b shows that the inelastic contribution in CPDF is limited to $r < 2.5$ Å. The CPDF analysis also provides a method to scale the simulated and experimental data based on the raw PDF, so that the analyses on ΔPDF is scaled independently. In this work, this scaling factor c_s was obtained by matching the height of the first OO peak in Extended Data Fig. 6a between experiment and theory. The obtained c_s was applied to both the χ^2 fitting and the temperature analyses.

The extracted CPDF at five different time windows are shown in Extended Data Fig. 6c. Once the height of the 2nd OO shell in CPDF is determined (Extended Data Fig. 6d), the g_2 can be determined with two calibration points. Here we use: 1) the starting temperature ($t < 0$) was 275 K (see ‘‘LUES data collection’’ section in Methods); and 2) CPDF=0 corresponds to $g_2=1$ by definition.

Equilibrium water simulation

The static water is modeled by classical MD with 4054 molecules in a $50 \times 50 \times 50$ Å boxes in GROMACS software suite using the TIP4P-Ew force-field³⁷, which has been demonstrated for the prediction of static water structure for both electron scattering¹⁶ and X-ray scattering³⁷ experiments. TIP4P-Ew force-field for equilibrium water simulations is chosen to maintain consistency with our previous work¹⁶ on static water analysis and determine the initial temperature of the sample. We have verified that, the neural networks potential(NNP)²¹, used for pump-probe simulation to achieve a higher accuracy for the femtosecond dynamics, provides results in good agreement with experiments and consistent TIP4P-Ew in the short range ($r < 6$ Å). However, the NNP does not provide accurate ΔPDF for $r > 6$ Å (Extended Data Figure 11). This may be because the NNP was trained against a set of

simulated trajectories that was computed using only 64 molecules²¹. In the main text, simulations in Fig. 1b and Fig. 4b are carried out with TIP4P-Ew force-field, and simulations in Fig. 2b-c and Fig. 3a are carried out with the neural network potential.

The classical MD trajectories were transformed into time-averaged RDF $g(r)$ using the VMD package, and the elastic scattering pattern was simulated using a formula given by Dohn et al³⁸,

$$I_{elastic}^{Electron}(Q) = \sum_l N_l f_l(Q)^2 + \sum_{l,m} f_l(Q) f_m(Q) \frac{N_l(N_m - \delta_{l,m})}{V} \times \int_0^{R_{box}} 4\pi r^2 [g_{l,m}(r) - 1] \frac{\sin(Qr)}{Qr} \frac{\sin(\frac{\pi r}{L})}{\frac{\pi r}{L}} dr \quad (7)$$

where the indices l, m are the type of atoms (O and H here), N_l is the number of atom type l , $f_l(Q)$ is the atomic form factor for l , $\delta_{l,m}$ is the Kronecker delta function, V is the volume of the simulation box, R_{box} is the length of the simulation box, $g_{l,m}(r)$ is the RDF of atom pair lm and L is half the length of the simulation box. The first term is the atomic component that does not contain structural information, and the second term is the molecular component that contains structural information.

The inelastic scattering cross-sections for electron and X-ray are related as³⁹:

$$I_{inelastic}^{Electron}(Q) = Q^{-4} I_{inelastic}^{X-ray}(Q) \quad (8)$$

where X-ray scattering is expressed in units of the Thompson X-ray scattering constant, and electron scattering is expressed in units of the characteristic Rutherford constant. The Q^{-4} factor comes from the r^{-1} Coulomb potential³⁴. The simulated inelastic scattering form factor (Fig. 1b in the main text) is obtained by adopting the singles- and doubles- configuration interaction quantum chemical simulation from Wang et al.⁴⁰ with the Q^{-4} factor applied. Once the scattering pattern is simulated, we use the same method as the experimental data analysis (equation (1) and equation (3)) to calculate the PDF and Δ PDF.

To validate the routine of RDF \rightarrow scattering pattern \rightarrow PDF, we compared the Δ PDF calculated both through this routine, and directly using equation (4) then a smoothing by convoluting with a Gaussian kernel. The result is shown in Extended Data Fig. 10.

Pump-probe MD simulation

To model the pump-probe experiment, MD simulations were carried out with periodic boundary conditions on a cubic box with side length of 25.05 Å, containing 522 water molecules, corresponding to a density of $\rho=0.994$ g/cm³. Water molecules were modeled according to the neural networks potential²¹ (NNP) trained on *ab initio* MD (AIMD) water structures based on the revised Perdew–Burke–Ernzerhof (RPBE)⁴¹ density functional with vdW corrections using the D3 method⁴². This machine-learning potential accurately represents the *ab initio* potential-energy surface of water and overcomes the bottleneck of the high computational costs and cubic scaling of AIMD simulations. Moreover, by adopting the vdW corrections, which consist of atom-pairwise specific dispersion coefficients and cutoff radii computed from first principles, NNP-based simulations are able to correctly predict the

density maximum and melting temperature of water²¹.

The system was initially prepared at 300 K with an NVT run by means of stochastic velocity rescaling⁴³ for 200 ps. After this run, additional 200 ps at 300K were performed, saving the atomic configuration (positions + velocities) every ps, in order to obtain the 200 independent replicas. Two different approaches, referred to as ‘classical’ and ‘quantum’, were used to model the excitation induced by the IR pump. In each case, 5% of the molecules (i.e. 26 molecules) were randomly excited following the experimentally estimated excitation ratio.

In the classical sampling, the molecules were excited by means of the generalized Langevin equation (GLE) thermostat^{22,23}, tuned at the OH stretch frequency ($\omega=3531\text{ cm}^{-1}$, computed from the Fourier transform of the velocity-velocity autocorrelation function) of the H₂O vibrational spectrum. Parameters for the GLE thermostat are provided in the Supporting Information. The thermostat was applied to 5% of the molecules for 100 fs and the system relaxation was observed without any thermostat coupling for 3 ps. The ‘classical’ excitation raises the instantaneous kinetic temperature of the OH stretch by $\sim 3000\text{ K}$. The first delay point after the 100-fs excitation phase is used as a reference point to calculate the difference signals in the main text figures.

Within the approximation of distinguishable particles, the path integral formalism enables a variety of approaches to sample equilibrium nuclear quantum distributions and dynamics⁴⁴⁻⁴⁶. Conversely, modeling vibrational excitation and relaxation at a quantum mechanical level still poses a severe methodological challenge. Here we opt for a semi-classical approach in which the quantum excitation is modeled according to the Wigner distribution function and the relaxation is classical. This approach is justified by the verification that zero-point energy leakage is slower than the sub-picosecond time scale of the local hydrogen-bond relaxation dynamics observed in the experiments (see section “**Zero-point energy leakage time**” in the SI).

In the quantum sampling, the excitation process was assumed instantaneous and localized to one of the two OH bonds with initial conditions for the excited OH stretch generated from the $\nu_{\text{OH}}=1$ Wigner distribution of the refined Lippincott–Schroeder model⁵. As shown by comparing to 1D and 2D NNP based OH stretching potentials in a frozen-environment picture (Section “**2D stretching NNP vs. Lippincott-Schroeder model**” in SI), this model provides a simple yet reasonable 1D description of the OH stretch motion. This inter- and intramolecular localized initial condition sampling rests on the assumption that the vibrational decoherence time of the expectedly collective excitation is fast compared to the excitation pulse. Specifically, starting from the classically sampled equilibrium phase-space distributions, the displacement of the H atom along the excited OH bond in the excited molecules as well as the corresponding components of the atomic velocities of the O and H atoms were resampled from the $\nu_{\text{OH}}=1$ Wigner distribution of the Lippincott–Schroeder model by rejection sampling. The unexcited OH bonds in the excited molecules were resampled from the corresponding $\nu_{\text{OH}}=0$ Wigner distribution. The quantum sampling was restricted to the region of phase space with positive-valued Wigner distribution. To separate

the effect of the excitation process from the change inevitably induced by replacing the classical with the quantum sampling, the Δ PDF calculations were computed with reference to simulations with initial conditions for both OH bonds in the excited molecules sampled from the $\nu_{OH}=0$ quantum distribution. The vibrational eigenstates were obtained from direct diagonalization of the Fourier Grid Hamiltonian on a position grid of 1024 points ranging from 0.8 to 4.0 a.u. The $\nu_{OH}=0,1$ eigenstates of the Lippincott–Schroeder model and the corresponding Wigner functions obtained by discrete inverse Fourier transform are shown in Extended Data Figure 7. The average between 0 and 25 fs of the $\nu_{OH}=0$ dynamics is used as a reference point to calculate the difference signals in the main text figures.

As shown in Extended Data Figure 9c, the quantum excitation brings the instantaneous kinetic temperature of the OH stretch to ~ 5500 K which is compatible with the photon energy of ~ 4800 K in the experiments. Nonequilibrium simulations were averaged over 200 independent replicas, where every replica is characterized by a different set of initial atomic positions, atomic velocities (as explained above) and by a different subset of excited molecules. The equations of motion are integrated with a time-step of $\delta t=0.25$ fs. Long-range electrostatic interactions are calculated using the particle-particle particle-mesh solver algorithm⁴⁷. All simulations were carried with the LAMMPS simulation package⁴⁸.

In the simulations, the R_I position (Fig. 2e-f) is calculated by means of a weighted average of the RDF $g_{OO}(r;t)$

$$R_1(t) = \frac{\int_{r_1}^{r_2} r g_{OO}(r;t) dr}{\int_{r_1}^{r_2} g_{OO}(r;t) dr} \quad (9)$$

where r_1 is 2.4 Å and r_2 is 3.3 Å, taken from the isosbestic points reported by Skinner et al.¹⁹.

Determining instantaneous kinetic temperature from pump-probe MD simulation

Instantaneous kinetic temperature of vibrational modes was computed by considering specific components of the atomic velocities. The temperature of OH stretching modes was computed by projecting the difference between oxygen and hydrogen velocities on the unit vector identifying the OH bond,

$$T_{stretch} = \frac{2}{k_B} \cdot \frac{\mu}{2} \left[(v_O - v_H) \cdot \frac{\overrightarrow{d_{OH}}}{d_{OH}} \right]^2 \quad (10)$$

where μ is the reduced mass for O and H atoms, $\overrightarrow{d_{OH}}$ is the vector pointing from O atom to H atom, v_O and v_H are the velocities for O and H atoms. The temperature of rotational modes was calculated by considering only the hydrogen velocity components perpendicular to the OH bond, once the velocity of the molecular center of mass was subtracted

$$T_{rot} = \frac{1}{k_B} \frac{m_H}{2} \left[(v_H - v_{COM}) \times \frac{\overrightarrow{d_{OH}}}{d_{OH}} \right]^2 \quad (11)$$

where m_H is the mass of H atom, and v_{COM} is the velocity of the molecular center of mass. In this case, T_{rot} involves mostly bending and libration modes. The simulated temperature evolution for the quantum and classical excitation are shown in Extended Data Fig. 9.

***Ab initio* electron scattering simulation**

The *ab initio* electron scattering is used to predict the inelastic and elastic signal change of the first vibrationally excited OH stretching state ($\nu_{OH}=1$) in comparison to the ground state ($\nu_{OH}=0$). The simulation (Extended Data Fig. 1) is performed on a single isolated water molecule using an OH distance of 1.021 Å for the $\nu_{OH}=1$ excited bond and 0.994 Å for the unexcited (corresponding to $\nu_{OH}=0,1$ level at an R_1 distance of 2.80 Å) and 0.989 Å for $\nu_{OH}=0$ (R_1 distance of 2.85 Å), computed as position expectation values of the refined Lippincott–Schroeder model (see **Pump-Probe MD simulation** section above). Rotationally averaged elastic and inelastic scattering signals were computed at the complete active space self-consistent field level of theory with the aug-cc-pVDZ⁴⁹ basis set and an active space containing 8 electrons in 7 orbitals ($2a_1, 3a_1, 1b_2, 1b_1, 4a_1, 2b_2, 2b_1$). The signals were evaluated using a Q -grid ranging from 0.0 to 10.0 Å⁻¹ (increments of 0.1 Å⁻¹) and a 590-point Lebedev quadrature using the implementation in the TeraChem program⁵⁰⁻⁵² presented in previous work⁵³. Cosine and sine squared angular distributions were used to simulate the contribution from the excited and unexcited fractions, respectively. The simulation predicts a sharp increase of inelastic scattering that is maximized at $Q=0$ and significantly stronger than the change in elastic scattering at small Q . This sharply increasing $Q\Delta S$ signal as Q approaches 0 matches with both our $Q\Delta S$ data around time zero and the characteristic shape of inelastic electron scattering (see, e.g. Ref.54). For the $Q\Delta S$ signal at $Q>1$ Å⁻¹, they do not match the characteristic shape of inelastic scattering. Therefore, we concluded that they belong to the elastic component (see Fig. 1c caption) and were used in the Fourier-sine transform to compute ΔPDF .

Comparison to time-resolved X-ray scattering

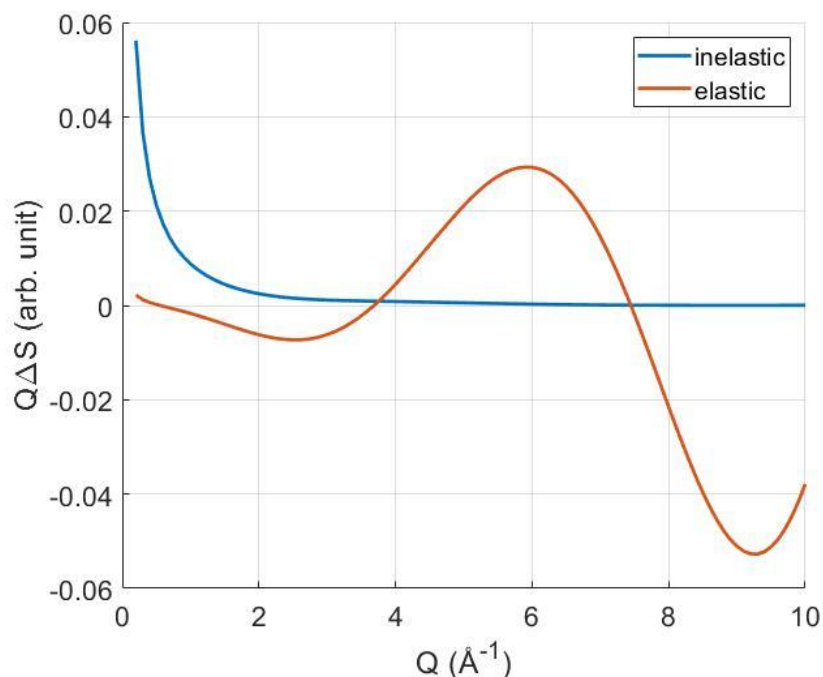
Time-resolved X-ray scattering (TRXS) is a well-established experimental technique that can also measure atomic motions on picosecond (using synchrotrons) and femtosecond (using XFELs) timescale. Therefore, it is useful to discuss the key differences between LUES and TRXS, especially in the context of this particular experiment. For this experiment, four key differences are worth noting:

1. The available maximum Q range in this work is 11.8 Å⁻¹ while the state-of-the-art TRXS with femtosecond resolution is roughly 6.5 Å⁻¹, using an XFEL with 12.7 KeV photon energy (See, e.g. Ref. 55). A comparable Q range would require a photon energy of ~25 KeV. Such a photon energy is not yet demonstrated in TRXS experiments using XFELs, but is expected to be achieved in the near future (e.g. SLAC LCLS-II facility or European XFEL facility).
2. For liquid samples, one of the advantages of TRXS over LUES is the option of using a regular round jet (with a typical thickness of 50-100 μm) rather than a flat jet (with a thickness of ~100 nm), thanks to its higher penetration depth. A thicker jet is much easier to

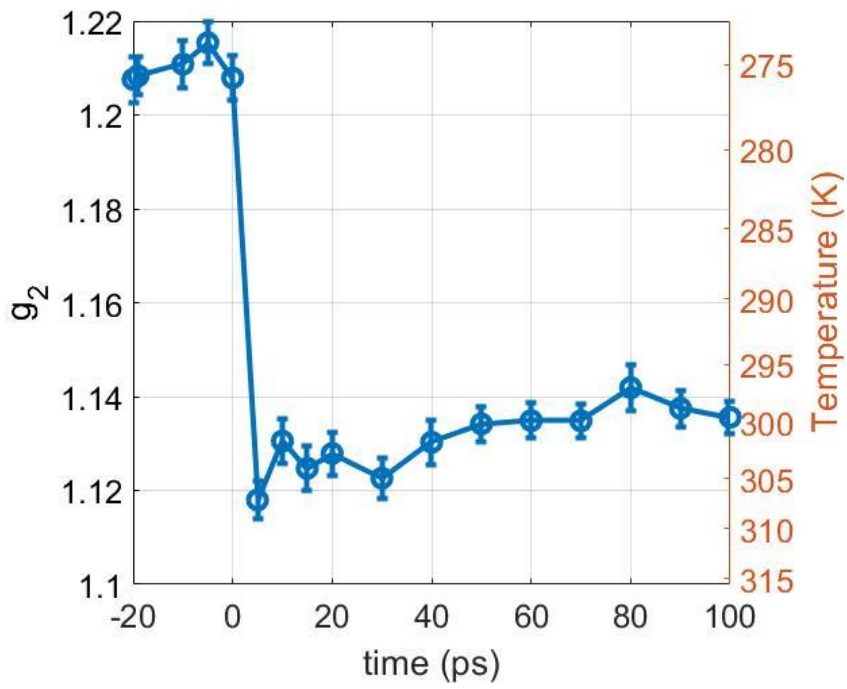
operate under vacuum. However, this would not work for this particular experiment, because the penetration depth of the pump laser is only ~ 800 nm. This is to say that TRXS would have to use a flat jet as well. The combination of hard X-ray pulses from XFEL with ultrathin liquid jet in vacuum is a non-trivial technique that is still under R&D phase.

3. The small-angle inelastic scattering is a unique feature to electron scattering.

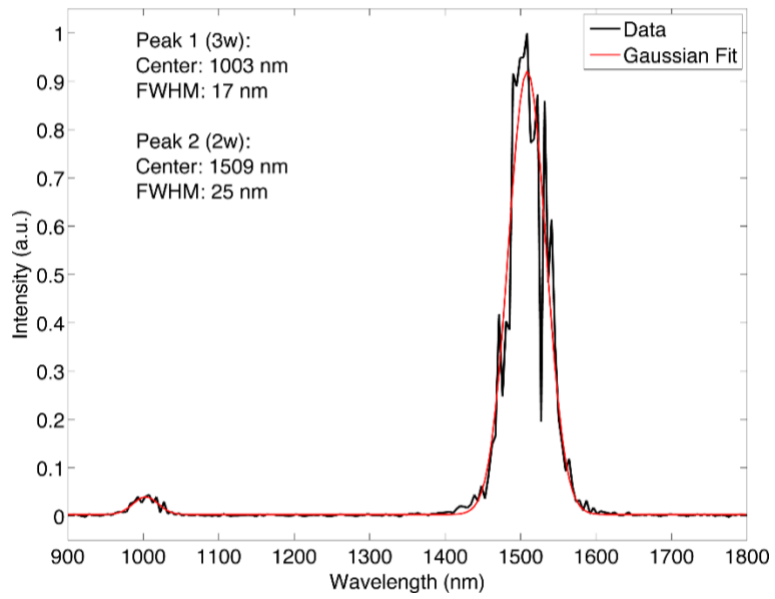
4. Protons are visible in LUES while not visible in TRXS thanks to the Coulomb interaction. Therefore, analyses in Fig. 3 will not be possible with TRXS.



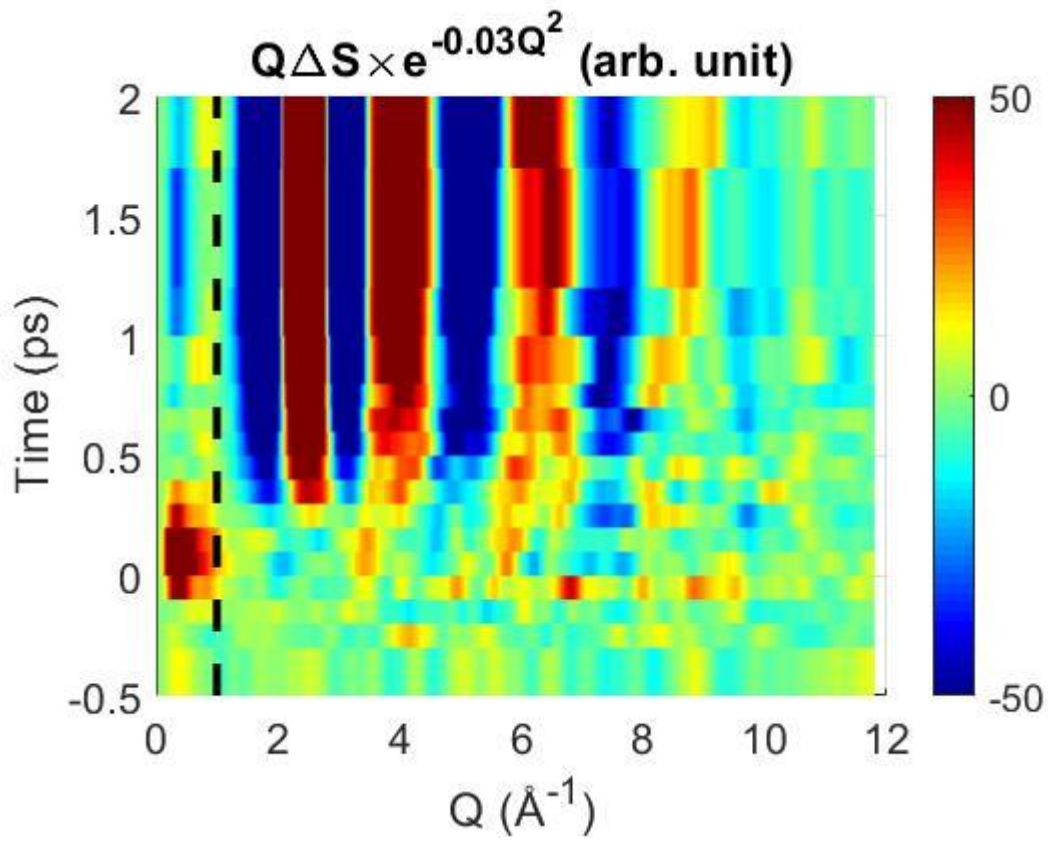
Extended Data Figure 1 | Ab initio simulation of the inelastic and elastic scattering signal change for $\nu_{\text{OH}}=1$ in comparison to $\nu_{\text{OH}}=0$. The simulation is performed on a single water molecule with OH bond lengths adjusted to the equilibrium length for each vibrational state as predicted by Bakker et al⁵, more details see Methods.



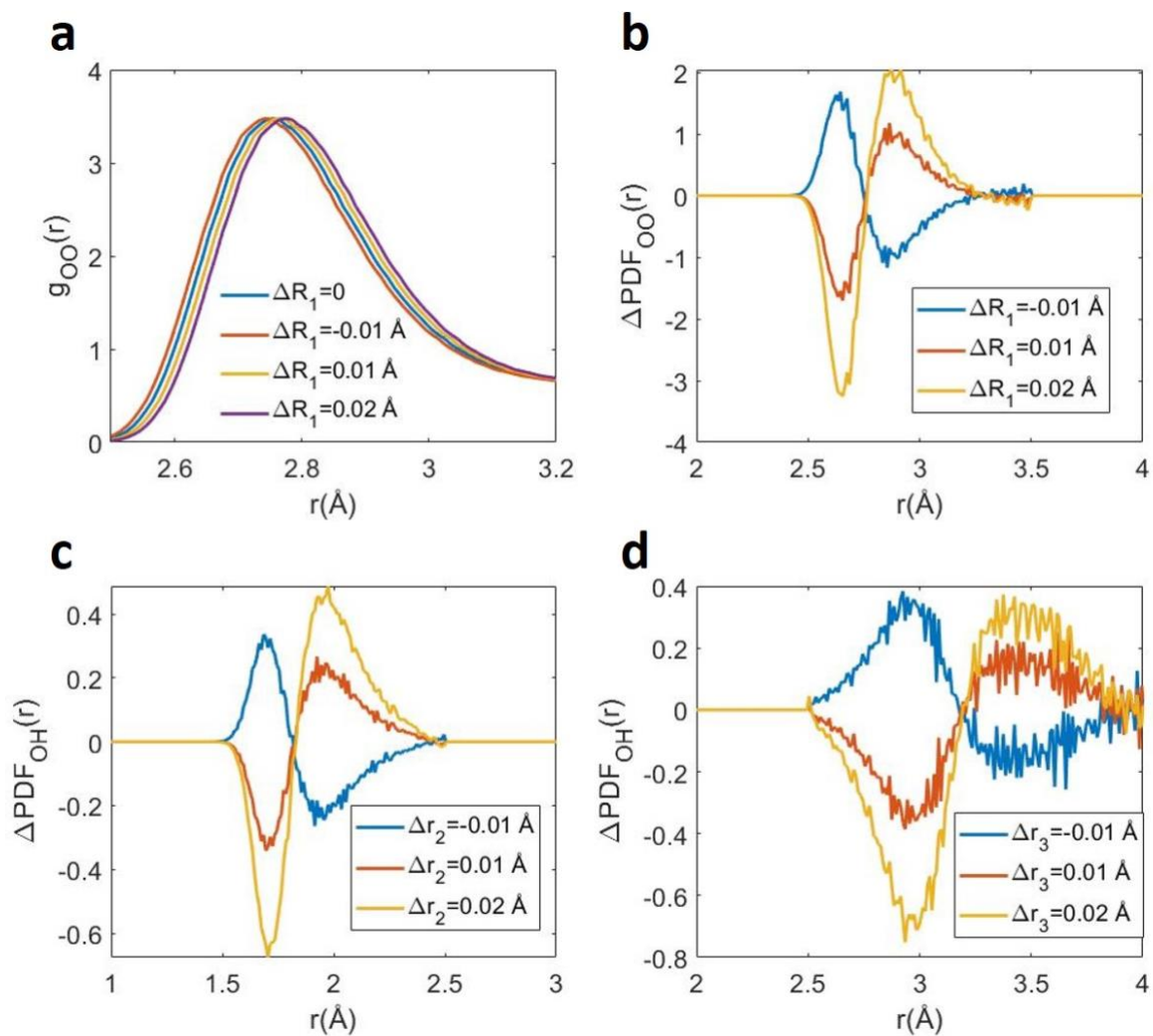
Extended Data Figure 2 | Experimental g₂ and temperature evolution up to 100 ps.



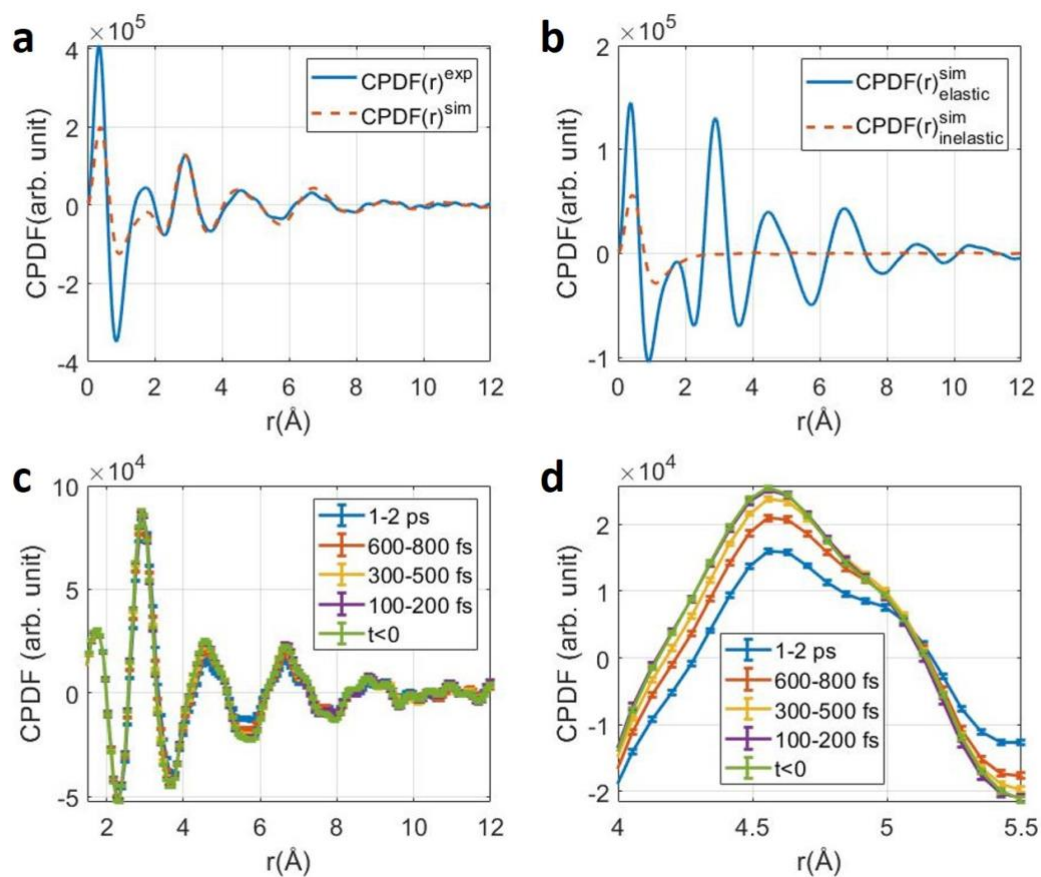
Extended Data Figure 3 | Spectrum of the second and the third harmonics of the pump laser.



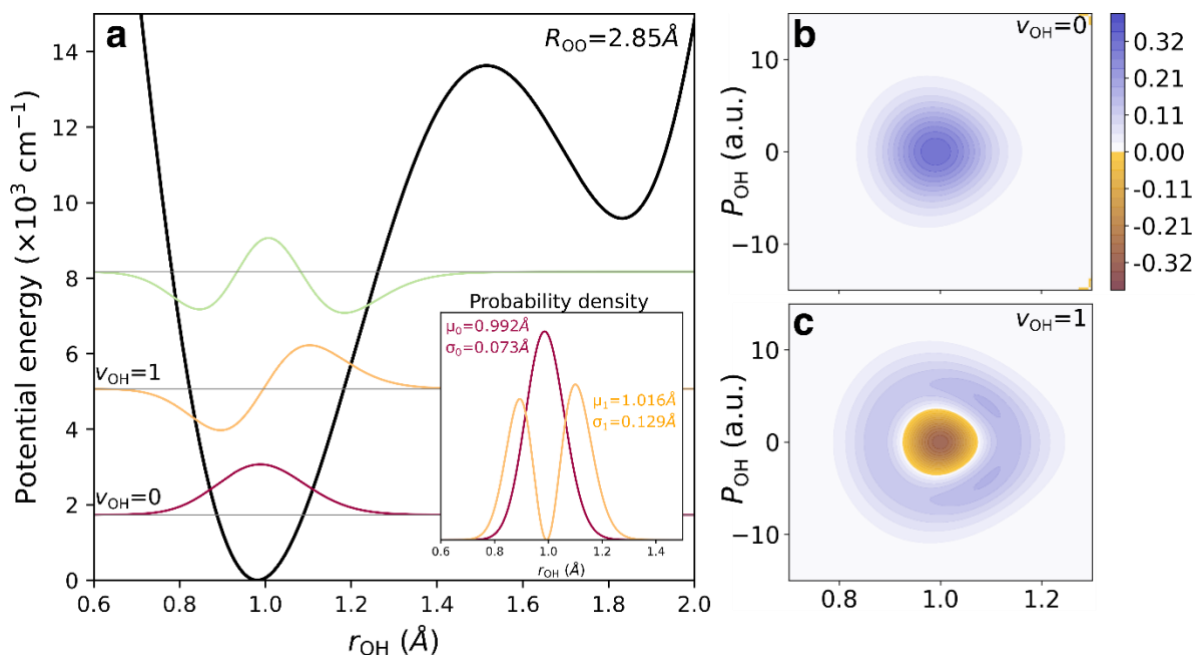
Extended Data Figure 4 | Damped $Q\Delta S$ from experimental data. This is related to the Fig. 1c in the main text by the damping term $e^{-0.03Q^2}$, see equation (3) in Methods.



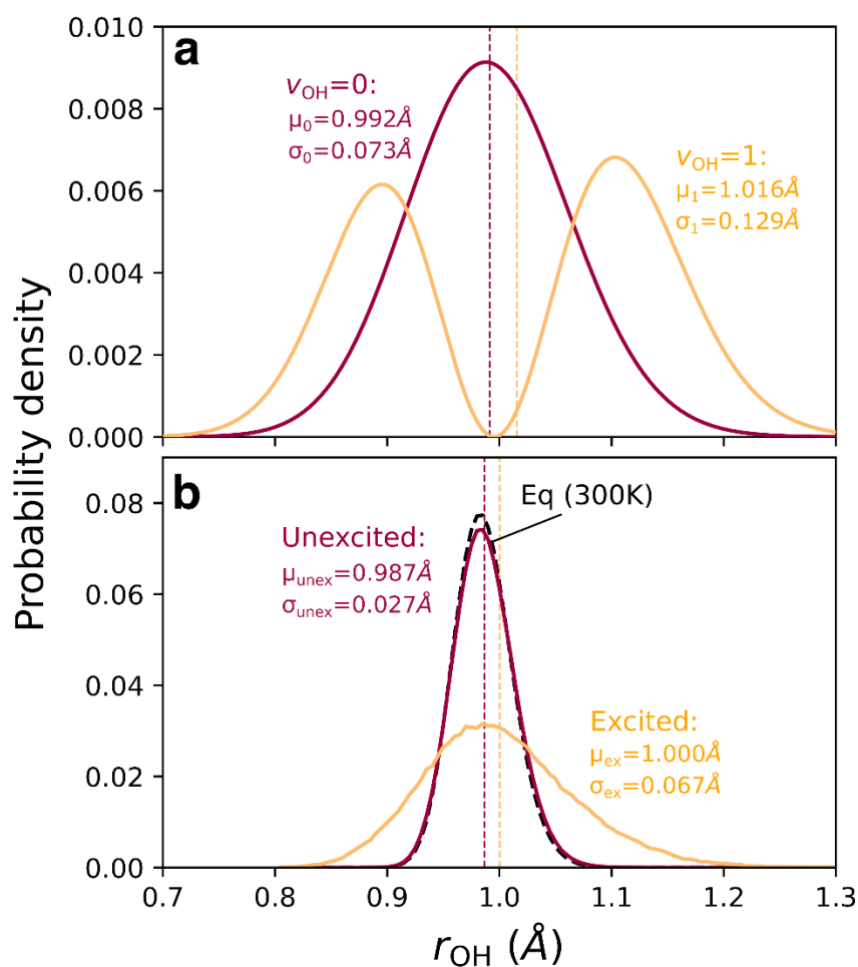
Extended Data Figure 5 | Examples of pair distances shift. **a**, $g_{OO}(r)$ around the 1st OO peak for four different ΔR_1 . **b**, ΔPDF_{OO} for three different ΔR_1 . **c**, ΔPDF_{OH} for three different Δr_2 . **d**, ΔPDF_{OH} for three different Δr_3 .



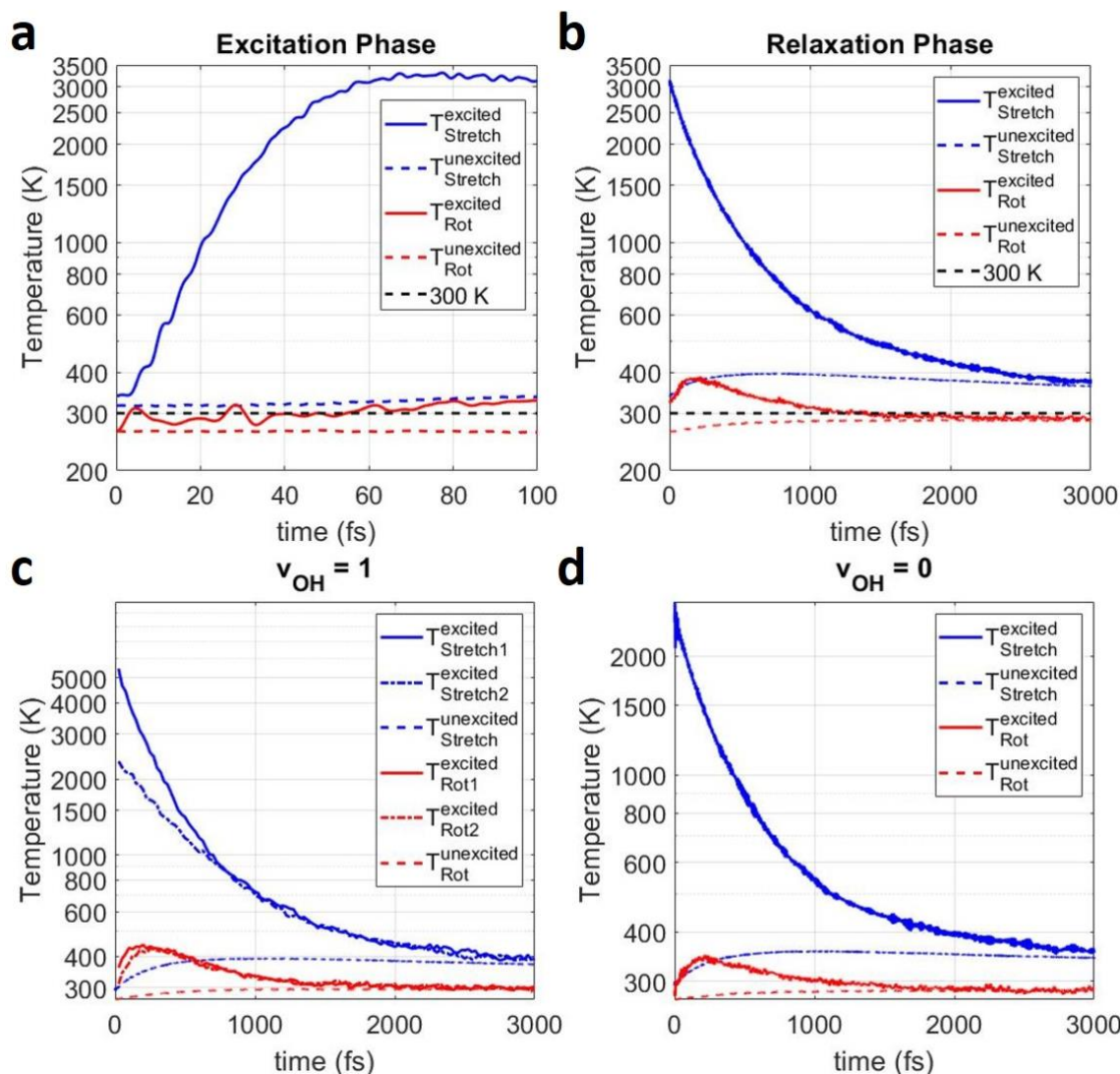
Extended Data Figure 6 | CPDF analysis (defined by equation (6), see Methods). **a**, A comparison of experimental and simulated CPDF. The overall scaling factor is achieved by matching the height of the 1st OO between experimental and simulated curves. The simulation is a 275 K water box under equilibrium condition. **b**, The simulated elastic and inelastic components of the CPDF, the inelastic component is concentrated to $r < 2.5$ Å. Sim. = simulated. Exp. = experimental. **c**, CPDF for five delay windows (labeled in the legend) in full r range. **d**, CPDF for five delay windows (labeled in the legend) around the 2nd OO shell. The peak height around 4.6 Å is used to extract g_2 for Fig. 4a in the main text.



Extended Data Figure 7 | Wigner sampling. **a**, The three lowest eigenstates (colored lines) and eigenvalues (horizontal gray lines) of the Lippincott-Schroeder model potential (black line). Insert: the probability distribution of the $v_{\text{OH}} = 0$ and $v_{\text{OH}} = 1$ states, μ and σ represent mean and standard deviation. **b-c**, Wigner distribution for $v_{\text{OH}} = 0$ and 1, respectively. The region of phase space with negative values of the $v_{\text{OH}} = 1$ distribution (orange shades) was excluded from the sampling. Note the different color gradient used for negative function values. Lippincott-Schroeder model ($R_{\text{OO}} = 2.85 \text{\AA}$) is used for sampling of the initial displacements and velocities along the OH bonds of the excited molecules.

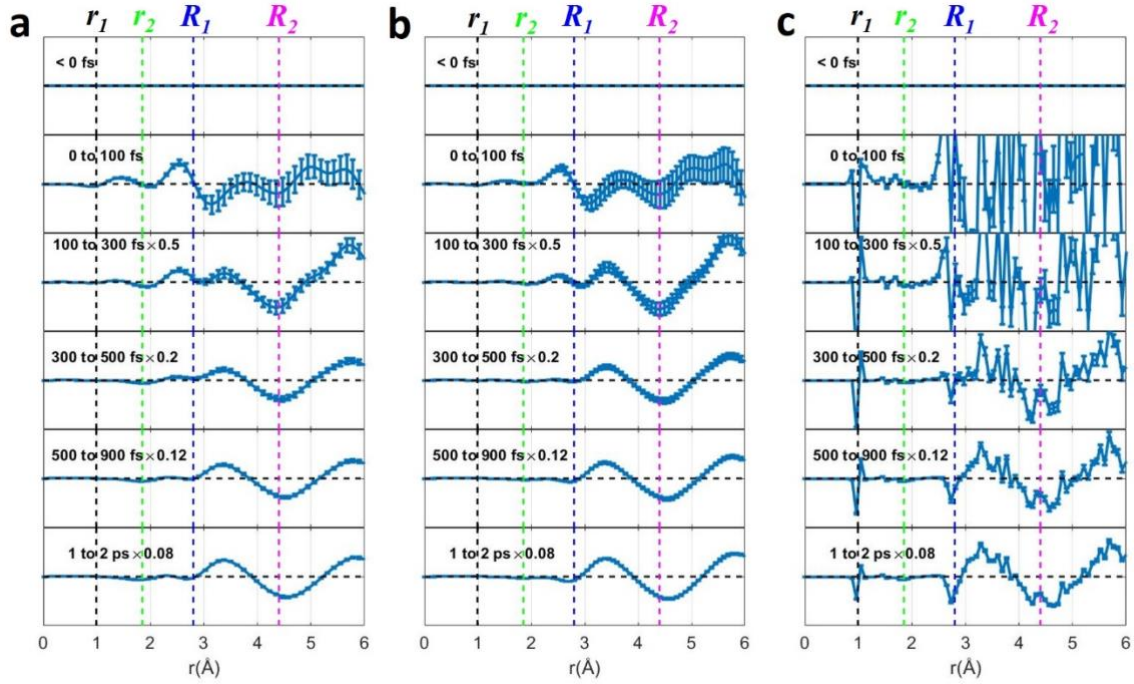


Extended Data Figure 8 | Probability density from classical and Wigner sampling. a, Wigner sampling. Magenta represents $v_{OH}=0$, yellow represents $v_{OH}=1$. **b,** Classical sampling. Magenta and yellow represent unexcited and excited molecules, respectively, calculated by averaging over the final 10-fs window during the excitation phase. Dashed black represents the equilibrium water before excitation. The vertical dotted lines represent the equilibrium distance for each curve, and μ and σ represent the mean and standard deviation of each curve, respectively.

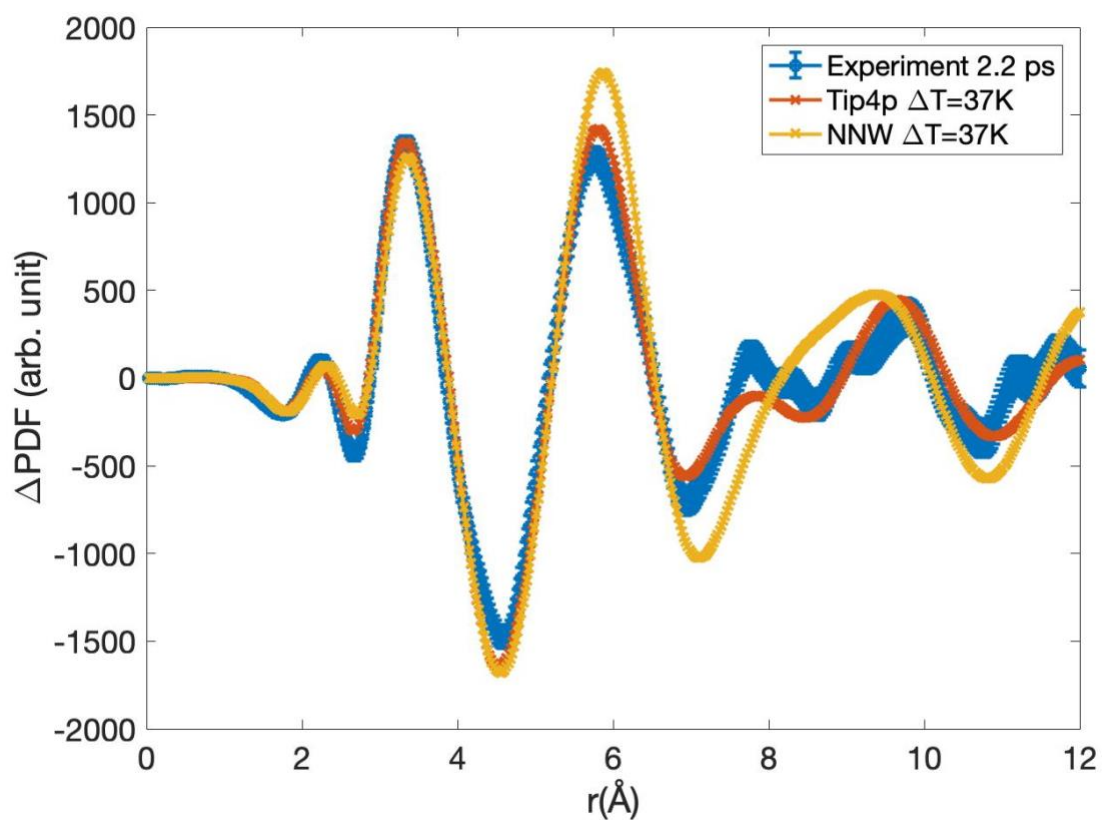


Extended Data Figure 9 | Simulated instantaneous kinetic temperature evolution. a-b, classical excitation. **a,** During the 100-fs excitation phase. **b,** during the 3-ps relaxation phase. **c-d,** quantum excitation.

c, $\nu_{\text{OH}} = 1$. **d,** $\nu_{\text{OH}} = 0$. T_{stretch} and T_{rot} are defined in equations (10) and (11). In part **c**, the subscript “Stretch1” and “Rot1” indicate the OH bond corresponding to $\nu_{\text{OH}} = 1$ Wigner sampling, and the “Stretch2” and “Rot2” indicate the OH bond corresponding to $\nu_{\text{OH}} = 0$ Wigner sampling. The superscript “excited” indicates Wigner sampling. Excited and unexcited molecules are calculated separately. The initial temperature before excitation is 300 K.



Extended Data Figure 10 | Δ PDF simulated using different methods. **a**, The Δ PDF simulated using the same method as Fig. 2b in the main text, i.e. by first simulating the electron scattering pattern using equation (7), then transforming to real space using equation (3). **b**, The Δ PDF simulated by directly applying equation (4), and smoothed by convolution with a Gaussian kernel with a FWHM of 0.53 Å. The weight of OO, OH and HH pairs are chosen to be 1, 0.4 and 0.16, respectively, obtained by atomic scattering cross section and the relative number of each types of atom pairs. The 0.53 Å FWHM of the Gaussian Kernel is obtained using $2\pi/Q_{\max}$, where $Q_{\max}=11.8\text{\AA}^{-1}$ is the maximum Q range in this experiment. **c**, The Δ PDF simulated by directly applying equation (4) without Gaussian smoothing. The vertical scales of all sub-panels are identical.



Extended Data Figure 11 | Comparison of equilibrium ΔPDF simulation. ΔPDF from experiment at 2.2 ps (blue with error bars), simulation using Tip4p-Ew force field (orange) and simulation using machine-learning force field (yellow).

References

- 1 Stillinger, F. H. Water Revisited. *Science* **209**, 451-457, doi:10.1126/science.209.4455.451 (1980).
- 2 Perakis, F. *et al.* Vibrational Spectroscopy and Dynamics of Water. *Chem. Rev.* **116**, 7590-7607, doi:10.1021/acs.chemrev.5b00640 (2016).
- 3 Lindner, J. *et al.* Vibrational relaxation of pure liquid water. *Chem. Phys. Lett.* **421**, 329-333, doi:<https://doi.org/10.1016/j.cplett.2006.01.081> (2006).
- 4 Ramasesha, K., De Marco, L., Mandal, A. & Tokmakoff, A. Water vibrations have strongly mixed intra- and intermolecular character. *Nat. Chem.* **5**, 935-940, doi:10.1038/nchem.1757 (2013).
- 5 Bakker, H. J. *et al.* Transient absorption of vibrationally excited water. *J. Chem. Phys.* **116**, 2592-2598, doi:10.1063/1.1432687 (2002).
- 6 Fecko, C. J., Eaves, J. D., Loparo, J. J., Tokmakoff, A. & Geissler, P. L. Ultrafast Hydrogen-Bond Dynamics in the Infrared Spectroscopy of Water. *Science* **301**, 1698-1702, doi:10.1126/science.1087251 (2003).
- 7 Ashihara, S., Huse, N., Espagne, A., Nibbering, E. T. J. & Elsaesser, T. Ultrafast Structural Dynamics of Water Induced by Dissipation of Vibrational Energy. *The Journal of Physical Chemistry A* **111**, 743-746, doi:10.1021/jp0676538 (2007).
- 8 Auer, B. M. & Skinner, J. L. IR and Raman spectra of liquid water: Theory and interpretation. *J. Chem. Phys.* **128**, 224511, doi:10.1063/1.2925258 (2008).
- 9 Amann-Winkel, K. *et al.* X-ray and Neutron Scattering of Water. *Chem. Rev.* **116**, 7570-7589, doi:10.1021/acs.chemrev.5b00663 (2016).
- 10 Sellberg, J. A. *et al.* Ultrafast X-ray probing of water structure below the homogeneous ice nucleation temperature. *Nature* **510**, 381-384, doi:10.1038/nature13266 (2014).
- 11 Beyerlein, K. R. *et al.* Ultrafast nonthermal heating of water initiated by an X-ray Free-Electron Laser. *Proceedings of the National Academy of Sciences of the United States of America* **115**, 5652-5657, doi:10.1073/pnas.1711220115 (2018).
- 12 Wen, H., Huse, N., Schoenlein, R. W. & Lindenberg, A. M. Ultrafast conversions between hydrogen bonded structures in liquid water observed by femtosecond x-ray spectroscopy. *J. Chem. Phys.* **131**, 234505, doi:10.1063/1.3273204 (2009).
- 13 Perakis, F. *et al.* Coherent X-rays reveal the influence of cage effects on ultrafast water dynamics. *Nature Communications* **9**, 1917, doi:10.1038/s41467-018-04330-5 (2018).
- 14 Kim, K. H. *et al.* Direct observation of bond formation in solution with femtosecond X-ray scattering. *Nature* **518**, 385-389, doi:10.1038/nature14163 (2015).
- 15 van Driel, T. B. *et al.* Atomistic characterization of the active-site solvation dynamics of a model photocatalyst. *Nat. Commun.* **7**, 13678, doi:10.1038/ncomms13678 (2016).
- 16 Nunes, J. P. F. *et al.* Liquid-phase mega-electron-volt ultrafast electron diffraction. *Struct. Dyn.* **7**, 024301, doi:10.1063/1.5144518 (2020).
- 17 Koralek, J. D. *et al.* Generation and characterization of ultrathin free-flowing liquid sheets. *Nature Communications* **9**, 1353, doi:ARTN 1353 10.1038/s41467-018-03696-w (2018).
- 18 Ihee, H. Visualizing Solution-Phase Reaction Dynamics with Time-Resolved X-ray Liquidography. *Acc. Chem. Res.* **42**, 356-366, doi:10.1021/ar800168v (2009).
- 19 Skinner, L. B., Benmore, C. J., Neuefeind, J. C. & Parise, J. B. The structure of water around the compressibility minimum. *J. Chem. Phys.* **141**, 214507, doi:10.1063/1.4902412 (2014).

- 20 Haldrup, K. *et al.* Observing Solvation Dynamics with Simultaneous Femtosecond X-ray Emission Spectroscopy and X-ray Scattering. *The Journal of Physical Chemistry B* **120**, 1158-1168, doi:10.1021/acs.jpcc.5b12471 (2016).
- 21 Morawietz, T., Singraber, A., Dellago, C. & Behler, J. How van der Waals interactions determine the unique properties of water. *Proc. Natl. Acad. Sci. U.S.A.* **113**, 8368-8373, doi:10.1073/pnas.1602375113 (2016).
- 22 Dettori, R. *et al.* Simulating Energy Relaxation in Pump-Probe Vibrational Spectroscopy of Hydrogen-Bonded Liquids. *J. Chem. Theory Comput.* **13**, 1284-1292, doi:10.1021/acs.jctc.6b01108 (2017).
- 23 Dettori, R., Ceriotti, M., Hunger, J., Colombo, L. & Donadio, D. Energy Relaxation and Thermal Diffusion in Infrared Pump-Probe Spectroscopy of Hydrogen-Bonded Liquids. *J. Phys. Chem. Lett.* **10**, 3447-3452, doi:10.1021/acs.jpcclett.9b01272 (2019).
- 24 Gilli, P., Bertolasi, V., Ferretti, V. & Gilli, G. Evidence for resonance-assisted hydrogen bonding. 4. Covalent nature of the strong homonuclear hydrogen bond. Study of the O-H...O system by crystal structure correlation methods. *Journal of the American Chemical Society* **116**, 909-915, doi:10.1021/ja00082a011 (1994).
- 25 Lippincott, E. R. & Schroeder, R. One-Dimensional Model of the Hydrogen Bond. *J. Chem. Phys.* **23**, 1099-1106, doi:10.1063/1.1742196 (1955).
- 26 Staib, A. & Hynes, J. T. Vibrational predissociation in hydrogen-bonded OH...O complexes via OH stretch-OO stretch energy transfer. *Chem. Phys. Lett.* **204**, 197-205, doi:[https://doi.org/10.1016/0009-2614\(93\)85627-Z](https://doi.org/10.1016/0009-2614(93)85627-Z) (1993).
- 27 McKenzie, R. H., Bekker, C., Athokpam, B. & Ramesh, S. G. Effect of quantum nuclear motion on hydrogen bonding. *J. Chem. Phys.* **140**, 174508, doi:10.1063/1.4873352 (2014).
- 28 Grabowski, S. J. What Is the Covalency of Hydrogen Bonding? *Chem. Rev.* **111**, 2597-2625, doi:10.1021/cr800346f (2011).
- 29 Shibata, S. & Bartell, L. S. Electron-Diffraction Study of Water and Heavy Water. *J. Chem. Phys.* **42**, 1147-1151, doi:10.1063/1.1696094 (1965).
- 30 Ceriotti, M. *et al.* Nuclear Quantum Effects in Water and Aqueous Systems: Experiment, Theory, and Current Challenges. *Chem. Rev.* **116**, 7529-7550, doi:10.1021/acs.chemrev.5b00674 (2016).
- 31 Weathersby, S. P. *et al.* Mega-electron-volt ultrafast electron diffraction at SLAC National Accelerator Laboratory. *Rev. Sci. Instrum.* **86**, 073702, doi:10.1063/1.4926994 (2015).
- 32 Bertie, J. E. & Lan, Z. Infrared Intensities of Liquids XX: The Intensity of the OH Stretching Band of Liquid Water Revisited, and the Best Current Values of the Optical Constants of H₂O(l) at 25°C between 15,000 and 1 cm⁻¹. *Applied Spectroscopy* **50**, 1047-1057 (1996).
- 33 Sorenson, J. M., Hura, G., Glaeser, R. M. & Head-Gordon, T. What can x-ray scattering tell us about the radial distribution functions of water? *J. Chem. Phys.* **113**, 9149-9161, doi:10.1063/1.1319615 (2000).
- 34 Brockway, L. O. Electron diffraction by gas molecules. *Reviews of Modern Physics* **8**, 0231-0266, doi:10.1103/RevModPhys.8.231 (1936).
- 35 Hubbell, J. H. *et al.* Atomic form factors, incoherent scattering functions, and photon scattering cross sections. *J. Phys. Chem. Ref. Data* **4**, 471-538, doi:10.1063/1.555523 (1975).
- 36 Yang, J. *et al.* Structure retrieval in liquid-phase electron scattering. *arXiv:2006.04234* (2020).
- 37 Horn, H. W. *et al.* Development of an improved four-site water model for biomolecular simulations: TIP4P-Ew. *J. Chem. Phys.* **120**, 9665-9678, doi:10.1063/1.1683075 (2004).

- 38 Dohn, A. O. *et al.* On the calculation of x-ray scattering signals from pairwise radial distribution functions. *Journal of Physics B-Atomic Molecular and Optical Physics* **48**, 244010, doi:Artn 244010
10.1088/0953-4075/48/24/244010 (2015).
- 39 Bartell, L. S. & Gavin, R. M. Effects of Electron Correlation in X-Ray and Electron Diffraction. *Journal of the American Chemical Society* **86**, 3493-3498, doi:DOI 10.1021/ja01071a019 (1964).
- 40 Wang, J. H., Tripathi, A. N. & Smith, V. H. Chemical-Binding and Electron Correlation-Effects in X-Ray and High-Energy Electron-Scattering. *J. Chem. Phys.* **101**, 4842-4854, doi:Doi 10.1063/1.467407 (1994).
- 41 Hammer, B., Hansen, L. B. & Nørskov, J. K. Improved adsorption energetics within density-functional theory using revised Perdew-Burke-Ernzerhof functionals. *Physical Review B* **59**, 7413-7421, doi:10.1103/PhysRevB.59.7413 (1999).
- 42 Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **132**, 154104, doi:10.1063/1.3382344 (2010).
- 43 Bussi, G., Donadio, D. & Parrinello, M. Canonical sampling through velocity rescaling. *J. Chem. Phys.* **126**, 014101, doi:10.1063/1.2408420 (2007).
- 44 Marx, D. & Parrinello, M. Ab initio path integral molecular dynamics: Basic ideas. *J. Chem. Phys.* **104**, 4077-4082, doi:10.1063/1.471221 (1996).
- 45 Cao, J. & Voth, G. A. The formulation of quantum statistical mechanics based on the Feynman path centroid density. III. Phase space formalism and analysis of centroid molecular dynamics. *J. Chem. Phys.* **101**, 6157-6167, doi:10.1063/1.468503 (1994).
- 46 Markland, T. E. & Ceriotti, M. Nuclear quantum effects enter the mainstream. *Nature Reviews Chemistry* **2**, 0109, doi:10.1038/s41570-017-0109 (2018).
- 47 Hockney, R. W. & Eastwood, J. W. *Computer simulation using particles*. (Taylor & Francis, Inc., 1988).
- 48 Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **117**, 1-19, doi:<https://doi.org/10.1006/jcph.1995.1039> (1995).
- 49 Jr., T. H. D. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *J. Chem. Phys.* **90**, 1007-1023, doi:10.1063/1.456153 (1989).
- 50 Ufimtsev, I. S. & Martínez, T. J. Quantum Chemistry on Graphical Processing Units. 1. Strategies for Two-Electron Integral Evaluation. *J. Chem. Theory Comput.* **4**, 222-231, doi:10.1021/ct700268q (2008).
- 51 Ufimtsev, I. S. & Martinez, T. J. Quantum Chemistry on Graphical Processing Units. 2. Direct Self-Consistent-Field Implementation. *J. Chem. Theory Comput.* **5**, 1004-1015, doi:10.1021/ct800526s (2009).
- 52 Ufimtsev, I. S. & Martinez, T. J. Quantum Chemistry on Graphical Processing Units. 3. Analytical Energy Gradients, Geometry Optimization, and First Principles Molecular Dynamics. *J. Chem. Theory Comput.* **5**, 2619-2628, doi:10.1021/ct9003004 (2009).
- 53 Yang, J. *et al.* Simultaneous observation of nuclear and electronic dynamics by ultrafast electron diffraction. *Science* **368**, 885-889, doi:10.1126/science.abb2235 (2020).
- 54 Shibata, S., Sekiyama, H., Tachikawa, K. & Moribe, M. Chemical bonding effect in electron scattering by gaseous molecules. *J. Mol. Struct.* **641**, 1-6, doi:Pii S0022-2860(01)00962-0
Doi 10.1016/S0022-2860(01)00962-0 (2002).

55 Kim, J. G. *et al.* Mapping the emergence of molecular vibrations mediating bond formation. *Nature* **582**, 520-524, doi:10.1038/s41586-020-2417-3 (2020).