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THz Excitation of Water

Ultrafast Energy Transfer to Liquid Water by Sub-Picosecond High-Intensity Terahertz Pulses: An Ab Initio Molecular Dynamics Study**

Pankaj Kr. Mishra, Oriol Vendrell, and Robin Santra*

Liquid water is the single most important medium in which chemical and biological processes take place.[1–3] Rather than acting as a passive environment, the dynamics of water during chemical and biological processes play a fundamental role in the solvation and stabilization of reaction intermediates.[4] Recent THz spectroscopy measurements probing collective, low-frequency modes show that water is a key actor in enzymatic reactions and protein folding.[5–7] Free-electron lasers (FELs) operating in the THz domain have been available for some time now.[8] Recently, the generation of THz radiation from X-ray FELs (XFELs) in full synchronization with the X-ray pulse has been demonstrated.[9–11] This opens extremely interesting avenues for pump–probe-type experiments in which a THz pulse initiates a chemical process of interest in, for example, solid-state or biological samples, followed by an ultrashort X-ray pulse that interrogates the system at a well-defined time delay.[10,12] At low intensity, THz light couples to low-energy collective modes of the liquid.[6,13] However, not much is known about the sub-picosecond response of liquid water to intense and ultrashort (few cycle) THz pulses, mostly owing to the lack of high-intensity THz sources with pulse durations in the sub-picosecond regime until recently.

Herein, we report an ab initio molecular dynamics (AIMD) study of the response of liquid water to a sub-picosecond THz pulse. Such pulse is given generally by Equation (1),

$$\mathbf{E}(t) = \varepsilon(t)\mathbf{u}_z \cos(\omega_c t + \phi) \tag{1}$$

where $\varepsilon(t)$ is a Gaussian envelope with a full width at half maximum (fwhm) of 250 fs and intensity of 10^{10} W cm^{-2}. This intensity is achievable at state-of-the-art THz sources[14] assuming a focus of the THz light to a spot of 1 mm^2 and a total pulse energy of 25 μJ. The photon energy ω_c is 100 cm^{-1} (about 3 THz). At this photon energy, one cycle of the electromagnetic field oscillation takes about 330 fs, meaning that our pulse is between a half and a full cycle long. $\mathbf{u}_z$ is the polarization direction of the electric field and ϕ is the carrier to envelope phase (CEP), which we set to $\pi/2$. We also tried other CEPs and obtained very similar results. Pulses with these characteristics match the design specifications of THz sources available at FELs.[11,14] We find that such a THz pulse transfers a large amount of energy to the liquid medium in a sub-picosecond time scale. Moreover, we are able to explain the basic mechanism by which energy is quickly transferred to the liquid medium, first to relative translational motion of the water monomers, and later how the vibrational energy redistributes into librational and intramolecular degrees of freedom. The large amount of energy per monomer transferred to the liquid changes its structure significantly, disrupting the hydrogen bond network and the tetrahedral coordination of water molecules on an ultrafast time scale. Moreover, we show that time-resolved X-ray diffraction (TR-XRD) measurements[15–17] should be able to capture such structural modifications.

AIMD simulations were performed using the CP2K molecular dynamics program,[18,19] in which nuclear motion is described classically and the electronic structure is described quantum mechanically by density functional theory (DFT).[20] The THz pulse was included explicitly, its envelope was centered at $t = 0$ and trajectories were started at $t = -250$ fs. TR-XRD patterns of the system were obtained by Fourier transform of the electron density of snapshots during the dynamics.[21] We averaged over the 15 available trajectories. Further technical details are provided as Supporting Information.

The THz pulse transfers a large amount of energy to the liquid in a sub-picosecond time scale. We partition the total kinetic energy (KE) of each water monomer into three contributions: translational energy (TE) of its center of mass, rotational energy (RE) around its center of mass, and intramolecular vibrational energy (VE). The latter contribution includes the intramolecular bending and stretching motion, which for this analysis have not been separated. The TE and RE contributions correspond to hindered rotations and librational motion of the water monomers in the liquid. Figure 1 a shows the mean value of the total KE per water monomer as a function of time, as well as the TE, RE, and VE contributions. The KE per monomer at $t = -250$ fs corresponds to the equilibrium temperature of 300 K. The KE

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[*] P. K. Mishra, Dr. O. Vendrell, Prof. Dr. R. Santra
Center for Free-Electron Laser Science, DESY
Notkestraße 85, 22607 Hamburg (Germany)
P. K. Mishra, Prof. Dr. R. Santra
Department of Physics, University of Hamburg
Jungiusstraße 9, 20355 Hamburg (Germany)
P. K. Mishra, Dr. O. Vendrell, Prof. Dr. R. Santra
Center for Ultrafast Imaging, University of Hamburg
Luruper Chaussee 149, 22761 Hamburg (Germany)
E-mail: oriol.vendrell@cfel.de
Homepage: http://desy.cfel.de/cfel_theory_division/

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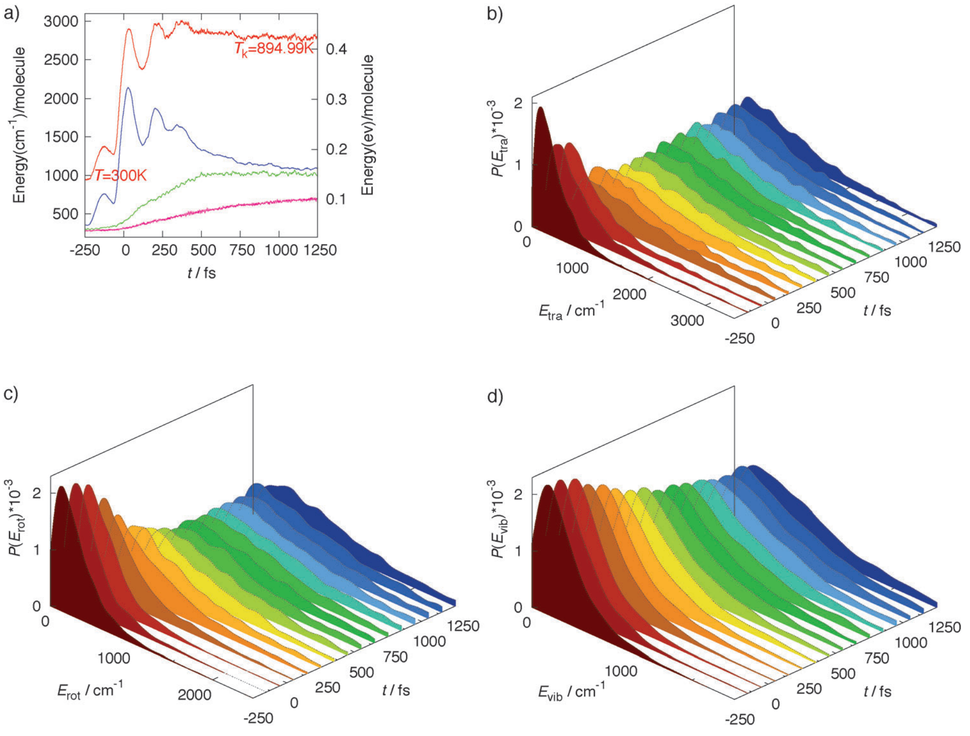

Figure 1. a) Average kinetic energy of each monomer paritioned according to; red: total kinetic energy, blue: translational kinetic energy, green: rotational kinetic energy, and pink: vibrational kinetic energy. T_k and T refer to kinetic and equilibrium temperatures, respectively. Probability distributions per water molecule of translational (b), rotational (c), and vibrational (d) energies for different time delays. These are Maxwell–Boltzmann distributions for $t=-250$ fs (see the Supporting Information) and are normalized at all times $\int_0^\infty P(E)dE=1$.

per monomer quickly increases during the duration of the pulse and remains constant after the pulse is over. The energy jump of more than 2000 cm^{-1} corresponds to a final kinetic temperature of about 900 K and to an absorption of about 25 THz photons per molecule during the pulse. Initially, most of the energy increase corresponds to TE, which is due to the sudden modification of the intermolecular potential, especially the modification of the strength of the hydrogen bonds by the THz pulse. This effect has already been reported for water clusters exposed to static electric fields.[22] Some tens of femtoseconds before the pulse is over, both the RE and VE contributions start to increase as a consequence of the molecular collisions taking place between the highly mobile water molecules. Quantum effects could influence the energy transfer rate to vibrations, which is not considered in the present study. In the case of a hot environment however, one can expect the corresponding correction factor to be small.[23] Rotational and vibrational modes still gain energy well after the pulse is over, indicating that the THz pulse does not excite these modes directly, or only to a small extent. This is clearly seen in simulations of individual water molecules and small clusters reported as Supporting Information.

Figure 1 b,c,d shows the energy distribution of the TE, RE, and VE as a function of time. At $t=-250$ fs the three distributions take the form of the equilibrium Boltzmann distribution at $T=300$ K. The THz pulse immediately flattens the TE distribution within 100 fs, which is the time the water monomers need to start moving relative to one other in the bulk. The RE distribution shifts to larger energies after about 150 fs and also extends its tail to energies that had almost zero probability to be found at equilibrium. The vibrational distribution also shifts to larger energy and becomes wider, but retains a shape similar to its equilibrium distribution at all times (note the different energy scales in Figure 1).

The large amount of energy transferred to the liquid causes large structural changes. A convenient probe of the structural transformations of the material is the coherent X-ray diffraction pattern, which is given by the modulus squared of the Fourier transform of the electron density and which for bulk water is well-known for an ample range of temperatures and pressures.[24,25] The double peak structure of the TR-XRD pattern at $t=-250$ fs in Figure 2 agrees with previously reported experimental and theoretical calculations of the XRD pattern of liquid water at $T=300$ K.[21] The peak at about 2 Å^{-1} is related to typical oxygen–oxygen distances in tetrahedrically coordinated water, whereas the lower peak at about 3 Å^{-1} is related to features in the density connected to the hydrogen-bonding structure. At times between -50 and 150 fs, the TR-XRD transitions into a pattern with a single peak at about 2.2 Å^{-1}, which is indicative of a dramatic modification of the tetrahedral structure of the liquid and a disruption of the hydrogen bond network. The pattern obtained after the pulse has ended is similar to the XRD pattern of water at $T=1500$ K and a pressure of 12 GPa,[24] where a complete disruption of the shell structure of the normal liquid was found, and which is indicative of the kind of

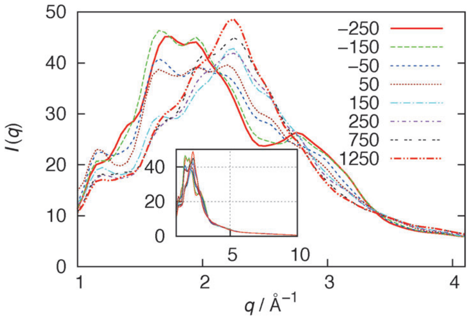

Figure 2. Coherent X-ray diffraction intensity at different time delays between the THz and X-ray pulse. Time is given in femtoseconds.

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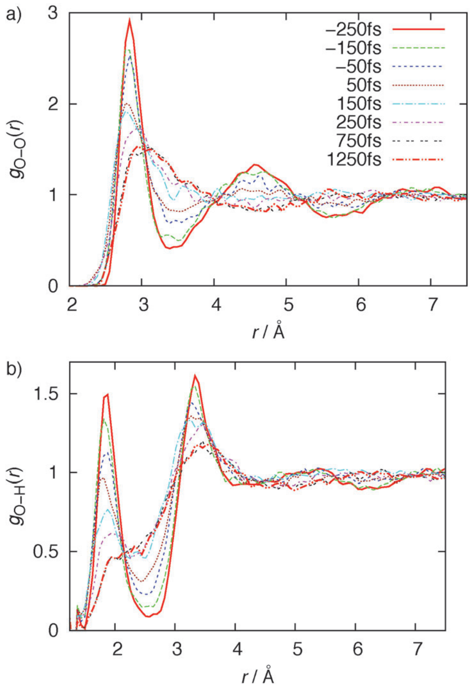

Figure 3. a) Radial distribution functions a) $g_{O-O}(r)$ and b) $g_{O-H}(r)$ at different time delays under the effect of a THz pulse. Times are in femtoseconds.

extreme conditions achieved in the liquid within a sub-picosecond time scale. Figure 3a shows the $g_{O-O}(r)$ radial distribution function (RDF) calculated as a function of time. As in the TR-XRD, $g_{O-O}(r)$ transitions from two peaks, which is indicative of the first two solvation shells around each molecule, into a flat RDF typical of a gas. This change occurs between −50 and 150 fs after the start of the THz pulse. Similarly, the $g_{O-H}(r)$ RDF in Figure 3b shows a very fast disruption of the hydrogen bond network, clearly seen by the disappearance of the peak at about 2 Å, which is related to the oxygen–hydrogen distance in a hydrogen bond. We remind that the structural changes occur isochorically since there is no time for the bulk to change its volume in the picosecond time scale of the excitation.

In conclusion, we have shown how a sub-picosecond intense THz pulse achievable at modern facilities is able to transfer a large amount of energy to liquid water and create a hot and structureless environment. The water molecules mostly acquire energy as they start to move relative to each other in response to changes in the hydrogen-bond strengths and through collisions the translational energy redistributes in a few hundred femtoseconds into monomer librations and vibrations. These changes can be monitored by time-resolved measurements of the X-ray diffraction pattern of the liquid. The transient and hot environment achieved by the THz pulse could have interesting properties as a matrix to study activated chemical processes. This will be the subject of future investigations.

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