Strong Anisotropy in Liquid Water upon Librational Excitation using Terahertz Laser Fields

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Orienting water molecules in the homogeneous liquid is challenging due to the ultrafast dissipation of rotational excitation energy through the hydrogen-bonded network. Here we demonstrate strong transient anisotropy of liquid water through librational excitation using single-color pump-probe experiments at 12.3 THz, with the birefringence exceeding previously reported values by three to five orders of magnitude. Using a theory that replaces the third order response with a material response property amenable to molecular dynamics simulation, we show that the rotationally damped motion of water molecules in the librational band is resonantly driven at this frequency, thereby enhancing the liquid anisotropy by the external Terahertz field. By addition of salt (MgSO₄), the hydration water is instead dominated by the local electric field of the ions, resulting in reduction of water molecules that can be dynamically perturbed by THz pulses.

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INTRODUCTION

Orienting molecules in the gas phase has been possible for more than two decades using both static electric fields\(^1\)–\(^3\) and oscillating laser fields\(^4\),\(^5\). Terahertz-Kerr (THz-Kerr) techniques, that typically use resonant pump pulses at around 1 THz and an off-resonant optical probe, have shown initial success in enhancing alignment of liquid acetonitrile and biphenyl by resonant excitation of librational modes\(^4\)–\(^13\). However, for bulk liquid water, orienting molecules using a laser source is still a challenge because the rotational motion of individual molecules is hindered by an extensive hydrogen-bonded network that can rapidly dissipate external excitations\(^14\)–\(^17\). Non-equilibrium molecular dynamics simulations have shown a rapid loss of the excitation energy of a single rotationally excited water molecule in the liquid on the sub-100 fs timescale, where the dominant dissipation pathway involves rotation of the hydrogen-bonded molecules in the first hydration shell of a central water\(^18\). This dissipation timescale is commensurate with previous experimental and theoretical studies showing that librational motions relax on a sub-200 fs timescale\(^18\)–\(^23\), with a characteristic reorientational decay time of 75 fs\(^24\),\(^25\). As a result, the third-order birefringence induced in water by either static fields\(^26\),\(^27\) or laser excitation\(^28\)–\(^37\) has been found to be small, \(3.1 \cdot 10^{-16} \frac{cm^2}{V^2}\) and \(2.6 \cdot 10^{-18} \frac{cm^2}{V^2}\), respectively.

Here, we report single-color THz pump–THz probe experiments carried out on the ultra-bright free electron laser FELIX that provides an unprecedented degree of laser induced transient birefringence in bulk liquid water, which is found to be five orders of magnitude larger at 12.3 THz than previously reported values for excitations in the infrared, optical, and low-frequency THz ranges. Using supporting theory that replaces the four point time correlation of the third order response with a material response property that can be simulated with molecular dynamics, we demonstrate that the birefringent enhancement is the result of resonance of the water modes at the lower frequency end of the librational band, colloquially referred to as “rocking” of the water dipole in the collective hydrogen-bonded network\(^38\),\(^39\). This resonant enhancement of the angular displacements of the water dipole compared to the ground state thereby increases the ability for increasing the anisotropy of the liquid through the applied electric field.

Furthermore, we would expect that water molecules undergoing dynamical realignment with the external field will be reduced if a locally stronger orienting electric field is present, as in the case of hydration waters near the ions in a salt solution. Interestingly, our experiments show that a 0.6 M MgSO\(_4\) solution exhibits a significantly decreased birefringent response with respect to bulk water, and simulations of MgSO\(_4\) solution at the same concentration also show a decreased signal of comparable magnitude. A detailed analysis of the simulation results reveals that the peak of the frequency spectrum
of the water molecules in the hydration shell of the ions, in particular of Mg$^{2+}$, is blue-shifted with respect to bulk water. Therefore, the water molecules in the proximity of the ions don't contribute as much to the response when the system is excited at the resonant frequency of bulk water.

Our ability to induce an enormous birefringence is proof that the THz pump pulse creates a strong anisotropy in the bulk liquid, and furthermore can be modulated with addition of simple salt solutes. This paves the way for future THz pump-probe experiments, interpretable with a theory that yields tractable simulated observables using molecular dynamics, which can measure and/or alter the strength of anisotropic effects of water at biological and materials interfaces in a controlled way.

**RESULTS**

Figure 1 shows the experimental setup of the ultra-bright free electron laser FELIX. The beam is split into the pump and probe parts: the pump beam is vertically polarized (V) with respect to the optical table and the probe beam is polarized at an angle $\theta$ with respect to the pump direction (Fig. 1a). After the liquid sample, we rotate the polarizer (analyzer) to detect the vertical and horizontal components of the probe light. The resulting $T_V$ and $T_H$ transmissions are shown in Fig. 1b when the pump laser is blocked, and in Fig. 1c when the pump is on. Further details on the pump-probe experiment can be found in the **Methods** section.

Our goal is to measure the peak magnitude of the third-order response $\chi^3$, which at a given pump-probe delay of $t = 0$ (see eq.(4.1.20) in Ref. 40) is given by:

$$
\chi^3 = \frac{\Delta n(0)}{I} \frac{n^2}{(283 \frac{\mu^2}{W})}
$$

(1)

where $I$ is the pump peak power, $n$ is the index of refraction of the sample at equilibrium, and $\Delta n$ is given in Eq. (2)$^6,13,41$:

$$
\Delta n(t) = n_V(t) - n_H(t) = \frac{\lambda \varepsilon(t)}{2 \pi d^*}
$$

(2)

where $n_V(t)$ and $n_H(t)$ are the index of refraction parallel and perpendicular to the pump polarization direction, respectively, $\lambda$ is the wavelength, and $d^*$ is the penetration depth of the probe radiation. The amplitude of the birefringence $\varepsilon(t)$ is approximately related to the birefringent signal $\epsilon(\theta, t)$ through

$$
\epsilon(\theta, t) = \varepsilon(t)(\cos^3(\theta) - \cos(\theta))
$$

(3)

where $\theta$ is the polarization of the probe beam.
**Figure 1.** Experimental configuration of the THz pump-probe experiments using the FELIX electron laser. The beam is split into a pump (green) and a 70x weaker probe (red) component. A 4” diameter off-axis parabolic mirror (PM) with 4” effective focal length (EFL) focuses both pump and probe beams at the sample position. The temporal overlap was found by placing a 200 µm metal pinhole at the sample position (see Fig. S1 in the Supporting Information and the description therein). The liquid sample is loaded into a static liquid cell with diamond windows. The sample thickness is $d \approx 25 \mu m$ (Kapton spacer) and the penetration depth, $d^* \approx 6 \mu m$ at 12.3 THz$^{42,43}$, is assumed equal to the size of the active medium emitting the non-linear signal. The sample temperature was actively stabilized at 20±0.05 °C with a recirculating chiller. In order to suppress the pump scatter at the detector, the pump and probe beams do not propagate along the same direction and overlap only at the sample position. After the sample, a second PM with 5” EFL collects radiation from the probe beam. A polarizer (analyzer) with 10$^4$:1 extinction ratio is placed before the detector to allow detection of either the vertical, $T_V$ (green), or horizontal, $T_H$ (blue), components of the probe transmission.

At equilibrium, when the pump is blocked (Fig. 1b), the vertical (V) and horizontal (H) probe light intensities transmitted by the analyzer are $T_V(\theta) = e^{-\alpha d \cos^2 \theta}$ and $T_H(\theta) = e^{-\alpha d \sin^2 \theta}$, where $\alpha$ is the absorption coefficient at equilibrium, and $d$ the sample thickness. When the pump is active (Fig. 1c), the parallel and perpendicular absorption coefficients, $\alpha_V(t)$ and $\alpha_H(t)$, can change due to a change in the excited libration population. Furthermore, the probe acquires a birefringent component $\epsilon(\theta, t)$, with $t$ the pump-probe delay. The pump-perturbed transmission coefficients, $T_V^*$ and $T_H^*$, transmitted by the analyzer when the pump is on are:

$$T_V^*(\theta, t) = e^{-\alpha_V(t) d^* - \alpha(d - d^*) \cos^2(\theta + \epsilon(\theta, t))}$$

(4)
\[ T_H^*(\theta, t) = e^{-\alpha_H^*(t)d^* - \alpha(d-d^*) \sin^2(\theta + \epsilon(\theta, t))} \]  

where we assumed that the pump-induced transient signal originates from a sample with a thickness equal to one penetration depth, \(d^*\). The pump-probe measurements were performed in balance-detection mode\(^{44-48}\). We measure the difference between the intensity of the probe beam and the reference beam, which is a co-propagating duplicate of the probe delayed by 20 ns, at each pump-probe delay \(t\). In this way we can directly access the relative variation of the sample transmission and measure the pump-probe traces:

\[
\frac{\Delta T_V(\theta, t)}{T_V(\theta)} = \frac{T'_V(\theta,t) - T_V(\theta)}{T_V(\theta)} = e^{-\Delta \alpha_V(t)d^* \cos^2(\theta+\epsilon(\theta,t))} - 1
\]

\[
\frac{\Delta T_H(\theta, t)}{T_H(\theta)} = \frac{T'_H(\theta,t) - T_H(\theta)}{T_H(\theta)} = e^{-\Delta \alpha_H(t)d^* \sin^2(\theta+\epsilon(\theta,t))} - 1
\]

where \(\Delta \alpha_V(t) = \alpha'_V(t) - \alpha\) and \(\Delta \alpha_H(t) = \alpha'_H(t) - \alpha\) are the time-dependent absorption changes along and perpendicular to the pump polarization direction. Thus to estimate the third order response \(\chi^3\) from an experiment at a pump intensity \(I\) and probe polarization \(\theta\), we measure the pump-probe traces, \(\frac{\Delta T_V(\theta, t)}{T_V(\theta)}\) and \(\frac{\Delta T_H(\theta, t)}{T_H(\theta)}\), and then use Eqs. (6) and (7) to solve for \(\epsilon(\theta, t), \Delta \alpha_V(t), \) and \(\Delta \alpha_H(t)\). By measuring the pump-probe traces at two different probe-polarization angles and focusing just on the pump-probe delay around \(t=0\) we can obtain an overdetermined system of linear equations that we can solve numerically to estimate \(\epsilon(\theta), \Delta \alpha_V, \) and \(\Delta \alpha_H\). Finally, by insertion of \(\epsilon(\theta)\) into Eqs. (1), (2) and (3) we obtain \(\chi^3\).

It is also important to note that our experiments are different than an optical Kerr experiment as follows. When \(\Delta \alpha_V(t)d^*, \Delta \alpha_H(t)d^*, \epsilon(\theta, t) \ll 1\) we obtain from Eqs. (6) and (7)

\[
\frac{\Delta T_V(\theta, t)}{T_V(\theta)} \approx -\Delta \alpha_V(t)d^* - 2\epsilon(\theta, t) \tan \theta
\]

\[
\frac{\Delta T_H(\theta, t)}{T_H(\theta)} \approx -\Delta \alpha_H(t)d^* + 2\epsilon(\theta, t) \cot \theta
\]

In the case that there is no absorption change (\(\Delta \alpha_V = \Delta \alpha_H = 0\)), as in a typical off resonant optical Kerr experiment, Eqs. (8) and (9) coincide with equations reported previously\(^{6,13,41}\), and the birefringence \(\epsilon\) is related to the instantaneous response of the electronic system, i.e., to the induced dipole which stems from polarizability\(^{49,50}\). In the present case, the transient absorption terms \(\Delta \alpha_V\) and \(\Delta \alpha_H\) cannot be neglected, as both pump and probe are resonant with a sample excitation, and both absorption terms can
be different than zero ($\Delta \alpha_v \neq 0; \Delta \alpha_h \neq 0$). As another extreme, ultrafast dichroism\textsuperscript{19,20,24,25,51–54} represents a sub-class of resonant experiments where the pump-probe signal is dominated by anisotropic transient absorption ($\Delta \alpha_v \neq \Delta \alpha_h \neq 0$). For a summary of previous results on aligning water molecules and other liquids, see Table S1 in the Supporting Information (SI).

We carried out the single-color THz pump–THz probe experiments at 7.8, 12.3, and 13.9 THz using the experimental setup and analysis described above. The single-color pump-probe experiment at 12.3 THz for probe polarization angles of $\theta=40^\circ$ and $\theta=50^\circ$ measure a negative vertical (Fig. 2a) and positive horizontal (Fig. 2b) pump-probe trace around pump-probe delay $t=0$, which indicates that the probe light polarization acquires ellipticity at pulse overlap, and thus that the interaction between water and the pump pulses induces an ultra-fast ($\ll 5$ ps) anisotropy in the bulk liquid. Because the pump-probe signal depends on the probe polarization angle, it confirms that the signal is birefringent ($\varepsilon(\theta, t) \neq 0$). Furthermore, the maximum modulus of the signal for vertical (Fig. 2a) and horizontal (Fig. 2b) pump-probe traces differs, which implies that the pump-probe signal is partially dichroic ($\Delta \alpha_v(t) \neq \Delta \alpha_h(t) \neq 0$). The probe ellipticity therefore originates from both the dichroism and the birefringence induced in the bulk liquid by the pump pulses. The pump-probe signal scales linearly with the pump intensity, as expected for a third-order experiment (see Fig. S2 in the SI).

![Figure 2](image.png)

*Figure 2. Polarization-dependent pump-probe of bulk liquid water at 12.3 THz.* The pump-probe traces are recorded when the analyzer is set to the vertical (a) or horizontal (b) position. The pulse length is 3.6 ps and the pump-probe overlap is $\sim 5$ ps. The pump is always vertically polarized and the peak power is 900 MW/cm$^2$. See Methods for details. The probe polarization angle is set to 40° (dark green in panel (a); dark blue in (b)) or 50° (light green in panel (a); light blue in (b)) with respect to the pump laser (V). The noise level is less than $\pm 2 \cdot 10^{-3}$. From the peak pump-probe measured values, we determine that the birefringent third-order response of bulk water at 12.3 THz is $\chi^3 = (2.5 \pm 0.2) \cdot 10^{-13} \text{ cm}^2/\text{V}^2$. This value is about three orders of magnitude
larger than for static fields\textsuperscript{26,27} ($3.1 \cdot 10^{-16} \text{ cm}^2/\text{V}^2$) and exceeds by 5 orders of magnitude the non-linear response of pure water at optical, near-infrared\textsuperscript{32,33,35–37,55–58}, and low THz\textsuperscript{28} frequencies, $2.6 \cdot 10^{-18} \text{ cm}^2/\text{V}^2$.

As a further control we also carried out single-color pump-probe experiments at 7.8 and 13.9 THz with the probe polarization set to $\theta=45^\circ$ with respect to the vertically-polarized pump (Figure 3). At 13.9 THz, pump energies deposited in the librational band of liquid water should be similar to that at 12.3 THz\textsuperscript{42,43,59,60}, and one would expect similar transient changes as described by $\Delta \alpha$ and $\Delta n$. We in fact observe a qualitatively similar signal at 13.9 THz compared to the 12.3 THz result, with a negative vertical pump-probe trace and a positive horizontal pump-probe signal at pulse overlap (comparing blue and green curves in Figures 3a and 3b). However, the penetration depth of liquid water\textsuperscript{42,43} at 13.9 THz is reduced ($d^* \approx 4 \mu m$) when compared to the penetration depth at 12.3 THz ($d^* \approx 6 \mu m$), and consequently the pump-probe signals are expected to be smaller. The measurement noise is $\sim 5\times$ larger at 13.9 THz which is attributed to an increase in atmospheric absorption at this frequency compared to 12.3 THz\textsuperscript{61,62}.

![Figure 3. Frequency-dependent pump-probe signal in water.](image)

In panels (a) and (b) we show the transient response acquired with the polarizer set to pass vertically- or horizontally-polarized light, respectively. The single-color measurements are performed in pure water at 13.9 THz (blue), 12.3 THz (green), and 7.8 THz (red). The probe polarization is set to $\theta=45^\circ$ in all these measurements. The pump-probe trace at 13.9 THz (7.8 THz) is multiplied by a factor $x900/800$ ($x900/470$) to account for the different source brilliance. The measurements are noisier at 13.9 THz and 7.8 THz due to atmospheric absorption\textsuperscript{61,62}, thus all the data shown here are re-binned: every 4 consecutive points are replaced with their average. This reduces the temporal resolution from $\sim 35$ fs to $\sim 140$ fs. (c). From Eq. (9) we can visually separate the horizontal pump-probe trace at 12.3 THz shown in panel (b) into contributions from the birefringence (purple) and the transient absorption (black). The purple and black curves are guides to the eyes. Panels (b) and (c) share the same y-axis.

At 7.8 THz the absorption coefficient is reduced and the experimental noise is increased compared to the measurements at 12.3 THz. But in addition, at 7.8 THz the laser energy is deposited into both the intramolecular hydrogen-bond stretch as well as into a librational mode\textsuperscript{43}. While the librational excitation facilitates the reorientation of the water molecules, excitation of the intermolecular...
hydrogen-bond stretch does not lead to any notable anisotropy\textsuperscript{6,7,43,63}. Thus, we predict a decrease of the birefringence, $\Delta n$, for pump-probe signals at 7.8 THz compared to 12.3 THz, as confirmed by the experiment (red vs. green curves in Figures 3a and 3b). The small negative horizontal pump-probe signal observed at 7.8 THz is consistent with a fast relaxation process, as expected for the hydrogen-bond stretch\textsuperscript{43,63}. As a consequence the increase in $\Delta \alpha_H$ (negative black signal in Fig. 3c) overcompensates a smaller birefringent signal expected at 7.8 THz, resulting in a net negative signal at 7.8 THz (red in Fig. 3b).

Having determined an unprecedentedly large birefringence in liquid water at 12.3 THz that exceeds previously reported values by five orders of magnitude, it is worth noting that both diffusion-limited and non-diffusive heating effects are negligible as outlined in the Methods section. Furthermore, we will discuss below pump-probe experiments at 12.3 THz for a low concentration MgSO$_4$ solution that has a slight change in the absorption at equilibrium, but for which we observe a significant decrease in the transient birefringence, thus confirming that heating can be excluded as a main source of the signal.

To gain insight into the molecular mechanisms responsible for the extremely large experimental birefringent response, we would in principle aim to simulate the experiments computationally. Unfortunately, direct simulation of the pump-probe experiment requires the acquisition of a four-point correlation function in the time-domain, a task that remains prohibitively expensive for all but the simplest systems.\textsuperscript{21} For this reason, we derive an approximation to the $\chi^2$ experimental response by a simpler time evolving variable that can be calculated using molecular dynamics simulations. To show this, we begin with the frequency-dependent expression for a heterodyne-detected signal:

$$ S(\omega) = \Im \left[ E_2^*(\omega) \langle \hat{P}(\omega) \rangle \right] $$

where $\Im$ stands for the imaginary part, $E_2^*(\omega)$ is the complex conjugate of the probing electric field envelope, and $\hat{P}(\omega)$ is the material polarization operator in the frequency-domain that contains field-matter interactions to arbitrary-order. Rigorously, pump-probe experiments require that we expand the material polarization operator $\hat{P}$ to 3rd order in the field-matter interaction. However, we can include the pumping field directly in the Hamiltonian so that the pumping is handled non-perturbatively. Expanding $\hat{P}(\omega)$ to 1st order in the probe field, we obtain

$$ \langle \hat{P}(\omega) \rangle = \langle \hat{\mu}(\omega) \rangle = \frac{1}{\hbar} \int dt \ e^{i\omega t} \int dt' \ E(t - t') \ Tr[(\hat{\mu}(t'), \hat{\mu}(0))\rho(0)] $$

where $\hat{\mu}$ is the dipole operator, so that the first equality is just the dipole approximation and $\rho$ is the material density matrix. We have replaced the full vector electric field by its scalar amplitude $E$ so that $\hat{\mu}$ is the projection of the dipole along the electric field. Substituting the spectral envelope for the temporal E-field allows integration over $t$, giving
\[ \langle \mathbf{P}(\omega) \rangle = \frac{i}{\hbar} E(\omega) \int dt \, e^{i\omega t} \, Tr\left[ (\hat{\mu}(t'), \hat{\mu}(0)) \rho(0) \right] \]  

(12)

The key quantity here is therefore the Fourier transform of the material response function, \( J(t) = FT^{-1}[S(\omega)] \):

\[ J(t) = \frac{i}{\hbar} Tr\left[ (\hat{\mu}(t'), \hat{\mu}(0)) \rho \right] = \frac{i}{\hbar} Tr\left[ (\hat{\mu}(t'), \rho) \hat{\mu}(0) \right] \]  

(13)

where we have used the cyclic invariance of the trace. The Fourier transform of this quantity gives the frequency domain response of the material system and thus contains all information about the light-matter interaction within this approximation. In the classical limit (the proof is given in the SI) we can write Eq. (13) as:

\[ J(t) = \mu^2 \langle \cos \theta(0) \frac{d}{dt} [\cos \theta(t)] \rangle \]  

(14)

where \( \theta \) is the angle between the electric field and the molecular dipole. The integration over all initial conditions with respect to arbitrary time origins leads to:

\[ J(t) = \langle \frac{d}{dt} [\cos \theta(t)] \rangle \]  

(15)

which using the identity \( J(t) = FT^{-1}[S(\omega)] \) we can finally rewrite as:

\[ S(\omega) = FT \left[ \langle \frac{d}{dt} [\cos \theta(t)] \rangle \right] \]  

(16)

This quantity, \( S(\omega) \), can be computed using molecular dynamics simulations. Details regarding the simulations are provided in Methods.

At equilibrium (i.e. no pump or zero-field), the frequency spectrum of the rotational motion of bulk water molecules, \( S(\omega) \) in Eq. (16), exhibits a relatively broad peak at 12-20 THz (Fig. 4). It is worth noting that the theoretical frequency spectrum shown in Fig. 4b is on the lower end of the librational band in standard IR experiments\(^{42,59} \), which peaks at ~21 THz and contains multiple other dynamical modes\(^{43} \). In this case the theory predicts that the underlying natural dynamics of damped dipole reorientations within the hydrogen-bond network are excited in the THz pump-probe experiment, inducing water dipole reorientations that span a large angular displacement on ultra-fast timescales of ~30-120 fs. This is confirmed when we apply an oscillating electric field in the simulations and characterize the response of the system, for which we find that the spectrum \( S(\omega) \) yields a much larger resonant response at \( \omega_{pump} = 12.3 \) THz pump frequency than at \( \omega_{pump} = 1.0, 7.8, \) or 200 THz (Fig. 4d). This is quantified using \( I_{rel} \), the ratio between the relative peak amplitudes of \( S(\omega) \) at \( \omega_{pump} \) (illustrated in Fig. 4c), with the simulations showing the expected quadratic dependence of the intensity on the field strength (Fig. 4e). Thus the simulated results are in excellent concordance with the THz pump-probe experiments, and provide a molecular interpretation that the large birefringence in the bulk liquid arises...
from resonance of the THz pulse with the softer librational modes of dipole reorientations that create a more anisotropic liquid.

**Fig. 4. Results from molecular dynamics simulations of water.** (a) An example of the time evolution of $\theta(t)$ and $d\cos\theta/dt$ in a 2 ps time-interval and (b) $S(\omega)$ for a system with 64 water molecules calculated from Eq. (16) in the absence of an applied electric field; the polarizable force field AMOEBA\textsuperscript{64} agrees well with the results from ab initio molecular dynamics using the B97M-rV density functional\textsuperscript{65}. (c) $S(\omega)$ for systems with 512 water molecules in the presence of an applied oscillating electric field of 2 MV/cm at 7.8 and 12.3 THz. The definition of the relative peak amplitude, $I_{\text{rel}}$, is illustrated. (d) Ratio between $I_{\text{rel}}$ for electric fields applied at frequencies at 1.0, 12.3, and 200 THz with respect to the $I_{\text{rel}}$ at 7.8 THz. Similar to the experiments, a larger effect is observed at 12.3 THz, and not for other frequencies. (e) Dependence of $I_{\text{rel}}$ as a function of the amplitude of the applied electric field with a frequency of 12.3 THz.
We emphasize again that if the pump-probe signal in the 12-20 THz range were to originate from heating, the response by pure water and a salt solution should be identical since the equilibrium absorption coefficient of the salt solution, specifically the 0.6 M MgSO₄ aqueous solution that we study, is only ~1% different than liquid H₂O at 12.3 THz. However, the results of the pump-probe measurements of a 0.6 M MgSO₄ aqueous solution at 12.3 THz (Fig. 5a-e) show a statistically significant drop of the signal at pump-probe overlap, −16 ± 7% (as estimated by Gaussian fits), when compared to bulk water. Thus, we can rule out that the pump-probe signals are due to transient heating effects.

Figure 5. Polarization-dependent pump-probe of 0.6 M MgSO₄ aqueous solution at 12.3 THz. We report in panels (a)-(b) and (c)-(d) the vertical, \( \Delta T_V(\theta, \ell) / T_V(\ell) \), and horizontal, \( \Delta T_H(\theta, \ell) / T_H(\ell) \), pump-probe signals, respectively. The probe polarization is set to \( \theta = 40^\circ \) (dark green in panel (a); dark blue in panel (c)) and to \( \theta = 50^\circ \) (light green in panel (b); light blue in panel (d)) with respect to the pump polarization direction (V). The pump-probe signals measured in pure water are shown in black lines for comparison. All the pump-probe signals are ~16% smaller in the salt solution. The data are not re-binned. All panels share the same time delay axis. (e) Results from molecular dynamics simulations of a 0.5 M MgSO₄ solution in the presence of an applied oscillating electric field of 2 MV/cm at 12.3 THz. The \( S(\omega) \) arising exclusively from the water molecules in the first solvation layer of Mg and SO₄ ions is shown in red and yellow, respectively. The full \( S(\omega) \) of the salt solution is shown in blue. In the inset we compare the full \( S(\omega) \) of the MgSO₄ solution (blue) to the one of bulk water (black). The decreased response of water molecules in the salt solution with respect to bulk water is clear.

To determine the origin of the reduction in the pump-probe signal in the presence of salt we have performed molecular dynamics simulations of a comparable (0.5 M) MgSO₄ solution and calculated the frequency spectrum \( S(\omega) \) of all the water molecules, as well as the \( S(\omega) \) of just the water molecules in the hydration shell of the Mg²⁺ and SO₄²⁻ ions (Fig. 5e). The strong interaction between water and the ions, in particular with the Mg²⁺ cation, manifests as a strong blue shift of ~8 THz of the resonant
frequency, which effectively moves the response of the water in the hydration of Mg\(^{2+}\) outside the resonant experimental frequencies. In the inset of Fig. 5e we compare the \(S(\omega)\) of MgSO\(_4\) solution (blue) and pure water (black) focusing on the response around the resonant peak at 12.3 THz. The comparison reveals a reduction in the birefringent third-order response (as quantified by \(I_{rel}\)) of \(-20 \pm 3.5\%\), which is in good agreement with the experiment \((-16 \pm 7\%)\). The strong electrostatic interaction between the divalent ions and water shifts the natural frequency of the rotational motion of the water molecules in the solvation shell cage towards higher frequencies. Therefore, when pumping the salt solution at the resonant frequency of bulk water molecules (e.g. 12.3 THz), the birefringent signal is decreased because the stiffened librational mode of the hydration water is out of the range of that frequency.

CONCLUSION
We have presented single-color pump-probe experiments at 7.8, 12.3, and 13.9 THz to induce transient anisotropy in the bulk liquid phase. We observe a giant third-order birefringent signal of pure water at 12.3 THz that exceeds by multiple orders of magnitude that found for optical, near-infrared, and low-frequency THz fields. We have presented new theory in which the four-point time correlation function, that typically would be required to simulate the third order birefringent response, can be replaced with a formalism that implicitly represents the pump while only needing the two-point time correlation at the resulting probe frequency. Together, experiment and theory have shown that the pump-probe experiment at the 12.3 THz laser frequency is resonant to the reorientation timescale of water dipoles in their hydration cages, and that application of an external field at this frequency leads to driven water dipole reorientations that creates a transient anisotropy in a homogeneous liquid phase. The experimentally observed birefringence at 13.9 THz is qualitatively similar, but with a decrease attributable to the smaller penetration depth and poorer signal-to-noise at this specific frequency. At 7.8 THz we observe a distinct, substantially smaller transient signal. The decrease in signal magnitude is also observed in the simulation and is attributed largely to the fact that the timescale of the driving field is detuned with respect to natural librational dynamics of the water molecules in their extensive hydrogen-bonded network.

We also report the results of a pump-probe signal from a low concentration MgSO\(_4\) salt solution which is decreased by \(-16\text{--}20\%\) with respect to pure water, a value supported both by experiment and theory. This change in direction, i.e. a reduction of the birefringence signal, is understood to arise from the fact that fewer water molecules can participate in the resonantly driven reorientational motions faster than \(<5\) ps imposed by the THz radiation. Because of the stiffer rotational response of the water molecules close to the ions, especially of those waters near the Mg\(^{2+}\) cation, their frequency spectrum is
blue-shifted and thus cannot follow the dynamical alignment driven by the THz field at 12.3 THz. The pump-probe THz spectroscopy from experiment and theory that we have presented here for water and simple salt solution holds the promise to manipulate and/or map hydration dynamics by the presence of strong AC and DC electric fields. This may open the door to new ways to probe or even control solvation behavior in more complicated environments, e.g. at interfaces and to induce chemical transformations in water by using THz fields.

METHODS

Source. As a radiation source we used the free electron laser FELIX in Nijmegen. The source emits “macro-pulses” with a repetition rate of 10 Hz. Each macro-pulse consists of 200 individual pulses with a temporal separation of 40 ns (25 MHz). The individual pulse length used was 3.6 ps full-width at half-maximum (FWHM) resulting in a pump-probe overlap of ~5 ps. The source emission frequency is tunable within the “terahertz gap”, spanning between about 8 THz and 16 THz. While it is challenging to generate intense pulses of light at these frequencies, accessing the terahertz gap is of interest because it overlaps with the librational absorption of liquid water. In order to completely suppress the pump scattering at the detector, we chose a non-collinear pump-probe configuration (Fig. 1a) and a sample thickness ~4 times larger than the penetration depth (42,43,59,60) at 12.3 THz. When FELIX is tuned to emit radiation at 12.3 THz, and taking into account the reflection losses at the cell window, the typical fluence of each individual pump pulse was 3.1 mJ/cm², resulting in a peak power (field strength) of 900 MW/cm² (0.9 MV/cm) at the sample. The time zero calibration procedure and the spot sizes are reported in the SI. Further details on the pump-probe setup at FELIX can be found in Ref.44–48.

Sample. Ultra-pure liquid water (Fig. 2, Fig. 3) and 0.6M MgSO₄ aqueous solutions (Fig. 5) were loaded into a static cell with diamond windows. A Kapton spacer with thickness $d = 25 \mu m$ is placed in between the diamond windows. The temperature of the diamond cell was actively stabilized at 20±0.05 °C with a recirculating chiller.

Diffusion-limited heat. The diffusion-limited thermalization time is approximately \( \tau = \frac{r^2}{D} \), where $D$ is the diffusivity and $r$ is the radius of a sphere of volume equal to the photoexcited volume. Considering the pump spot size of ~700 \( \mu m \) and \( d^* \approx 6 \mu m \), we have $r \sim 80 \mu m$. The thermal diffusivity of water is \( 1.47 \times 10^{-7} \frac{m^2}{s} \) and the diffusion-limited thermalization time of the liquid water sample is $\tau \approx 44 \text{ ms}$ in our experiments. Each macro-pulse of FELIX is as short as 200 · 40 ns = 8 \( \mu s \). Thus, we expect negligible thermal build-up during each macro-pulse ($8\mu s / 44 ms < 2 \cdot 10^{-4}$). $\tau$ is also the
cooling time, and the temporal separation between two macro-pulses is 100 ms (10 Hz duty cycle): during this delay, the chiller stabilizes the sample temperature to 20±0.05 °C. For these reasons, diffusion-limited heating is negligible.

**Non-diffusive heating.** It is not always possible to assign an effective time-dependent temperature to a system which is perturbed by an ultra-short light pulse\textsuperscript{75,76}. During the light-matter interactions the population of the excited transitions is inconsistent with a Boltzmann distribution and the temperature is ill-defined\textsuperscript{75,76}. To the best of our knowledge, the decay time of such a thermal component displays a decay time exceeding 20 ps in liquid water\textsuperscript{19,75,77,78}. In our measurements we could detect signal almost exclusively at pulse overlap, thus indicating that non-diffusive thermalization effects are not dominant. In some cases, there is a tiny negative signal beyond pulse overlap (e.g., about -2·10\textsuperscript{-3} at t=10 ps in Fig. 3c), which we associate to a small heat-induced absorption.

**Molecular dynamics.** We performed molecular dynamics simulations using the TINKER molecular dynamics package\textsuperscript{79} and the polarizable force field AMOEBA, specifically the AMOEBA14 water model\textsuperscript{64}. We study two different systems: a pure water system with 512 water molecules packed at a density of 1 g/cm\textsuperscript{3}, and a MgSO\textsubscript{4} solution with 975 water molecules and an salt concentration of 0.5 M (10 Mg\textsuperscript{2+} and 10 SO\textsubscript{4}\textsuperscript{2-} ions). All the simulations are carried out in the NVT ensemble at room temperature using a Nose-Hoover thermostat with a coupling constant of 0.1 ps and a Beeman integrator. The timestep in all the simulations is 0.5 fs. Each trajectory has a length of 25 ps, enough to sample the ultra-fast rotational modes of interest. The oscillating external field is implemented by adding a component to the permanent electrostatic field that changes in time according to a sinusoidal function, i.e. $E = A \sin(\omega_{pump} t)$, where $A$ is the amplitude of the electric field and $\omega_{pump}$ is the frequency. We performed simulations at $\omega_{pump} = 1.0, 7.8, 12.3,$ and 200 THz, at three different amplitudes of the electric field 1 MV/cm, 2 MV/cm, and 3 MV/cm, and for 3 different polarization directions. The results show in the all the figures correspond to the average among the different polarization directions. From the simulation trajectories we calculate the angle $\varphi_i(t)$ between the electric field $\vec{E}$ and the dipole moment of the $i$-th water molecule $\vec{\mu}_i$ at time $t$. From these time series of the orientation angles is trivial to calculate $\langle \frac{d}{dt} [\cos(\varphi(t))] \rangle$, and hence $S(\omega)$ using Eq. (16). The angular brackets indicate the average over all the molecule in the system in the canonical ensemble. In order to validate the AMOEBA force field, we compared the $S(\omega)$ of pure water from two different force-field water models (AMOEBA14 and TIP4P-Ew) to the results from ab initio molecular dynamics (AIMD) based on density functional theory and the functional B97M-rV (Fig. S3). We find that while AMOEBA (the polarizable force field) is in good agreement with the AIMD results, the classical force field with fixed charges TIP4P-Ew
strongly disagrees.

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**Author contributions**

F. N., G. S., and M. H. proposed the experiments. F. N., F. S., E. A., C. H., T. O., A. C. performed the measurements. N. D., K. S. I., N. S., V. E., and L. V. helped during the experiments. N. D., N. S., and L. V. developed the optical system. N. D. optimized the pump-probe setup. F. N. performed the data analysis. K. C. B. derived the theory. L. R. P. and T. H.-G. developed the simulated model. L. R. P. performed MD calculations. F. N., L. R. P., G. S., T. H.-G. and M. H. discussed and interpreted the data. F. N., L. R. P., T. H.-G., and M. H. wrote the manuscript with help from all authors.
Competing interests
The authors declare no competing financial interests.

Materials & Correspondence
The data are available from the corresponding authors on reasonable request.