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Terahertz Driven Ultrafast Energy Dissipation in Aqueous Ionic Solutions

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ABSTRACT. Solvation of ions changes the physical, chemical and thermodynamic properties of water. The microscopic origin of this process is believed to be the ion-induced perturbation in the structure and dynamics of the hydrogen (H)-bonding network of water. Here, we provide microscopic insight on the local structural deformation of the H-bonding network of water by ions, via investigating the dissipation of external energy in salt solutions by a novel time-resolved terahertz (THz)-Raman spectroscopy. We resonantly drive the low-frequency rotational dynamics of water molecules by intense THz pulses and probe the Raman response of their intermolecular translational motions. We find that the intermolecular rotational-to-translational energy transfer is enhanced by highly-charged cations and it is drastically reduced by highly-charged anions, scaling with the ion surface charge density and concentration. Our molecular dynamics simulations further reveal that the water-water H-bond strength between the first and the second solvation shells of cations (anions) increases (decreases), signifying the opposite effects of cations and anions on the local structure of water. The impact of ion polarity on the ultrafast energy dissipation in water, resembles the effect of ions on stabilization and denaturation of proteins.

Introduction

Ions are ubiquitous in nature and their solvation is of fundamental importance in chemical and biological reactions.^{1,2} They affect folding and unfolding of proteins and enzymes,^{3–6} they are responsible for the transmission of neural signals in organisms⁷, they affect chemical equilibria⁸ and define the efficiency of electrochemical reactions^{9–11}. In most, if not all, of these processes, strong interactions between ions and water molecules are believed to play a central role. Due to electrostatic interactions, ions perturb the dynamics and the local structure of hydrogen (H)-bonding network of water, although the extent of these effects is not yet fully understood.^{12–14} Ions are typically categorized into structure-makers and -breakers. Relative to the strength of water-water interaction, the former stabilizes the water structure, due to their high surface charge density (SCD),¹⁵ while the latter, consisting of ions with low SCD, interact weakly with water molecules and promote disorder in the H-bonding network of water.^{15,16} However, this SCD-based categorization neglects the polarity of ions. Moreover, the distinct solvation mechanisms of cations and anions is not grounded on a comprehensive molecular level description.^{17,18}

Extensive theoretical^{19–22} and experimental^{23–25} studies have been conducted for gaining microscopic insight on ion solvation. However, due to the complexity of this process and the selective sensitivity of employed methods, the emerged pictures are still elusive and in many cases contradictory. Some methods are inherently more sensitive to either of anions or cations. For instance, ultrafast vibrational spectroscopy, in which the stretch vibration of water's hydroxyl group is used as a local probe to measure the orientational correlation time of water molecules, is more sensitive to anionic effects.^{22,26} Employing this technique, Bakker and co-workers resolved slow H-bonding dynamics of water hydrating anions²⁶ and almost no effect on the re-orientational dynamics of water surrounding cations^{27,28}. In contrast, dielectric relaxation which probes the dynamics of the molecular permanent dipole moment, is more sensitive to the motion of water molecules in the first hydration shell of cations.^{29,30} This method showed only local ionic effects, limited to the water molecules in the first solvation shell.³¹ On the other hand, neutron scattering resolves the distortion of the H-bonding network, well beyond the first solvation shell

of ions with the structural modification similar to the impact of pressure on water, but with marginal impact on H-bonding between water molecules.³²

Interestingly, methods that directly interrogate the H-bonding network dynamics of water, such as THz and low-frequency Raman spectroscopies turned out to be triumphant on revealing further details of ion solvation. For sub-1THz region, Netz and co-workers theoretically predicted^{33,34} and later experimentally resolved³⁵ the ion-water and ion-ion correlation signatures, connecting the ion mobility to the macroscopic electrolyte conductivity. Using high frequency THz spectroscopy, Havenith and co-workers resolved resonances due to the vibrational motion of ions inside their water cages.^{36,37} The polarization-resolved ultrafast Raman spectroscopy by Meech and co-workers, showed the hydrogen bond vibrational mode, formed between anions and their surrounding water molecules.^{31,38} Notably, all these methods measure the time dependent, ensemble averaged two-point correlation function $\langle A(0), A(t) \rangle$, with A being the dipole moment vector in THz spectroscopy, the polarizability tensor elements in Raman spectroscopy and particle density in neutron scattering. More recently, Hamm and co-workers introduced a combined Raman-THz spectroscopy, which measures three-point cross-correlation of the dipole moment vector μ and the polarizability tensor elements Π , i.e. $\langle \Pi(0), \mu(t_1), \mu(t_2) \rangle$. They demonstrated the heterogeneity of the local structures of water, surrounding cations by resolving the photon-echo response of aqueous ionic solutions and demonstrated the ability of cations to structure the H-bonding network of water.¹⁸

Here we employ a similar approach and study the local structural dynamics of water in aqueous ionic solutions. However, in contrast to Hamm's approach, we induce the third-order nonlinear effect by two THz-electric-field interaction with the collective permanent dipole moment of liquids and one-field optical-Raman interaction with the collective polarizability of the system, which gives rise to the three-point response function of the form $\langle \mu(0), \mu(0), \Pi(t) \rangle$. In this hybrid THz-Raman technique, the ultrafast dissipation of the deposited THz energy to the associated modes/processes of the H-bonding network dynamics of water can be traced in time. Using this technique, we recently demonstrated that the resonant excitation of the rotational degrees of freedom of water at ~ 1 THz leads to an ultrafast (faster than 300 fs) energy transfer to its collective translational motions.³⁹ The latter process is the result of an intermolecular coupling between the rotational and the translational motions in the H-bonding network of water, see Fig. 1.

In the current study, we use the latter THz-Raman technique to study the impact of ions on the local structural dynamics of water. The amplitude of the resolved signal is increased in the solutions with strong cations and reduced by strong anions, suggesting the respective enhancement and disruption of energy transfer within the H-bonding network of water by cations and anions. By employing *ab initio*, as well as polarizable classical molecular dynamics (MD) simulations, we attribute these effects to the strengthening and weakening of the H-bonds between water molecules in the first and second solvation shells of cations and anions, respectively.

Experiment

The THz-Raman experiment is performed in the THz Kerr effect (TKE) configuration whose details are given elsewhere.^{40,41} Briefly, as shown schematically in Fig. 1a, a linearly polarized THz electric field with a strength of ~ 2 MV/cm pumps the aqueous salt solutions.⁴¹ The liquid samples (thickness of 100 μm) are held between a rear glass window and a 150 nm thick silicon nitride (SiN) membrane as the entrance window.⁴² The SiN thin window exhibits a negligible Kerr signal and therefore, ease challenges for separating the liquid response from that of the window. The pump-induced optical birefringence $\Delta n(t)$ is measured by a probe pulse (800 nm, 2 nJ, 8 fs) whose linear polarization acquires ellipticity by traversing the sample. The induced transient birefringence is measured by a temporally delayed and collinearly propagating probe pulse whose incident linear polarization is set to an angle of 45° relative to the THz electric field polarization. Due to the pump-induced birefringence, the probe field components polarized parallel ($\parallel$) and perpendicular ($\perp$) to the pump field acquire a phase difference $\Delta\phi$ when propagating through the sample, thereby resulting in elliptical polarization. The $\Delta\phi$ is detected with a combination of a quarter-wave plate and a Wollaston prism, which split the incoming

Fig. 1. TKE of water. a, An intense THz pump pulse with peak frequency of ~ 1 THz induces optical birefringence in water. The effect is monitored by an optical probe pulse that becomes elliptically polarized upon traversing through the medium. b, Upon excitation of the rotational degrees of freedom of water with an intense THz field, corresponding to two THz E-field interaction with this system, the deposited energy is almost instantaneously transferred to the translational degrees of freedom and increases its kinetic energy, causing an increase in the collision between molecules and accordingly the collision-induced polarizability. The latter is resolved by a Raman interaction with the system.

beam in two perpendicularly polarized beams with power $P_{\parallel}$ and $P_{\perp}$. In the limit $|\Delta\phi| \ll 1$, the normalized difference $P_{\parallel} - P_{\perp}$ fulfills: $\frac{P_{\parallel} - P_{\perp}}{P_{\parallel} + P_{\perp}} \approx \Delta\phi$. The measured phase shift is related to the change in the refractive index Δn of the liquid, i.e. $\Delta\phi = \Delta n L \omega c^{-1}$, where L is the thickness of the sample, ω is the probe frequency and c is the speed of light.

For a systematic study, we chose a series of salts, formed by highly charged anions and cations, including both “hard”, monoatomic, as well as “soft”, polyatomic ions. The counter-ions, namely Na^+ and Cl^- are chosen such that their interaction with water is comparable with water-water interaction.^{43,44} All samples were prepared volumetrically, by adding Milli-Q water to the weighted amount of salt. The salts were all handled in a glove box in order to avoid further water uptake during the preparation and gain maximum control of the water concentration in each solution. All solutions were prepared at concentrations of 2 and 4 mol/L (M), where possible, otherwise in certain cases with reduced solubility (i.e. Na_2SO_4 and Na_2CO_3), we reached the solubility limit and prepared also an intermediate concentration. Finally, for studying the effect of F^- , we chose K^+ as its counter-ion, due to its similarity with Na^+ in the ion-induced effects on water and the fact that higher concentrations could be reached.

Molecular Dynamics Simulations

In order to simulate the effect of the THz pulse on the solutions, we have employed non-equilibrium polarizable force field molecular dynamics (pFFMD) simulations using the AMOEBA force field.⁴⁵ We have performed pFFMD simulations on the ionic solutions MgCl_2 and Na_2SO_4 . In aqueous ionic solutions, a combination of very strong ionic electric fields and field gradients, long range interactions, and the interplay of polarization and charge transfer effects, make the simulations a challenging feat.⁴⁶ For instance, ignoring the charge transfer polarization effects, as is done in simple point charge models, can lead to the erroneous conclusion that all ions are structure-makers.^{47–49} Even for a simple electrolyte such as NaCl , the force fields based on point charges were found unable to reproduce the concentration dependence of important thermodynamic properties under ambient conditions.⁵⁰

Compared to simple point-charge models, AMOEBA assigns to each atom a permanent partial charge, a dipole, and a quadrupole moment. Electronic many-body effects are also represented using a self-consistent dipole polarization procedure. Due to the immense electric fields of ions, this explicit treatment of polarization becomes important in order to reproduce the THz Kerr response and its concentration dependence (See Fig. S8).

Fig. 2. TKE response of aqueous salt solutions. **a**, THz driven transient optical birefringence of a series of salts with strong cations and Cl^- as their counterion, at 4M concentration. The flipped relaxation tail of the signals decays with $\tau \approx 0.5$ ps and gains amplitude with $\text{MgCl}_2 > \text{LiCl} > \text{LiCl} > \text{NaCl} > \text{H}_2\text{O}$. **b**, Same as panel **a**, but for strong anions with their counterion either Na^+ or K^+ . Here also the tail of the signal relaxes with $\tau \approx 0.5$ ps, but drops in amplitude with $\text{Na}_2\text{CO}_3 < \text{Na}_2\text{SO}_4 < \text{KF} < \text{H}_2\text{O}$.

Results

The resulting THz electric-field-induced optical birefringence of all solutions including chloride salts and sodium salts are displayed in Fig. 2a and Fig. 2b, respectively. In both panels the signals are compared with that of pure water. Two main contributions can be discerned: (i) a coherent instantaneous electronic response which carries no information on the nuclear dynamics of the liquid and (ii) a flipped relaxation tail. The amplitude of the latter contribution is highly sensitive to the ionic content of the solutions; it is enhanced for the solutions with chloride salts of strong cations (which we denote “strong cations” for brevity) and reduced for solutions of sodium salts of strong anions (strong anions), both relative to the TKE signal of water. Moreover, the relaxation tail of all signals can be fit with a single exponential with decay times in the range ~ 0.5 - ~ 0.8 ps (see Fig. S2 and Fig. S3).

The variation of the TKE signal amplitude of all ionic solutions (relative to that of pure water) as function of salt concentration is shown in Fig. 3a. While for strong cations the signal amplitude increases by increasing the salt concentration, the trend is reversed for the strong anions and the amplitude drops with increasing concentration. We further compare the TKE signal amplitude against the gas phase surface charge density, SCD of ions.⁵¹ As shown in Fig. 3b, the normalized amplitude of the TKE signals of the highest salt concentrations (4 M) declares a linear dependence of the TKE amplitude on SCD, again with opposite trends for cations and anions. Notably, the slope of the linear fit to the signal amplitudes in both panels is much steeper for anions, which may indicate stronger anionic effects on water structural dynamics relative to that of cations.

Discussion

Optical birefringence. In the THz Kerr effect experiment, due to the action of the pump field, polarized along x (see Fig. 1a), the probe pulse, polarized at 45° relative to x , encounters a transient difference $\Delta n = n_x - n_y$ between the refractive indices along x and y directions. The resulting birefringence is given by⁵²

$$\Delta n \propto \langle \Delta \Pi_{xx} - \Delta \Pi_{yy} \rangle, \quad (1)$$

where $\Delta \Pi_{ij}$ is the pump-induced change in the collective electronic polarizability tensor element Π_{ij} . Here, Π refers to the liquid phase and contains contributions from interactions/collisions between

Fig. 3. TKE concentration and SCD dependence. **a**, The amplitude of the TKE signal relative to that of pure liquid water is plotted against the salt molar concentrations. The solid lines correspond to the best linear fit. **b**, The amplitude of the TKE signal relative to that of pure liquid water is plotted against the gas phase charge density of the salts. The solid lines provide visual aids showing the trend of anions and cations. Note that the TKE amplitude of SO_4^{2-} and CO_3^{2-} at 4M is obtained by extrapolating the TKE amplitudes at two lower concentrations. The error bars indicate the noise level in the corresponding TKE signals.

molecules in condensed phase. The variation $\Delta\Pi$ can, in principle, be written as a sum $\Delta\Pi^M + \Delta\Pi^I$, whose two contributions arise, respectively, from the intrinsic gas-phase molecular polarizability Π^M and the intermolecular interactions and collisions Π^I in condensed phase.^{47,53}

$\Delta\Pi^M$ characterizes the degree of anisotropy of the unperturbed Π and is usually labeled $\Delta\alpha$ for single gas phase molecules. Averaging $\Delta\Pi^M$ over all molecules according to Eq. (1) yields an expression for Δn_{rot} that scales with the degree of molecular alignment $\langle P_2(\cos\theta) \rangle = \langle 3 \cos^2 \theta - 1 \rangle / 2$ and the molecular polarizability anisotropy $\Delta\Pi^M$ i.e. $\Delta n_{\text{rot}} \propto \Delta\Pi^M \langle P_2(\cos\theta) \rangle$. The averaged $\Delta\Pi^I$ makes another contribution to the transient birefringence and arises from directly or indirectly pump-induced changes in the collision-induced polarizability.

THz Kerr effect of water. Intermolecular interactions in water are highly complex and are affected by the breaking and reforming of hydrogen bonds, a process that strongly depends on both molecular rotations and translations.^{54,55} As shown in Fig. S1, the low-frequency intermolecular dynamics of water includes restricted rotational and translational motions whose energies span over 1000 cm^{-1} .⁵⁶ These contain various contributions including the hindered rotation of single molecules at $\sim 600 \text{ cm}^{-1}$ (librations), the H-bond stretch vibration at $\sim 200 \text{ cm}^{-1}$, H-bond bending at $\sim 60 \text{ cm}^{-1}$ and the collective rotational motions at lower frequencies.⁵⁷ Our recent study³⁹ and also the work by Zhang and co-workers⁵⁸ demonstrate that the TKE of water manifests a coupling between the rotational and the translational motion of water molecules, in contrast to the TKE response of simple molecular liquids whose dynamics are dominated by the single molecules rotational motion.⁵⁹

As displayed schematically in Fig. 1b, the deposited THz energy to the rotational degrees of freedom is transferred to the translational motion of water molecules and increase their kinetic energy (KE). In Ref.39 we demonstrated that the decay of the TKE signal's tail may be explained by the relaxation of the translational motion of water molecules, most likely that of the H-bond bending mode due to its spectral proximity to the excitation frequency. Note that the rotation-to-translation energy transfer is concomitant with a coherent increase in the rate of the collision between the molecules and accordingly changes in the refractive index of the liquid via $\Delta\Pi^I$. As such, the TKE signal of water can measures $\Delta\Pi^I$ and may be used to estimate the water-water intermolecular interactions in aqueous ionic solutions.

THz Kerr effect of aqueous ionic solutions. As shown in Fig. 2 and Fig. 3b, the amplitude of the flipped side of the TKE signal of ionic solutions is very sensitive to the polarity and the SCD of ions.

Fig 4. Simulated polarizability anisotropy of the salt solutions. Total polarizability anisotropy $\Delta\Pi$ of **a**, aqueous solutions of MgCl_2 at 1M, 2M and 4M concentration **b**, and Na_2SO_4 aqueous solution at 1M. Arrows indicated the increase and decrease of $\Delta\Pi$ relative to that of pure water. **c** and **d**, show single molecule $\Delta\Pi^M$ and collision induced $\Delta\Pi^I$ polarizability components of the total polarizability for MgCl_2 solution at 4M and for Na_2SO_4 at 1M, respectively. While $\Delta\Pi^I$ has the dominant contribution in the $\Delta\Pi$ for the MgCl_2 solution, its contribution is minor in the Na_2SO_4 solution.

Given our previous finding that the TKE signal amplitude measures the strength of the intermolecular water-water interaction, the ion-induced enhancement or weakening of the TKE signals suggests in the variation in the strength of the intermolecular water-water H-bonding interaction, such that the strong cations strengthen the water-water interaction and the strong anions weaken it. Note also that the tail of all TKE signals relaxes on sub-ps time constant (see Fig. S2 and Fig. S3). This finding is in-line with the low-frequency Raman studies of aqueous ionic solutions, in which the bandwidth of the intermolecular H-bond bending mode of water is shown to remain all in the same range and further show the soundness of our suggested assignment of the H-bond bending mode as the origin of the observed TKE signal.^{60,61}

To gain microscopic insight into the details of the ion-induced changes in the local structure of water, we resort to MD simulations with the AMOEBA polarizable force field. Fig. 4 shows the calculated THz electric-field induced polarizability anisotropy $\Delta\Pi(t)$ for MgCl_2 and Na_2SO_4 solutions. This was obtained from the MD trajectories using the extended dipole-induced dipole (XDID) model as described by Torri⁶² but modified to include the second hyperpolarizabilities (See SI for details of MD setup, force field parameters, and XDID model). We have also calculated $\Delta\Pi(t)$ for NaF which is given in Fig. S7.

In Fig. 4a, we display the concentration dependence of $\Delta\Pi(t)$ for the MgCl_2 solutions. Interestingly, the $\Delta\Pi(t)$ amplitude of all three solutions at 1M, 2M and 4M concentrations are larger than that of pure water (black line) and it increases by increasing the concentration, in-line with our experimental results in Fig. 3a. In Fig. 4b we compare the polarizability anisotropy of water and 1M solution of Na_2SO_4 . In contrast to the MgCl_2 solutions, the $\Delta\Pi$ calculated for 1M of Na_2SO_4 shows an amplitude drop, again in-

Fig 5. Molecular kinetic energy. Temporal evolution of the ratio of the molecular translational KE to the total instantaneous KE of aqueous ionic solutions obtained from polarizable FFMD simulations. The deviation of the ratio from the equilibrium value of one-third is plotted so that a positive value indicates a relative increase in the respective KE contribution in comparison to an equilibrium (equipartitioned) distribution.

line with the experimental results (see Fig. 2b). Note that the $\Delta\Pi(t)$ amplitude drop of Na_2SO_4 is not as large as that signal amplitude drop observed in the experiment, this is likely due to the force field (FF) of Na_2SO_4 in need for further optimization. However, we observe larger amplitude drop for 1M solution of NaF (see Fig. S7a) which better presents the $\Delta\Pi(t)$ amplitude drop of the strong anions.

In Fig. 4c and 4d we show the decomposition of $\Delta\Pi$ into the contributions $\Delta\Pi^M$ and $\Delta\Pi^I$ for MgCl_2 at 2M and for Na_2SO_4 at 1M. Interestingly, while in the MgCl_2 solution the collision induced polarizability anisotropy $\Delta\Pi^I$ has the dominant contribution, its contribution in the Na_2SO_4 solution is minor. The dominance of $\Delta\Pi^M$ in the total polarizability anisotropy in the solution of the strong anions is also observed for the 1M NaF solution, see Fig. S7. Notably, as the THz energy is initially deposited into the rotational degrees of freedom of water molecules, the enhancement/weakening of $\Delta\Pi^I$ may imply an underlying enhancement/weakening of the rotation-to-translation coupling. In other words, the rotational-to-translational energy transfer within the H-bonding network of water is enhanced by strong cations and reduced by anions. This conclusion is further corroborated by our MD simulations, at least for the strong cationic solutions of MgCl_2 . As shown in Fig. 5, the evolution of the translational KE relative to the KE at the equilibrium state of molecules shows a strong enhancement for the MgCl_2 solutions, compared to KE of water molecules in pure water³⁹. For the 1M Na_2SO_4 solution, although we do not observe the expected decrease of the translational KE relative to pure water, its increase is not as large as 1M MgCl_2 solution. This again might be an issue with the employed FF parameters for Na_2SO_4 .

To connect the latter findings to the local intermolecular interactions in water in the presence of ions, we calculate the strength of hydrogen bonds between water molecules in the first and the second solvation shells of ions. For quantifying the strength of the H-bonds, we employ the energy decomposition analysis for condensed phase systems based on absolutely localized molecular orbitals (ALMO-EDA)^{63,64} within Kohn–Sham density functional theory (See computational details in SI). Conceptually, ALMO-EDA decomposes intermolecular interaction energies by first filtering out the frozen electrostatic and polarization effects from the total many-body intermolecular binding energy. The remaining charge transfer contribution is then split into pairwise two-body terms, each corresponding to an individual HB or ion-water interaction in the system. These two-body terms are obtained self-consistently under fully periodic boundary conditions. The water-water H-bond strength

Fig. 6. Water-water H-bond strength in salt solutions. H-bonds and their properties are obtained from AIMD, as the average of equilibrium trajectories. Every water molecule in the system is classified into one of four categories: In the solvation shell of a cation (red) or an anion (blue), shared between a cation and an anion (green), or bulk (remaining molecules). Average water–water H-bond strength as quantified by ALMO-EDA. Note that for water molecules in the first solvation shell of ions, the H-bonds reported are those between water molecules in the first and the second solvation shells of the ion. The dotted line marks the value of the corresponding quantity in pure water. We have used a simple geometric definition of a Hydrogen bond, with an O-O distance < 3.5 angstrom and an angle < 30°. ⁵⁴

is then calculated for all pairs of molecules. The H-bonds are categorized into four classes: those between the first and second solvation shells of an anion, similarly for cations, those involving one water molecule which is simultaneously shared in the first solvation shell of an anion and a cation, and those between the remaining bulk-type water molecules.

As shown in Fig. 6, by comparing the water-water H-bond strength around ions with that for the bulk type water, the following conclusions may be drawn. In MgCl₂ solutions, the Mg²⁺ ions with their high charge density, lead the water-water H-bonds in their immediate surrounding to be 2-3 KJ/mol stronger than more distant H-bonds. This agrees with the MD calculations by Urbic et al.⁶⁵ and the recent experimental study by Shalit et al. in which they denote the ability of strong cations such as Mg²⁺ to structure the H-bonding network of water.^{18,66} On the other hand, in the Na₂SO₄ solution the sulfate ions SO₄²⁻ show an opposite trend to Mg²⁺, with neighboring H-bonds that are slightly weaker. The weakening of the water-water H-bonding strength in the presence of strong anions has also been reported in previous MD simulations.⁶⁵ Yadav et al. via analyzing the changes in the OH-stretch vibration frequency of water molecules in the first and second solvation shells of carbonate (CO₃²⁻) resolved the weakening of the water-water H-bonding strength.⁶⁷

We further calculated the H-bond strength of the MgSO₄ solution, in which both the anion and the cation are highly charged. Interestingly, the average of all ion-mediated contributions becomes slightly larger than the bulk type water-water H-bond strength, signifying the “cationic character” of this solution, i.e. the effect of the magnesium ion subtly prevails that of sulphate. Interestingly, this can be realized from the TKE response of this solution as well. As shown in Fig. S6, the TKE signal of MgSO₄ has a slightly larger amplitude compared to the signal amplitude of pure water.

Our finding shows that highly-charged ions influence the water-water intermolecular interactions between their first and the second solvation shells: cations strengthen this interaction and anions weaken it. The latter ion-induced change in water-water interaction, alters the intermolecular coupling strength between the rotational and the translational degrees of freedom as well. Hence, the THz energy initially

deposited into the rotational degrees of freedom of water, funnels into the translational motions of water molecules with the efficiency given by the ionic content of the solution.

In conclusion, we have reported a joint experimental and MD simulation study of the THz electric field induced optical birefringence in a large set of aqueous ionic solutions. We have found that strong cations enhance the total polarizability anisotropy of water, whereas strong anions weaken this effect relative to the effect observed in pure water. The polarizable classical MD simulations successfully reproduce the experimental results and further show that the collision/interaction induced polarizability is enhanced in the presence of strong cations and it is weakened by strong anions. The origin of these effects is attributed by ab initio MD simulations to the changes in the water-water H-bonding interaction by ions; strong cations make H-bonds stronger while strong anions weaken it. Hence, THz energy initially deposited into the rotational degrees of freedom, is transferred to the translational motions with the efficiency given by the ionic content of the solution, it increases by strong cations and decreases by strong anions. Our success to reproduce THz Kerr effect signal of aqueous solutions via MD simulations and gaining microscopic insight into the structural modification of water by ions, shows the overall soundness of employed polarizable force fields for such studies.

The opposite effects of strong ions on energy dissipation in water is the first experimental observable, found in-line with the impact of ion polarity on the denaturation and stabilization of proteins' tertiary structures in aqueous solutions (i.e. the Hofmeister effect).^{68,69,70} While strongly hydrated cations are believed to denature proteins, mainly by direct preferential binding to the polar amide groups or by pairing with the protein's negatively charged carboxylate groups,^{5,71–73} the molecular picture of protein stabilization by strongly hydrated anions, remains elusive. Our finding in anion-mediated weakening of the water-water H-bond strength may support the mechanism suggested by Collins et al., in which the protein stabilization is attributed to the “interfacial effects of strongly hydrated anions near the surface of proteins”.⁷⁴ Less efficient energy transfer in water and weaker water-water interaction may result in changing the liquid to a “less good solvent” by strong anions. As a result, one might speculate that a poor solvent drives the protein to minimize its solvent accessible surface area by folding.⁷⁴ Interestingly, for the MgSO₄ solution both the TKE experiment (see Fig. S6) and ab initio MD simulations (see Fig. 5) suggest the dominance of cationic effects in strengthening the water-water interactions by Mg²⁺, which is again in-line with the denaturing behavior of this salt on proteins.⁷⁵

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Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper including the codes may be requested from the authors.

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