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Rattling in the Cage: Ions as Probes of Sub-picosecond Water Network Dynamics

Diedrich A. Schmidt,[†] Özgür Birer,[†,§] Stefan Funkner,[†] Benjamin P. Born,[†]
Ramachandran Gnanasekaran,[‡] Gerhard W. Schwaab,[†] David M. Leitner,[‡] and
Martina Havenith*,[†]

Department of Physical Chemistry II, Ruhr-University Bochum, 44780 Bochum, Germany, and
Department of Chemistry, University of Nevada, Reno, Nevada 89557

Received October 1, 2009; E-mail: Martina.Havenith@rub.de

Abstract: We present terahertz (THz) measurements of salt solutions that shed new light on the controversy over whether salts act as kosmotropes (structure makers) or chaotropes (structure breakers), which enhance or reduce the solvent order, respectively. We have carried out precise measurements of the concentration-dependent THz absorption coefficient of 15 solvated alkali halide salts around 85 cm^{-1} (2.5 THz). In addition, we recorded overview spectra between 30 and 300 cm^{-1} using a THz Fourier transform spectrometer for six alkali halides. For all solutions we found a linear increase of THz absorption compared to pure water (THz excess) with increasing solute concentration. These results suggest that the ions may be treated as simple defects in an H-bond network. They therefore cannot be characterized as either kosmotropes or chaotropes. Below 200 cm^{-1}, the observed THz excess of all salts can be described by a linear superposition of the water absorption and an additional absorption that is attributed to a rattling motion of the ions within the water network. By providing a comprehensive set of data for different salt solutions, we find that the solutions can all be very well described by a model that includes damped harmonic oscillations of the anions and cations within the water network. We find this model predicts the main features of THz spectra for a variety of salt solutions. The assumption of the existence of these ion rattling motions on sub-picosecond time scales is supported by THz Fourier transform spectroscopy of six alkali halides. Above 200 cm^{-1} the excess is interpreted in terms of a change in the wing of the water network librational mode. Accompanying molecular dynamics simulations using the TIP3P water model support our conclusion and show that the fast sub-picosecond motions of the ions and their surroundings are almost decoupled. These findings provide a complete description of the solute-induced changes in the THz solvation dynamics for the investigated salts. Our results show that THz spectroscopy is a powerful experimental tool to establish a new view on the contributions of anions and cations to the structuring of water.

Introduction

Water's importance in a variety of phenomena, ranging from simple aqueous salt solutions to complex biomolecule hydration, makes it a paramount material of experimental and theoretical investigation, as evidenced by recent extensive reviews.[1−4] An open question concerns the ability of a solute to change the water structure beyond its hydration shell. Kosmotropes (structure makers) are expected to enhance the water structure, while chaotropes (structure breakers) reduce the solvent order. While the optimum method to decide whether a specific solute shows kosmotropic or chaotropic behavior is still under debate, Marcus[4] proposed the average number of hydrogen bonds per water molecule as the most satisfactory description of the water structure. Experimentally, this should show up as a change in the spectral response in the frequency region where the hydrogen network absorbs, i.e., the terahertz (THz, 10^{12} Hz) regime.

The water network,[5−7] where hydrogen bonds are formed and broken on picosecond time scales,[7−9] has long been used to explain the unique physical, chemical, and structural properties of water. Neutron diffraction, X-ray scattering, and femtosecond IR techniques have been essential in determining either static or dynamic structural information.[10−15] However, to obtain a deeper understanding of the interaction of the network-coupled

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[†] Ruhr-University Bochum.

[‡] University of Nevada.

[§] Current address: Department of Chemistry, Koç University, 34450 Istanbul, Turkey.

(1) Ohtaki, H.; Radnai, T. *Chem. Rev.* **1993**, *93*, 1157.
(2) Ball, P. *Chem. Rev.* **2008**, *108*, 74.
(3) Bakker, H. J. *Chem. Rev.* **2008**, *108*, 1456.
(4) Marcus, Y. *Chem. Rev.* **2009**, *109*, 1346.
(5) Ohmine, I. *J. Phys. Chem.* **1995**, *99*, 6767.
(6) Silvestrelli, P. L.; Bernasconi, M.; Parrinello, M. *Chem. Phys. Lett.* **1997**, *277*, 478.
(7) Matsumoto, M.; Baba, A.; Ohmine, I. *J. Chem. Phys.* **2007**, *127*, 134504.
(8) Eaves, J. D.; Loparo, J. J.; Fecko, C. J.; Roberts, S. T.; Tokmakoff, A.; Geissler, P. L. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 13019.
(9) Boero, M.; Terakura, K.; Ikeshoji, T.; Liew, C. C.; Parrinello, M. *Phys. Rev. Lett.* **2000**, *85*, 3245.
(10) Soper, A. K.; Bruni, F.; Ricci, M. A. *J. Chem. Phys.* **1997**, *106*, 247.
(11) Wernet, Ph.; Nordlund, D.; Bergmann, U.; Cavalleri, M.; Odelius, M.; Ogasawara, H.; Näslund, L. Å.; Hirsch, T. K.; Ojamäe, L.; Glatzel, P.; Pettersson, L. G. M.; Nilsson, A. *Science* **2004**, *304*, 995.
(12) Smith, J. D.; Cappa, C. D.; Wilson, K. R.; Messer, B. M.; Cohen, R. C.; Saykally, R. J. *Science* **2004**, *306*, 851.

10.1021/ja9083545 © 2009 American Chemical Society

motions with the ions, it is necessary to use precise techniques capable of probing collective motions on picosecond time scales, i.e., at THz frequencies.

Indeed, we have previously shown that THz absorption spectroscopy provides a sensitive tool to study solvation dynamics. The method has been applied to carbohydrates,[16,17] model peptides,[18] and proteins.[19,20] For aqueous salt solutions, we qualitatively expect that an increase (decrease) in the average number of hydrogen bonds results in an increase (decrease) of the broadband water absorption due to the change of the oscillator density for kosmotropes and chaotropes, respectively. For a change in other hydrogen bond parameters, like bond angles and distances, further changes in absorbance, line shape, and center frequency are to be expected.

To reduce systematic effects in the vibrational spectrum due to contributions from the solvent spectrum or solute−water vibrational contributions, we have chosen 15 monovalent alkali halide salt solutions. The fundamental significance of hydrated metal ions originates from their essential role in aqueous chemical reactions, particularly in biological systems. Techniques such as femto- and picosecond IR and Raman spectroscopies,[21−23] neutron scattering,[10] and molecular dynamic (MD) simulations have been used to disentangle essential points of hydration, including hydration structure,[24] ion−water distances,[25] dynamical properties,[22] and collective motions.[26] Understanding the microscopic solvation picture of these ions is particularly difficult, due to the restricted experimental accuracy in neutron and X-ray diffraction experiments, which is a consequence of the fact that the ion−water distance is almost the same as the oxygen−oxygen distance in bulk water. Moreover, these techniques require high ion concentrations which limit the study to short-range dynamics. In addition, the hydration shells can be quite flexible on certain time scales due to the exchange of water molecules in the first and second hydration shells, most notably for anions.

Here, we report on the concentration-dependent narrow-band THz absorption for most of the alkali (Li, Na, K, Rb, Cs) halide (Cl, Br, I) salts. For all salt solutions we find an increase in THz absorption compared to pure water (THz excess) within our frequency range (2.3−2.8 THz). More specifically, we observe a strong cation mass-dependent absorption, with a maximum absorbance associated with K^+ for all halides and much less dependence of the THz excess on the anion. These findings can be explained by the model of ionic rattling motions, i.e., oscillations of the anions and cations, respectively, that are driven by the THz field in “cages” provided by the surrounding water network. We could corroborate the existence of these ion rattling motions on sub-picosecond time scales by THz Fourier transform spectroscopy of six alkali halides to extend the frequency range, and by accompanying MD simulations.

Experimental Section

All conclusions are based on precise measurements of the concentration-dependent changes in narrow-band THz absorption coefficients around 85 cm^{-1} with our unique p-Ge laser THz difference spectrometer[17] and by wideband (30−300 cm^{-1}) scans with a Bruker Vertex 80 V FTIR spectrometer. For the p-Ge laser difference measurements, liquid samples were held at 20.0 ± 0.1 °C and under purged conditions with <8% humidity and measured in standard Bruker liquid cells with fixed polytetrafluoroethylene (PTFE) spacers (51.3 μm ± 0.3 μm, determined from Fourier transform infrared (FTIR) spectroscopy) and 4.0 mm ± 0.1 mm thick z-cut quartz windows. Signals were averaged over 30 000 laser pulses. Absorption coefficients (α, in cm^{-1}) were determined using Beer’s law. Each salt series was measured at several concentrations between 0 and 4 M against water as reference liquid, with the maximum salt concentration depending on solubility.

THz FT spectra of salt solutions were also measured on a Bruker Vertex 80 V FTIR spectrometer under purged conditions at 20 ± 1 °C. Liquid samples were measured in standard Bruker liquid cells with fixed PTFE spacers (42 μm ± 1 μm, determined from FTIR spectroscopy) and 500 μm ± 100 μm thick chemical vapor deposition-grown diamond windows (Diamond Materials, GmbH). The cell for the FT measurements was chosen slightly thinner to improve the signal-to-noise ratio at higher frequencies. Each spectrum was measured with 1 cm^{-1} resolution and averaged three times over 128 scans. In total, 384 measurements were obtained at each concentration. Spectra were then smoothed with a running average of 29 points, or 27 cm^{-1}, to smooth out etalon effects from the diamond windows and PTFE spacer (see Supporting Information for experimental details).

Theoretical Section

Classical MD simulations were performed using the GROMACS software package.[27] All ions were modeled using Lennard-Jones parameters[28,29] developed and implemented in GROMACS. Water was described by the TIP3P[30] model using the optimized potentials for liquid simulations (OPLS) force fields.[31] The simulations were performed within a cubic box of side length 25 Å and periodic boundary conditions, so that the systems contained approximately 500 water molecules. For 1 M NaCl the box contained 491 water molecules with 10 cations and 10 anions. In all cases the ions were placed initially in random positions within the simulation box. The isothermal−isobaric ensemble (NPT) simulations were run at 300 K using a Berendsen thermostat and at 1 atm with a Berendsen barostat.[32] Cutoffs of 1.2 nm were used for the Lennard-Jones potentials and for the short-range nonbonded interactions. The particle mesh Ewald (PME) method[33,34] was applied to calculate

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(13) Winter, B.; Aziz, E. F.; Hergenhahn, U.; Faubel, M.; Hertel, I. V. *J. Chem. Phys.* **2007**, *126*, 124504.

(14) Omta, A. W.; Kropman, M. F.; Woutersen, S. W.; Bakker, H. J. *Science* **2003**, *301*, 347.

(15) Park, S.; Fayer, M. D. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 16731.

(16) Heugen, U.; Schwaab, G.; Bründermann, E.; Heyden, M.; Yu, X.; Leitner, D. M.; Havenith, M. *Proc. Natl. Acad. Sci. U.S.A.* **2006**, *103*, 12301.

(17) Heyden, M.; Bründermann, E.; Heugen, U.; Niehues, G.; Leitner, D. M.; Havenith, M. *J. Am. Chem. Soc.* **2008**, *130*, 5773.

(18) Born, B.; Weingärtner, H.; Bründermann, E.; Havenith, M. *J. Am. Chem. Soc.* **2009**, *131*, 3752.

(19) Ebbinghaus, S.; Kim, S. J.; Heyden, M.; Yu, X.; Heugen, U.; Gruebele, M.; Leitner, D. M.; Havenith, M. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 20749.

(20) Born, B.; Kim, S. J.; Ebbinghaus, S.; Gruebele, M.; Havenith, M. *Faraday Discuss.* **2009**, *141*, 161.

(21) Laenen, R.; Thaller, A. *Chem. Phys. Lett.* **2001**, *349*, 442.

(22) Kropman, M. F.; Bakker, H. J. *Science* **2001**, *291*, 2118.

(23) Walrafen, G. E.; Pugh, E. *J. Sol. Chem.* **2004**, *33*, 81.

(24) Mancinelli, R.; Botti, A.; Bruni, F.; Ricci, M. A.; Soper, A. K. *J. Phys. Chem. B* **2007**, *111*, 13570.

(25) Ikeda, T.; Boero, M.; Terakura, K. *J. Chem. Phys.* **2007**, *126*, 034501.

(26) Kim, S. J.; Born, B.; Havenith, M.; Gruebele, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 6486.

(27) Van der Spoel, D.; Lindahl, E.; Hess, B.; Groenhof, G.; Mark, A. E.; Berendsen, H. J. C. *J. Comput. Chem.* **2005**, *26*, 1701.

(28) Chandrasekhar, J.; Spellmeyer, D. C.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1984**, *106*, 903.

(29) Åqvist, J. *J. Phys. Chem.* **1994**, *98*, 8253.

(30) Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.

(31) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. *J. Am. Chem. Soc.* **1996**, *118*, 11225.

(32) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. *J. Chem. Phys.* **1984**, *81*, 3684.

(33) Darden, T.; York, D.; Pedersen, L. *J. Chem. Phys.* **1993**, *98*, 10089.

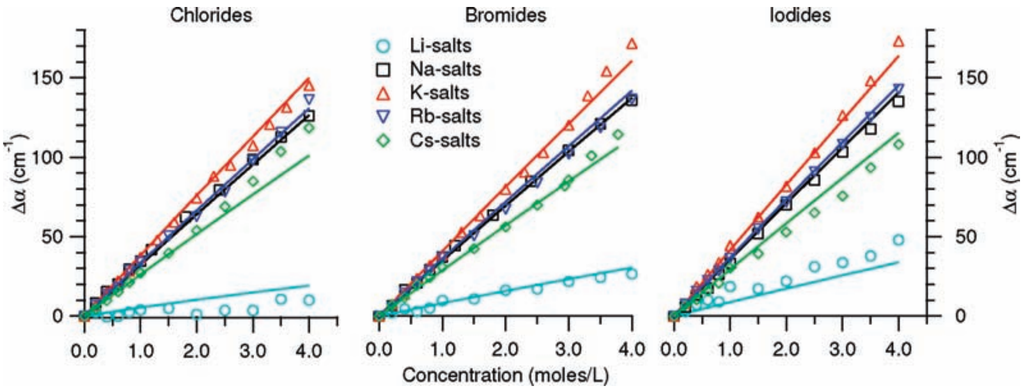

Figure 1. THz excess data and fits vs concentration. Concentration-dependent THz excess experimental data (points) and theoretical fits (solid lines) to LiCl (○), NaCl (□), KCl (Δ), RbCl (∇), and CsCl (◇) for the chlorides (left panel), bromides (middle panel), and iodides (right panel).

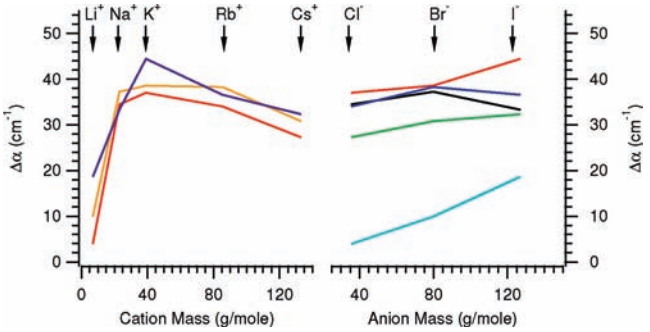

Figure 2. THz absorption vs ionic mass at 1 M concentration. (Left panel) Δα vs cation mass for chlorides (red), bromides (orange), and iodides (purple). (Right panel) Δα vs anion mass for Li^+ (cyan), Na^+ (black), K^+ (red), Rb^+ (blue), and Cs^+ (green).

all long-range electrostatic interactions using a 0.12 nm grid and fourth-order interpolation. The time correlation functions were computed using data from 8 ns simulations. The MD simulations were performed using the standard leapfrog algorithm with 1 fs time steps.

Results and Discussion

Using the p-Ge laser difference spectrometer, we have measured the difference $\Delta\alpha(c_S,\nu)$ between the absorption coefficient of a salt solution and that of pure water, which is given by

$$\Delta\alpha(c_S, \nu) = \alpha_{\mathrm{sample}}(c_S, \nu) - \alpha_{\mathrm{water}}(\nu) \tag{1}$$

where c_S is the concentration (in mol/L), and $\alpha_{\mathrm{sample}}(c_S, \nu)$ and $\alpha_{\mathrm{water}}(\nu)$ are the absorption coefficients of the sample and reference at frequency ν. For the narrow-band p-Ge laser measurements we set $\alpha_{\mathrm{water}}(2.55\ \mathrm{THz})$ to 419 cm^{-1}, the average value obtained for the 2.3−2.8 THz region using FT spectroscopy of pure water.

Experimentally, we obtained the following results. (a) All salt solutions show a THz excess in the 2.3−2.8 THz range ($\Delta\alpha > 0$, see Figure 1) with a linear dependence on the concentration, in contrast to what was found previously for biomolecule hydration.[16−20] (b) At a fixed concentration, a strong systematic dependence of Δα on cation mass and a weaker one on anion mass (see Figure Figure 2) is obtained. For all concentrations studied here, Δα has the following general dependence on alkali cations: $Li^+ < Cs^+ < Rb^+ \approx Na^+ < K^+$, whereas the dependence of Δα on anion is weaker and generally follows $Cl^- < Br^- < I^-$. Dodo et al. found a similar order for some of the lighter alkali halides between 40 and 80 cm^{-1}.[35] However, only 2 M concentrations were measured, and the heavier alkali halide salts were not investigated.

Previous results for the THz spectroscopy of solutes indicated that the data can be well described assuming a three-component model with the solute, bulk water, and water in the dynamical hydration shell which shares a distinct fast network dynamics and therefore a distinct THz absorption. The need for a third component was given by the observation of a nonlinear response when increasing the concentration.[17] In contrast, the linearity of the salt THz absorption when increasing the concentration indicates that the THz absorption coefficients of the solvation shells are approximately equal to those of bulk water and/or the dynamic hydration shell is very small, suggesting a treatment of the ions as simple defects in an H-bond network. The strong dependence of Δα on cation mass indicates a resonance that is tuned across the observed frequency range.

To fit the experimental data, we therefore used a model that is based on the following assumptions:

1. The molar absorption cross section σ_{water} of water is assumed to be independent of c_S. To obtain the amount of water in the solution the Masson equation is used (see Supporting Information for further details).
2. The frequency (ν)-dependent molar absorption cross sections $\sigma_A(\nu)$ and $\sigma_C(\nu)$ of the anions and cations, respectively, are described by reduced-mass resonance absorptions of ionic rattling modes, similar to those previously described by Dodo et al.[35]
3. The total absorption is a linear superposition of the individual contributions, i.e., $\alpha_{\mathrm{solution}}(c_S, \nu) = \sigma_{\mathrm{water}}(\nu)c_{\mathrm{water}}(c_S) + \sigma_C(\nu)c_S + \sigma_A(\nu)c_S$, where $c_{\mathrm{water}}(c_S)$ is the water concentration as a function of the salt concentration (see Supporting Information for details).

This yields

$$\Delta\alpha(c_S, \nu) = \sigma_C(\nu)c_S + \sigma_A(\nu)c_S - \sigma_{\mathrm{water}}(\nu)c_S\left(\frac{\phi^0_{V,S}}{V^0_w} + \frac{\sqrt{c_S}S^*_{V,S}}{V^0_w}\right) \tag{2}$$

for the difference in absorption. Here, V^0_w is the molar volume of pure water, $\phi^0_{V,S}$ is the salt's apparent molal volume at infinite dilution, and $S^*_{V,S}$ is the experimental slope of the Masson

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(34) Essmann, U.; Perera, L.; Berkowitz, M. L.; Darden, T.; Lee, H.; Pedersen, L. G. *J. Chem. Phys.* **1993**, *98*, 10089.

(35) Dodo, T.; Sugawa, M.; Nonaka, E.; Honda, H.; Ikawa, S. *J. Chem. Phys.* **1995**, *102*, 6208.

Table 1. Fit Parameters for Reduced Mass and Apparent Molal Volume Ionic Absorption Model

γ_C (THz)	15.46(22)
k_C (kg/s^2)	12.32(11)
γ_A (THz)	10.62(30)
k_A (kg/s^2)	63.1(14)
s_C (g/mol)	40.1(10)

equation, which varies with electrolyte type and charge.[36] A small nonlinear term arises in the concentration dependence of $\Delta\alpha$ from the Masson equation which is attributed to the loss in water oscillator number density at higher concentrations.

We were able to carry out a simultaneous fit of the concentration-dependent absorption coefficients of the 15 salts under investigation using five adjustable parameters (the damping constant for anions and cations, $\gamma_{A,C}$; the force constant for anions and cations, $k_{A,C}$; and a reduced mass fitting parameter, s_C, for the cations). The result is in very good agreement with the experimental data (see Figure 1), with minimal differences at high concentrations for the heavier salts.

Table 1 summarizes the resulting fit parameters. The damping constant is the rate of dissipation for the oscillating charge in a confined potential and is close to the inverse time scale of the water librational motion (~0.15 ps).[37] The force constants are interpreted as strengths of confinement related to the modes of water that interact with the ions. The larger force constants for the anions are interpreted as increased confinement within the H-bond network cage due to smaller anion−hydrogen distances, compared to the weaker cation confinement due to larger cation−oxygen distances. Consequently, we expect the rattling modes of the anion to be shifted to higher frequencies compared to the cation modes. As an example, the Cl^- mode is expected around 175 cm^{-1}, as it is indeed observed in our THz FT spectra (see below). The reduced mass constraint, s_C, is a fit parameter that accounts for the cation mass-dependent resonance behavior (see Figure 2) and was found to be ~40 amu, or approximately two water molecules. The reduced mass fitting parameter for the anions was found to be approximately equal to the anion mass. With the fitted force constant, we therefore expect no resonance behavior for the anions within the accessible frequency range of the p-Ge laser.

To test the validity of this simple model over a wider frequency range, we used it to predict wideband ion spectra by omitting the water contribution in eq 2. In Figure 3 we compare the model spectra (thin solid lines) to difference spectra which were measured using our THz FT spectrometer. We measured six alkali halide salts at 1, 2, and 3 M concentrations (dotted, dashed, and thick solid lines, respectively). The arrows indicate the center frequency of the p-Ge measurements for reference. To correct for the reduced water concentration and to leave only the ionic contributions, a scaled pure water spectrum was subtracted from the salt solution spectra. The scaling factor amounts to the ratio of the number of moles of water at a given salt concentration (in mol/L) as derived from standard density measurements to the moles of water in pure water (in mol/L), i.e., $c_{water}(c_S)/55.423$.

Both experiment and model predictions show very good qualitative agreement for all alkali halide salt solutions. The proportionality to concentration of the THz FT difference spectra confirms the general validity of our simple linear superposition model in the frequency range from at least 30 to 250 cm^{-1}. Except for LiCl, all of the alkali halide salts show two modes between 30 and 200 cm^{-1} in both the experimental and model spectra. The experimental peak at ~180 cm^{-1}, which shows little or no dependence on the cation, is attributed to the Cl^- rattling mode. This is confirmed by the measurement of LiBr, where the 180 cm^{-1} is missing while two peaks at ~150 and ~100 cm^{-1} are observed that are attributed to the Li^+ and Br^- rattling modes, respectively. Returning to the chloride measurements, the second peak at lower wavenumber, which is more sensitive to the cation in solution, is primarily attributed to the rattling modes of the cations. For LiCl, both ionic rattling modes are at nearly the same wavenumber, resulting in a single undistinguishable mode. All difference spectra also show an increased high-frequency absorption from the tail of the libration band.

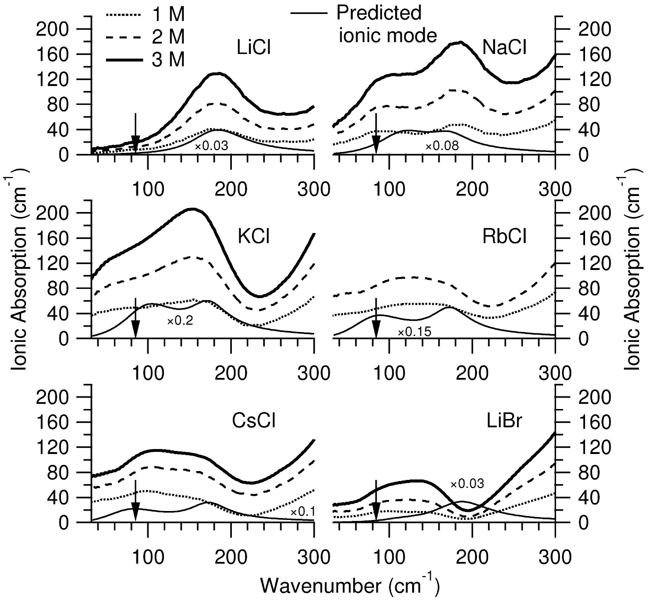

Figure 3. Experimental and predicted ionic absorption. THz FT (solid) and predicted (dotted) ionic absorption spectra of 1, 2, and 3 M concentration alkali halide salt solutions. All spectra are pure-water-subtracted and corrected for the loss of water. The arrows indicate the center frequency of the p-Ge laser.

In addition to the cation mass-dependent shifting of peaks to lower frequencies, there is also a cation size-dependent broadening of the experimental cation and anion peaks. If one uses the cation−water distance (see ref 4, Table 4) as a gauge of the ion diameter in the water network, those ions (i.e., Li^+, Na^+) that are smaller than $d_{water} = 0.276$ nm (the diameter of a water molecule) express sharper peaks, while those ions that are about the size of or larger than water (i.e., K^+, Rb^+, Cs^+) show broadened peaks. We take this as experimental evidence for a change in the static (on time scales >1 ps) rearrangement of the ionic solvation cages with size: On sub-picosecond time scales, small ions show a well-defined solvation cage, while large ions do not fit into the H-bond network, resulting in a distribution of local ion environments, e.g., cage sizes, with different interaction strengths. As a consequence, we find inhomogeneously broadened lines in the THz range.

In order to come to a microscopic description of the observed THz spectra, we have carried out accompanying MD simulations. The theoretical radial distribution functions (RDFs) of 1 M salt concentrations are shown in Figure 4. The RDFs for oxygen−oxygen of pure water (gray, dotted) and chloride−oxygen

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(36) Horne, R. A., Ed. *Water and Aqueous Solutions*; John Wiley & Sons, Inc.: New York, 1972.

(37) Laage, D.; Hynes, J. T. *Proc. Natl. Acad. Sci. U.S.A.* **2007**, *104*, 11167.

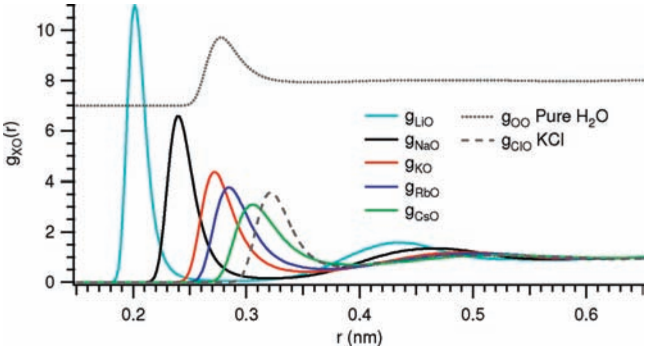

Figure 4. Radial distribution functions for cations (1 M salt solutions): g_{LiO} (cyan), g_{NaO} (black), g_{KO} (red), g_{RbO} (blue), and g_{CsO} (green). g_{OO} (gray, dotted) of pure water and g_{ClO} (gray, dashed) of 1 M KCl are shown for reference. g_{OO} is offset by 7 units for clarity.

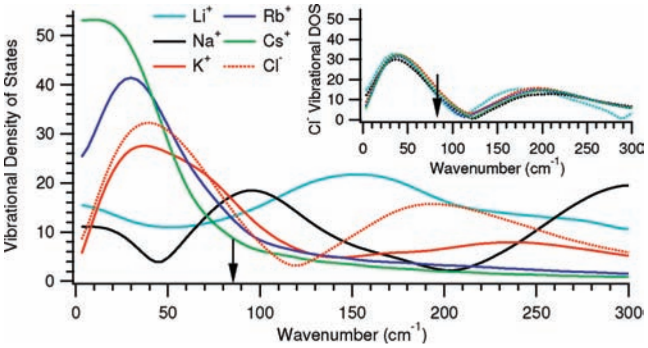

Figure 5. FT velocity autocorrelation plots for Li (cyan), Na (black), K (red), Rb (blue), Cs (green), and Cl (red, dotted) solutions at 1 M concentration. The inset shows the FT velocity autocorrelation of Cl for each alkali chloride solution (same color code). The arrows indicate the center frequency of the p-Ge laser.

(gray, dashed) of 1 M KCl are shown for comparison. Consistent with literature data of ion radii,[4] there is a clear shift of the first peak to larger cation−oxygen distances from Li^+ (cyan) to Cs^+ (green). In addition, the first peak in the cation−oxygen RDF broadens from Li^+ to Cs^+, indicating a weaker interaction and a less well defined ion−oxygen distance for the larger cations. This supports our view of the larger cations experiencing a wider distribution of local solvating environments. In contrast, the RDFs for chloride−oxygen and oxygen−oxygen of the 1 M solutions (see Supporting Information) show very little difference with changes in electrolyte or to pure water, in the case of g_{OO}.

Fourier transform velocity autocorrelation data as deduced from our MD simulations provide additional evidence for our interpretation of the THz FT difference spectra as rattling modes of the ions (Figure 5; the center frequency of the p-Ge laser experiments is indicated by an arrow). Specifically, we see that at ∼200 cm^{-1} there is a strong contribution in the density of states (DOS) of Cl^-, which is near the peak for Li^+ (∼160 cm^{-1}), resulting in a single rattling mode for the solution, in agreement with our experiment. The Na^+ DOS peak at ∼100 cm^{-1}, in combination with the Cl^- DOS peak at ∼200 cm^{-1}, agrees well with the double-peak structure seen in the experimental spectra of solvated NaCl. For the salts with larger ionic diameters (K^+, Rb^+, and Cs^+), there is a dominant peak in the DOS at lower wavenumbers between ∼10 and 70 cm^{-1}, which probably is responsible for the broad secondary peaks in the THz FT difference spectra. Finally, the computed FT velocity autocorrelation functions give rise to an ordering of the rattling mode DOS similar to the ordering of the measured THz excess. The shifts in the predicted peaks for Li^+, Na^+, and K^+ are consistent with the observed variation as a function of cation mass.

Summarizing our experimental results in combination with MD simulations, we conclude that, for aqueous solutions of structureless, monovalent binary salts, the THz absorption in the frequency range from 30 to 200 cm^{-1} can be described as a linear superposition of the THz water absorption and ionic oscillations, or rattling modes, in a water cage defined by the solvating waters. Above 200 cm^{-1}, all observed salts show an increase in absorption that is attributed to the tail of the librational motion of water. The strong linear behavior in the observed 30−200 cm^{-1} THz excess indicates that the normal-mode spectra of the solvation shells and of bulk water are not changed by the influence of the salts within the frequency range that corresponds to time scales in between those for hydrogen bond breaking (>1 ps) and the librational motion (∼0.15 ps) and includes the frequency region of the hydrogen bond stretch vibration.

In principle, this could be explained in two ways: (1) On the sub-picosecond time scale, the presence of the investigated ions does not appreciably affect the dynamic behavior of the H-bond network, i.e., the number of hydrogen bonds and their line strength. (2) The variation in absorption due to a change in average number of H-bonds is subtly compensated by a change in the line strength per H-bond. However, the latter alternative seems highly unlikely, considering the large number and variety of salts investigated and the frequency range covered. This makes a classification of any of the investigated alkali halides as kosmotrope or chaotrope questionable. In comparison, previous work has shown general agreement that anions tend to have little or no effect on the H-bond network (with two notable exceptions[38,39]). For example, Smith et al.[40] have shown in a combination of IR spectroscopy and computer simulations that the influence of halide anions in aqueous solution on the O−H vibrational spectrum can be understood in terms of the actions of the ions' electric field on adjacent water molecules. For cations so far, the discussion is still controversial regarding their effect on the H-bond network.[1,3,14,15,21,22,35,37−46]

Our results are in full agreement with neutron diffraction data of Mancinelli et al.,[24] which show that NaCl and KCl have negligible effects on the O−H and H−H RDFs, i.e., the hydrogen bond network, and that the modification in the O−O RDF is very similar to that of pure water under pressure. This pressure effect has been accounted for in our model by the use of a constant absorption per mole of water molecules.

Conclusion

We have performed a systematic narrow-frequency 2.3−2.8 THz absorption spectroscopy study of 15 alkali halide salts producing structureless ions in aqueous solution and a wideband

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(38) Schultz, J. W.; Hornig, D. F. *J. Phys. Chem.* **1961**, *65*, 2131.
(39) Terpstra, P.; Combes, D.; Zwick, A. *J. Chem. Phys.* **1990**, *92*, 65.
(40) Smith, J. D.; Saykally, R. J.; Geissler, P. L. *J. Am. Chem. Soc.* **2007**, *129*, 13847.
(41) Ohtomo, N.; Arakawa, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2755.
(42) Chizhik, V. *Mol. Phys.* **1997**, *90*, 653.
(43) Rull, F. *Pure Appl. Chem.* **2002**, *74*, 1859.
(44) Kropman, M. F.; Bakker, H. J. *J. Am. Chem. Soc.* **2004**, *126*, 9135.
(45) Cappa, C. D.; Smith, J. D.; Wilson, K. R.; Messer, B. M.; Gilles, M. K.; Cohen, R. C.; Saykally, R. J. *J. Phys. Chem. B* **2005**, *109*, 7046.
(46) Harsányi, I.; Pusztai, L. *J. Phys. Condens. Matter* **2007**, *19*, 335208.

THz FT study of a subset of six alkali halides in order to unravel their induced change on the water network. All of the investigated salts show a THz excess that is nearly linearly dependent on the salt concentration. The narrow-frequency THz excess is physically modeled by two damped simple harmonic oscillators with an apparent molal volume relative to water and fit to the data with only four physically meaningful parameters and an additional reduced mass fitting parameter. The model well predicts the behavior of the absorption of monovalent aqueous alkali halide solutions. In addition to the qualitative model, we have carried out MD simulations that show an ion-specific frequency dependence in the vibrational density of states that can be related to a rattling motion of the ions in the water network. Our results support earlier theories that absorption in the 70−100 cm^{-1} range is due to cationic oscillations in a potential well defined by the solvating waters. We find that the ions have negligible effect on the sub-picosecond dynamic behavior in the H-bond stretch frequency region of the water network, making a classification of any of the investigated ions as kosmotrope or chaotrope questionable. Yet this does not exclude any nondynamic rearrangement of the H-bond network in order to accommodate the ionic defects. The result is in full agreement with less general results of neutron scattering data.[24] We have provided a general molecular description of the influence on the sub-picosecond solvation dynamics that explains all our observed THz spectra in the frequency range of network motions. We propose that all results can be explained assuming no significant changes on the surrounding water network but an ion rattling motion that accounts for the observed increase in THz absorption. Although beyond the scope of the present paper, a detailed investigation of the concentration-dependent line shapes of the rattling modes will provide important information on the local anion and cation environments.

Finally, it is interesting to note that, in contrast to the more complex solutes we studied previously (e.g., sugars, proteins, model peptides), for alkali halides we find no indication of long-range dynamical changes in the water network. This raises the question, What are the limitations of the linear superposition model described here? Will it also hold for multivalent ions with higher charge density or multi-atom ions where solute−solvent THz intermolecular vibrational modes might be expected?

As has been shown above, THz spectroscopy provides a powerful tool to investigate solute-induced changes in the solvation dynamics. It allows us to separate different physical effects contributing to the absorption of aqueous solutions with alkali halides as a kind of absorption standard that shows no measurable effect on the hydrogen bond network of the solvation shells and/or bulk water.

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Supporting Information Available: Experimental details on p-Ge laser setup and Fourier transform measurements; computational details; computational radial distribution functions; linear superposition model for total absorption of salt absorption; detailed fitting routine; table of partial molar volumes of investigated compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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