Ion effects on the structure of water studied by terahertz time-domain spectroscopy

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Summary: We have investigated dielectric relaxation in aqueous ionic solutions by terahertz time-domain spectroscopy to elucidate the ionic hydration effect on the structure of water. Our finding suggests the dissolved ion induces the “structure breaking effect” which weakens the hydrogen bonding of water beyond the ion hydration shell.

Introduction: hydration in aqueous solutions has long been a subject of great interest to chemists and biologists. The dissolved ion significantly affects various macroscopic properties of water, such as viscosity and heat capacity, thereby determining the chemical and biological properties of ionic solutions.

It is well known that water molecules in first hydration shells are tightly bound to the ion and slowed down in their mobility as compared with those in pure water. On the other hand, outside the first hydration shell, the water molecules have been considered to show the “faster” motion, since the hydrogen bonding structure is disrupted by ions [1]. The verification of the existence of the long-range “structure breaking effect” of the ion is one of the long standing problems in solution chemistry, but it still remains unresolved.

To solve this problem, we focused on the “fast” dielectric relaxation in water which appears in the terahertz (THz) frequency [2]. The “fast” relaxation is attributed to that of the “free water molecules” which exist in liquid water and contribute little to the hydrogen bonding network [2]. When an ion dissolves in water, the “fast” relaxation would be modified, since the fraction and the dynamics of “free water molecules” in aqueous ionic solutions have to be changed from those in pure water by the long-range interaction. Since the modification in the “free water molecules” can affect the dielectric spectra in the THz region, the existence of a long-range ion effect would be revealed by THz spectroscopy. In this study, we investigated the ion effects on the “fast” dielectric relaxation by applying THz time-domain spectroscopy (THz-TDS) [3].

Methods: A 1 kHz pulse train centered at 800 nm with a pulse duration of 120 fs and a pulse energy of 800 μJ was provided from a Ti:sapphire regenerative amplifier, was split into two light pulses by a wedge plate. The transmitted major pulse was used for THz generation by optical rectification in a Mg-$LiNbO_3$ prism with pulse front control. A small portion of 800 nm light was used for probing the waveform of the generated THz pulse. The THz pulse was introduced into the solution sample cell. The transmitted THz pulse from the cell was detected by electro-optic (EO) sampling in a ZnTe crystal. The detectable frequency of the THz probe pulse ranged from 0.2 to 1.8 THz. To obtain the complex dielectric spectra of the sample solution, the THz waveforms transmitted from the reference (pure water) and sample solutions were measured in a series of measurements. The solution cell consists of two 1-mm-thick quartz windows separated by a 0.1-mm-thick plumbic spacer.

Results and Discussion: We measured the dielectric spectra of aqueous solutions of various 1:1 electrolytes and found the significant effects of dissolved cations. Figure 1 shows the imaginary part of the dielectric constant, $\varepsilon''(\nu)$, which reflects absorption of THz light by the sample solution. Especially in the high frequency region (Fig. 1. inset), the amplitude of the dielectric spectra of the aqueous solutions is significantly larger than that of pure water. This behavior cannot be explained by the hydration effects within the first hydration shell, because this effect reduces the absorption of THz light in aqueous ionic solution as compared with that in pure water as observed in the previous MW studies [4]. This characteristic behavior observed here should be related to the effect other than hydration.

To quantitatively investigate the ion effect on the “fast” relaxation that appears in the THz region, here, we expressed the observed dielectric spectra as the sum of the contributions from MW “slow” relaxation, $\varepsilon''_{\mathrm{MW}}(\nu)$; THz “fast” relaxation, $\varepsilon''_{\mathrm{THz}}(\nu)$; and intermolecular stretching vibration between water molecules, $\varepsilon''_{\mathrm{vib}}(\nu)$. The spectra of the “fast” relaxation, $\varepsilon''_{\mathrm{THz}}(\nu)$, was obtained by subtracting the “slow” relaxation component and the vibrational term from the observed spectra. The “slow” dielectric relaxation spectra, $\varepsilon''_{\mathrm{MW}}(\nu)$, were calculated from the spectroscopic parameters reported in the previous MW studies [4] and are shown in Fig. 1 as the solid curves. The vibrational term, $\varepsilon''_{\mathrm{vib}}(\nu)$, have been estimated from the previous study for pure water [2]. In the estimation, we corrected the amplitude of the vibration by the fraction of water molecules in each solution. The calculated vibrational term, $\varepsilon''_{\mathrm{vib}}(\nu)$, is shown as the dotted line in Fig. 1.

The resultant spectra of the "fast" dielectric relaxation, $\varepsilon''_{\mathrm{THz}}(\nu)$, for the aqueous solutions are shown in Fig. 2. In the same figure, we also show the $\varepsilon''_{\mathrm{THz}}(\nu)$ of pure water for comparison. Notable feature is that the spectra of the aqueous solutions shift to the higher frequency side from that of pure water. By nonlinear least squares fitting of the spectra with the single Debye model, the relaxation strength and time was obtained. We found that the relaxation time of all the aqueous solutions was smaller than that of pure water, which indicates that the reorientation of water molecules is enhanced by ions in the THz frequency region. This finding strongly suggests the presence of the "structure breaking effect" in which the number and the mobility of "free water molecules" are enhanced by the dissolved ion.

The "structure breaking effect" was further confirmed by the ion concentration dependence of the dielectric spectra. The "fast" relaxation component increased in amplitude as the ion concentration increased in all the aqueous solutions investigated here. From nonlinear least squares fitting of the spectra, we found the relaxation strength, which shows the population of "free water molecules," increased with increasing salt concentration. This is clear evidence of the ion-induced "structure breaking effect."

From above results, we have concluded that the ions in solution induces the structure breaking effects which weaken the hydrogen bonding network of water in addition to the hydration effect.

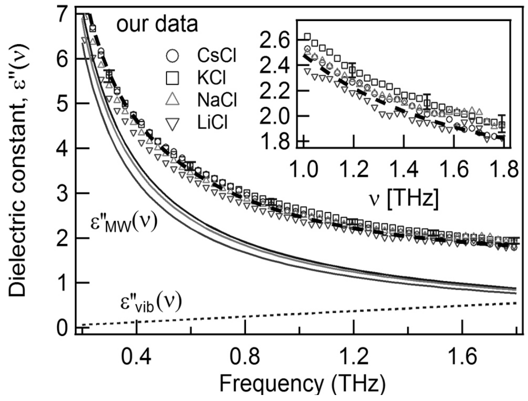

Figure 1: Imaginary part of dielectric spectra of pure water (thick dashed line) and 1 mol/L aqueous ionic solutions (dots). The inset is a magnification in vertical direction in 1.0-1.8 THz.

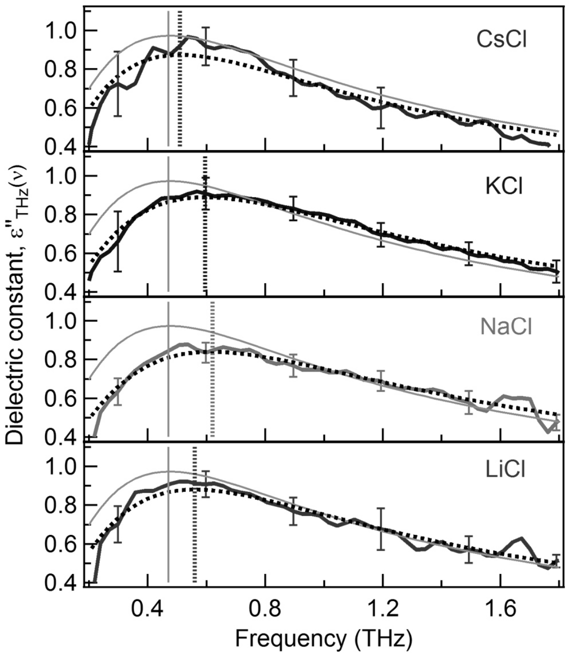

Figure 2: "Fast" dielectric relaxation spectra, $\varepsilon''_{\mathrm{THz}}(\nu)$, of pure water (thin solid line) and aqueous ionic solutions (thick solid lines). The thick dotted lines represent the fitting results to the observed spectra by the single Debye model.

References:

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