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# Negligible cation effect on the vibrational relaxation dynamics of water molecules in $NaClO_4$ and $LiClO_4$ aqueous electrolyte solutions

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In this study, the cation effects on the vibrational relaxation dynamics of water molecules in $NaClO_4$ and $LiClO_4$ aqueous solutions are investigated *via* polarization selective IR pump probe experiments. The distinct peak splitting of the OD stretch of HOD molecules in concentrated $NaClO_4$ and $LiClO_4$ aqueous solutions enables us to investigate the specific cation effects on the dynamics of water molecules that are hydrogen bonded to $ClO_4^-$. The reorientation of $ClO_4^-$-bound water molecules shows a bi-exponential decay and the slow component of the reorientation time constant is sensitive to the function used to describe the rotational anisotropy decay. We also show that the rotational dynamics of water molecules that are hydrogen bonded to anions is restricted and cannot decay to zero in the concentrated $NaClO_4$ and $LiClO_4$ aqueous solutions. Furthermore, the cation effects ($Li^+$, $Na^+$) on the vibrational relaxation dynamics of water molecules hydrogen bonded to $ClO_4^-$ are observed to be relatively negligible.

## 1. Introduction

Aqueous electrolyte solutions have been of interest in chemistry, biology, and atmospheric environment sciences and have been investigated for many years. Valuable information has been gained regarding the structure and dynamics of water molecules in aqueous electrolyte solutions.[1–7] It is generally accepted that anions have more pronounced effects than cations on the water structure and dynamics in aqueous solutions.[8,9] The effects of ions on the water structure usually follow the order of the Hofmeister series and are originally arranged according to their ability to salt out or salt in proteins.[10] The Hofmeister series has been utilized for more than 100 years, where ions are classified as "structure making" or "structure breaking" resulting from the effect on the structure of water molecules.[10–16] The concept of the Hofmeister series is mainly based on the macroscopic properties of aqueous solutions, such as viscosity, surface tension and entropy of solvation measurements. However, the terms "structure making" and "structure breaking" have been disputed for many years.[17] Also, the mechanism of specific ion effects on protein denaturation is still not well addressed at the molecular level and is lacking microscopic explanations. One of the central topics in the field of aqueous electrolyte solutions is to obtain the correlations between the ion hydration and the resulting molecular dynamics and structures which inevitably relies on the development of new spectroscopic techniques.

Ultrafast IR spectroscopy has been demonstrated as a useful method to unravel the ion hydrations in aqueous electrolyte solutions at the molecular level.[18–22] Bakker and co-workers firstly investigated the aqueous electrolyte solutions containing $ClO_4^-$ using ultrafast IR pump probe spectroscopy, and found that the presence of ions does not lead to an enhancement or breakdown of the hydrogen-bond network in bulk liquid water.[17,23] While the rotational dynamics of anion-bonded water molecules slowed down significantly. Fayer and co-workers also showed that water molecules interacting with ions can have much slower fluctuation dynamics.[24–27] More recently, the exchange dynamics between anion and water in the $NaClO_4$ and $NaBF_4$ aqueous solutions have been well studied using two dimensional infrared (2DIR) spectroscopy.[25,28,29] The exchange dynamics between water–water and water–anion hydrogen bonds occurs several times slower than the rate of hydrogen bond rearrangement dynamics in pure water. It also showed that water molecule shifts its donated hydrogen bonds between water and $ClO_4^-$ anions by a large and prompt angular rotation.[25,28,30–32]

However, in most of electrolyte aqueous solution studies probed with ultrafast IR spectroscopy, the pronounced anion and water interaction is extensively investigated. The cation effect on the hydrogen bond network and dynamics of water is usually less studied and there is still no consensus regarding the specific cation effect on the rotational dynamics of water. Bakker and co-worker originally reported that cations were not able to affect the rotational dynamics of water in the $NaClO_4$

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aqueous solution.[17,23] While in a subsequent report, they showed there is small but significant cation effect on the vibrational lifetime of water molecules in aqueous salt solutions.[33] Recent studies further showed that cations and anions affect each other's hydration shell dynamics in a subtle way[34–36] and the effect of ions and counterions on water can be strongly interdependent and nonadditive.[5]

In the concentrated electrolyte aqueous solutions (>3 mol $kg^{-1}$), the effects of ion and ion interactions, including cation/anion and anion/anion interactions, need to be considered to analyze the ion effects on the water dynamics. Previous MD simulations showed that certain amounts of ion pairing and clustering can be expected in the concentrated strong electrolyte aqueous solutions.[37,38] Recently, we developed the intermolecular mode specific vibrational energy transfer method and successfully applied this method to the electrolyte aqueous solution systems.[39,40] We found that ions form significant amount of clusters in KSCN aqueous solutions.[41–44] We further investigated the different behavior of rotational dynamics of water molecules and anions due to the structural inhomogeneity and discussed the anion and cation effects.[43,44]

To investigate the specific cation effect on the water dynamics in electrolyte aqueous solution, it is necessary to separate the contribution from dynamics of water in anionic hydration shell and water dynamics in the bulk liquid. The electrolyte aqueous solution containing $ClO_4^-$ provides a unique system because of the large frequency shift (~130 $cm^{-1}$) of anion bonded hydroxyl stretch. In this work, we investigated the specific cation effects on the vibrational relaxation dynamics of water molecules in $NaClO_4$ and $LiClO_4$ aqueous solutions using ultrafast IR pump probe spectroscopy. The cation effects are investigated in terms of the vibrational lifetime and reorientation of the OD-stretch in $NaClO_4$ and $LiClO_4$ aqueous solutions. We found there are slightly small cation effects on the vibrational relaxation dynamics of anion bonded water molecules in the systems studied even at concentration up to 5.5 mol $kg^{-1}$. We further showed that rotational dynamics of water molecules that hydrogen bonded to anions is restricted and cannot decay to zero in the concentrated aqueous solutions.

## 2. Experimental details

The experimental setup for the ultrafast IR spectroscopy has been described elsewhere.[39,41,44,45] Briefly, a ps amplifier and a fs amplifier are independently operated and synchronized with the same seed pulse from a Ti-sapphire oscillator. The ps amplifier pumps an OPA to produce ~1 ps Mid-IR pulses with a bandwidth ~18 $cm^{-1}$ at 1 kHz repetition rate. The fs amplifier pumps another OPA to produce ~140 fs Mid-IR pulses with a bandwidth ~200 $cm^{-1}$ at 1 kHz repetition rate. In the polarization selective IR pump probe experiments, the ps IR pulse is the pump beam. The fs IR pulse is the probe beam which is frequency resolved by a spectrograph. Two polarizers are added into the probe beam path to selectively measure the parallel or perpendicular polarized signal relative to the pump beam. Vibrational lifetimes are obtained from the rotation free signal $P_{\text{life}} = P_{\parallel} + 2 \times P_{\perp}$, where $P_{\parallel}$ and $P_{\perp}$ are parallel and perpendicular signal respectively. Rotational relaxation times are obtained from the waiting time dependent anisotropy $R = (P_{\parallel} - P_{\perp})/(P_{\parallel} + 2 \times P_{\perp})$.

All chemicals were purchased from Sigma-Aldrich Company. The isotopically mixed water solution of HOD in $H_2O$ was prepared by mixing 2 wt% $D_2O$ with $H_2O$. All concentrations are reported in moles of solute per kilogram of solvent. All the FTIR spectra were obtained with Nicolet IS10 spectrometer (Thermo Scientific) with 1 $cm^{-1}$ resolution. The samples were sandwiched in a home-made cell composed of two $CaF_2$ windows separated by a Teflon spacer. The thickness of the spacer was controlled at 50 μm and can be adjusted depending upon the optical densities. The experimental optical path and apparatus after the generation of mid-IR pulses was purged with $CO_2$ and $H_2O$ free clean air. All the measurements were carried out at room temperature (22 ± 1 °C), and the humidity in the room is controlled around 40%.

## 3. Results and discussion

### 3.1. Concentration-dependent FTIR spectra of the stretch of OD groups in $NaClO_4$ and $LiClO_4$ aqueous solutions

Fig. 1 A and B shows the FTIR spectra of $NaClO_4$ and $LiClO_4$ in the OD stretching region in HOD (2 wt% $D_2O$ in $H_2O$) solutions with different concentrations. Two distinct peaks can be clearly observed, especially at higher salt concentrations (>3 mol $kg^{-1}$). It is generally accepted that the two distinct peaks correspond to two types of hydrogen bond configurations in the aqueous ionic solutions containing the $ClO_4^-$ anions.[29] The OD stretch frequency positioned at around 2509 $cm^{-1}$ is assigned to the $OD_w$ groups hydrogen bonded to other water molecules in the solution. While the OD stretch in the higher frequency (~2630 $cm^{-1}$) is assigned to the $OD_a$ groups hydrogen bonded to the anions in the solution. The central frequencies of $OD_w$ stretch blue shift at higher ion concentration in both $NaClO_4$ and $LiClO_4$ solutions and the results are plotted in Fig. 2A. It is known that the blue shifts of $OD_w$ frequency at higher ion concentrations is an indication of disruption of hydrogen bond networks in the $MClO_4$ (M = Li, Na) solutions. Also the amplitudes of $OD_w$ frequency shifts are only dependent on the ion concentration, regardless of the nature of cations (Li, Na). The observed results here are consistent with our general understanding that the anions have more significant effects on the vibrational spectra of water molecules because of its direct binding to positively charged hydrogen atoms of water molecules and weaken the force constant of the OD stretch.[44,46,47] On the other hand, the interactions between cation and water do not directly interfere with the OD bonds due to its binding to the negatively charged electron pairs on the oxygen atoms of the water molecules.

As we mentioned earlier, the new peak in the higher frequency positioned at around 2630 $cm^{-1}$ is assigned to the $OD_a$ groups hydrogen bonded to the $ClO_4^-$ anions. The central frequencies of $OD_a$ stretch remain unchanged with the increase of salt concentration in both $NaClO_4$ and $LiClO_4$ aqueous solutions, shown in Fig. 1. However, the peak amplitude of $OD_a$

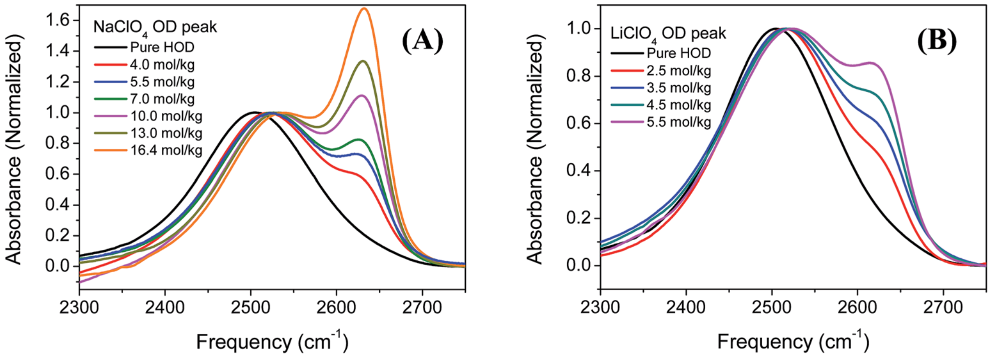

Fig. 1 FTIR spectra of (A) $NaClO_4$ and (B) $LiClO_4$ aqueous solutions (HOD, 2 wt% $D_2O$ in $H_2O$) in the OD stretch frequency region at different salt concentrations. FTIR spectrum of the OD stretch of HOD water is shown for comparison. All the spectra are normalized at the OD stretch frequency positioned at around 2509 $cm^{-1}$ which is assigned to OD groups hydrogen bonded to other water molecules. The $H_2O$ background has been subtracted in the spectra. The unit of concentration is molality mol $kg^{-1}$.

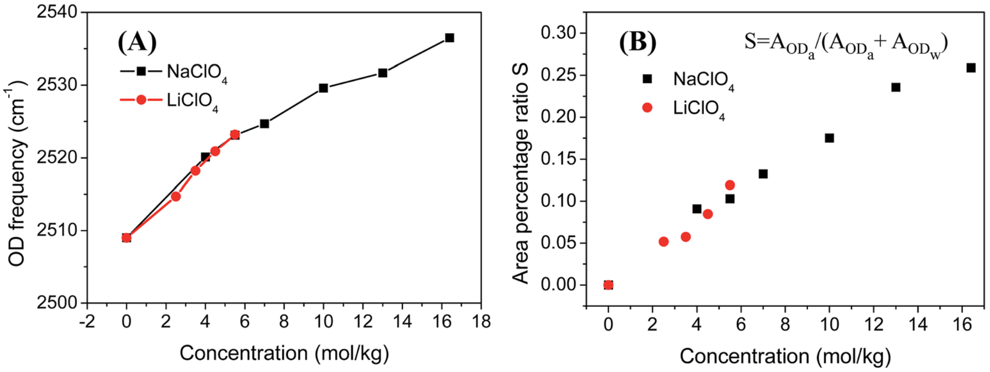

Fig. 2 (A) Central frequencies of $OD_w$ stretch in $NaClO_4$ and $LiClO_4$ aqueous solutions. (B) The percentage of $OD_a$ species (S) in the $NaClO_4$ and $LiClO_4$ aqueous (2 wt% $D_2O$ in $H_2O$) solutions of different concentrations. $S$ is defined as $S = A_{OD_a}/(A_{OD_a} + A_{OD_w})$ where $A_{OD_a}$ is the peak area of $OD_a$ stretch in $NaClO_4$ and $LiClO_4$ aqueous solutions and is obtained through the decomposition of FTIR spectra in Fig. 1 into two contributions fitted using two Gaussian peak functions.

stretch increase significantly as the salt concentrations increase. Here we define $S = A_{OD_a}/(A_{OD_a} + A_{OD_w})$ where $A_{OD_a}$ is the peak area of $OD_a$ stretch in $NaClO_4$ and $LiClO_4$ aqueous solutions and is obtained through the curve fitting using two Gaussian functions. The results were shown in Fig. 2B. We can clearly see that the ratio $S$ increases almost linearly as the salt concentrations increase and is independent on the nature of cations.

Similar phenomenon of peak splitting of OD stretch was also observed in the aqueous ionic solutions containing $BF_4^-$ and $PF_6^-$ and reported in previous literatures.[25,48,49] The distinct peak splitting of OD stretch shown in Fig. 1 enables us to investigate the specific ion effects on the structure and dynamics of water molecules in electrolyte aqueous solutions which will be presented in following sections. Bakker *et al.* investigated the ion effect on the orientational dynamics of the bulk water molecules ($OD_w$ stretch) in $NaClO_4$ aqueous solutions.[50] Here, we will mainly focus on the study of ion effects on the orientational dynamics of water molecules ($OD_a$ stretch) hydrogen boned to $ClO_4^-$ anion.

### 3.2. Cation ($Li^+$, $Na^+$) effects on the vibrational relaxation dynamics of water molecules

In the IR pump probe experiment, a narrow band (~15 $cm^{-1}$) IR pulse with high pump energy is used to excite the water molecules from the ground state ($\upsilon = 0$) to the first excited states ($\upsilon = 1$). Then the relaxation of the excited molecules is monitored by an independent and broadband probe pulse at different delay times. The two beams are generated from two independent OPAs and its frequency can be tuned independently which make it suitable for quantitative analysis of the vibrational relaxation dynamics data with weak signal.[39] Fig. 3 shows a typical pump probe measurement of $OD_a$ stretch ($\upsilon = 0$–1 transition) in 5.5 mol $kg^{-1}$ (4.3mol $L^{-1}$) $LiClO_4$ aqueous solution. The decay of the pump probe signal is because of the vibrational population relaxation and orientational relaxation. These two contributions can be separated through the polarization dependent measurement which is extensively adopted in the IR pump probe measurement. Here the heat effect from the vibrational relaxation is very small and further heat removal procedure is not needed for the vibrational population decay analysis.[40]

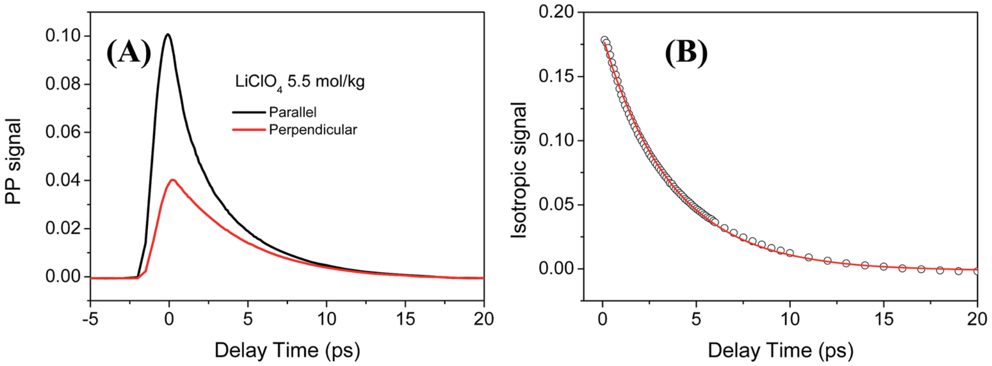

Fig. 3 (A) The raw pump probe data of $OD_a$ stretch ($\upsilon = 0$–1 transition) for 5.5 mol $kg^{-1}$ $LiClO_4$ aqueous solution under two different polarizations of polarized signal relative to the pump beam. The pump frequency and probe frequency were fixed at 2630 $cm^{-1}$. (B) The isotropic (rotation free) signal $P_{life}$ obtained from $P_{\parallel} + 2 \times P_{\perp}$ where the vibrational lifetime of OD stretch can be determined. The solid line is the fitting curve using a single exponential decay function.

For the 5.5 mol $kg^{-1}$ $LiClO_4$ aqueous solution, the isotropic signal was fitted using a single exponential decay function: $P_{life}(t) = A\exp(-t/T)$. The vibrational lifetime of $OD_a$ stretch from the $\upsilon = 0$–1 transition (2630 $cm^{-1}$) was determined to be $T = 3.7 \pm 0.1$ ps, shown in Fig. 3B. For comparison, we also performed the polarization selective IR pump probe measurement for the OD stretch of HOD in the neat water solution. The vibrational lifetime of OD stretch in neat water solution was determined to be $T = 1.7 \pm 0.1$ ps which agrees well with previous reports.[51,52] Previous studies showed that OD stretch interacting with anions usually have a longer lifetime than OD in pure water.[26,27,53–55] The slowing down of the vibrational relaxation of $OD_a$ stretch is explained by the weaker hydrogen bond interaction between water and anions which leads to a decrease of the anharmonic interaction between the OD stretch vibration and the hydrogen bond mode.[33]

The vibrational lifetime of $OD_a$ stretch in $NaClO_4$ aqueous solutions with concentration at 5.5 mol $kg^{-1}$ (4.3 mol $L^{-1}$) and 16.4 mol $kg^{-1}$ (8.6 mol $L^{-1}$) were also studied in order to observe the specific cation ($Li^+$ and $Na^+$) effects on the vibrational population dynamics of water molecules. The results were shown in Fig. 4. The vibrational lifetime of the $OD_a$ stretch in 5.5 mol $kg^{-1}$ $NaClO_4$ was determined to be $T = 3.8 \pm 0.1$ ps which is almost the same compared with the results obtained from 5.5 mol $kg^{-1}$ $LiClO_4$ solution considering the experimental uncertainty. In 16.4 mol $kg^{-1}$ $NaClO_4$ solution, the vibrational lifetime of $OD_a$ stretch was determined to be $T = 6.3 \pm 0.1$ ps. The results here indicated that the vibrational lifetime of $OD_a$ is mainly affected by the anions in the aqueous solution, while the cation effects ($Li^+$ and $Na^+$) are negligible on the vibrational population decay of water molecules for the system studied here. Previous literature showed that the vibrational lifetimes of water molecules in a series of alkali halides solutions were observed having a small but significant dependence on the nature of the cation.[33] However, due to the solubility of $KClO_4$ and $CsClO_4$ in water is less than 0.1 mol $kg^{-1}$, we cannot perform more systematic measurement of the cation effect on the vibrational population decay of water molecule in $ClO_4^-$ containing aqueous solutions.

### 3.3. Cation ($Li^+$, $Na^+$) effects on the rotational dynamics of water molecules

The orientational anisotropy of $OD_a$ in both $LiClO_4$ and $NaClO_4$ aqueous solutions were obtained and shown in Fig. 5. It is clear that the anisotropy curve does not decay all the way to zero. One of possible reason is that the vibrational lifetime of $OD_a$ stretch is too short to observe the anisotropy decay in a wider time delay window. We also measured the OD stretch rotational dynamics in isotopically mixed water which can be described by a single exponential decay with a time constant of $2.6 \pm 0.2$ ps. The result is consistent with previous reports,[44,52,56] and is also plotted in Fig. 5. Interestingly, the anisotropy decay of OD stretch in neat isotopically mixed water can decay to zero even the data quality is not good compared with that in $LiClO_4$ and $NaClO_4$ solutions. The main reason is that OD stretch has a relatively short vibrational lifetime of $1.7 \pm 0.1$ ps in neat isotopically mixed water.[52]

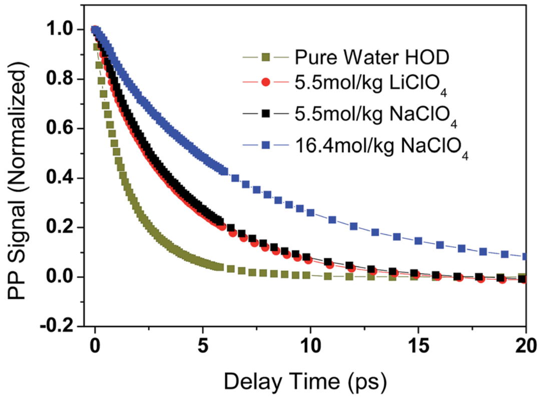

Fig. 4 The vibrational population decay of OD groups that hydrogen-bonded to $ClO_4^-$ ions in 5.5mol $kg^{-1}$ $LiClO_4$, 5.5 mol $kg^{-1}$ $NaClO_4$ and 16.4 mol $kg^{-1}$ $NaClO_4$ aqueous solutions with pump frequency at 2630 $cm^{-1}$. All curves can be fitted using a single exponential decay function. The vibrational population decay of the OD of HOD in isotopically mixed water measured at 2509 $cm^{-1}$ is also shown for comparison.

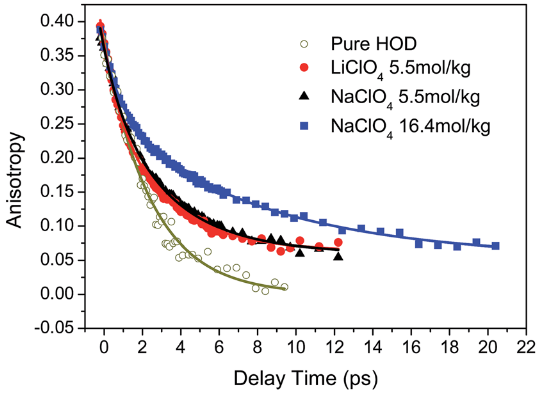

Fig. 5 The anisotropy decay data of OD stretch in pure water (2 wt% $D_2O$ in $H_2O$), 5.5 mol $kg^{-1}$ $LiClO_4$, 5.5 mol $kg^{-1}$ and 16.4 mol $kg^{-1}$ $NaClO_4$. The solid lines are the fitting results.

In 5.5 mol $kg^{-1}$ $LiClO_4$ and $NaClO_4$ aqueous solutions, it is clear that the orientational anisotropy of $OD_a$ decays slowly than that of water molecules in isotopically mixed water. However, the anisotropy decay can not be described by a single exponential decay. As we discussed in Section 3.1, the water molecules that interacting with anions or other water molecules should have different rotation times. A bi-exponential decay with general function expressed as $R(t) = b_0 + b_1\exp(-t/\tau_1) + b_2\exp(-t/\tau_2)$ can fit the data very well. Here, the anisotropy decay is described by a fast ($\tau_1$) and slow ($\tau_2$) components. The fast component ($\tau_1$) is believed to correlate with the wiggling motion of the OD while keeping its hydrogen bond to the anion intact.[34] The slow component is associated with the rotational diffusion of hydration shell water molecules on the anion surface. The constant term $b_0$ is also given in the expression. In previous reports, the constant term $b_0$ is fixed as zero or sometimes not mentioned in the data analysis, here we will discuss the constant term $b_0$ which can greatly affect the rotational time constants.

Firstly, if we do not fix the constant term $b_0$ to zero during the anisotropy decay fitting, the rotational time constant results are listed in Table 1. For 5.5 mol $kg^{-1}$ $LiClO_4$ solution, a bi-exponential decay give time constants of 0.9 ps (33%) and 3.2 ps (67%). At the same concentration of 5.5 mol $kg^{-1}$, a bi-exponential decay give time constants of 1.0 ps (28%) and 3.3 ps (72%) in the $NaClO_4$ solution. At higher ion concentration of 16.4 mol $kg^{-1}$, the rotational time constants are 1.0 ps (32%) and 7.9 ps (68%) in the $NaClO_4$ solution. The constant term $b_0$ is determined to be $0.06 \pm 0.01$ for these three studied solutions. The physical origin of nonzero $b_0$ is tentatively discussed and presented in the following section.

Secondly, if we set the constant term $b_0$ to zero during the curve fitting, the anisotropy decay curve in Fig. 5 can still be fit very well and the rotational time constants are listed in Table 1. For 5.5 mol $kg^{-1}$ $LiClO_4$ solution, a bi-exponential decay give time constants of 1.0 ps (46%) and 7.3 ps (54%). The fast component remains the same, while the slow component is determined to be $7.3 \pm 0.3$ ps which is two times slower than the value of $3.2 \pm 0.3$ ps assuming the constant term $b_0$ is not zero. For 5.5 mol $kg^{-1}$ $NaClO_4$ solution, a bi-exponential decay give time constants of 1.0 ps (38%) and 7.0 ps (62%). At the concentration of 16.4 mol $kg^{-1}$, a bi-exponential decay give time constants of 1.0 ps (35%) and 13.8 ps (65%).

### 3.4. Correlations between rotational dynamics and viscosity in electrolyte aqueous solution

In the concentrated solutions, *e.g.*, 5.5 mol $kg^{-1}$ of $NaClO_4$, where on average there is one cation or anion for every ten water molecules, there is certain amount of water molecules stay close to cation or anions in the confined environment. The anisotropy decay of water molecules in the confined environment should behave very different from the water molecules in bulk-like system and is not necessarily a single exponential. In our previous work, we showed that the rotational dynamics of the anions and water molecules behave in very different ways in concentrated MSCN (M = Li, Na, K, Cs) electrolyte aqueous solutions.[44] The rotational dynamic segregation between $SCN^-$ and water molecules is because of structural inhomogeneity in the solutions. Furthermore, the rotational time constants of anions scaled linearly with the change of solution viscosity. However, the water dynamics were only slightly affected by the solution viscosity and depend on nature of the cation. At 5 mol $kg^{-1}$, the OD rotational time constant (4.8 ps for a single exponential) in LiSCN solution is about 1.3 times that (3.7 ps) of the NaSCN solution. However, we showed there is relatively small cation effect on the rotational water dynamics in the $LiClO_4$ and $NaClO_4$ solutions.

Fig. 6 displays the concentration-dependent viscosity of $LiClO_4$ and $NaClO_4$ aqueous solutions. It is clear that with the concentration lower than 5.5 mol $kg^{-1}$, the viscosity is slightly

Table 1 Concentration dependent rotational time constants of $OD_a$ stretch in $LiClO_4$ and $NaClO_4$ aqueous solutions. The anisotropy decays were fit using a bi-exponential function: $R(t) = b_0 + b_1\exp(-t/\tau_1) + b_2\exp(-t/\tau_2)$ under two different conditions with $b_0 = 0$ and $b_0 \neq 0$. For pure water, the anisotropy decay of OD stretch was fit using a single exponential function: $R(t) = b_1\exp(-t/\tau_1)$

| | Solution | $b_0$ | $b_1$ | $\tau_1$ (ps) | | |
|---|---|---|---|---|---|---|
| | Pure water | 0 | $0.37 \pm 0.02$ | $2.6 \pm 0.2$ | $b_2$ | $\tau_2$ (ps) |
| Fitting case 1 | $LiClO_4$ (5.5 mol $kg^{-1}$) | $0.06 \pm 0.01$ | $0.11 \pm 0.02$ | $0.9 \pm 0.1$ | $0.22 \pm 0.02$ | $3.2 \pm 0.3$ |
| | $NaClO_4$ (5.5 mol $kg^{-1}$) | $0.06 \pm 0.01$ | $0.09 \pm 0.01$ | $1.0 \pm 0.1$ | $0.23 \pm 0.01$ | $3.3 \pm 0.3$ |
| | $NaClO_4$ (16.4 mol $kg^{-1}$) | $0.05 \pm 0.01$ | $0.10 \pm 0.01$ | $1.0 \pm 0.1$ | $0.21 \pm 0.01$ | $8.2 \pm 0.4$ |
| Fitting case 2 | $LiClO_4$ (5.5 mol $kg^{-1}$) | 0 | $0.18 \pm 0.01$ | $1.0 \pm 0.1$ | $0.21 \pm 0.01$ | $7.3 \pm 0.3$ |
| | $NaClO_4$ (5.5 mol $kg^{-1}$) | 0 | $0.15 \pm 0.01$ | $1.0 \pm 0.1$ | $0.24 \pm 0.01$ | $7.0 \pm 0.3$ |
| | $NaClO_4$ (16.4 mol $kg^{-1}$) | 0 | $0.13 \pm 0.01$ | $1.0 \pm 0.1$ | $0.24 \pm 0.01$ | $13.8 \pm 0.4$ |

changed with the increase of salt concentrations. At concentration of 5.5 mol $kg^{-1}$, the viscosity increases about 24% for $LiClO_4$ ($n_r = 1.24$) and 21% for $NaClO_4$ ($n_r = 1.21$) aqueous solutions. Based on our discussion in previous section, if we do not fix the constant term $b_0$ to zero during the anisotropy fitting, the rotational dynamics of water ($\tau_2 = 3.2$ ps) in 5.5 mol $kg^{-1}$ $LiClO_4$ slows about 23% which scales very well with the change of solution viscosity. For $NaClO_4$ at the concentration of 5.5 mol $kg^{-1}$, the rotational dynamics of water ($\tau_2 = 3.3$ ps) slows about 27% which also scales linearly with the change of solution viscosity within the experimental uncertainty. However, on the other hand, if we fix the constant term $b_0$ to zero for the rotational anisotropy fitting of 5.5 mol $kg^{-1}$ $LiClO_4$, the rotational dynamics of water ($\tau_2 = 7.3$ ps) slows almost 3-fold which is obviously not supported by the viscosity measurement.

The solubility of $LiClO_4$ in water can only go up to 5.6 mol $kg^{-1}$ (59.8 g per 100 g water at 25 °C), we cannot observe the water rotational dynamics at higher concentration in $LiClO_4$ solution. For $NaClO_4$, the saturated concentration is 17.1 mol $kg^{-1}$ (209.6 g per 100 g water at 25 °C). The viscosity of a 16.4 mol $kg^{-1}$ $NaClO_4$ solution is 4.5 times that of pure water, shown in Fig. 6. However, the $OD_a$ rotational time constant ($\tau_2 = 8.2$ ps) is only about 3.2 times that of the pure water. The reason that water rotational dynamics does not follow the viscosity change at higher concentration is mainly because of the dynamic segregation of anions and water molecules from our previous studies.[43,44] We surmise the ion clustering may also be formed in the $LiClO_4$ and $NaClO_4$ solutions. The nature of the dynamic segregation and the possible ion clustering in the $LiClO_4$ and $NaClO_4$ solutions warrants further investigation.

Our previous studies showed that cation can significantly affect the reorientational motions of water molecules in alkali thiocyanate aqueous solutions.[44] The water dynamics are slower in a solution with a smaller cation due to the larger charge density ($Li^+ > Na^+$). However, we observed there is negligible cation effect on the water dynamics in the $LiClO_4$ and $NaClO_4$ aqueous solutions. Since the $OD_a$ groups that hydrogen bonded to $ClO_4^-$ anions and $OD_w$ groups that hydrogen bonded to other water molecules have large frequency shift, which is different from the case in alkali thiocyanate solution system where the OD groups hydrogen bonded to $SCN^-$ and other water molecules are overlapped. Both Bakker and Gaffney investigated the rotational dynamics of water molecules hydrogen boned to $ClO_4^-$ anions at the concentration of 6 M (about 9 mol $kg^{-1}$ in molality) $NaClO_4$ solution.[29,34,50] They observed the slow rotational anisotropy of $OD_a$ decay with a time constant of 7.3 ± 0.6 ps. In their experiments, they used a broad band excitation pulse (FWHM ~120 $cm^{-1}$) in the IR pump probe setup.[34] Both the water molecules hydrogen bonded to anions and to other water molecules can be excited at the same time which make the rotational water dynamics complicated. Here we use a narrowband IR pulse (FWHM ~18 $cm^{-1}$) which can selectively excite the $OD_a$ stretch and observe its rotational dynamics. Thus the cation effects ($Li^+$, $Na^+$) on the vibrational relaxation dynamics of water molecules in the hydration shell of $ClO_4^-$ in $NaClO_4$ and $LiClO_4$ aqueous solutions can be clearly observed.

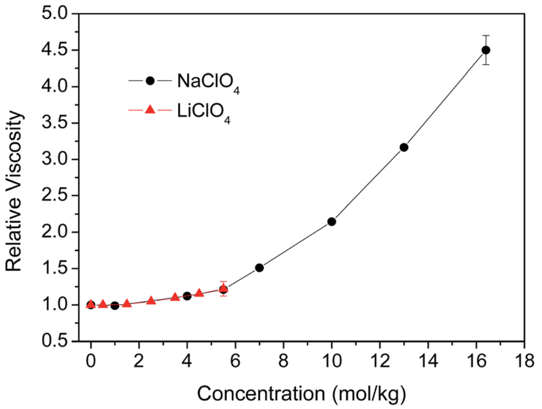

Fig. 6 The concentration dependent relative viscosity in $LiClO_4$ and $NaClO_4$ aqueous solutions.

From the viscosity measurement, we think it is more appropriate to use the general expression $R(t) = b_0 + b_1 \exp(-t/\tau_1) + b_2 \exp(-t/\tau_2)$ to describe the rotational dynamics of water molecules in the $NaClO_4$ and $LiClO_4$ aqueous solutions. The physical meaning of nonzero $b_0$ may indicate that rotational dynamics of water molecules that hydrogen bonded to anions is restricted and cannot decay to zero in the concentrated electrolyte aqueous solution. This phenomenon is similar to interfacial water dynamics measured in the confined water pool inside reverse micelle systems which were reported by Fayer and co-worker.[21,53,54,56–59] However, the exact reason for the restricted rotational dynamics of water molecules hydrogen bonded to anions observed here is not clear yet and is subject to future experimental and theoretical studies.

## 4. Conclusion

In this report, we investigated the specific cation effects on the vibrational relaxation dynamics of water molecules in the hydration shell of $ClO_4^-$ in $NaClO_4$ and $LiClO_4$ aqueous solutions using polarization selective IR pump probe experiment. The distinct peak splitting of OD stretch of HOD molecules in concentrated $NaClO_4$ and $LiClO_4$ in isotopically diluted water (2% $D_2O$ in $H_2O$) enables us to investigate the specific cation effects on the dynamics of water molecules that hydrogen bonded to $ClO_4^-$ in aqueous electrolyte solutions. The reorientation of the perchlorate-bound water molecules show a bi-exponential decay and the slow component reorientation time constant is sensitive to function used to fit the rotational anisotropy decay. We showed that rotational dynamics of water molecules that hydrogen bonded to anions is restricted and cannot decay to zero in the concentrated solution. The cation effects ($Li^+$, $Na^+$) on the vibrational relaxation dynamics of water molecules hydrogen bonded to $ClO_4^-$ are relatively negligible even at concentration where the molar ratio between cation and water is 1 : 10. Due to the solubility of $LiClO_4$ can only go up to 5.6 mol $kg^{-1}$ in water solution, other ionic aqueous solution systems containing $BF_4^-$ and $PF_6^-$ will be investigated in the future.

## Conflicts of interest

There are no conflicts to declare.

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