

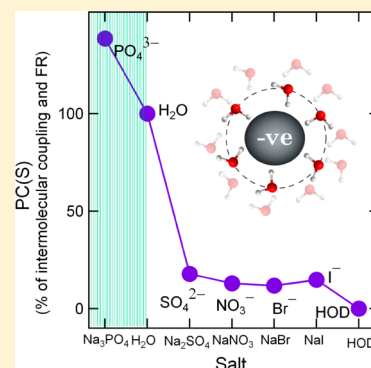
# How Ions Affect the Structure of Water: A Combined Raman Spectroscopy and Multivariate Curve Resolution Study

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## S Supporting Information

**ABSTRACT:** Raman spectroscopy in combination with multivariate curve resolution (Raman-MCR) is used to explore the interaction between water and various kosmotropic and chaotropic anions. Raman-MCR of aqueous Na-salt ( $\text{NaI}$ ,  $\text{NaBr}$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{Na}_3\text{PO}_4$ ) solutions provides solute-correlated Raman spectra (SC-spectra) of water. The SC-spectra predominantly bear the vibrational characteristics of water in the hydration shell of anions, because  $\text{Na}^+$ -cation has negligible effect on the OH stretch band of water. The SC-spectra for the chaotropic  $\text{I}^-$ ,  $\text{Br}^-$ , and  $\text{NO}_3^-$  anions and even for the kosmotropic  $\text{SO}_4^{2-}$  anion resemble the Raman spectrum of isotopically diluted water ( $\text{H}_2\text{O}/\text{D}_2\text{O} = 1/19$ ; v/v) whose OH stretch band is largely comprised by the response of vibrationally decoupled OH oscillators. On the other hand, the SC-spectrum for the kosmotropic  $\text{PO}_4^{3-}$  anion is quite similar to the Raman spectrum of  $\text{H}_2\text{O}$  (bulk). Comparison of the peak positions of SC-spectra and the Raman spectrum of isotopically diluted water suggests that the hydrogen bond strength of water in the hydration shell of  $\text{SO}_4^{2-}$  is comparable to that of the isotopically diluted water, but that in the hydration shell of  $\text{I}^-$ ,  $\text{Br}^-$ , and  $\text{NO}_3^-$  anions is weaker than that of the latter. Analysis of integrated area of component bands of the SC-spectra reveals  $\sim 80\%$  reduction of the delocalization of vibrational modes (intermolecular coupling and Fermi resonance) of water in the hydration shell of  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  anions. In the case of trivalent  $\text{PO}_4^{3-}$ , the vibrational delocalization is presumably reduced and the corresponding decrease in spectral response at  $\sim 3250\text{ cm}^{-1}$  is compensated by the increased signal of strongly hydrogen bonded (but decoupled) water species in the hydration shell. The peak area-averaged wavenumber of the SC-spectrum increases as  $\text{PO}_4^{3-} < \text{SO}_4^{2-} < \text{NO}_3^- < \text{Br}^- < \text{I}^-$  and indeed suggests strong hydrogen bonding of water in the hydration shell of  $\text{PO}_4^{3-}$  anion.



## INTRODUCTION

Water is a ubiquitous solvent for innumerable chemical reactions occurring in living and nonliving systems. Water, being a dipolar molecule with hydrogen bond donating and accepting abilities, can participate in specific and nonspecific interactions with charged/dipolar solutes. These strong interactions make charged/dipolar solutes miscible with water. On the contrary, nonpolar solutes, because of the lack of strong interactions, self-aggregate in water. The interplay and delicate balance between various interactions (e.g., water–water, water–solute, and solute–solute) govern the solubility/miscibility and aggregation behavior of solutes/macromolecules.<sup>1–5</sup> Ion-induced change in solubility of proteins (Hofmeister effect) is a classic example of such delicate balance of those interactions.<sup>6–8</sup> When different anions are arranged in order of their ability to precipitate certain proteins, the following series (Hofmeister series) is obtained:  $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{HPO}_4^{2-} > \text{CH}_3\text{COO}^- > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^- > \text{ClO}_4^- > \text{SCN}^-$ .<sup>9</sup> Here, the anions on the left-hand side of  $\text{Cl}^-$  favor the folded state of protein (precipitation/salting-out) and those on the right side promote the unfolded state (denaturation/salting-in). Initially, it was believed that the ions on the left side of the series bind more strongly with water than water binds itself in bulk solution (kosmotrope or structure

maker)<sup>2,10–14</sup> and makes water less aggressive to a protein (solute), thus helping the protein to retain its native/folded structure (stabilization). On the other hand, ions on the right side of the series interact less strongly with water (weaker than water binds itself in bulk) and are known as chaotropes or structure breakers, which make water more aggressive to a solute (protein) and promotes denaturation (destabilization). In agreement with this view, it has been found that the so-called kosmotropic anions increase the viscosity of water (positive Jones–Dole viscosity coefficient,  $B$ ) whereas the chaotropic anions decrease the same (negative  $B$  coefficient).<sup>2,4</sup> When some of the anions are arranged on the basis of their  $B$ -coefficient values, the following series is obtained:  $\text{PO}_4^{3-}$  ( $B = 0.495$ )  $> \text{CO}_3^{2-}$  (0.294)  $> \text{CH}_3\text{COO}^-$  (0.25)  $> \text{SO}_4^{2-}$  (0.206)  $> \text{F}^-$  (0.107)  $> \text{Cl}^-$  (−0.005)  $> \text{Br}^-$  (−0.033)  $> \text{NO}_3^-$  (−0.043)  $> \text{I}^-$  (−0.073), which is in conformity with their order in the Hofmeister series. Because of this conformity, it was believed that the Hofmeister effect and the change in viscosity of water have a common origin, which is the modification of the H-bond network in liquid water in the

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presence of anions. However, the change of viscosity in the presence of certain ions does not necessarily mean that these ions affect the hydrogen bond (H-bond) network of bulk water at long-range like that of temperature.<sup>1,15</sup> Recent studies,<sup>16,17</sup> in fact, suggested that the ions perturb water in their hydration shells and do not have a long-range effect. In other words, the physicochemical properties of water in the hydration shells are important. Extensive experimental<sup>18–29</sup> and theoretical<sup>30–33</sup> efforts have been devoted to understand the properties of water in the hydration shell of ions/solutes.

Raman spectroscopy in combination with multivariate curve resolution (Raman-MCR) is a promising technique to unravel the properties of water in the hydration shell of ions/solutes.<sup>34–37</sup> Unlike conventional difference spectroscopy,<sup>10,38,39</sup> factor analysis,<sup>40</sup> and peak fitting (with presumed fitting functions),<sup>11,41</sup> MCR does not have any assumption about the amplitude, position, and width of spectral bands (except the absence of negative concentration and intensity<sup>34</sup>). Recent Raman-MCR studies of aqueous alkali halide<sup>21</sup> and amphiphilic molecules<sup>36,37,42–44</sup> revealed the structural transformations (e.g., modification of H-bonding, coupling between vibrational modes, dangling, and tetrahedral structures) of water in the hydration shells. Such kinds of structural modifications are likely to affect the properties of water either as a solvent or as an active reaction component/catalyst.<sup>45–47</sup>

The OH stretch band of water, which typically has three component bands (centered at 3250, 3450, and 3600  $\text{cm}^{-1}$ , respectively) essentially reflects the combined response of intermolecular coupling, Fermi resonance (FR), and the H-bond interaction of water. For instance, strongly (weakly) H-bonded water has weaker (stronger) O–H bonds and its OH stretch vibration appears in the low (high) frequency region of the OH stretch band. Similarly, intermolecular coupling, which promotes delocalization of the vibrational mode among several water molecules (collective vibration), decreases the energy of the OH stretch vibration and results in relative higher intensity in the red region of the OH stretch band ( $\sim 3250 \text{ cm}^{-1}$ ) in Raman/IR measurements.<sup>48–51</sup> Finally, FR, i.e., the coupling between the OH stretch fundamental ( $\sim 3400 \text{ cm}^{-1}$ ) and HOH bend overtone ( $2 \times 1645 = 3290 \text{ cm}^{-1}$ ) further deforms the OH stretch band by increased response at  $\sim 3250 \text{ cm}^{-1}$ .<sup>52–54</sup> As a result, in liquid water, it is not straightforward to correlate the spectral changes in the OH stretch regions with either the H-bond strength and/or the coupling effects (intermolecular coupling and FR). Upon isotopic dilution (e.g.,  $\text{H}_2\text{O}/\text{D}_2\text{O} = 1/19$  (v/v); abbreviated as HOD or isotopically diluted water), because of the off-resonance of the OH stretch mode with other modes in diluted water, intermolecular coupling and FR are significantly reduced (H-bond strength does not change upon isotopic dilution). So, the response of HOD in the OH stretch region mainly bears the signature of H-bond strength of water and makes the interpretation of the OH stretch band simple.

We compared the SC-spectra of  $\text{H}_2\text{O}$  that are obtained by Raman-MCR analysis of aqueous electrolyte solutions with the Raman spectrum of HOD to unravel the H-bond strength and intermolecular coupling (collective vibration) of  $\text{H}_2\text{O}$  in the hydration shell of kosmotropic and chaotropic anions. The SC-spectra for a series of Na-salts (NaI, NaBr,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{Na}_3\text{PO}_4$ ) revealed that the H-bond strength of water in the hydration shell of  $\text{SO}_4^{2-}$  is comparable to that of isolated OH mode in liquid water (HOD) whereas that in the hydration shell of  $\text{NO}_3^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  anions are weaker than that of HOD.

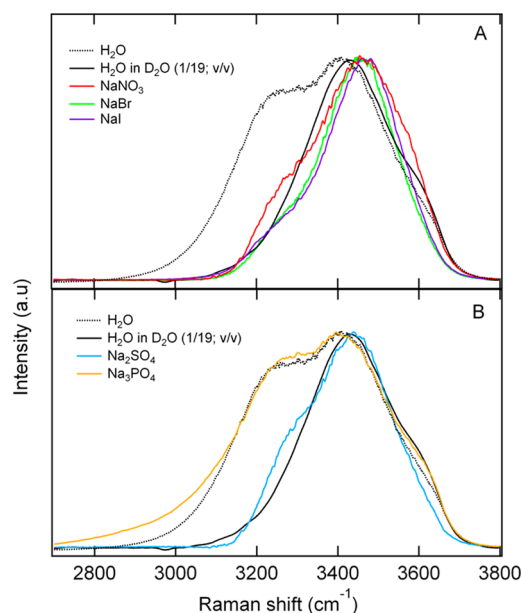
Quantitative analysis of the area-normalized SC-spectra reveals that there is  $\sim 80\%$  reduction of intermolecular coupling and FR in the hydration shell of all the anions studied, except for  $\text{PO}_4^{3-}$ . Presumably, the water molecules are decoupled in the hydration shell of  $\text{PO}_4^{3-}$ , too, and the decrease in vibrational response due to decoupling (at  $\sim 3250 \text{ cm}^{-1}$ ) is compensated by the increase in response of strongly H-bonded decoupled water in the hydration shell of the  $\text{PO}_4^{3-}$  anion.

## EXPERIMENTAL SECTION

Heavy water ( $\text{D}_2\text{O}$ ,  $>99.9$  atom % D) and the Na-salts ( $\geq 99.0\%$ ; NaI, NaBr,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SO}_4$ , and  $\text{Na}_3\text{PO}_4$ ) were purchased from Sigma Aldrich. Milli-Q water ( $18.2 \text{ M}\Omega \text{ cm}$  resistivity) was used for all the measurements. The spontaneous Raman spectra of the samples were recorded using a STR-300 micro-Raman spectrometer (SEKI Technotron, Japan). The sample solution ( $\sim 0.5 \text{ mL}$ , maximum concentration  $1.2 \text{ mol dm}^{-3}$ ) was taken in a quartz cell of  $2 \text{ mm}$  optical path length and excited at  $532 \text{ nm}$  (power  $\sim 20 \text{ mW}$  at the sample spot, DPSS) using a  $10\times$  objective lens (Olympus). The scattered light was collected through a fiber-coupled  $300 \text{ mm}$  spectrograph (Acton series SP 2300i,  $1200 \text{ gr/mm}$ ) and detected by a therm-electric cooled ( $-75^\circ\text{C}$ ) charge-coupled device (CCD). The acquisition time was  $200 \text{ s}$  or more for a single spectral measurement. To avoid the uncertainty in sample volume probed in successive measurements, we used a Z-stage of  $0.1 \mu\text{m}$  resolution as the sample stage and focused the laser beam with a long focal length objective lens ( $10\times$ ). To obtain reproducible results, the spectra were acquired at the same experimental conditions. A constant background that leads to almost zero signal in the off-resonant spectral region ( $\sim 4000 \text{ cm}^{-1}$  in the present study) was subtracted from the experimental spectra. The baseline-subtracted spectra were put into the columns of a matrix (the first column is the neat water (no salt) spectrum) which was used for multivariate analysis using Igor Pro 6.22A software. The details of the multivariate analysis have been described elsewhere.<sup>34,55–58</sup> One of the component spectra obtained after multivariate analysis corresponds to the SC-spectrum, which in the case of Na-salts predominantly bears the vibrational characteristics of water in the hydration shell of anions.<sup>21</sup> To compare the SC-spectra with the Raman spectrum of isotopically diluted water, which is free from intra/intermolecular coupling and FR, we used a largely diluted  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixture ( $\text{H}_2\text{O}/\text{D}_2\text{O} = 1/19$  (v/v) i.e.,  $\text{H}_2\text{O}/\text{HOD}/\text{D}_2\text{O} = 0.25/90.25/9.5$ ). The  $\text{H}_2\text{O}-\text{D}_2\text{O}$  mixture is described as diluted water (HOD) and the neat water as undiluted water ( $\text{H}_2\text{O}$ ), in this paper.

## RESULTS

**Solute-Related Raman Spectra of Water.** Figure 1 shows the SC-Raman spectra of  $\text{H}_2\text{O}$  in the presence of various Na-salts. The experimentally recorded Raman spectra (raw spectra) of a few aqueous electrolyte solutions are shown in Figure S1 of the Supporting Information (SI). The SC-Raman spectra provide the vibrational characteristics of water in the hydration shell of solutes/ions.<sup>37</sup> Thus, the SC-spectrum of each of the Na-salts (Figure 1) contains the combined spectral response of water in the hydration shell of  $\text{Na}^+$ -cation and the corresponding anion. It has been observed that the OH stretch band of water is more affected by anions (halide ions) than by  $\text{Na}^+$  cation.<sup>4,59</sup> Moreover, the SC-spectra of different alkali chloride salts (NaCl, KCl, and LiCl) are very similar to each



**Figure 1.** SC-Raman spectra of water in the OH stretch regions for various (A) chaotropic and (B) kosmotropic anions as mentioned in the graph panel. Raman spectra of HOD ( $\text{H}_2\text{O}/\text{D}_2\text{O} = 1/19$ ; v/v) and  $\text{H}_2\text{O}$  are shown for comparison.

other,<sup>21</sup> which means that  $\text{Na}^+$  (or even  $\text{Li}^+$ ) cation has a negligible effect on the OH stretch band of water compared to that of the  $\text{Cl}^-$  anion. In other words, the SC-spectra of various Na-salts represent the vibrational response of water in the hydration shell of the respective anions. The Raman spectra of  $\text{H}_2\text{O}$  and HOD (diluted water) are also shown for comparison with the SC-spectra. The spectrum of  $\text{H}_2\text{O}$  shows three typical bands centered at  $\sim 3250$ ,  $3450$ , and  $3600\text{ cm}^{-1}$ , respectively. Because the water molecules in liquid bulk phase are in dynamic equilibrium of making and breaking of hydrogen bonds with neighboring water molecules,<sup>60</sup> the bulk water, at any instant, can be thought of as a mixture of three types of water species of varying H-bond strength, whose center frequency appears at  $\sim 3250$ ,  $3450$ , and  $3600\text{ cm}^{-1}$ , respectively. Of course, vibrational delocalization due to intermolecular coupling and FR also affect the response, especially in the red region of the OH stretch band (discussed in the third paragraph of Introduction).

Upon isotopic dilution, the relative intensity below  $3400\text{ cm}^{-1}$  is largely reduced and that above  $3400\text{ cm}^{-1}$  does not change significantly. As can be seen from Figure 1A, the SC-spectra of the chaotropic anions ( $\text{NO}_3^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ) look like the Raman spectrum of HOD (isolated OH oscillator). Similar SC-spectra have been reported for the halide ions (except  $\text{F}^-$ ) by previous Raman-MCR measurement.<sup>21</sup> These results suggest that the  $\text{H}_2\text{O}$  molecules in the hydration shell of chaotropic anions behave more like HOD than  $\text{H}_2\text{O}$ . Nevertheless, the maximum of the SC-spectra are blue-shifted compared to that of HOD. The blue-shift indicates that water forms weaker H-bond in the hydration shell of the chaotropic anions than that in bulk.

Unlike the chaotropic anions, the SC-spectrum of kosmotropic  $\text{PO}_4^{3-}$  anion shows significant intensity at  $\sim 3250\text{ cm}^{-1}$ , and the relative intensity below  $3100\text{ cm}^{-1}$  is higher than that of bulk  $\text{H}_2\text{O}$ . These features suggest that the water in the hydration shell of  $\text{PO}_4^{3-}$  is strongly H-bonded. We note that the SC-spectrum for  $\text{PO}_4^{3-}$  ion is marginally broader than the

Raman spectrum of  $\text{H}_2\text{O}$ . In this situation, the SC-spectrum may be affected by rotational ambiguity, and the MCR analysis, instead of the true SC-spectrum, may provide the minimum area SC-spectrum.<sup>34</sup> The rotational ambiguity in the MCR analysis may be viewed as an uncertainty in drawing the boundary between the hydration shell and bulk water, and the MCR analysis in this case overemphasizes the regions of the true SC-spectrum that differ from the solvent spectrum (minimum area SC-spectrum). As a result, the minimum area SC-spectrum typically shows zero signals at one point in the spectral window of the pure solvent. Under such circumstances, the true SC-spectrum is a combination of the minimum area SC-spectrum and a contribution of the bulk solvent spectrum. However, in the present case, the SC-spectrum for the  $\text{PO}_4^{3-}$  anion does not have a vanishingly small signal at any point within  $2900\text{--}3700\text{ cm}^{-1}$  (OH stretch band of  $\text{H}_2\text{O}$ ), which suggests that the SC-spectrum for  $\text{PO}_4^{3-}$  is not significantly affected by rotational ambiguity.

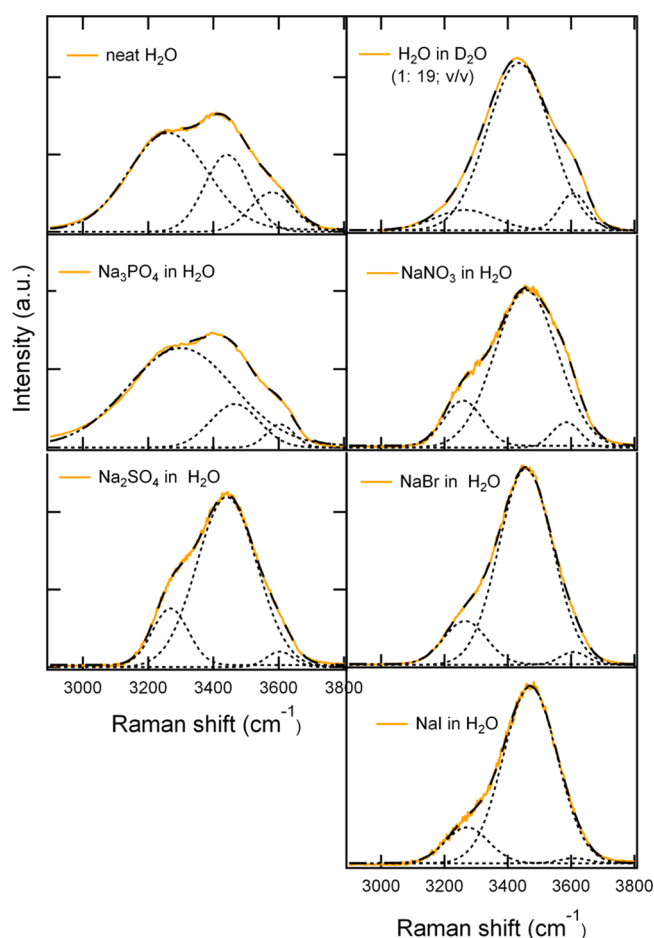
In contrast to  $\text{PO}_4^{3-}$ , the SC-spectrum for  $\text{SO}_4^{2-}$ , which is also a strong kosmotropic anion (positioned in extreme left side of Hofmeister series), shows significantly reduced intensity at  $\sim 3250\text{ cm}^{-1}$  regions. In other words, the SC-spectrum of  $\text{SO}_4^{2-}$  ion resembles that of the Raman spectrum of HOD or the SC-spectra of the structure-breaking  $\text{NO}_3^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  anions (Figure 1A and 1B). The maximum of the SC-spectrum for  $\text{SO}_4^{2-}$  is very close to the peak position of the Raman spectrum of HOD. These results indicate that the H-bond strength of  $\text{H}_2\text{O}$  in the hydration shell of  $\text{SO}_4^{2-}$  is comparable to that of bulk HOD, which is in sharp contrast to the belief that water forms a stronger H-bond (than bulk HOD) with  $\text{SO}_4^{2-}$  anion.<sup>39,61</sup> To obtain more meaningful and quantitative information about the H-bond strength and intermolecular coupling of water in the hydration shell of various kosmotropic and chaotropic anions, we fitted the Raman/SC-spectra with multiple Gaussian bands as described in the following section.

**Component Analysis of the SC-Spectra.** Figure 2 shows three-component Gaussian fits of the area-normalized Raman spectra of  $\text{H}_2\text{O}$  and HOD, and the SC-spectra of the salt solutions (a minimum of three components are required to fit the experimental spectra<sup>62</sup>). The fitted spectra (dashed line) as well as the component bands (dotted line) are shown in Figure 2. The fitting parameters and the relative integrated area of the component bands are summarized in Table 1.

From the relative integrated areas in Table 1, it is obvious that upon isotopic dilution, the relative contribution of the  $3250\text{ cm}^{-1}$  band (component-1) decreases and that of the  $3450\text{ cm}^{-1}$  band (component-2) increases. A similar trend has been observed in the SC-spectra of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions. However, in the presence of  $\text{PO}_4^{3-}$ , the relative contribution of component-1 increases from that of bulk  $\text{H}_2\text{O}$ . The contribution of component-3, which is a minor component even in bulk  $\text{H}_2\text{O}$ , does not change significantly with the addition of  $\text{D}_2\text{O}$  or Na-salts in  $\text{H}_2\text{O}$ .

The integrated intensities of the three bands (centered at  $\sim 3250$ ,  $3450$ , and  $3600\text{ cm}^{-1}$ ) are plotted against the Na-salts in Figure 3. It is observed that the relative populations of the three components do not change significantly in the presence of  $\text{PO}_4^{3-}$ . However, in the case of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  anions, the relative contribution of component-1 is significantly lower, and that of component-2 is higher than that in  $\text{H}_2\text{O}$ . In the presence of  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  ions, the spectral width (fwhm) of component-2 and component-3 does not





**Figure 2.** Multiple Gaussian peak fits of the Raman spectra of H<sub>2</sub>O, HOD (H<sub>2</sub>O/D<sub>2</sub>O = 1/19; v/v), and the SC-spectra of salt solutions. The fitted spectra and component bands are shown by black dashed and dotted lines.

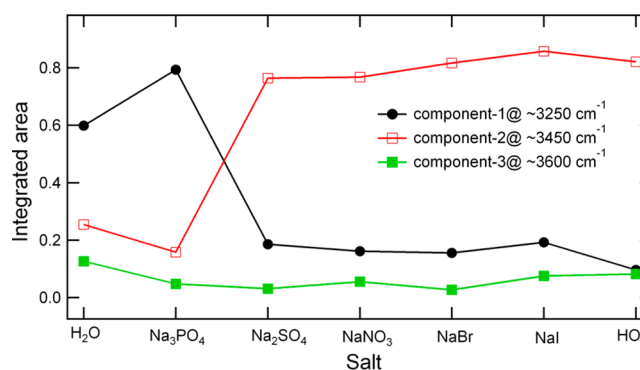
change much, but that of component-1 is much lower than that of H<sub>2</sub>O (Figure S2 in SI).

## DISCUSSION

The results presented above provide important insights into the H-bond strength and collective vibrations (intermolecular coupling) of water in the hydration shell of different kinds of anions. With the addition of D<sub>2</sub>O in H<sub>2</sub>O, the H-bond strength of water does not change but the intermolecular coupling and FR decreases (contribution of intramolecular coupling is relatively weak,<sup>52</sup> and at high pressure FR may reappear in diluted water<sup>63</sup>), which is revealed by reduced relative intensity around 3250 cm<sup>-1</sup> regions in the Raman spectrum of HOD. Qualitatively, the band shapes of the SC-spectra (for SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>) are different from the Raman spectrum of bulk H<sub>2</sub>O but similar to that of bulk HOD (Figure 1A). This suggests that, like in HOD, the OH stretch mode of H<sub>2</sub>O is not coupled in the hydration shell of these anions. As shown by component analysis in Figure 2, the center frequency of the major component (component-2) in the SC-spectra of chaotropic anions shifts toward higher frequency, which reveals weaker H-bonding (stronger O–H bond) of H<sub>2</sub>O in the hydration shell of those anions compared to that in bulk HOD. Weaker H-bonding increases the energy of symmetric OH stretch vibration and decreases that of the HOH bend mode<sup>64,65</sup> of H<sub>2</sub>O. Consequently, the energy difference

**Table 1.** Fitting Parameters: Center Wavenumber ( $\nu_c$ ), fwhm ( $\Gamma$ ), and Relative Integrated Area of Different Component Bands

Raman/SC-spectra	$\nu_c$ , cm <sup>-1</sup>	$\Gamma$ , cm <sup>-1</sup>	relative integrated area
H <sub>2</sub> O	3261	283	0.599
	3441	160	0.254
	3579	156.5	0.1266
HOD (H <sub>2</sub> O/D <sub>2</sub> O = 1/19; v/v)	3264	221.5	0.096
	3435	233	0.821
	3608	106	0.082
Na <sub>3</sub> PO <sub>4</sub>	3300	379.3	0.793
	3465	176.5	0.158
	3605	100	0.0478
Na <sub>2</sub> SO <sub>4</sub>	3268	128	0.1858
	3441	216.5	0.764
	3603	98	0.0310
NaNO <sub>3</sub>	3260	140	0.1617
	3458	233	0.7678
	3585	105	0.055
NaBr	3265	158	0.1554
	3457	200	0.8171
	3608	116.5	0.0268
NaI	3271	161.5	0.171
	3471	200	0.762
	3610	111.5	0.067



**Figure 3.** Variation of integrated area of the component bands in the Raman/SC-spectra in the OH stretch regions.

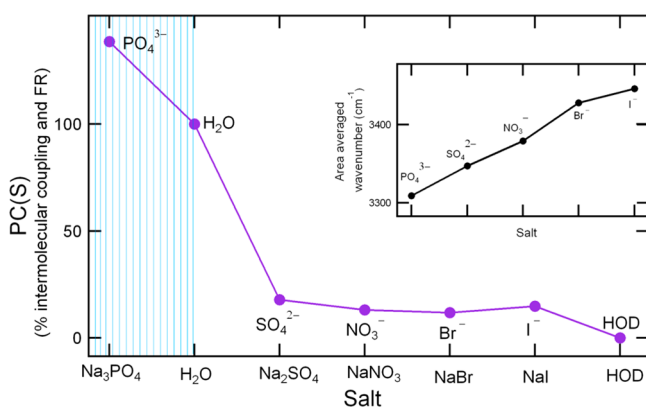
between the OH stretch fundamental and bend overtone increases in the hydration shell water. The increased energy difference reduces the coupling between stretch fundamentals and bend overtones (FR) of H<sub>2</sub>O. A recent Raman study from our group showed that water in the hydration shell of halide ion has significantly reduced FR in the hydration shell of halide ions.<sup>54</sup> Moreover, because of the weaker H-bonding in the hydration shell, the frequency of the OH stretch vibration of water in the hydration shell gets mismatched with that of the neighboring bulklike water. The frequency mismatch discourages the delocalization of vibrational mode (collective vibration) in the hydration shell. In other words, the water molecules in the hydration shell are energetically decoupled from neighboring bulklike water. Apart from the energetic mismatch, the strong electric field at the immediate vicinity of an anion leads to a time-averaged preferential orientation of water at the surface of the anion, and with increasing charge density (of the anion), the water in the hydration shell approaches closer to the anion.<sup>1,5,30</sup> It follows that the water in the (first) hydration shell is polarized by the ion's electric field

and experiences a significant spacial patterning (orientations and intermolecular distances) and dynamical perturbations,<sup>12,16,66–68</sup> which are likely to promote localization of vibrational modes in the hydration shell. Finally, due to excluded volume, on average the water molecules in the first hydration shell that directly interacts with the anion have a lower number of accessible H<sub>2</sub>O molecules than that in the bulk, which leads to decreased intermolecular coupling in the hydration shell.

The integrated areas of the component bands (Figure 2 and Table 1) enable estimation of relative coupling effects (intermolecular coupling and FR) of water in the hydration shell of anions. The OH stretch mode in HOD is vibrationally decoupled so that the component-1 is mainly due to the contribution of strongly H-bonded water molecules (free from the response of the collective OH oscillator and FR). In other words, for diluted water (H<sub>2</sub>O/D<sub>2</sub>O = 1/19; v/v), the integrated area of component-1 (0.096) is an estimation of the relative population of strongly H-bonded (maximum 3264 cm<sup>-1</sup>) water in HOD. However, in the case of neat H<sub>2</sub>O (undiluted water), the corresponding area (0.599) is an estimation of strongly H-bonded (maximum 3261 cm<sup>-1</sup>) water as well as the contribution of collective OH oscillators (intermolecular coupling) and FR in bulk H<sub>2</sub>O. Assuming the contribution of intermolecular coupling and FR in bulk H<sub>2</sub>O as 100, the percentage of the combined intermolecular coupling and FR in the hydration shell of an ion/solute (PC(S)) can be calculated by eq 1.

$$\text{PC(S)} = \frac{A_1(\text{S}) - A_1(\text{HOD})}{A_1(\text{H}_2\text{O}) - A_1(\text{HOD})} \times 100 \quad (1)$$

where  $A_1(i)$  is the relative integrated area of component-1 for the respective area-normalized Raman/SC-spectra; S stands for the solute (ion). A plot of PC(S) vs Na-salts of various chaotropic and kosmotropic anions is shown in Figure 4. It is



**Figure 4.** Variation of percentage coupling (intermolecular coupling and FR) of water in the hydration shells of kosmotropic and chaotropic anions. The coupling in H<sub>2</sub>O (undiluted) is assumed as 100%. Inset: Peak area-averaged wavenumber of the SC-spectra in the OH stretch regions.

observed that there is more than 80% reduction of PC(S) in the hydration shell of chaotropic anions such as NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>. Interestingly, water in the hydration shell of kosmotropic SO<sub>4</sub><sup>2-</sup> has almost equal PC(S) value to that of the chaotropic halide and nitrate anions. In the case of SO<sub>4</sub><sup>2-</sup> (as observed in Figure 2), there is almost no change in the peak position compared with that of HOD, which means that SO<sub>4</sub><sup>2-</sup> does not make a

stronger H-bond with water than water does with bulk water. This means for SO<sub>4</sub><sup>2-</sup> anion, the energy mismatch between the OH stretch fundamental and bend overtone as well as that between OH stretch fundamentals of neighboring water molecules in the hydration shell are not as large as those for NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> anions. Therefore, from the point of energetic mismatch, the intermolecular coupling and FR are expected to be less perturbed in the hydration shell of SO<sub>4</sub><sup>2-</sup> than those in the hydration shell of chaotropic NO<sub>3</sub><sup>-</sup>/Br<sup>-</sup>/I<sup>-</sup> anions.<sup>54</sup> However, the comparable PC(S) value for SO<sub>4</sub><sup>2-</sup> with those of the NO<sub>3</sub><sup>-</sup>/Br<sup>-</sup>/I<sup>-</sup> suggests that there is almost equal (~80%) reduction of coupling effects in the hydration shell of all these anions.

The reduction of intermolecular coupling of H<sub>2</sub>O in the hydration shell of SO<sub>4</sub><sup>2-</sup> ion is assignable to the stronger electric field at the vicinity of the divalent SO<sub>4</sub><sup>2-</sup> anion (higher charge density than the monovalent chaotropic NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> anions). Accordingly, the ions with even higher charge density (like trivalent PO<sub>4</sub><sup>3-</sup>) are expected to have even stronger electric field, and hence weaker coupling (lower PC(S) than that of SO<sub>4</sub><sup>2-</sup>). In contrast, the PC(S) value for PO<sub>4</sub><sup>3-</sup> is much larger than that of SO<sub>4</sub><sup>2-</sup>, as if the water in the hydration shell of PO<sub>4</sub><sup>3-</sup> has efficient intermolecular coupling and FR (Figure 4). This apparent anomaly can be resolved on the basis of significant contribution of strongly H-bonded water species (~3250 cm<sup>-1</sup>) in the hydration shell of trivalent PO<sub>4</sub><sup>3-</sup> anion. The strongly H-bonded water in the hydration shell of PO<sub>4</sub><sup>3-</sup> enhances the relative Raman intensity in the red region (~3250 cm<sup>-1</sup>) of the OH stretch band. In fact, the SC-spectrum for PO<sub>4</sub><sup>3-</sup> anion shows larger intensity in the red region of the OH stretch band (<3100 cm<sup>-1</sup>) than the Raman spectrum of H<sub>2</sub>O (Figure 1B). The intensity enhancement in the red region is compensated to some extent by the reduction of intermolecular coupling of water due to strong electric field and the excluded volume effect in the hydration shell. As a result, the SC-spectrum for PO<sub>4</sub><sup>3-</sup> apparently looks similar to the Raman spectrum of bulk H<sub>2</sub>O, and the PC(S) value is little larger than that of bulk H<sub>2</sub>O (blue shaded region in Figure 4). Thus, the large PC(S) value for PO<sub>4</sub><sup>3-</sup> signifies that the vibrational response due to collective OH oscillators (~3250 cm<sup>-1</sup>) is replaced by the response of strongly H-bonded isolated OH oscillators in the hydration shell. The peak area-averaged wavenumber ( $\nu_a$ ) of the SC-spectrum, which is defined as  $\nu_a = \sum A_i \nu_i$  ( $A_i$  and  $\nu_i$  are the relative integrated area and center wavenumber of the  $i$ th component band) provides a qualitative measure of the average O–H bond strength, and inversely, that of the H-bond strength (i.e., when  $\nu_a$  increases, O–H bond strength increases and consequently the H-bond strength decreases) of water in the hydration shell of the anions studied. As shown in the inset of Figure 4, the  $\nu_a$  value for PO<sub>4</sub><sup>3-</sup> is lowest among all the anions studied (PO<sub>4</sub><sup>3-</sup> < SO<sub>4</sub><sup>2-</sup> ≈ bulk HOD < NO<sub>3</sub><sup>-</sup> < Br<sup>-</sup> < I<sup>-</sup>), indicating stronger H-bonding of water in the hydration shell of PO<sub>4</sub><sup>3-</sup>. Thus, although SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> anions exhibit similar Hofmeister effects (salting-out), they do not have the same effect on the H-bond strength of water in their hydration shell. The trivalent PO<sub>4</sub><sup>3-</sup> anion increases the H-bond strength of water in its hydration shell, but the divalent SO<sub>4</sub><sup>2-</sup> does not. The different charge density of the anion is presumably responsible for the dissimilar behavior. The H-bond interaction of water, which is largely electrostatic in nature, is stronger with trivalent PO<sub>4</sub><sup>3-</sup> anion than that with divalent SO<sub>4</sub><sup>2-</sup> anion. Nevertheless, the collective nature of the

OH stretch vibration is significantly lost in the hydration shell of  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ , and halide ions.

## CONCLUSIONS

We have investigated the intermolecular coupling and H-bond strength of water in the hydration shell of various kosmotropic and chaotropic anions using Raman spectroscopy and the multivariate curve resolution method (Raman-MCR). Raman-MCR extracts the vibrational response of water in the hydration shell of ions (SC-spectrum). The peak positions of the SC-spectra show that the H-bond strength of  $\text{H}_2\text{O}$  in the hydration shell of  $\text{SO}_4^{2-}$  is comparable to that of bulk HOD but that in the case of  $\text{I}^-$ ,  $\text{Br}^-$ , and  $\text{NO}_3^-$  anions is weaker than that of bulk HOD. Comparison of integrated areas of component bands of the SC-spectra with that of the Raman spectrum of  $\text{H}_2\text{O}$  and HOD enables quantification of the modification of intermolecular coupling (collective OH stretch) of water at the immediate vicinity of different kinds of anions. It is observed that there is  $\sim 80\%$  reduction of coupling effects (intermolecular coupling and FR) in the hydration shell of  $\text{I}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  ions. In the case of  $\text{PO}_4^{3-}$ , the water is strongly hydrogen bonded with reduced intermolecular coupling. The stronger hydrogen bonding of water in the hydration shell of  $\text{PO}_4^{3-}$  is evident from the lower value of the peak area-averaged wavenumber of its SC-spectrum.

## ASSOCIATED CONTENT

### Supporting Information

Raman spectra of water in the presence of different salts. Variation of fwhm of component bands for the SC-spectra of different anions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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