

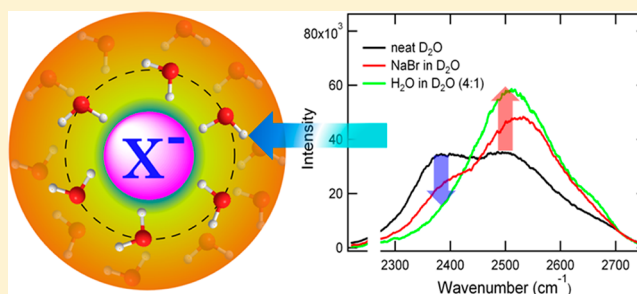
# Water in the Hydration Shell of Halide Ions Has Significantly Reduced Fermi Resonance and Moderately Enhanced Raman Cross Section in the OH Stretch Regions

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## S Supporting Information

**ABSTRACT:** Water in the presence of electrolytes plays an important role in biological and industrial processes. The properties of water, such as the intermolecular coupling, Fermi resonance (FR), hydrogen-bonding, and Raman cross section were investigated by measuring the Raman spectra in the OD and OH stretch regions in presence of alkali halides (NaX; X = F, Cl, Br, I). It is observed that the changes in spectral characteristics by the addition of NaX in D<sub>2</sub>O are similar to those obtained by the addition of H<sub>2</sub>O in D<sub>2</sub>O. The spectral width decreases significantly by the addition of NaX in D<sub>2</sub>O (H<sub>2</sub>O) than that in the isotopically diluted water. Quantitative estimation, on the basis of integrated Raman intensity, revealed that the relative Raman cross section,  $\sigma_H/\sigma_b$  ( $\sigma_H$  and  $\sigma_b$  are the average Raman cross section of water in the first hydration shell of X<sup>−</sup> and in bulk, respectively), in D<sub>2</sub>O and H<sub>2</sub>O is higher than those in the respective isotopically diluted water. These results suggest that water in the hydration shell has reduced FR and intermolecular coupling compared to those in bulk. In the isotopically diluted water, the relative Raman cross section increases with increase in size of the halide ions ( $\sigma_H/\sigma_b = 0.6, 1.1, 1.5$ , and  $1.9$  for F<sup>−</sup>, Cl<sup>−</sup>, Br<sup>−</sup>, and I<sup>−</sup>, respectively), which is assignable to the enhancement of Raman cross section by charge transfer from halide ions to the hydrating water. Nevertheless, the experimentally determined  $\sigma_H/\sigma_b$  is lower than the calculated values obtained on the basis of the energy of the charge transfer state of water. The weak enhancement of  $\sigma_H/\sigma_b$  signifies that the charge transfer transition in the hydration shell of halide ions causes little change in the OD (OH) bond lengths of hydrating water.



## INTRODUCTION

Interactions between ions and water play important roles in biological, environmental, and industrial processes. To understand these interactions, vibrational spectroscopy is widely used, since the vibrational transitions are highly sensitive to the local environments of a molecule. In principle, a comparison of spectral width, position, and intensity of the vibrational spectrum of neat water with those of aqueous electrolyte solutions would reveal the interactions between ions and water. Earlier vibrational studies<sup>1–4</sup> of aqueous alkali halide solutions showed that the alkali cations have negligible effect on the properties of water, but the halide ions reduce the width of the OH stretch band and shifts the band position toward blue, which is often described as the “structure breaking” properties of halide ions. Moreover, unlike the IR absorption in the OH stretch regions, the Raman intensity (in the blue region of the OH stretch band) increases with increasing concentration of alkali halides in water. This was qualitatively explained by the change in polarizability of the OH bonds in presence of halide ions.<sup>5,6</sup> However, these straightforward spectral analysis may not fully account the observed spectral changes, since the band shape and the intensity of the OH stretch band are heavily affected by the intermolecular coupling and Fermi resonance (FR),<sup>7–10</sup> which may be affected in the presence of ions.<sup>7–10</sup>

In aqueous electrolyte solutions or charged interfaces, water is preferentially oriented in the hydration shell of the charged groups/ions.<sup>11–13</sup> Water in the first hydration shell experiences an anisotropic environment, since it is sandwiched between charged group/ion and the water molecules in the second hydration shell.<sup>14–17</sup> The anisotropic environment (at the vicinity of halide ions) is likely to affect the intermolecular coupling and FR of hydrating water, which in turn would alter the Raman scattering cross section ( $\sigma$ ) of water.<sup>18–21</sup> Moreover, the charge transfer from halide ions to the hydrating water leads to enhanced Raman intensity in the OH stretch regions.<sup>6,18</sup> Therefore, it is important to understand the intermolecular coupling and Fermi resonance of water and the role of these couplings on the Raman cross section of water while interacting with halide ions.

In this paper, we investigated the intermolecular coupling, FR, and the Raman cross section of water in the hydration shell of halide ions by comparing the Raman spectra of water (D<sub>2</sub>O and H<sub>2</sub>O) and isotopically diluted waters (D<sub>2</sub>O/HOD/H<sub>2</sub>O = 1/18/81 and 81/18/1) in the presence of varying concen-

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trations of alkali halides (NaX). Our results show that the effect of NaX on the OD stretch band of D<sub>2</sub>O is similar to the effect of H<sub>2</sub>O in D<sub>2</sub>O. It is observed that, on isotopic dilution (addition of H<sub>2</sub>O in D<sub>2</sub>O), the OD stretch bandwidth (fwhm) decreases and the integrated Raman intensity increases due to reduced intermolecular coupling and FR. Addition of NaX in D<sub>2</sub>O leads to similar spectral changes. In isotopically diluted water, addition of NaX leads to smaller change in fwhm and intensity in the OD (OH) stretch bands compared to those in D<sub>2</sub>O (H<sub>2</sub>O). Quantitative estimation revealed that the relative Raman cross section,  $\sigma_{\text{H}}/\sigma_{\text{b}}$  ( $\sigma_{\text{H}}$  and  $\sigma_{\text{b}}$  are the Raman cross section of water in the first hydration shell and in bulk), in D<sub>2</sub>O (H<sub>2</sub>O) is higher than that in isotopically diluted water. These results suggest that the hydrating water has reduced FR and intermolecular coupling than those in bulk water. In alkali halide solutions of isotopically diluted water, the experimentally determined relative Raman cross sections are smaller than the calculated values based on the energy of the charge transfer excited state of water. The smaller values of  $\sigma_{\text{H}}/\sigma_{\text{b}}$  suggest that the charge transfer from halide ions does not significantly change in the OD (OH) bond lengths of hydrating water.

## EXPERIMENTAL SECTION

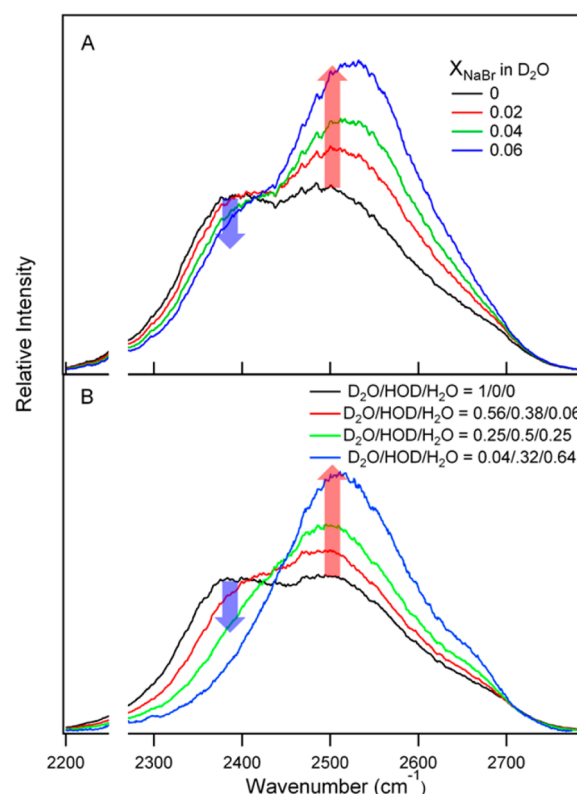
Salts, such as NaX (X = Cl, Br, I) and KF ( $\geq 99.0\%$ ) and heavy water (D<sub>2</sub>O,  $> 99.9$  atom %) were purchased from Sigma Aldrich. Milli-Q water (18.2 M $\Omega$  cm resistivity) was used for all measurements. The spontaneous Raman spectra of the samples were recorded using a STR-300 micro-Raman spectrometer (SEKI Technotron, Japan). The sample solution (2.5 mL) was taken in the round glass vial and excited at 532 nm (power  $\sim 20$  mW at the sample spot, DPSS) using a 10 $\times$  objective lens (Olympus). The scattered light was collected through fiber-coupled 300 mm spectrograph (Action series SP 2300i, 1800 gr/mm) and detected by a thermoelectric cooled ( $-75$  °C) charge-coupled device (CCD). The acquisition time was 200 s for a single spectral measurement. A Z-stage of 0.1  $\mu\text{m}$  resolution was used as the sample stage, and the laser beam was focused with 10 $\times$  (long focal length) lens to avoid the uncertainty in sample volume probed in successive measurements. A small concentration of acetonitrile was used as the internal standard, to account for the laser fluctuations during the acquisition. The small concentration of acetonitrile was found not to affect the integrated intensity in the OD stretch band, and reproducible spectra were acquired by measuring at the same experimental conditions. Background subtracted spectra were obtained using Peakfit v4.12 software. At least, two such background subtracted spectra were averaged for each of the spectra reported in this work.

## RESULTS AND DISCUSSION

**Effect of NaBr and H<sub>2</sub>O on the OD Stretch Band of D<sub>2</sub>O.** Figure 1A shows the concentration normalized Raman spectra of D<sub>2</sub>O in the OD stretch regions, with different mole fractions of NaBr. The concentration normalized Raman spectra ( $I_{\text{norm}}$ ) of NaBr solutions were calculated as follows.

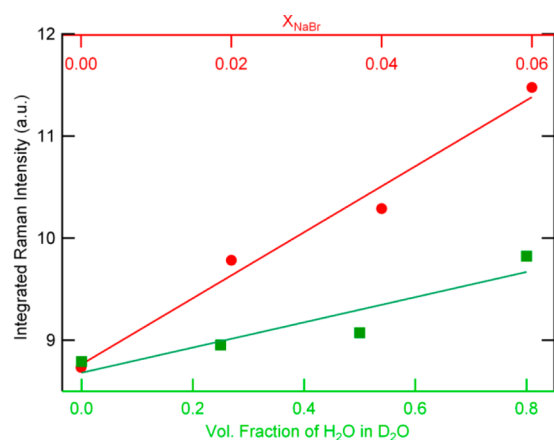
$$I_{\text{norm}} = I(C_0/C_1) \quad (1)$$

where  $I$  is the measured spectra of NaBr solutions, and  $C_0$  and  $C_1$  are the concentrations of D<sub>2</sub>O in neat D<sub>2</sub>O and in NaBr solutions, respectively. On increasing the concentration of NaBr, the intensity in the red regions of the OD stretch band (strongly H-bonded water) decreases and that in the blue



**Figure 1.** Concentration normalized Raman spectra in the OD stretch regions: (A) D<sub>2</sub>O with different mole fractions of NaBr and (B) D<sub>2</sub>O–H<sub>2</sub>O mixtures with different mole ratios as mentioned in the panel. The Raman spectra of H<sub>2</sub>O with different mole fractions of NaBr are shown in the Supporting Informations.

regions (weakly H-bonded water) increases (Figure 1A), which is quite similar to the effect of increasing temperature on the IR or Raman spectra of water.<sup>5,9,22</sup> These spectral changes indicate that the population of strongly H-bonded water decreases and that of the weakly H-bonded water increases in the presence of NaBr. Previous IR and Raman studies<sup>6,23–28</sup> have shown that the spectral change in the OD (OH) stretch band is primarily due to the halide ion ( $X^-$ ) and the alkali cation ( $Na^+$ ) has negligible effect on the OD (OH) stretch band of water. Moreover, the time-resolved IR studies<sup>29–32</sup> have also shown that the halide ions affect the water only in the (first) hydration shell and do not influence the H-bond network in the bulk of liquid water. Therefore, the spectral change in Figure 1A is assignable primarily to the reduced H-bond strength of water in the first hydration shell of Br<sup>−</sup>. It can be seen in Figure 1A that the increase in intensity in the blue region of the OD band (weakly H-bonded water) is significantly higher than the decrease in the red regions (strongly H-bonded water),<sup>5</sup> which leads to an increase in integrated Raman intensity with the concentration of NaBr (red line in Figure 2). The increase in Raman intensity suggests that the water that is perturbed by Br<sup>−</sup> has higher Raman cross section ( $\sigma$ ) than that of bulk water. Raman studies<sup>6,20,33</sup> of aqueous alkali halide solution qualitatively suggested that the average Raman cross section of water increases due to change in polarizability of the OH bonds by charge transfer from the halide ions. Interestingly, the spectral changes similar to that in Figure 1A (NaBr in D<sub>2</sub>O) are observed with gradual addition of H<sub>2</sub>O in D<sub>2</sub>O (Figure 1B). The normalized spectra ( $I_{\text{norm}}$ ) in Figure 1B are calculated by eq 2,

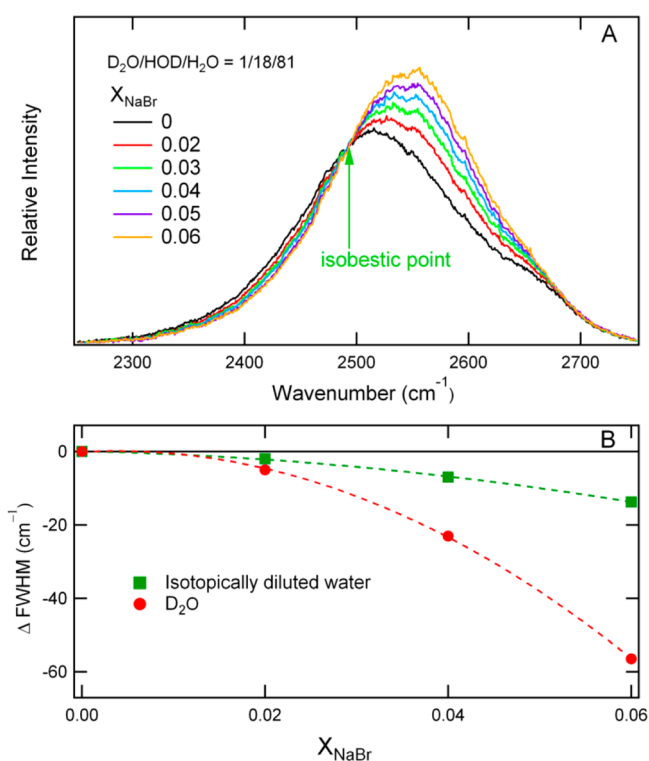


**Figure 2.** Plot of integrated Raman intensity (OD stretch band) against the mole fraction of NaBr in D<sub>2</sub>O (red) or the volume fraction of H<sub>2</sub>O in D<sub>2</sub>O (green).

$$I_{\text{norm}} = I\{C_0/(C_{\text{D}_2\text{O}} + C_{\text{HOD}}/2)\} \quad (2)$$

Here,  $I$  is the measured spectrum in D<sub>2</sub>O–H<sub>2</sub>O mixtures, and  $C_{\text{D}_2\text{O}}$  and  $C_{\text{HOD}}$  are the concentrations of D<sub>2</sub>O and HOD in the D<sub>2</sub>O–H<sub>2</sub>O mixtures. The concentration of HOD is divided by 2, since unlike the two OD bonds in D<sub>2</sub>O each HOD molecule has one OD bond. Like the addition of NaBr in D<sub>2</sub>O, on increasing isotopic dilution (gradual addition of H<sub>2</sub>O in D<sub>2</sub>O), the intensity in the red regions decreases and that in the blue regions increase, and the integrated Raman intensity also increases. On isotopic dilution, the intra/intermolecular coupling and FR of water decrease but the H-bond strength of water does not change.<sup>7–9,34</sup> Thus, the similarities between the spectral changes in Figure 1A and B suggest that the water in the hydration shell of Br<sup>−</sup> may also have reduced intermolecular coupling and FR compared to that of bulk water. To investigate this effect, the Raman spectra of isotopically diluted water, D<sub>2</sub>O/HOD/H<sub>2</sub>O = 1/18/81, which is free from the intermolecular coupling and FR (at atmospheric pressure<sup>35</sup>) in the OD stretch regions,<sup>7,36</sup> were measured in the presence of different concentrations of NaBr.

**Effect of NaBr on the OD Stretch Band of Isotopically Diluted Water.** Figure 3A shows the Raman spectra of isotopically diluted water (D<sub>2</sub>O/HOD/H<sub>2</sub>O = 1/18/81) in the OD stretch regions with different concentrations of NaBr. On increasing salt concentration, the intensity in the red regions of the OD stretch band decreases and that in the blue region increases with an isosbestic point at ~2490 cm<sup>−1</sup>. This shows that the hydrating water whose population increases with increasing concentration of Br<sup>−</sup> absorbs in the higher frequency regions of the OD stretch band compared to that of the bulk water. Moreover, comparing Figures 1A and 3A, it can be seen that the spectral width (fwhm) of the OD stretch band decreases significantly in D<sub>2</sub>O than that in the isotopically diluted water (see Figure 3B) with increasing concentration of Br<sup>−</sup>. In the OH stretch regions, similar spectral changes are observed by the addition of NaBr in H<sub>2</sub>O and isotopically diluted water, D<sub>2</sub>O/HOD/H<sub>2</sub>O = 81/18/1 (see the Supporting Information (SI)). Since the isotopically diluted water does not have significant intermolecular coupling and FR, the larger decrease in  $\Delta\text{fwhm}$  in D<sub>2</sub>O (H<sub>2</sub>O) than that in the isotopically diluted water reveals the significant reduction of intermolecular coupling and FR in the hydrating D<sub>2</sub>O (H<sub>2</sub>O).<sup>1,16</sup> In the isotopically diluted water, a small decrease in  $\Delta\text{fwhm}$  with a



**Figure 3.** (A) Raman Spectra of D<sub>2</sub>O–H<sub>2</sub>O mixture (D<sub>2</sub>O/HOD/H<sub>2</sub>O = 1/18/81) with different mole fractions of NaBr. The spectra are normalized according to eq 2. (B) Change in fwhm of the OD stretch band due to addition of NaBr in D<sub>2</sub>O (red circle) and in the isotopically diluted water (green square). The dashed lines are guides for the eye.

blue shift of the OD stretch band can be assigned to decreased H-bond strength of water with increasing concentration of NaBr. Recently, Perera et al.<sup>10</sup> have reported that ion correlated Raman spectrum of water obtained by multivariate Raman curve resolution shows significant reduction of intensity in the red regions of the OH stretch band (~3250 cm<sup>−1</sup>), which was assigned to the reduced FR of hydrating water.

It can be seen from Figure 3A that even in the isotopically diluted water the magnitude of the increase (in intensity) in the blue region of the OD band is larger than the magnitude of the decrease (in intensity) in the red regions. This suggests larger average Raman cross section of hydrating water than that of the bulk water.<sup>10,11</sup> To elucidate the intermolecular coupling and FR in the hydration shell of Br<sup>−</sup>, a quantitative analysis of the relative Raman cross section in isotopically diluted water and in D<sub>2</sub>O was performed in the following section.

**Relative Raman Cross Section of Water in the Hydration Shell of Br<sup>−</sup> in D<sub>2</sub>O and in Isotopically Diluted Water.** The area under the Raman spectrum of D<sub>2</sub>O recorded at constant excitation intensity is proportional to the average Raman cross section per D<sub>2</sub>O molecule and the number density of D<sub>2</sub>O.

$$\int I_0(\nu) d\nu \propto \sigma_b N_A C_{\text{D}_2\text{O}} \quad (3)$$

Here  $\sigma_b$  is the average Raman cross section of D<sub>2</sub>O in bulk, and  $N_A$  and  $C_{\text{D}_2\text{O}}$  are the Avogadro number and concentration of D<sub>2</sub>O, respectively. In aqueous NaBr solution, the integrated intensity can be approximated as the sum of the responses of water in the first hydration shell of Br<sup>−</sup> and in the bulk.<sup>1</sup>



Assuming that there is no significant effect of  $\text{Br}^-$  beyond its first hydration shell,<sup>29–32</sup> eq 3 takes the following form in presence of NaBr.

$$\int I_{\text{norm}}(\nu) d\nu \propto \{\sigma_{\text{H}} n N_{\text{A}} C_{\text{Br}^-} + \sigma_{\text{b}} N_{\text{A}} (C_{\text{D}_2\text{O}} - n C_{\text{Br}^-})\} \quad (4)$$

where  $n$  and  $\sigma_{\text{H}}$  are the average number of  $\text{D}_2\text{O}$  molecules and the Raman cross section of  $\text{D}_2\text{O}$  in the first hydration shell of  $\text{Br}^-$  respectively. Now,

$$\frac{\int I_{\text{norm}}(\nu) d\nu}{\int I_0(\nu) d\nu} \propto 1 + \left( \frac{\sigma_{\text{H}}}{\sigma_{\text{b}}} - 1 \right) \left( \frac{n}{C_{\text{D}_2\text{O}}} \right) C_{\text{Br}^-} \quad (5)$$

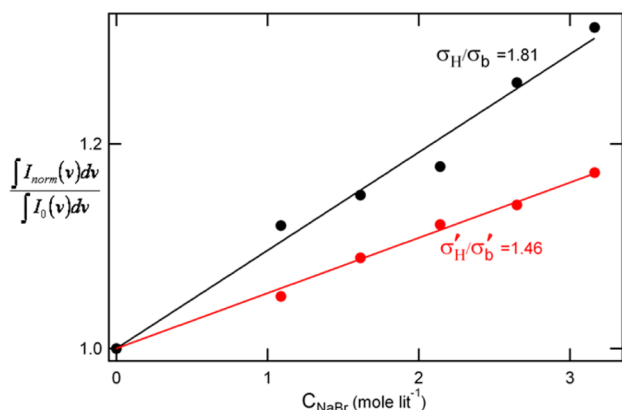
Here,  $\sigma_{\text{H}}/\sigma_{\text{b}}$  is the relative Raman cross section of  $\text{D}_2\text{O}$  in the first hydration shell of  $\text{Br}^-$ . The relative Raman cross section,  $\sigma_{\text{H}}/\sigma_{\text{b}}$ , provides a quantitative idea about the variation of the average Raman cross section in the hydration shell of halide ions.

In the case of NaBr in isotopically diluted water, eq 5 is reduced to

$$\frac{\int I_{\text{norm}}(\nu) d\nu}{\int I_0(\nu) d\nu} \propto 1 + \left( \frac{\sigma'_{\text{H}}}{\sigma'_{\text{b}}} - 1 \right) \left( \frac{0.19n}{C_{\text{HOD}}} \right) C_{\text{Br}^-} \quad (6)$$

$\sigma'_{\text{H}}/\sigma'_{\text{b}}$  is the relative Raman cross section of the isotopically diluted water. On the basis of relative populations of  $\text{D}_2\text{O}$  and  $\text{HOD}$  in the isotopically diluted water ( $\text{D}_2\text{O}/\text{HOD}/\text{H}_2\text{O} = 1/18/81$ ), the  $n$  in eq 5 is replaced by  $0.19n$  in eq 6.

Figure 4 shows a plot of the ratio of integrated intensity vs the concentration of NaBr in  $\text{D}_2\text{O}$  and in the isotopically



**Figure 4.** Plot of relative integrated intensity vs the concentration of NaBr in  $\text{D}_2\text{O}$  (black circles) and isotopically diluted water (red circles). The solid lines are the fitted functions as mentioned in the text.

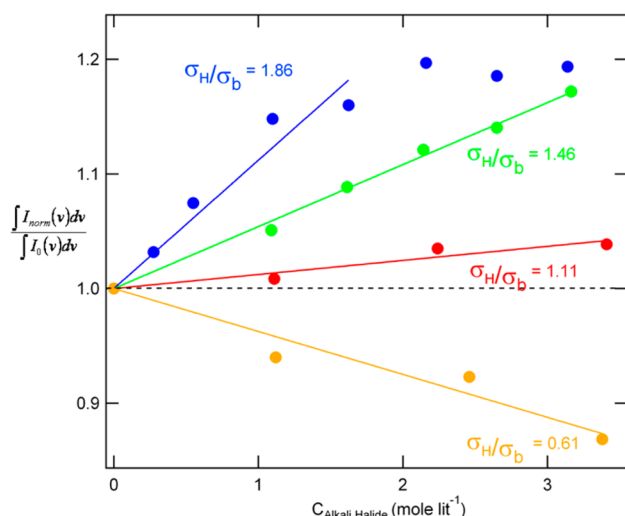
diluted water. In both cases, the ratio of integrated intensity was found to increase with increase in concentration of NaBr. However, the slope is higher in case of  $\text{D}_2\text{O}$  than that in the isotopically diluted water. In the OH stretch region as well, the plot of the ratio of integrated intensity vs concentration of NaBr (Figure S3 in the SI) shows larger slope for  $\text{H}_2\text{O}$  than that in the isotopically diluted water ( $\text{D}_2\text{O}/\text{HOD}/\text{H}_2\text{O} = 81/18/1$ ). The data points for  $\text{D}_2\text{O}$  (black circles in Figure 4) are fitted with eq 5 and those for the isotopically diluted water with eq 6, and the fitted functions are shown by the solid lines.

In the isotopically diluted water, the relative Raman cross section,  $\sigma'_{\text{H}}/\sigma'_{\text{b}}$ , is 1.46 for  $\text{Br}^-$ . Since the isotopically diluted

water is free from intermolecular coupling and FR,<sup>7,36</sup> the higher value of  $\sigma'_{\text{H}}$  than that of  $\sigma'_{\text{b}}$  is assignable to the preresonance enhancement of the Raman cross section by charge transfer from  $\text{Br}^-$  to the combined antibonding orbital of hydrating water<sup>6,20,37</sup> (vide infra). Similarly, if there is no change in the intermolecular coupling and FR of  $\text{D}_2\text{O}$  by the addition of NaBr, the  $\sigma_{\text{H}}/\sigma_{\text{b}}$  for  $\text{D}_2\text{O}$  is expected to be 1.46. However, as shown in Figure 4, the  $\sigma_{\text{H}}/\sigma_{\text{b}}$  for  $\text{D}_2\text{O}$  is higher (1.81) than that of the isotopically diluted water. This means that the intermolecular couplings and FR in  $\text{D}_2\text{O}$  are perturbed in the hydration shell. It is reported that the intramolecular coupling has lesser effect on the intensity and the position/width of the OD (OH) stretch band than the FR and intermolecular coupling in water.<sup>7–9,38</sup> Raman cross section of water increases either due a reduction in FR<sup>18</sup> or due to an increase in intermolecular coupling.<sup>7,19</sup> On average, a water molecule in the first hydration shell of  $\text{Br}^-$  interacts with lesser number of neighboring water molecules compared to those in the bulk, and experiences a rapidly varying electric field.<sup>11,39</sup> In a sense, the water in the first hydration shell experiences an anisotropic environment with lower probability of interaction with neighboring water and the intermolecular interaction is expected to be weaker; that is,  $\sigma_{\text{H}}/\sigma_{\text{b}}$  is expected to be  $<1.46$ . On the contrary, the experimentally determined  $\sigma_{\text{H}}/\sigma_{\text{b}}$  (1.81) is higher than that in the isotopically diluted water. The large enhancement of  $\sigma_{\text{H}}$  is assignable to the significant decrease in FR of  $\text{D}_2\text{O}$  in the hydration shell of  $\text{Br}^-$ . The decrease in FR can be explained by the perturbation of the stretching and bending vibrations of water in the hydration shell of halide ions. As shown in Figure 3, the maximum of the OD stretch band ( $\nu_{\text{OD}}$ ) shifts toward higher frequency with increasing concentration of NaX which means that the water in the hydration shell has weaker H-bonding than that of the bulk.<sup>15,31,32</sup> In the case of the bending vibration of water ( $\delta_{\text{OD}}$ ), the maximum of  $\delta_{\text{OD}}$  shifts toward lower frequency with decreasing interaction with neighboring molecules<sup>15,40,41</sup> and so is the overtone band ( $2\delta_{\text{OD}}$ ). Therefore, in the hydration shell of  $\text{Br}^-$ , the weakly interacting water has larger energy gap between  $\nu_{\text{OD}}$  and  $2\delta_{\text{OD}}$  (bending overtone) than that of the neat water, which results in weaker Fermi resonance coupling.

**Relative Raman Cross Section of Water in the Hydration Shell of Different Halide Ions in Isotopically Diluted Water.** Figure 5 shows a plot of relative integrated intensity vs the concentration of alkali halide ( $\text{MX}$ ;  $\text{M} = \text{Na}/\text{K}$  and  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) in the isotopically diluted water ( $\text{D}_2\text{O}/\text{HOD}/\text{H}_2\text{O} = 1/18/81$ ). The data points for different halide ion solutions are fitted with eq 6 with  $n = 5, 5.8, 6.2$ , and  $6.6$  for  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$ ,<sup>42–44</sup> and the fitted functions are shown as solid lines in Figure 5. It is observed that, except for  $\text{F}^-$ ,  $\sigma'_{\text{H}}/\sigma'_{\text{b}} > 1$  and increases as the size of the halide ions increases ( $\sigma'_{\text{H}}/\sigma'_{\text{b}} = 1.11$  for  $\text{Cl}^-$ , 1.46 for  $\text{Br}^-$ , and 1.86 for  $\text{I}^-$ ). With increasing size, the charge transfer ability of the halide ions to the combined antibonding orbitals of hydrating water increases and the energy of the lowest excited electronic state of hydrating water decreases.<sup>6,20</sup> So, the energy gap between the electronic excited state (UV region) and the virtual state (the excited state created by the 532 nm laser excitation in the present experiment) decreases, which causes an increase of the Raman cross section according to eq 7.<sup>45,46</sup>

$$\sigma \propto k\nu_0(\nu_0 - \nu_j)^3 \left[ \frac{\nu_e^2 + \nu_0^2}{(\nu_e^2 - \nu_0^2)^2} \right]^2 \quad (7)$$



**Figure 5.** Plot of the relative integrated intensity vs the concentration of MX: NaI (blue), NaBr (green), NaCl (red), and KF (orange) in the isotopically diluted water, D<sub>2</sub>O/HOD/H<sub>2</sub>O = 1/18/81. The solid lines are the fitted functions according to eq 6.

Here,  $\nu_e$  and  $\nu_0$  are the electronic absorption and excitation frequencies,  $\nu_j$  is the frequency of the  $j$ th vibrational transition, and  $k$  is a scaling constant. With decreasing energy gap between the electronic excited state ( $\nu_e$ ) and the virtual state ( $\nu_0$ ), the denominator in eq 7 decreases, which leads to an increase of  $\sigma$ . In this case,  $\sigma$  increases not by the resonant excitation, but due to closeness of the virtual state to the resonant excited state, and hence, the increase of the Raman cross section is known as preresonance enhancement. Raman measurements<sup>6,10,20,33,47</sup> and computational studies<sup>11,48</sup> suggested the increase in Raman intensity with increasing size of halide ions, which qualitatively agrees with our results in isotopically diluted water. In the following section, we modeled the increase in relative Raman cross section with eq 7.

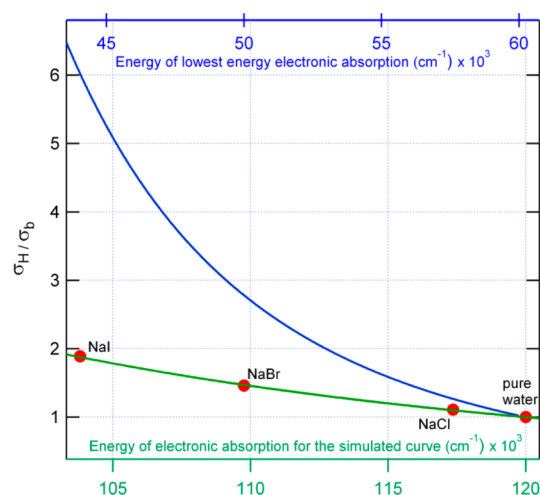
**Variation of Relative Raman Cross Section with the Energies of Lowest Excited Electronic States.** For the hydrating water, eq 7 takes the form,

$$\sigma_H \propto k' \nu_0 (\nu_0 - \nu_j')^3 \left[ \frac{\nu_{e(H)}^2 + \nu_0^2}{(\nu_{e(H)}^2 - \nu_0^2)^2} \right]^2 \quad (8)$$

Here,  $\nu_{e(H)}$  is the frequency of lowest energy electronic absorption of hydrating water. In aqueous halide ion solutions, the lowest energy electronic transition arises due to the transfer of electron from the halide ion to linear combination of antibonding orbitals of hydrating water.<sup>6,37,49,50</sup> Assuming a comparable scaling constant ( $k' \approx k$ ) and neglecting the small spectral shift in the OD stretch band in the presence of alkali halide ( $\nu_j' \approx \nu_j$ ), the relative Raman cross section of the isotopically diluted water takes the form,

$$\frac{\sigma'_H}{\sigma'_b} \approx \left[ \frac{\nu_{e(H)}^2 + \nu_0^2}{\nu_{e(b)}^2 + \nu_0^2} \right]^2 \left[ \frac{\nu_{e(b)}^2 - \nu_0^2}{\nu_{e(H)}^2 - \nu_0^2} \right]^4 \quad (9)$$

where  $\nu_{e(b)}$  is the frequency of lowest energy electronic absorption of bulk water (60240 cm<sup>-1</sup>). In aqueous NaX (X = Cl, Br, I) solutions, the lowest energy electronic excited state of water ( $\lambda_{\max} \sim 166$  nm) shifts toward lower energy as the size of the halide ions increases  $\lambda_{\max}$  (Cl<sup>-</sup>)  $\sim 173$  nm,  $\lambda_{\max}$  (Br<sup>-</sup>)  $\sim 200$  nm, and  $\lambda_{\max}$  (I<sup>-</sup>)  $\sim 227$  nm).<sup>6,20</sup> Figure 6 shows a plot of



**Figure 6.** Plot of relative Raman cross section vs the energy of electronic absorption of water (red circle) for different alkali halide solutions. Blue and green lines are the simulated curves corresponding to the lowest energy (60 240 cm<sup>-1</sup>, top horizontal axis) and higher energy (120 000 cm<sup>-1</sup>, bottom horizontal axis) electronic excited states of water.

the  $\sigma'_H/\sigma'_b$  vs the energy of the lowest energy absorptions band for different NaX solutions (red circles). As expected, the relative Raman cross section increases with decreasing the energy of the lowest excited electronic state of water (i.e., with decreasing the energy gap between  $\nu_{e(H)}$  and  $\nu_0$ ).

However, the experimental  $\sigma'_H/\sigma'_b$  (red circles) is lower than the calculated values (blue line) corresponding to the preresonance enhancement by the lowest energy electronic state. This shows that the preresonance enhancement of the Raman cross section of the hydrating water is only weakly mediated by the lowest energy excited state of water. In other words, the charge transfer in hydrating water causes little change in their O–H bond lengths. Simulation studies<sup>14,15</sup> revealed that halide ions do not directly increase the OD (OH) bond lengths of water but the mean water–water H-bond angle in the first hydration shell increase, which shifts the OD (OH) stretching mode of water to higher frequency. The results in Figure 6 can be modeled by the simulated curve (green line in Figure 6) corresponding to the preresonance enhancement by a higher energy excited electronic state ( $\nu_{e(b)} = 120\,000$  cm<sup>-1</sup>) of water. Recently, Xiong and Asher<sup>23</sup> measured the excitation wavelength dependence of the Raman cross section for the OH stretch band of water and predicted that the electronic state responsible for the preresonance enhancement lies in far UV regions (either 150 000 or 91 000 cm<sup>-1</sup>), which is consistent with the present results.

## CONCLUSIONS

We investigated the intermolecular coupling, Fermi resonance (FR), hydrogen-bonding, and the Raman cross section of neat and isotopically diluted water in presence of halide ions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>) by measuring the Raman spectra in the OD and OH stretch regions. Except for F<sup>-</sup>, all the halide ions cause blue-shift and enhancement of intensity in OD stretch regions, which are also observed by the isotopic dilution of D<sub>2</sub>O (H<sub>2</sub>O). Comparison of the spectral changes by the addition of alkali halides in D<sub>2</sub>O (H<sub>2</sub>O) and in the isotopically diluted water reveals that the magnitude of  $\Delta fwhm$  of the OD (OH) stretch band and the relative Raman cross section ( $\sigma_H/\sigma_b$ ) in D<sub>2</sub>O

(H<sub>2</sub>O) are higher than those in the respective isotopically diluted water. These results suggest that water has reduced FR and intermolecular coupling in the hydration shell of halide ions compared to those in bulk. In the isotopically diluted water, the increase in relative Raman cross section with the size of the halide ions ( $\sigma_{\text{H}}/\sigma_{\text{b}} = 0.6, 1.1, 1.5$ , and  $1.9$  for F<sup>−</sup>, Cl<sup>−</sup>, Br<sup>−</sup>, and I<sup>−</sup>, respectively) shows that the charge transfer from halide ions to the hydrating water leads to preresonance enhancement of the Raman cross section of hydrating water. Quantitative analysis, however, revealed that the Raman cross section of hydrating water is only weakly enhanced by the lowest energy charge transfer electronic excited state of water.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Raman spectra of H<sub>2</sub>O and isotopically diluted water (D<sub>2</sub>O/HOD/H<sub>2</sub>O = 81/18/1) in the presence of varying concentrations of NaX. Raman spectra of 0.06 mol fraction NaBr in D<sub>2</sub>O in the OD and OH stretch regions. 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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