

# **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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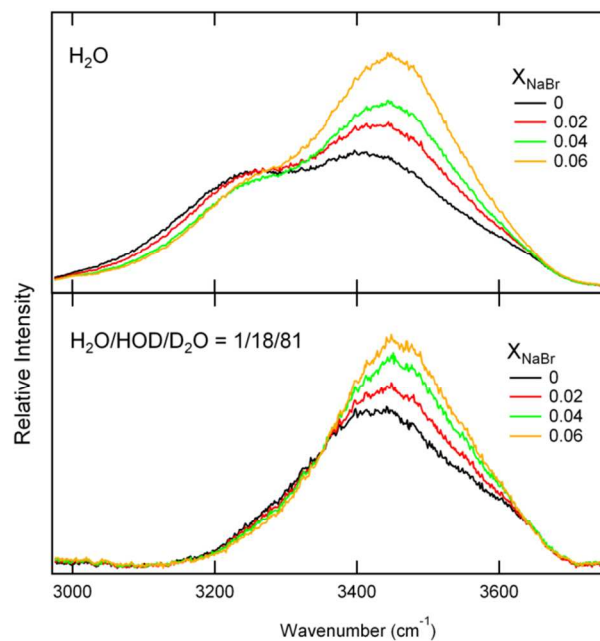
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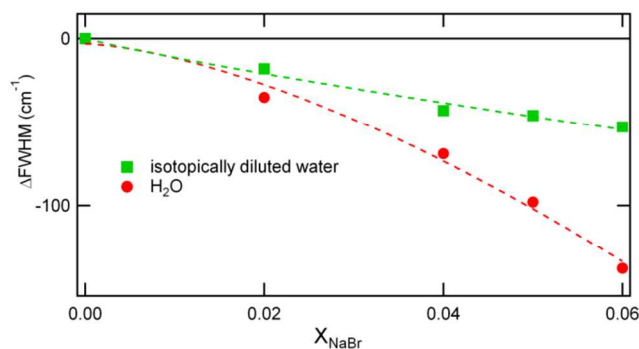
## **Supporting Informations:**

### **1. Effect of NaBr on the OH stretch bands of H<sub>2</sub>O and isotopically diluted water**

Figure S1 shows the Raman Spectra of H<sub>2</sub>O (top) and isotopically diluted water, D<sub>2</sub>O/HOD/H<sub>2</sub>O = 81/18/1, (bottom) with different mole fractions of NaBr. With increasing concentration of NaBr, the intensity in the blue region (weakly H-bonded) increases and that in the red regions (strongly H-bonded) decreases, which are quite similar to the spectral changes in the OD stretch regions (for D<sub>2</sub>O and isotopically diluted water D<sub>2</sub>O/HOD/H<sub>2</sub>O = 1/18/81) as discussed in the main text. The  $\Delta$ FWHM of the OH stretch band decreases with increasing concentration of NaBr (Figure S2) and the decrease in H<sub>2</sub>O is more than that in the isotopically diluted water for the same concentration of NaBr. This indicates that the effect of NaBr on D<sub>2</sub>O, H<sub>2</sub>O, and isotopically diluted water are quite similar, and does not depend on the spectral regions (OH or OD stretch bands) monitored.



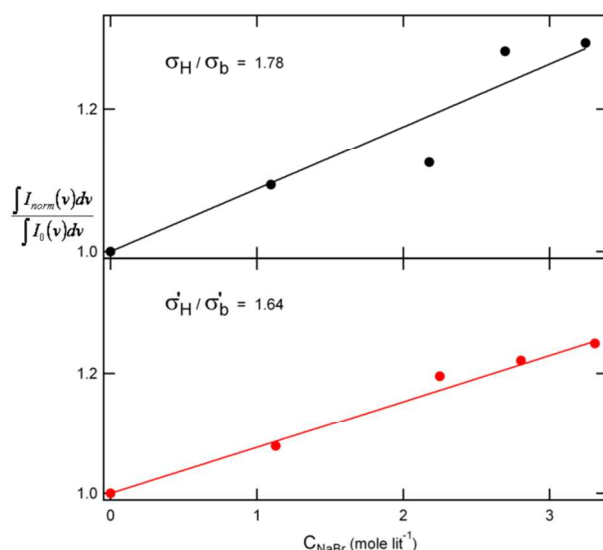
**Figure S1.** Raman Spectra of  $\text{H}_2\text{O}$  (top) and isotopically diluted water,  $\text{D}_2\text{O}/\text{HOD}/\text{H}_2\text{O} = 81/18/1$ , (bottom) with different mole fractions of NaBr. The spectra are normalized according to equation 1 and 2 in the main text.



**Figure S2.** Change in FWHM of the OH stretch band with increasing concentration of NaBr in  $\text{H}_2\text{O}$  (red circle) and in isotopically diluted water,  $\text{D}_2\text{O}/\text{HOD}/\text{H}_2\text{O} = 81/18/1$  (green square). The dashed lines are guides for the eye.

Figure S3 shows a Plot of relative integrated intensity vs. the concentration of NaBr in  $\text{H}_2\text{O}$  (top) and isotopically diluted water (bottom). The relative Raman cross-section,  $\sigma_{\text{H}}/\sigma_{\text{b}}$  in  $\text{H}_2\text{O}$  (1.78) is

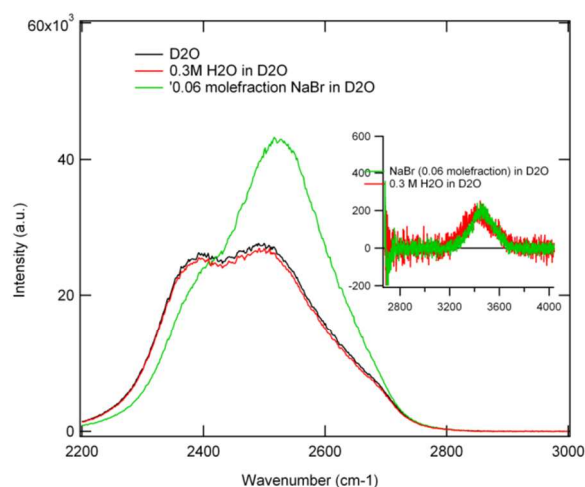
close to that of D<sub>2</sub>O (1.81). However, in the isotopically diluted water (D<sub>2</sub>O/HOD/H<sub>2</sub>O = 81/18/1), while measuring in the OH stretch regions, the relative Raman cross-section (1.64) is little higher than that in the corresponding OD stretch regions (1.46, as shown in the main text). The higher value of the relative Raman cross-section in the OH stretch region is due to the presence of H<sub>2</sub>O impurity in NaBr.



**Figure S3.** Plot of relative integrated intensity vs. the concentration of NaBr in H<sub>2</sub>O (top) and isotopically diluted water (bottom). The solid lines are the fitted functions as mentioned in the main text.

Presence of H<sub>2</sub>O impurity in NaBr has been confirmed by the appearance of Raman signal in the OH stretch region for the NaBr in D<sub>2</sub>O. The Raman spectrum of NaBr (0.06 mole fraction; the highest concentration of NaBr used in the present study) in D<sub>2</sub>O shows a weak band in the OH stretch regions (green spectrum in the inset of Figure S4) that indicates the presence of H<sub>2</sub>O as an impurity in the hygroscopic NaBr. From the comparative measurements of Raman intensity in the OH stretch regions, it is found that the concentration of H<sub>2</sub>O impurity corresponds to the presence of 0.3 M H<sub>2</sub>O in D<sub>2</sub>O (red line in the inset of Figure S4). Thus, the concentration of H<sub>2</sub>O in 0.06 mole fraction of NaBr in D<sub>2</sub>O is ~ 180 times less than that of D<sub>2</sub>O. Naturally, the H<sub>2</sub>O impurity added with NaBr will have negligible effect on the OD stretch band region. Figure S4 compares the

Raman spectra neat D<sub>2</sub>O (black line) and 0.3 M H<sub>2</sub>O in D<sub>2</sub>O (red line), which shows H<sub>2</sub>O impurity does not significantly affect the OD stretch band of D<sub>2</sub>O or the isotopically diluted water (D<sub>2</sub>O/HOD/H<sub>2</sub>O = 1/18/81). However, the OH stretch band of the corresponding isotopically diluted water (D<sub>2</sub>O/HOD/H<sub>2</sub>O = 81/18/1), is expected to attain significant intensity from the H<sub>2</sub>O impurity. This is why the relative Raman cross-section of isotopically diluted water in the OH stretch region (1.64) is higher than that of the corresponding OD stretch regions (1.46).



**Figure S4.** Raman spectra in the OD stretch regions for neat D<sub>2</sub>O (black), 0.3M H<sub>2</sub>O in D<sub>2</sub>O (red), and 0.06 mole fraction NaBr in D<sub>2</sub>O (green). **Inset:** Raman spectrum in the OH stretch regions for 0.06 mole fraction NaBr in D<sub>2</sub>O (green) and 0.3M H<sub>2</sub>O in D<sub>2</sub>O (red).