

Supporting Information

“Surface Cation Effects on Interfacial Water Organization of Aqueous Chloride

Solutions. I. Monovalent Cations”

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SUPPLEMENTARY FIGURES

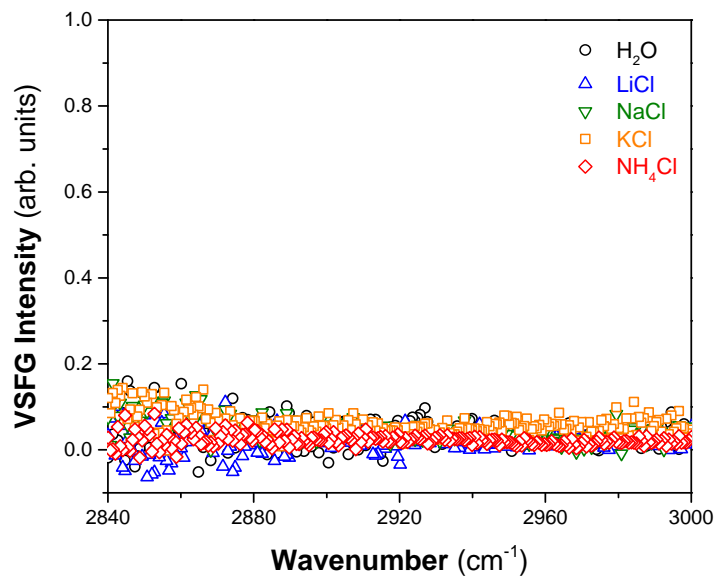


Figure S1. VSFG spectra of filtered chloride salt stock solutions in the CH stretching region.

Neat water spectrum is shown as a reference.

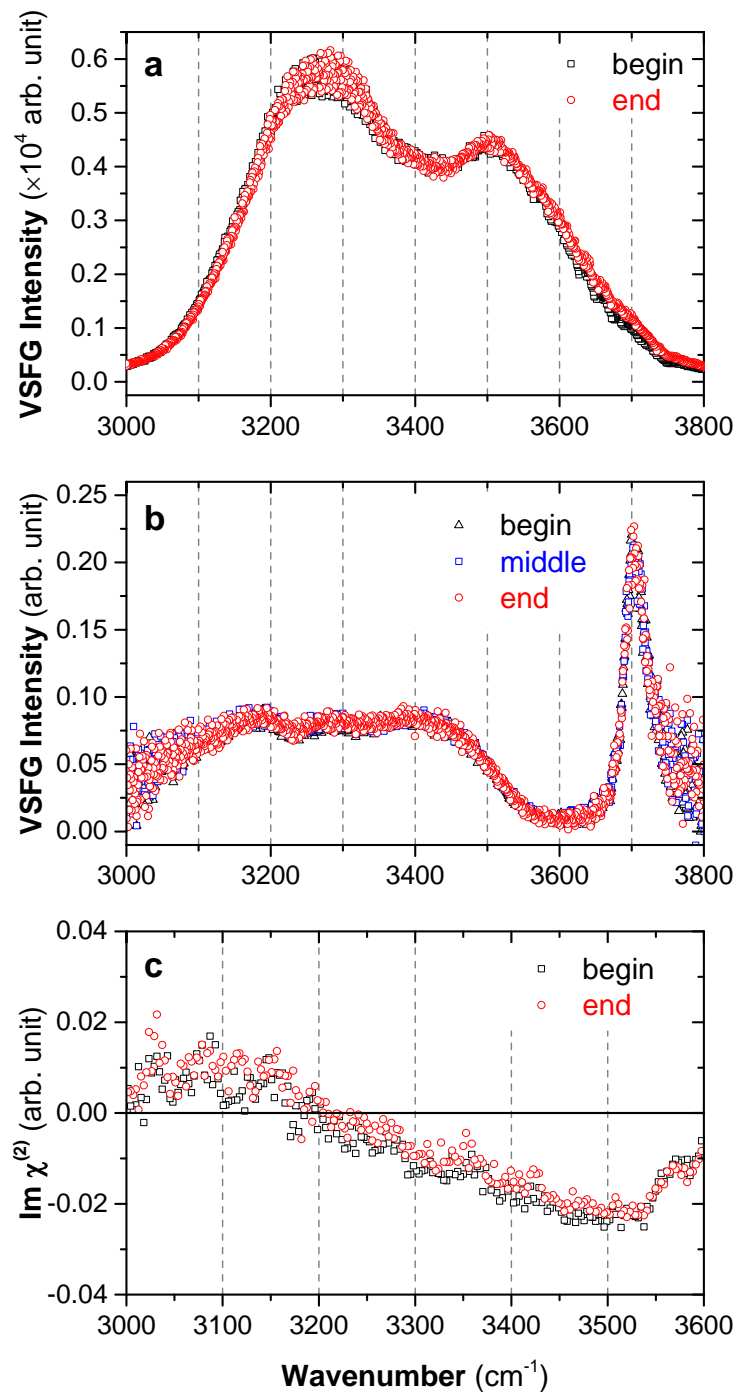


Figure S2. Stability of the SFG system shown by the GaAs profile, conventional VSFG and HD-VSFG $\text{Im } \chi_s^{(2)}(\omega_{\text{IR}})$ spectra of neat water in the OH stretching region (3000–3800 cm⁻¹). (a) GaAs(110) reference crystal profile and (b) conventional VSFG spectra in the OH stretching region, and (c) $\text{Im } \chi_s^{(2)}(\omega_{\text{IR}})$ spectra in the OH stretching region from 3000 to 3600 cm⁻¹.

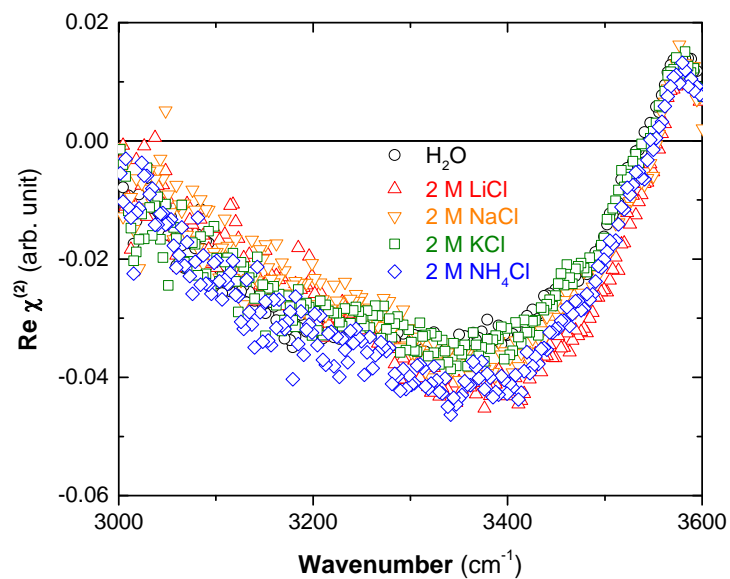


Figure S3. $\text{Re } \chi_s^{(2)}(\omega_{\text{IR}})$ spectra from HD-VSFG results of 2 M chloride salt solutions in the OH stretching region (3000–3600 cm^{-1}). Neat water spectra are shown as reference.

IR and Raman spectroscopy

Bulk infrared (IR) and Raman spectroscopy measurements were also performed for each aqueous chloride salt solutions (Figures S4–S7). The setups for both measurements have been described in detail elsewhere.¹ For the bulk IR measurements, attenuated total reflected (ATR-)IR spectroscopy was used in place of conventional IR transmission spectroscopy because of the unavoidable high molar absorptivity of water in aqueous solutions. IR spectra were not corrected for anomalous dispersion and wavelength dependency of the penetration depth. As shown by Chapados and co-workers,² the interpretation of the IR spectra is not influenced by anomalous dispersion because all samples contain water and are recorded by the same ATR unit. In the Raman measurements, two spectra were averaged for each solution for a total acquisition time of 10 min.

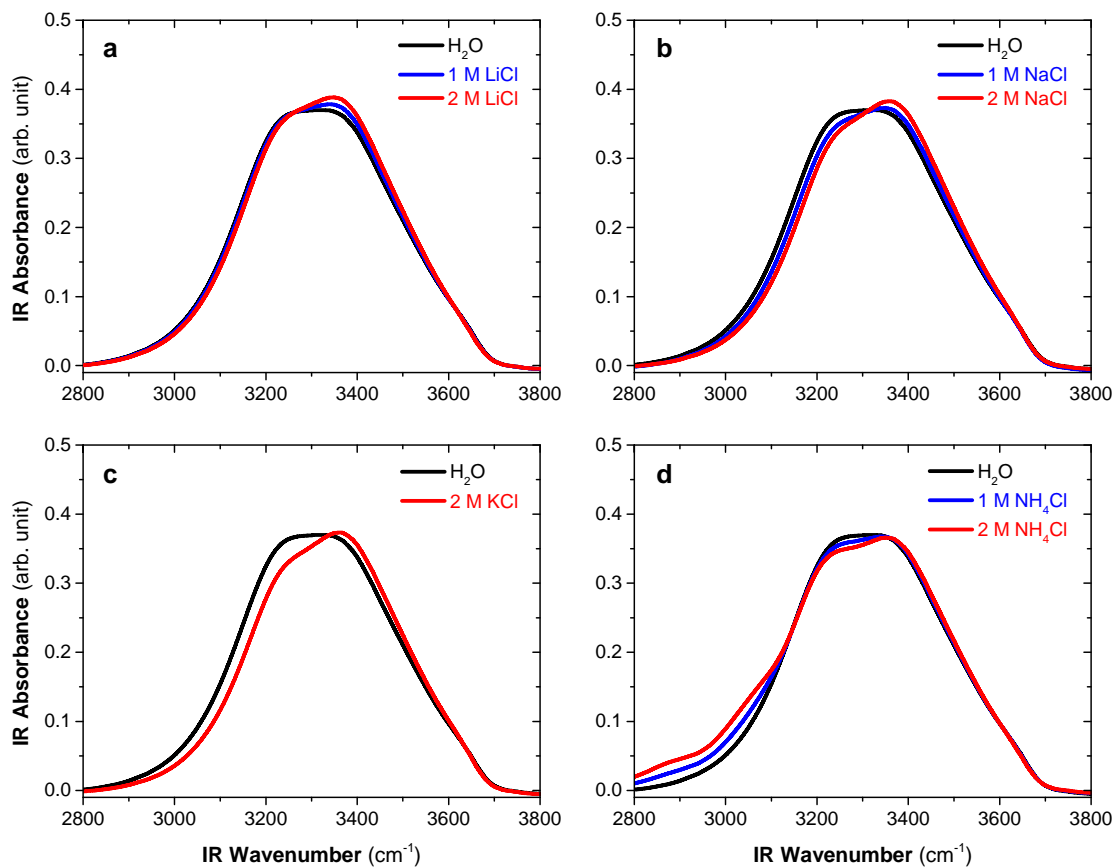


Figure S4. Bulk IR spectra of 1 and 2 M chloride salt solutions. (a) LiCl, (b) NaCl, (c) KCl, and (d) NH₄Cl. Neat water spectrum is shown as a reference.

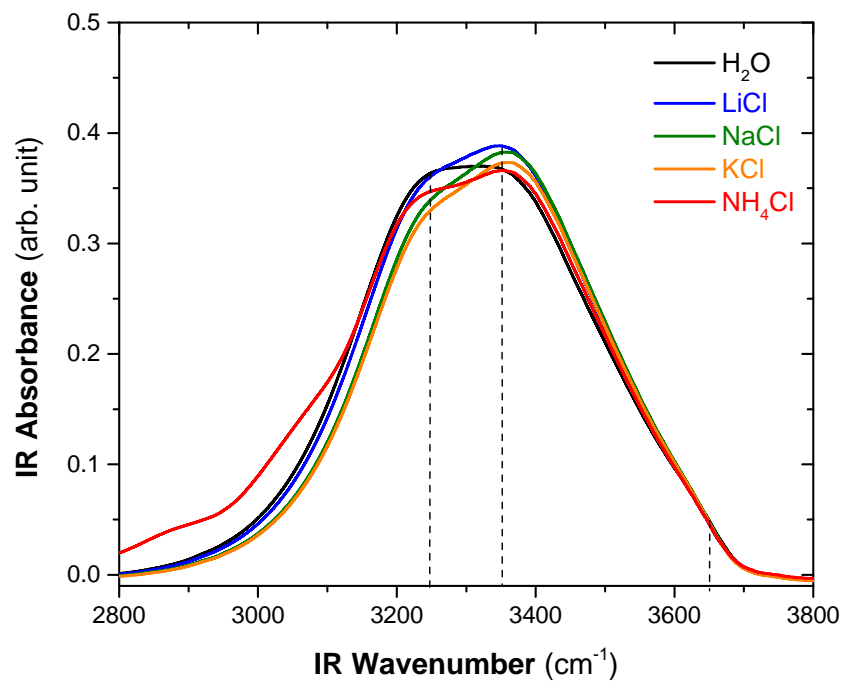


Figure S5. Comparison of bulk IR spectra of 2 M chloride salt solutions in the OH stretching region. Neat water spectrum is shown as a reference.

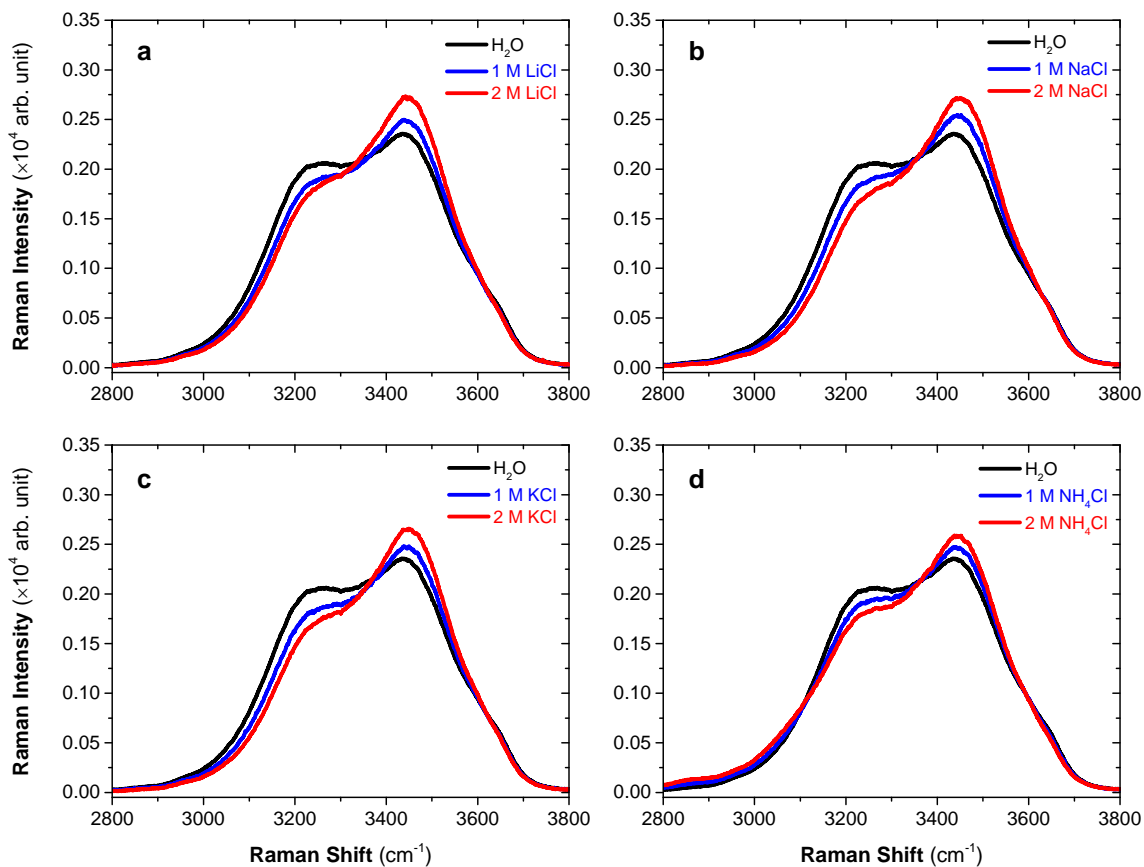


Figure S6. Bulk Raman spectra of 1 and 2 M chloride salt solutions. (a) LiCl, (b) NaCl, (c) KCl, and (d) NH_4Cl . Neat water spectrum is shown as a reference.

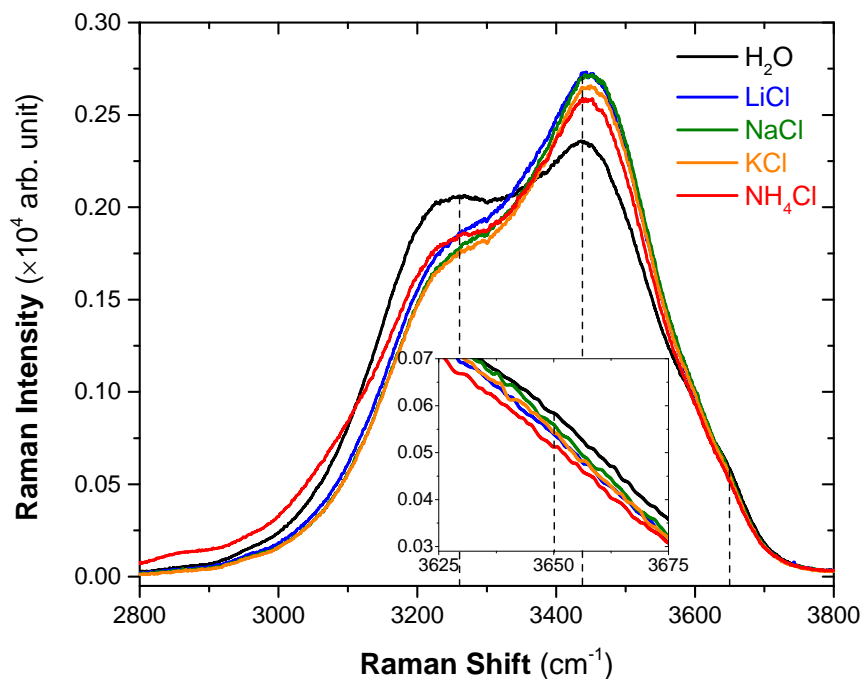


Figure S7. Comparison of bulk Raman spectra of 2 M chloride salt solutions in the OH stretching region. Neat water spectrum is shown as a reference. The region around the band ($\sim 3650\text{ cm}^{-1}$) associated with very weakly hydrogen-bonded water molecules (quasi-“free OH”) is shown in the inset.

REFERENCES

- (1) Huang, Z. S.; Hua, W.; Verreault, D.; Allen, H. C. Salty Glycerol Versus Salty Water Surface Organization: Bromide and Iodide Surface Propensities. *J. Phys. Chem. A* **2013**, *117*, 6346–6353.
- (2) Max, J. J.; Gessinger, V.; Driessche, C. v.; Larouche, P., Chapados, C. Infrared Spectroscopy of Aqueous Ionic Salt Solutions at Low Concentrations. *J. Chem. Phys.* **2007**, *126*, 184507/1–184507/14.