

**Supporting Information. Observation of hydronium ions at the air-aqueous acid interface:
Vibrational spectroscopic studies of aqueous HCl, HBr, and HI solutions**

Lori M. Levering, M. Roxana Sierra-Hernández, Heather C. Allen*

Department of Chemistry, The Ohio State University, 100 W. 18th Ave., Columbus, Ohio
43210; allen@chemistry.ohio-state.edu

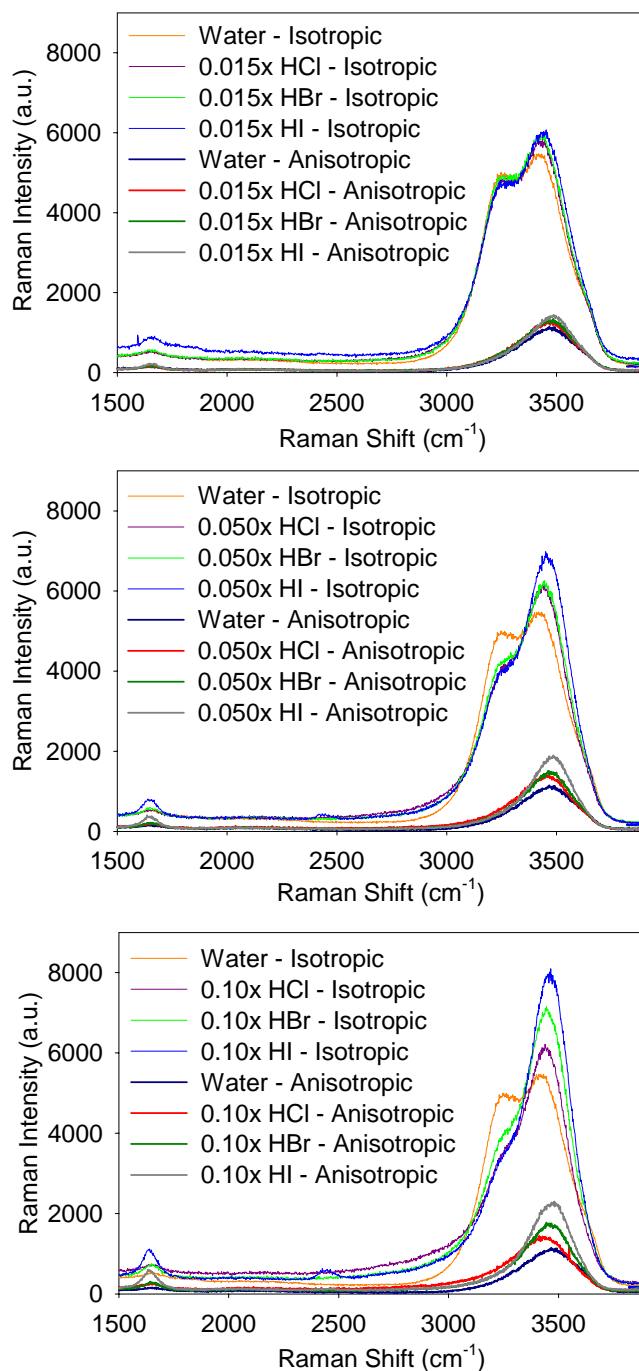


Figure S1. Isotropic and anisotropic Raman spectra of HCl, HBr, and HI aqueous acids plotted together for comparison.

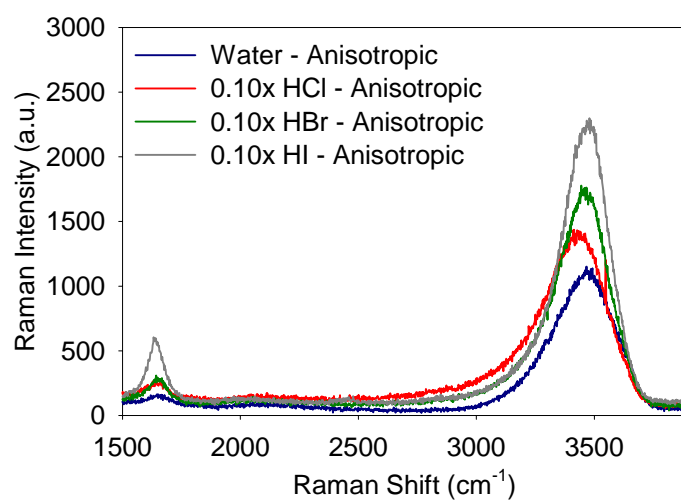
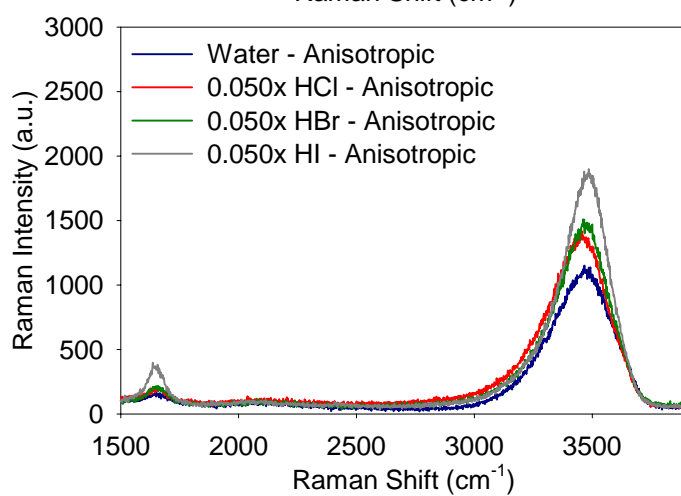
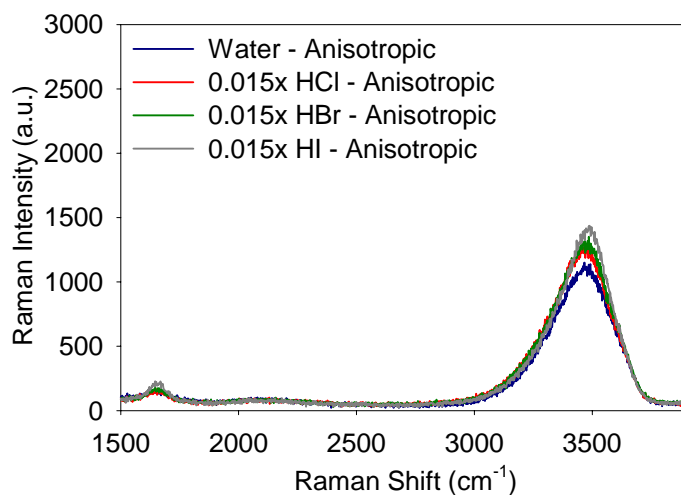


Figure S2. Anisotropic Raman spectra of HCl, HBr, and HI aqueous acids.

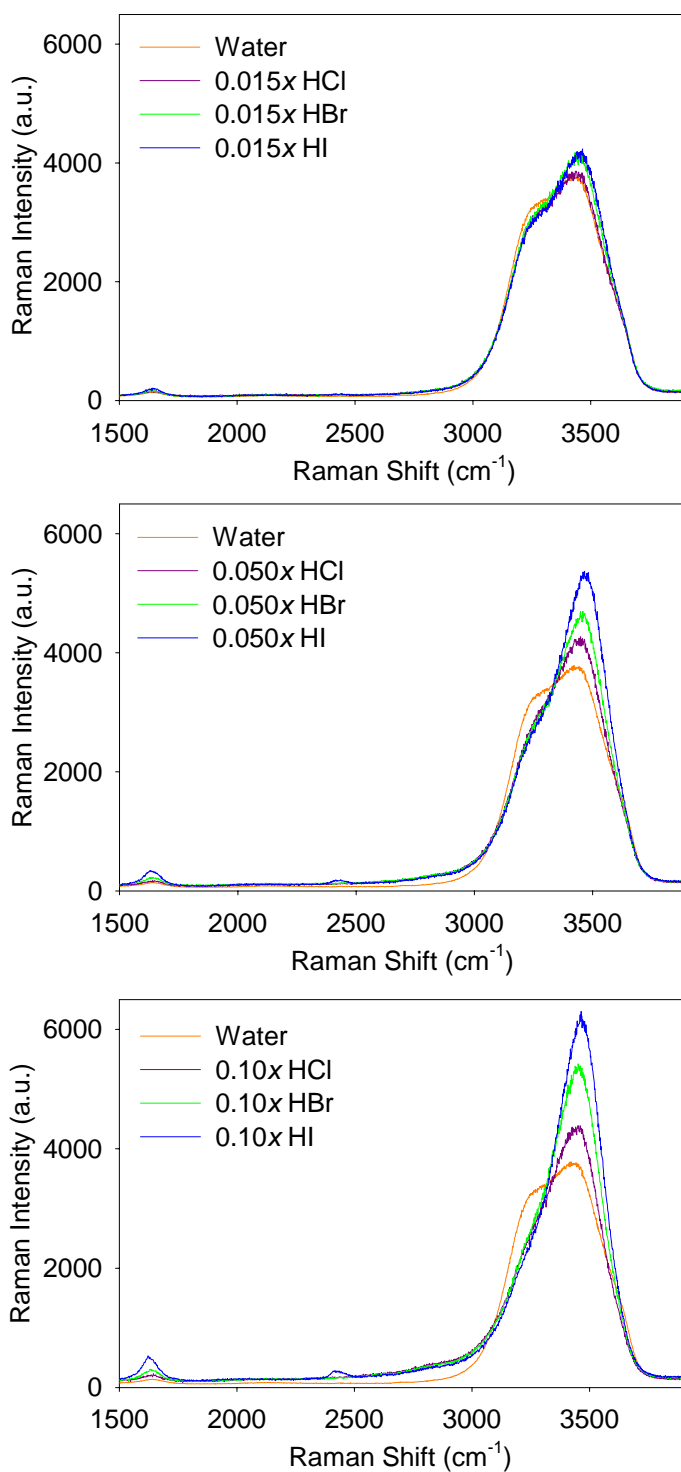


Figure S3. Higher resolution Raman spectra of HCl, HBr, and HI aqueous acids. 600 g/mm grating, Integration time: 30,000 ms, Slit Width: 10 μm , Bandpass: $\sim 2 \text{ cm}^{-1}$, Laser Power: 84 mW, Temp.: $23 \pm 1 \text{ }^\circ\text{C}$.

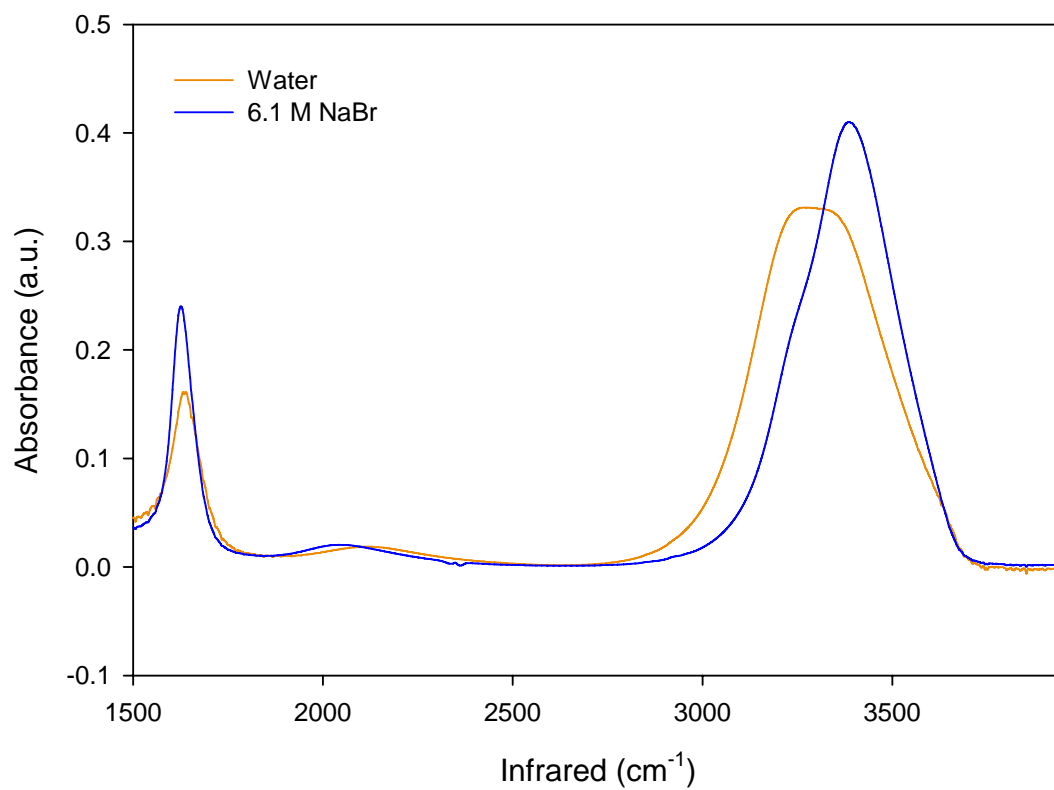


Figure S4. IR spectra of filtered 6.1 M NaBr using a zinc selenide (ZnSe) crystal (4 cm⁻¹ resolution, 64 scans). Neat water is shown for comparison.

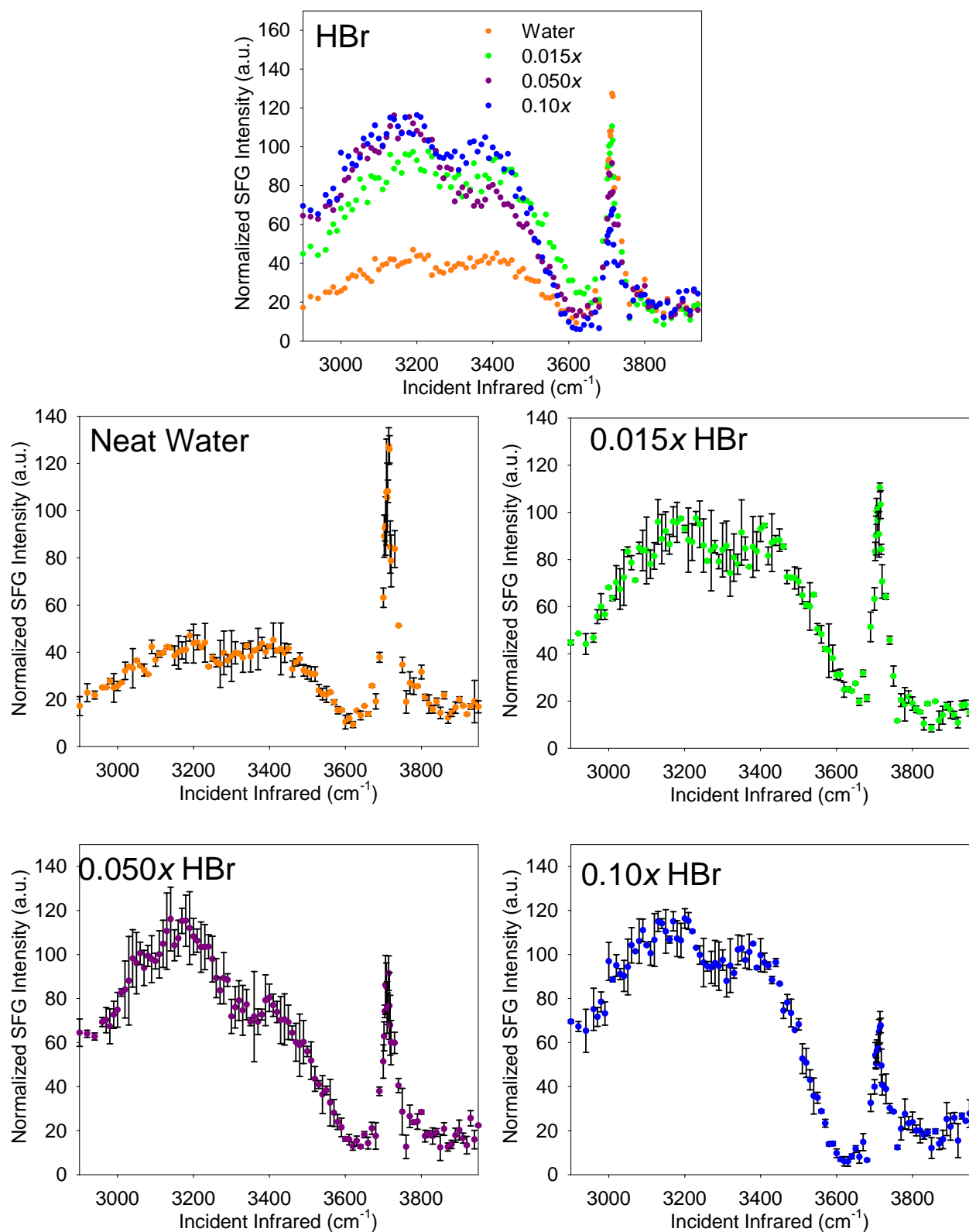


Figure S5. VSGF spectra of HBr concentration series. Error bars are ± 1 standard deviation.

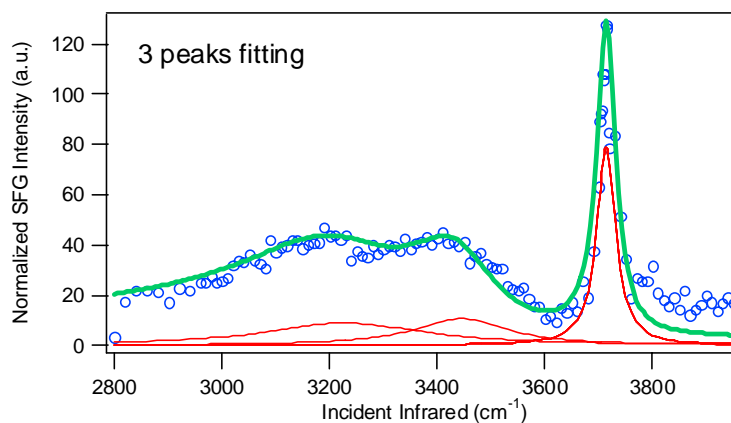
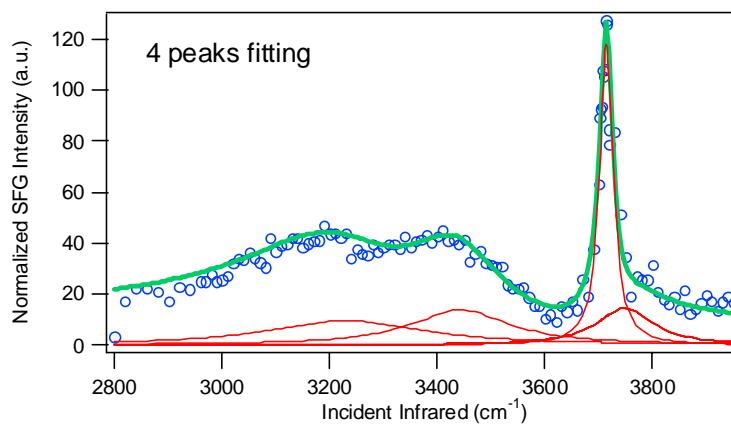
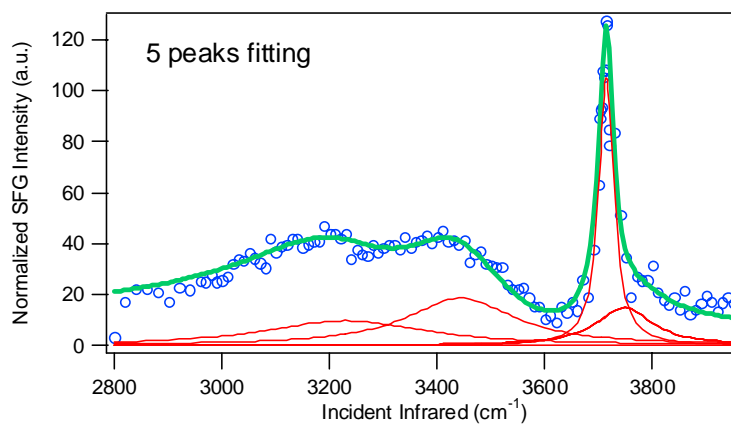


Figure S6. Spectral fits of the VSFG spectra of neat water. It is necessary to use 4 peaks (3229, 3443, 3714, and 3748 cm^{-1}) to fit the neat water spectra.

(5 peaks: 3229, 3443, 3569, 3714, and 3748 cm^{-1} ; 4 peaks: 3229, 3443, 3714, and 3748 cm^{-1} ; 3 peaks: 3229, 3443, and 3714 cm^{-1})

Table S1. Mole fractions and molarities of the aqueous acid and salt solutions.

	Mole Fraction (x)	Molarity (mol/L)
HCl	0.015	0.82
	0.050	2.7
	0.10	5.2
HBr	0.015	0.81
	0.050	2.5
	0.10	4.6
HI	0.015	0.79
	0.050	2.3
	0.10	4.0
NaCl	0.015	0.85
	0.050	2.9
	0.10	6.2
NaBr	0.015	0.85
	0.050	2.9
	0.10	6.2
NaI	0.015	0.85
	0.050	2.9
	0.10	6.2