Supporting Information

Water structure at the air-aqueous interface of divalent cation and nitrate solutions

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Fresnel factors and VSFG spectra normalization

The VSFG intensity, I_{VSFG}, is proportional to the absolute square of the effective sum frequency susceptibility, $\chi_{eff}^{(2)}$, and to the intensities of the visible and infrared incident pulses by[1,2]

$$I_{VSFG} = \frac{8\pi^3 \omega_{VSFG}{}^2 \sec^2 \theta_{VSFG}}{c^3 n_1(\omega_{VSFG}) n_1(\omega_{vis}) n_1(\omega_{IR})} |\chi_{eff}^{(2)}|^2 \, I(\omega_{vis}) I(\omega_{IR}) \tag{1}$$

with

$$\chi_{eff}^{(2)} = \left[\hat{e}(\omega_{VSFG}) \cdot L(\omega_{VSFG})\right] \cdot \chi^{(2)} : \left[L(\omega_{vis}) \cdot \hat{e}(\omega_{vis})\right] \cdot \left[L(\omega_{IR}) \cdot \hat{e}(\omega_{IR})\right] \tag{2}$$

where $n_1(\omega)$ is the refractive index of the bulk medium 1 at frequency ω, $\hat{e}(\omega)$ is the unit electric field vector, and $L(\omega)$ is the Fresnel factor at frequency ω. $\chi_{eff}^{(2)}$, the effective sum frequency susceptibility, is polarization dependent. Under polarization combinations ssp, sps, pss and ppp, $\chi_{eff}^{(2)}$ can be expressed as equation 3, 4, 5, 6, respectively.[1,2]

$$\chi^{(2)}_{eff,ssp} = L_{yy}(\omega_{VSFG})L_{yy}(\omega_{vis})L_{zz}(\omega_{IR})\sin\theta_{IR}\chi_{yyz} \quad (3)$$

$$\chi^{(2)}_{eff,sps} = L_{yy}(\omega_{VSFG})L_{zz}(\omega_{vis})L_{yy}(\omega_{IR})\sin\theta_{vis}\chi_{yzy} \quad (4)$$

$$\chi^{(2)}_{eff,pss} = L_{zz}(\omega_{VSFG})L_{yy}(\omega_{vis})L_{yy}(\omega_{IR})\sin\theta_{VSFG}\chi_{zyy} \quad (5)$$

$$\begin{aligned}\chi^{(2)}_{eff,ppp} &= -L_{xx}(\omega_{VSFG})L_{xx}(\omega_{vis})L_{zz}(\omega_{IR})\cos\theta_{VSFG}\cos\theta_{vis}\sin\theta_{IR}\chi_{xxz} \\ &- L_{xx}(\omega_{VSFG})L_{zz}(\omega_{vis})L_{xx}(\omega_{IR})\cos\theta_{VSFG}\sin\theta_{vis}\cos\theta_{IR}\chi_{xzx} \\ &+ L_{zz}(\omega_{VSFG})L_{xx}(\omega_{vis})L_{xx}(\omega_{IR})\sin\theta_{VSFG}\cos\theta_{vis}\cos\theta_{IR}\chi_{zxx} \\ &+ L_{zz}(\omega_{VSFG})L_{zz}(\omega_{vis})L_{zz}(\omega_{IR})\sin\theta_{VSFG}\sin\theta_{vis}\sin\theta_{IR}\chi_{zzz}\end{aligned} \quad (6)$$

According to above equations, the VSFG intensity is associated with the Fresnel factors. Therefore, when performing the normalization of VSFG spectra, the Fresnel factors should be considered in addition to infrared and visible intensities.

The Fresnel factors are functions of the refractive indices of the beam in different media, and the experimental geometry[1,2]

$$L_{xx}(\omega_i) = \frac{2n_1(\omega_i)\cos\gamma_i}{n_1(\omega_i)\cos\gamma_i + n_2(\omega_i)\cos\theta_i} \quad (7)$$

$$L_{yy}(\omega_i) = \frac{2n_1(\omega_i)\cos\theta_i}{n_1(\omega_i)\cos\theta_i + n_2(\omega_i)\cos\gamma_i} \quad (8)$$

$$L_{zz}(\omega_i) = \frac{2n_2(\omega_i)\cos\theta_i}{n_1(\omega_i)\cos\gamma_i + n_2(\omega_i)\cos\theta_i}\left(\frac{n_1(\omega_i)}{n'(\omega_i)}\right)^2 \quad (9)$$

where $n_m(\omega_i)$ is the refractive index of the bulk medium m (m = 1, 2, ′) at frequency ω_i (i = VSFG, vis, IR), $n'(\omega_i)$ is the effective refractive index of the interface that can be estimated by equation (10)[1] shown below. γ_i is refractive angle into medium 2 defined by

Snell's law $n_1(\omega_i)\sin\theta_i = n_2(\omega_i)\sin\gamma_i$. θ_i is the incident or reflection angle from the interface normal for the beam in consideration.

$$\left(\frac{1}{n'(\omega_i)}\right)^2 = \frac{4n_2^{\ 2}(\omega_i)+2}{n_2^{\ 2}(\omega_i)(n_2^{\ 2}(\omega_i)+5)} \tag{10}$$

For the ssp-polarized VSFG spectra at the air-aqueous interface, the relevant Fresnel factors are:

$$L_{yy}(\omega_{VSFG}) = \frac{2n_1(\omega_{VSFG})\cos\theta_{VSFG}}{n_1(\omega_{VSFG})\cos\theta_{VSFG} + n_2(\omega_{VSFG})\cos\gamma_{VSFG}} \tag{11}$$

$$L_{yy}(\omega_{vis}) = \frac{2n_1(\omega_{vis})\cos\theta_{vis}}{n_1(\omega_{vis})\cos\theta_{vis} + n_2(\omega_{vis})\cos\gamma_{vis}} \tag{12}$$

$$L_{zz}(\omega_{IR}) = \frac{2n_2(\omega_{IR})\cos\theta_{IR}}{n_1(\omega_{IR})\cos\gamma_{IR} + n_2(\omega_{IR})\cos\theta_{IR}}\left(\frac{n_1(\omega_{IR})}{n'(\omega_{IR})}\right)^2 \tag{13}$$

Refractive index of aqueous phase n_2, reflection angle θ of VSFG, refractive angles γ of VSFG and IR, and refractive index of the interface n' are all frequency dependent and therefore are considered when calculating the Fresnel factors and performing the spectra normalization. Refractive indices of water at different wavelengths or wavenumbers were obtained from literature[3,4] and are plotted in Figure S1. For the VSFG system used in this work, the input visible is at 532 nm, and IR varies from 2800 cm^{-1} to 3800 cm^{-1}. The incident angles of visible and IR beams were set to be 45° and 53° to the surface normal. Figure S2 gives the calculated Fresnel factors $L_{yy}(\omega_{VSFG})$ and $L_{zz}(\omega_{IR})$ at the air-neat water interface. $L_{yy}(\omega_{vis})$ of neat water has a value of 0.768.

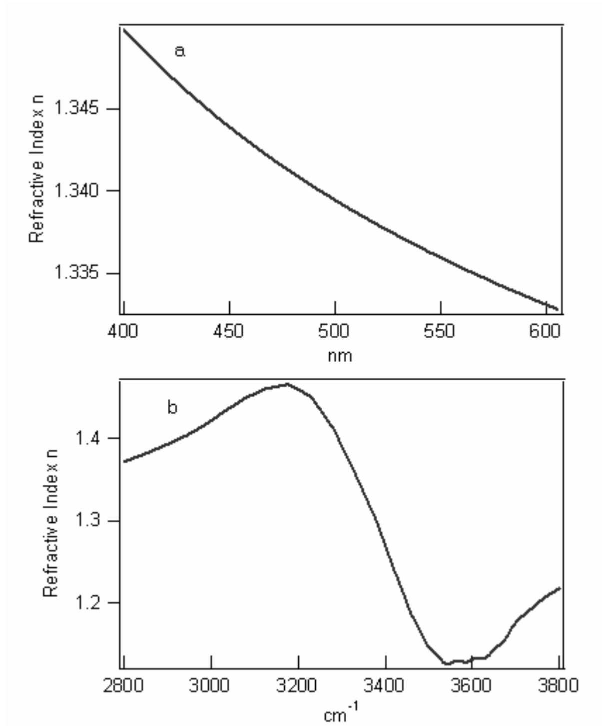

Figure S1. (a) Refractive index of water as a function of wavelength in the visible region; (b) Refractive index of water as a function of wavenumbers of IR.[3,4]

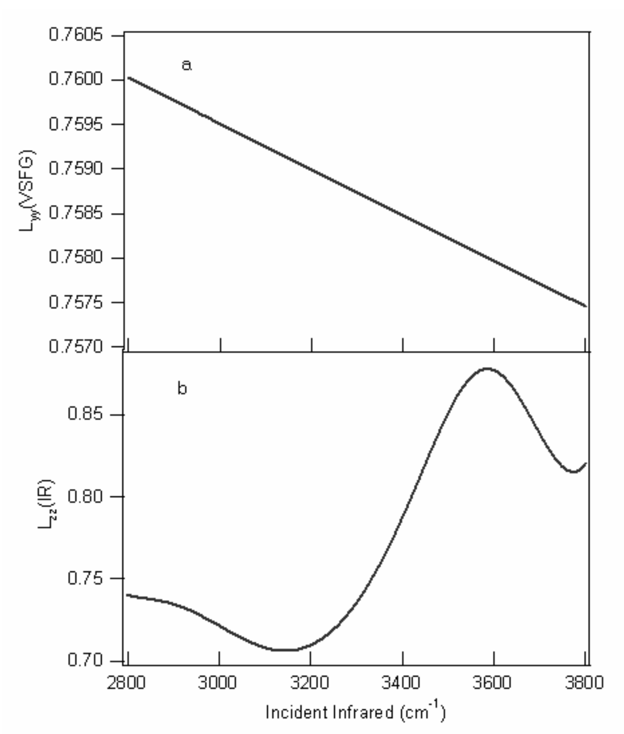

Figure S2. Fresnel factors $L_{yy}(\omega_{VSFG})$ and $L_{zz}(\omega_{IR})$ of neat water as a function of wavenumber of incident IR.

Figure S3a shows the VSFG spectra of neat water and nitrate aqueous solutions normalized to the real-time IR profiles. In the spectra shown in Figure S3b-c, ${\omega_{VSFG}}^2 \sec^2 \theta_{VSFG} \left(L_{yy}(\omega_{VSFG}) L_{yy}(\omega_{vis}) L_{zz}(\omega_{IR})\right)^2$ as well as the IR intensities were employed for the VSFG spectra normalization. In the spectra shown in Figure S3b, we assumed that the refractive indices of neat water and nitrate aqueous solutions are the same. Actually according to our IRRAS and Kramers-Kronig results, the refractive index differences between neat water and the nitrate solutions used in this study are within 5-10%. A difference of 6% in refractive index is therefore utilized in the normalization shown in Figure S3c. Small differences in the hydrogen-bonded OH stretching region are observed when using different normalization methods. In the VSFG spectra shown in Figure S3b-c that are normalized to the Fresnel factors and the real-time IR, the effects of different refractive indices in different media and the effects of experimental geometry that varies from laboratory to laboratory have been considered. However, the same experimental geometry was utilized for the VSFG experiments of water and nitrate solutions, and similar spectral changes are observed in the spectra shown in Figure S3b-c compared to the spectra in Figure S3a. Therefore it is reasonable that the article discussion focuses on the VSFG spectra normalized to IR only.

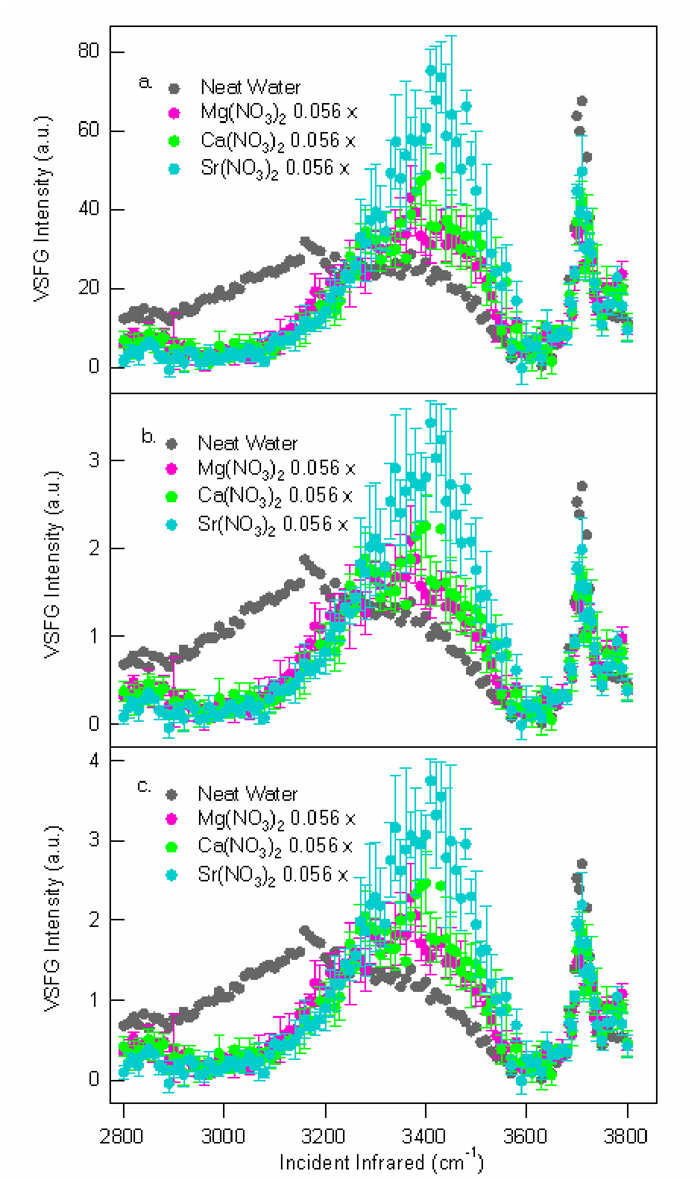

Figure S3. ssp-polairzed VSFG spectra at the air–aqueous interface: (a) VSFG spectra normalized to real-time IR; (b) VSFG spectra normalized to F factor (F= $\omega_{VSFG}{}^{2}\sec^{2}\theta_{VSFG}\left(L_{yy}(\omega_{VSFG})L_{yy}(\omega_{vis})L_{zz}(\omega_{IR})\right)^{2}$) and real-time IR, assuming that neat water and nitrate solutions have the same refractive indices; (c) VSFG spectra normalized to F factor (F= $\omega_{VSFG}{}^{2}\sec^{2}\theta_{VSFG}\left(L_{yy}(\omega_{VSFG})L_{yy}(\omega_{vis})L_{zz}(\omega_{IR})\right)^{2}$) and real-time IR, assuming that the refractive indices of nitrate solutions are 6% higher than that of neat water.

In Figure S4, Raman spectra of NaCl, NaBr, and $NaNO_3$ aqueous solutions are shown for comparison. Note that the bromide and chloride solutions enhance the 3400 cm^{-1} region over that of the nitrate system.

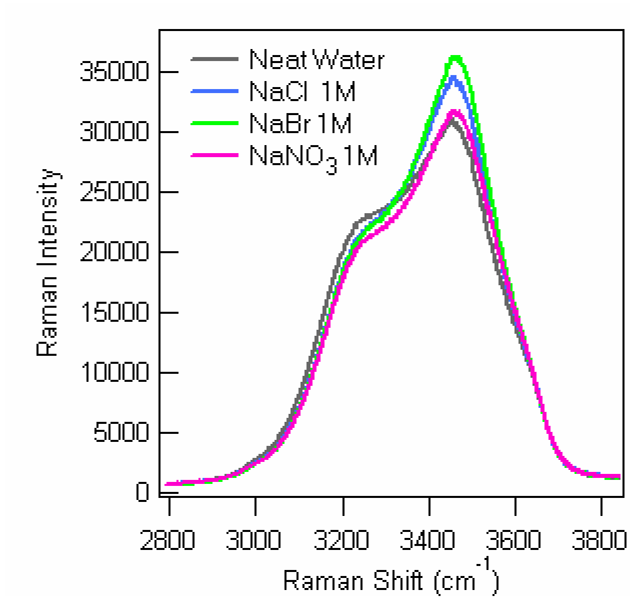

Figure S4. Raman spectra of NaCl, NaBr, and $NaNO_3$ aqueous solutions. Spectrum of neat water is plotted for comparison.

Supporting Information References

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(4) Segelstein, D. J. The Complex Refractive Index of Water. University of Missouri. 1981.