Observation of the Bending Mode of Interfacial Water at Silica Surfaces by Near-Infrared Vibrational Sum-Frequency Generation Spectroscopy of the [Stretch + Bend] Combination Bands

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Supporting Information

ABSTRACT: Vibrational sum-frequency generation (SFG) spectroscopy of interfacial water at mineral/aqueous interfaces is extended to the near-IR range containing the low cross section stretch + bend combination bands ($\nu_{\text{comb}} = \nu_{\text{OH}} + \delta_{\text{HOH}}$) of liquid water at silica surfaces near 5000–5300 cm$^{-1}$, for the first time. The assignments of SFG spectra are supported by FTIR and Raman spectroscopic measurements of the bulk water $\nu_{\text{comb}}$ modes. The SFG spectra contain significant contributions from two combinations, [\(\nu_s + \delta\)] $\approx$ 5060 cm$^{-1}$ and [\(\nu_{as} + \delta\)] $\approx$ 5300 cm$^{-1}$. These measurements provide the first, to our knowledge, reported probe of the bending mode of water at buried interfaces. The data suggest that the interfacial water bending mode is blue-shifted from that of bulk water.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis

Water at interfaces is an active research topic in bio-, geo-, and environmental chemistry. Of particular interest are the molecular structure, acid/base equilibria, and energy-transfer mechanisms at water/mineral interfaces,1−4 which are ubiquitous in the environment as well as in industrial applications. Sum-frequency vibrational spectroscopy (SFVS), or vibrational sum-frequency generation (VSFG) spectroscopy, has proven to be a powerful tool to investigate the properties and structure of water at various types of buried liquid/solid interfaces1,2,5−7 due to its intrinsic sensitivity to noncentrosymmetric environments.1,2

Traditionally, the SFVS of aqueous interfaces has focused on probing the fundamental OH stretch vibrations of interfacial hydroxyls ($\nu_{\text{OH}}$) $\approx$ 3000–3800 cm$^{-1}$, Figure 1A). However, the interpretation of water/mineral SFG spectra is often complicated due to the Fermi resonance between the symmetric OH stretch peak and the overtone of the bending mode.8,9 While the Fermi resonance can be avoided by using isotopic dilution,8,10 probing of HOD molecular species provides information on the local oscillators (O−H and O−D) rather than the collective motion of liquid H$_2$O. Other challenges include the practical inability to distinguish the water OH from surface-bound hydroxyls (e.g., SiOH, AlOH) due to the overlap of the broad hydroxyl stretch spectral responses, as well as the bulk absorption of water in the infrared ($\nu < 3700$ cm$^{-1}$) which limits investigations of buried electrochemical interfaces. The SFG spectra of the water bending mode, which is believed to participate in vibrational energy relaxation processes,11 have just been published for the air/water interface.12 However, due to the infrared absorption by liquid water and the bulk of minerals, the water bending mode is challenging to directly observe in SFG from water at silica and other mineral surfaces.

We believe that such obstacles can be overcome by performing SFVS of the higher-frequency vibrational transitions of interfacial hydroxyls such as combination modes and

Figure 1. SFG vibrational spectra of aqueous/silica interfaces in the fundamental OH stretch (A) and [stretch + bend] combination band (B) ranges. Scales are comparable. SFG spectra were obtained by normalizing raw sample spectra by IR pulse reference SFG spectra (gray shaded region) and the IR-frequency-dependent Fresnel factors ($|L_{zz}(\omega)_{\text{IR}}|^2$, Supporting Information). Red lines: respective fits based on eq 1 (Supporting Information). Note that the fits for SFG spectra from pH2/silica are the simultaneous fit over the range of 3000–5800 cm$^{-1}$.

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overtones, which lie in the near-IR frequency range (\(\sim 4000-8000 \text{ cm}^{-1}\)).\textsuperscript{13} Overtones provide information on anharmonicity and hence bond dissociation energies, while combination modes enable access to low-lying vibrations such as the in-plane and out-of-plane bending of aqueous and surface-bound hydroxyls, which frequently cannot be measured directly due to bulk absorption in the mid-IR by water or minerals.\textsuperscript{13} Thus, near-IR SFVS has the potential to become a powerful technique to investigate water and other interfacial molecules at buried interfaces because many materials are transparent in the near-IR.

The \([\text{bending} + \text{stretch}]\) mode of water \((\nu_{\text{comb}} = \nu_{\text{OH}} + \delta_{\text{HOH}})\) at \(\sim 5200 \text{ cm}^{-1}\) \(\lambda \approx 1.9 \mu\text{m}\)\textsuperscript{14} is unique due to the relatively high frequency of the water bending mode \(\delta_{\text{HOH}} \approx 1645 \text{ cm}^{-1}\)\textsuperscript{14} compared to that of other hydroxyl-containing species (e.g., SiOH, \(\delta \approx 800 \text{ cm}^{-1}\)). This enables direct, unambiguous detection of water in systems such as high-area silicates, zeolites, and so forth.\textsuperscript{13} However, in most previous near- and mid-IR studies, the sample had to be placed into an evacuated atmosphere to avoid complications due to ambient water.\textsuperscript{14} To the best of our knowledge, the surface sensitivity of SFVS has not been applied to the near-IR vibrational combinations and overtones of the interfacial hydroxyls. The most obvious reason is that the combination/overtone transitions are orders of magnitude weaker than fundamental. However, owing to the high signal-to-noise ratio (SNR) of our recently developed broad-band IR SFV spectrometer\textsuperscript{15} and additional enhancement of the resonant response due to a constructive interference with the tail of the intense fundamental stretching band (’self-heterodyning’), it is possible to observe the low cross section combination bands and characterize their spectral shapes precisely.

In the present study, we extend SFVS into the near-IR frequency range (\(\sim 4000 \text{ cm}^{-1}\)) to probe the \([\text{stretch} + \text{bend}]\) combination bands of water molecules at buried interfaces in situ. To complement the SFG, we performed bulk FTIR and Raman spectroscopic measurements in the 4700–5700 cm\(^{-1}\) frequency range. We show that the combination band spectroscopy of interfacial water molecules can access the symmetric and antisymmetric OH stretches individually, even for intramolecularly coupled hydroxyls (avoiding Fermi resonance occurring at around 3400 cm\(^{-1}\)).

For SFVS measurements, we used our newly developed ultra-broad-band spectroscopic setup, based on a noncollinear optical parametric amplifier (NOPA)\textsuperscript{15} that provides high SNR, thus allowing detection of the small cross-sectional vibrational modes in the near-IR. The central frequency of the broad-band IR was tuned to either \(\sim 3400 \text{ or } 5000 \text{ cm}^{-1}\), and SFG spectra were acquired in the two ranges without further tuning the NOPA (Figure 1a,b). The silica/water interface was created by placing IR-grade fused silica (IRFS) hemicylinder prisms on top of the silica/water interface at higher frequencies in the range of 4700–5700 cm\(^{-1}\) (Figure 1). Importantly, in the high-frequency range, the SFG signal decreases as the pH drops or as the salt concentration increases (Figure 2), in correspondence with the OH stretch spectra.\textsuperscript{1,6} The pH dependence of the SFG signal strength is commonly explained by the protonation of the surface SiOH at lower pH forming neutral silanols,\textsuperscript{1} leading to reduced surface charge, a smaller surface electric field into the bulk water, and consequently less contribution of water molecules aligned in the electric field and/or water molecules contributing to the second-order response.\textsuperscript{1,6} The effect of salt (Figure 2B) is to screen the surface electric field by ions.\textsuperscript{6} The similarity of the dependence of the SFG spectra on solution pH and salt concentration in the fundamental and combination band regions clearly supports the interfacial origin of the combination band SFG response. Determining the relative contributions of \(\chi^{(2)}\) and \(\chi^{(3)}\) to the response in the combination band region will require more detailed investigation. The comparison of the observed variation of the SFG spectra in the 4700–5700 cm\(^{-1}\) range with that in the fundamental stretch range (Figure 1) supports the assignment of the observed bands at \(\sim 5000–5300 \text{ cm}^{-1}\) to interfacial water molecules, namely, the stretch + bend combination modes.\textsuperscript{14}

The SFG intensity is related to the surface second-order nonlinear susceptibility, \(\chi^{(2)}\), which, in the case of inhomogeneously broadened oscillators, can be written as follows:\textsuperscript{1}

\[
\chi^{(2)} = \chi_{\text{NR}}^{(2)} \exp(i \varphi_{\text{NR}}) + \sum_{j} \int d\omega j \frac{B_j}{\omega - \omega_j + i\Gamma_j} \times \exp\left(-\frac{(\omega_j - \omega_0)^2}{\sigma_j^2}\right)
\]

(1)

where \(\chi_{\text{NR}}^{(2)}\) and \(\varphi_{\text{NR}}\) are the nonresonant susceptibility and its relative phase, respectively, \(B_j\) is the amplitude of the \(j\)th vibrational mode, \(\Gamma_j\) is the natural line width of the \(j\)th vibrational mode, \(\omega_0\) is the central frequency of the \(j\)th vibrational mode, and \(\sigma_j\) is the inhomogeneous (Gaussian) broadening. Each of the oscillator strength parameters \(B_j\) is related to the molecular second-order polarizabilities \(\beta_j^{(2)}\) via orientational factors. The individual second-order polar-
izabilities are proportional to the IR and Raman responses for the corresponding vibrational mode, \( \delta_{mn}^{\nu_\alpha} \propto (\partial \alpha^{(1)}_{\nu_\alpha}/\partial Q_i)(\partial \mu_{\beta}/\partial Q_j) \), where \( \delta_{mn}^{(1)} \) and \( \partial \alpha_{\nu_\alpha}/\partial Q_i \) are the partial derivatives of the Raman polarizability and IR dipole of the \( \nu_\alpha \) vibrational mode along its normal coordinate \( Q_i \) (the \( mn \) are the axes in the molecular coordinate system). Thus, to complement and achieve the best possible analysis of the SFG spectroscopic data in the 4700–5700 cm\(^{-1}\) range, we invoked the data available from the literature and our FTIR and Raman measurements of liquid water (Supporting Information).

In FTIR spectra of water vapor\(^{16}\) as well as liquid water,\(^{17}\) the combination band peak (\( \approx 5200 \text{ cm}^{-1} \)) has been assigned only to the combination of the antisymmetric stretch and bending [\( \nu + \delta \)] (i.e., \( \nu_3 + \nu_2 \)), although a mode at \( \approx 5000 \text{ cm}^{-1} \) (close to the frequency of the symmetric stretch + bend, [\( \nu_i + \delta \)]) is also typically observed as a shoulder. While FTIR data on the water [stretch + bend] combination are quite abundant in the literature, we found that the Raman spectroscopic data for this mode are practically limited to a single available report by Walrafen and Pugh,\(^{18}\) most likely due to the extreme weakness of the Raman response.

Similarly to previous FTIR studies, we detect an asymmetric peak for liquid water that could be decomposed into a main peak at \( \approx 5200 \text{ cm}^{-1} \) and a shoulder at \( \approx 5065 \text{ cm}^{-1} \) (Supporting Information). More importantly, in our newly measured parallel-polarized Raman spectra (vertical excitation—vertical detection, VV, ||) of the water combination band, we consistenly observe an extremely weak peak at \( \approx 5150 \pm 20 \text{ cm}^{-1} \) with a shoulder at \( \approx 4900 \pm 20 \text{ cm}^{-1} \). The lower-frequency shoulder disappears in the perpendicularly polarized Raman spectra (horizontal—horizontal, HH, Figure 3B). We note that the only available similar Raman spectroscopic investigation\(^{18}\) was performed with rather low resolution and did not involve polarization analysis. The closeness of the main peak positions (\( \approx 5150–5200 \text{ cm}^{-1} \)) in the FTIR and Raman spectra leads us to assign the main Raman peak to the [\( \nu + \delta \)] combination, similar to FTIR.\(^{14,16}\) Additional evidence for this assignment is a high depolarization ratio \( I_{VH}/I_{VV} \approx 0.6 \pm 0.2 \) of the high-frequency component (Figure 3B). The lower depolarization ratio compared to that of nontotally symmetric vibrations (0.75) is explained by imperfections of the polarization analyzer in the Raman spectroscopic setup. On the other hand, the high polarization of the 4900 cm\(^{-1}\) mode, as well as its frequency, suggests that this mode is a [\( \nu_i + \delta \)] combination. The latter assignment has not been fully considered for the vibrational spectroscopy of the liquid water [stretch + bend] mode. The central frequency of the shoulder in FTIR spectra (\( \approx 5060 \approx 3400 + 1650 \text{ cm}^{-1} \)) suggests that it actually must have some contribution from the [\( \nu_i + \delta \)] combination as well. What is more important for the current work is that the two combinations [\( \nu_i + \delta \)] and [\( \nu + \delta \)] are both IR- and Raman-active and can have nonzero oscillator strengths in SFG spectra. We use this conclusion in the analysis of SFG spectra.

The phase analysis of SFG spectra in the high-frequency range is facilitated by the similar magnitude of the resonant and nonresonant \( \chi^{(2)} \) surface nonlinearities, and thus, we can observe interference between them\(^1\) (Figure 1B). Briefly, our interpretation of SFG spectra in the 4000–6000 cm\(^{-1}\) range is based on the conclusions that (1) the phase \( \phi_{\text{NR}} \) of the nonresonant response \( \chi_{\text{NR}}^{(2)} \) relative to the oscillators is close to zero (assuming that \( \chi_{\text{NR}}^{(2)} > 0 \); Supporting Information) as follows from the “derivative”-like shape of the weak combination band peaks\(^{19}\) and (2) a major contribution of the SFG signal in the near-IR range is made by the protruding “tails” of the largely inhomogeneously broadened fundamental OH stretch peaks. Note that if \( \chi_{\text{NR}}^{(2)} < 0 \) is chosen, the relative phase shifts by \( \pi \), and the oscillator strengths change signs. Due to the interference of the intense OH stretch peaks with the nonresonant nonlinearity \( \chi_{\text{NR}}^{(2)} \), the SFG spectra go through a zero minimum at \( \approx 4000–4300 \text{ cm}^{-1} \) (Figure 1B). The appearance of the zero value in SFG spectra is another indication of the near-zero nonresonant phase \( \phi_{\text{NR}} \) with respect to the OH stretches (modeling of SFG spectra at around 4000–5000 cm\(^{-1}\) shows that \( \chi^{(2)} \) cannot cross zero for \( |\phi_{\text{NR}}| \approx \pi/2 \); Supporting Information). Note that the relative phase in the conditions of our experiment is expected to be zero. However, the inclusion of nonzero phase improved the fits significantly (Table S3, Supporting Information). This could be due to some unaccounted for relative phase shifts between the three evanescent waves as well as imperfections in the SFG setup. For charged silica surfaces (pH \( \geq 4 \)), the OH stretch SFG response is large, so that the spectra still have considerable intensity at \( \approx 5000 \text{ cm}^{-1} \) (Figures 1B and 2), on top of which lie the combination band features. (N.B. the y-scale of A in Figure 1 is \( \approx 100 \) times that of B.)

The above conclusions are strongly supported by the SFG spectra from the pH2/silica interface, which demonstrate a reduced contribution of the OH stretch oscillators in the 4000–6000 cm\(^{-1}\) range (Figure 3A). In the case of the pH2/silica surface, the spectrum in the 3000–3800 cm\(^{-1}\) range (Figure 1A) and the spectrum in the 4500–5800 cm\(^{-1}\) range are simultaneously fit while holding the OH stretch parameters fixed (Figure 3A). This analysis also required inclusion of a
mode at $\sim$5060 cm$^{-1}$ with an opposite sign to the 5300 cm$^{-1}$ mode (Figure 3A), which was not as obvious for the SFG spectra from the neat H$_2$O/silica surface due to a large contribution from the OH stretch peak shoulders.

By combining the bulk FTIR and Raman spectra with the SFG data, we developed the following assignments for the observed features in the surface-specific spectra. The frequency of the water combination band in SFG spectra from neat H$_2$O/silica appears at $\sim$5340 cm$^{-1}$, which is $\sim$100 cm$^{-1}$ blue-shifted from the position of a similar peak in FTIR and Raman spectra. The frequency of the hydrogen-bonded bending mode ($\delta \approx 1645$–1650 cm$^{-1}$ in bulk liquid water$^{14}$) suggests that the closest OH-stretching vibration that can form the 5340 cm$^{-1}$ combination band observed in SFG is the 3650 cm$^{-1}$ OH stretch mode (Supporting Information). Raman spectra of bulk water as well as HOD/D$_2$O$^{10}$ contain a similar peak at $\sim$3610–3620 cm$^{-1}$. Because this mode appears in deuterium-diluted samples, it cannot be $\nu_{as}$ and therefore, it is assigned to hydroxyls that are weakly hydrogen-bonded. On the basis of the Raman spectra of bulk water as well as HOD/D$_2$O samples, we assign the 3650 cm$^{-1}$ mode in SFG spectra to weakly hydrogen-bonded hydroxyls of asymmetrically bonded water molecules$^{21}$ (in contrast to the earlier suggestion that it is the antisymmetric OH stretch$^5$).

The assignment for the 5340 cm$^{-1}$ mode as $[\nu_{as}(OH_{3650}) + \delta]$ is partially supported by the fact that it is pronounced in the neat water/silica SFG spectra (Figure 1B), in agreement with the symmetry of the most intense peak in the vibrational (IR and Raman) spectra of bulk water ($\nu_{as}(OH_{3650}) + \delta$). Taking into account the $\sim 25$ cm$^{-1}$ spectral resolution of the ultra-broad-band SFG setup,$^{15}$ as well as $\sim 10$–20 cm$^{-1}$ red shift of the water combination band due to anharmonicity,$^{16}$ we conclude that the bending mode of interfacial water molecules at silica is most likely blue-shifted from the frequency of bulk water by $\sim 10$–20 cm$^{-1}$, or possibly more. A more precise determination would require a higher-resolution SFG measurement. The positive shift from the bulk value suggests increased hydrogen bonding of water molecules at charged silica surfaces.

Thus, we assign the 5340 cm$^{-1}$ combination band to a sum of the weakly hydrogen-bonded OH stretches of interfacial water molecules with the bending mode that is blue-shifted due to the increased hydrogen bonding experienced by the other hydroxyl. Such frequency behavior for the bending mode is consistent with a recent publication by the Benderskii group of this vibration at the air/water interface where it was observed at a blue-shifted value of 1656 cm$^{-1}$, while low-intensity modes were observed even at $>1700$ cm$^{-1}$. The 1656 cm$^{-1}$ mode was assigned to the bending of water molecules with one hydroxyl “sticking” out of the water into the vapor phase. $^{12}$

As the aqueous phase becomes more acidic (pH2), the SFG spectra show a pronounced mode at $\sim$5060 cm$^{-1}$. On the basis of our analysis of the Raman data (Figure 3B), we assign the 5060 cm$^{-1}$ mode in SFG spectra to the combination between the symmetric OH stretch decoupled from the Fermi resonance and the bending mode $[\nu_{s} + \delta]$. The SFG oscillator strength ratio, $B_{5060}/B_{3650}$, was determined to be $\sim 1.28$ at pH2 and $\sim 3.3$ for neat H$_2$O/silica. For both pH values, the peak positions for the two combination bands are close within the resolution of the system, although in the case of pH2, the frequency of the higher-intensity mode is at a slightly higher frequency ($\sim 5360 \pm 25$ cm$^{-1}$) than that at pH6 ($\sim 5325 \pm 25$ cm$^{-1}$). The bandwidths are close to $\sim 100$ cm$^{-1}$ and are consistently close to the widths of the fundamental OH stretches. The latter suggests that the surface bending mode width is relatively narrow compared to the hydroxyl stretch widths, consistent with $\sim 40$ cm$^{-1}$ widths observed for the water/air interface.$^{12}$ The frequency of the $[\nu_{b} + \delta]$ mode yields $\nu_{b} \approx 3400 \pm 50$ cm$^{-1}$, which is close to the uncoupled OH peak position ($\sim 3430$ cm$^{-1}$) in the isotropic Raman spectra of diluted HOD/D$_2$O (when intra- and intermolecular couplings are avoided).$^{9,20}$ Note also that the signs of the two modes at 5060 and 5300 cm$^{-1}$ are opposite, which reflects the opposite directions of the dynamic dipole moments.$^1$ This supports the suggestion that these modes correspond to distinct species.

Another possible assignment is that the 5340 cm$^{-1}$ mode is formed by the asymmetric stretch $\nu_{as} \approx 3550$ cm$^{-1}$ and a greatly blue-shifted bending mode $\sim 1780$–1800 cm$^{-1}$, while the 5060 cm$^{-1}$ mode in this case would be formed by the same bending mode and the symmetric stretch at $\sim 3280$ cm$^{-1}$. However, such a position of the bending mode is much higher than even that in crystalline ice ($\sim 1710$ cm$^{-1}$)$^{12}$ and seems unrealistic.

Several important conclusions are due. While in bulk water the most intense combination band is formed by the antisymmetric stretch, $\nu_{as} \approx 3550$ cm$^{-1}$ and the bending mode $\delta \approx 1650$ cm$^{-1},^{14}$ in SFG spectra, we observe the main combination band to be formed by the asymmetric weakly hydrogen-bonded hydroxyls, $\nu_{as} \approx 3650$ cm$^{-1}$ and the bending mode. These results require further detailed investigation, with involvement of theory. However, in general, such a change of coupling of the hydroxyl stretches with the bending mode may be associated with water molecules close to the interface that undergo asymmetric bonding with one of hydroxyls hydrogen-bonded weaker than the water molecules in the bulk.$^{14}$ Further, we believe that the current assignment of the observed combination peaks from bulk water in FTIR spectra exclusively to $[\nu_{as} + \delta]$ needs to be revisited as our Raman and SFG data clearly show a strong contribution from the $[\nu_{b} + \delta]$ mode. Lastly, the appearance of the two combination bands in SFG from charged surfaces and bulk Raman spectra (and possibly IR) indicates the similarity between these spectra.$^7$ Moreover, the similar ratio of the oscillator strengths $B_{5060}/B_{3650}$ for pH6/ silica and pH2/silica surfaces additionally indicates that the SFVS of silica/water within at least the pH 2–6 range probes the same molecular species, while only the number of the probed molecules and the averaged orientation angle are changing with pH according to the strength and extent of the penetration of the surface electric field into the liquid phase.

The observation of the water combination [stretch + bend] band in SFG spectra is significant because the combination is orders of magnitude weaker than the bend in FTIR and Raman spectra. Furthermore, it provides access to the bending mode of interfacial H$_2$O. Thus, we believe that, for the first time, our measurements detect the surface water bending mode at a buried interface, similar to the indirect assessment of the low-frequency deformation modes in silicates and zeolites via combination modes in the near-IR.$^{13}$ The fits of SFG spectra from pH2/silica indicate that the combination band oscillator strengths are $\sim 200$ times weaker than those of the OH stretch peaks (Supporting Information), which would be expected from FTIR and Raman data. (N.B. $B_{5060} \approx (\partial \mu/\partial Q) (\partial \mu/\partial Q)$, while $\partial \mu/\partial Q \approx (\partial \mu/\partial Q) \approx (\partial \mu/\partial Q)$.)

In summary, we have detected the SFG response of [bend + stretch] combination bands of water molecules at silica surfaces and provided their assignments, for the first time. We revisit FTIR and Raman spectra of the water combination bands in
the bulk and show that the SFG of water at charged SiO₂ as well as bulk water Raman and FTIR responses have contributions from \( \nu_s + \delta \) and \( \nu_a + \delta \). Such correspondence between spectra suggests similar structures of bulk water and H₂O/SiO₂ as was observed for water at charged surfactant surfaces, although the dynamics are much different.\(^3\) We believe that these are the first surface-specific spectroscopic measurements accessing the water bending mode at buried interfaces. The frequency of the interfacial water bending mode appears to be blue-shifted from that of the bulk water, while the near-IR SFVS data suggest that \( \delta \) couples with the asymmetric stretch of the weakly-hydrogen bonded hydroxyls. The data indicate the presence of asymmetrically-bonded water molecules with one hydroxyl undergoing increased hydrogen bonding at a charged silica/aqueous interface. In addition, SFG spectroscopy in the near-IR directly provides phase information for SFG spectra of mineral/water interfaces; the magnitude of the resonant SFG response in the near-IR is comparable to the nonresonant part so that their mutual cancellation yields near-zero net SFG spectra. Hence near-IR SFG has a potential to become a powerful technique to observe water and other interfacial molecules, in particular, low-frequency modes, at buried interfaces. The full potential of near-IR SFG should be realized with further technical advancements in SFG spectroscopy.

ASSOCIATED CONTENT

Supporting Information

Description of the experimental procedure, fitting analyses of the Raman spectra of bulk water, and fit results for SFG spectra from neat H₂O/silica and pH2/silica over the 3000–5800 cm⁻¹ range. 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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