

Sum-Frequency Vibrational Spectroscopy on Water Interfaces: Polar Orientation of Water Molecules at Interfaces

Yuen Ron Shen* and Victor Ostroverkhov†

Department of Physics, University of California, Berkeley, California 94720

Presented by Seok, Sangjun

□ Surface Sum-Frequency Vibrational Spectroscopy

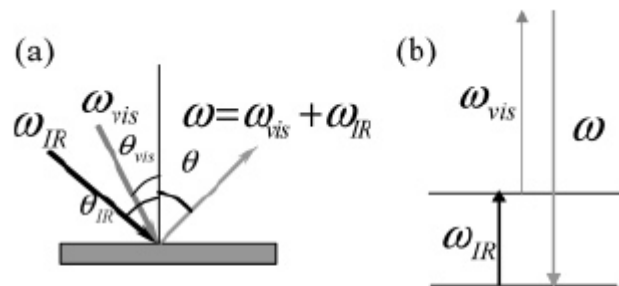


Figure 1. Schematic representation of (a) the sum frequency generation process at an interface detected in the reflection direction and (b) the sum-frequency generation process with ω_{IR} at resonance with a vibrational transition.

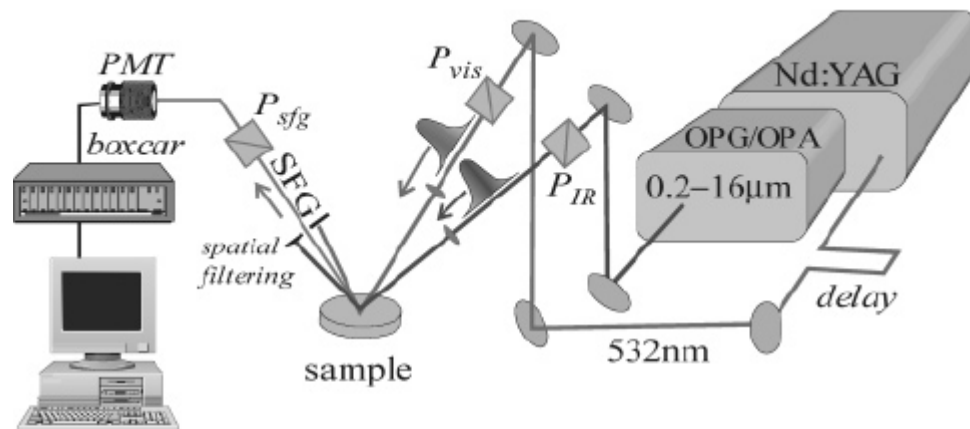
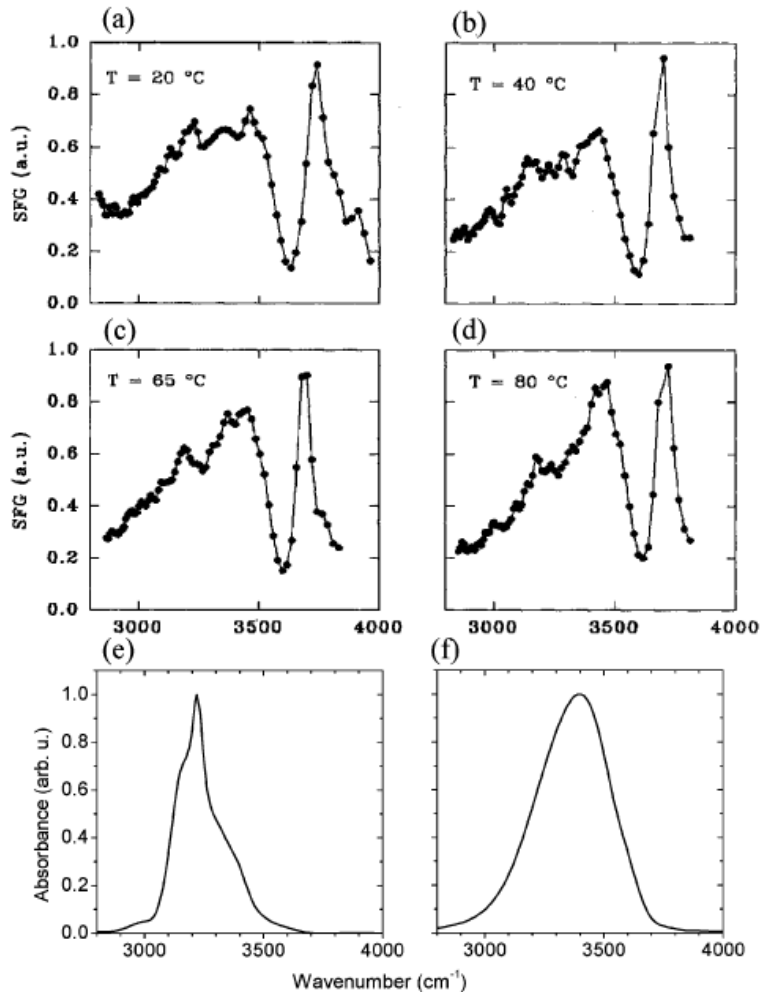


Figure 2. A typical experimental arrangement for SFVS. OPG/OPA refers to an optical parametric generator/amplifier system, and PMT denotes a photomultiplier tube. P_{vis} , P_{IR} , and P_{sfg} are polarizers for visible, IR, and sum-frequency beams, respectively. The propagation direction of the output SF beam is defined by the tangential wave vector matching condition at the interface: $k^{\parallel} = k_{vis}^{\parallel} + k_{IR}^{\parallel}$.

□ Sum-Frequency Vibrational Spectra of water

- Vapor/Water Interfaces



In the form of a mixed ordered and disordered hydrogen-bonding network

Figure 3. SFVS spectra (a–d) of the water/vapor interface at four temperatures collected with SSP polarization combination (Reprinted Figure 3 with permission from ref 23. Copyright 1993 by the American Physical Society. <http://link.aps.org/abstract/PRL/v70/p2313>), (e) Bulk absorbance of hexagonal ice (I_h) at 100 K (from data in Bertie et al., ref 59), and (f) bulk absorbance of bulk water (from data in Query et al., ref 60).

□ Sum-Frequency Vibrational Spectra of water

- Vapor/Water Interfaces

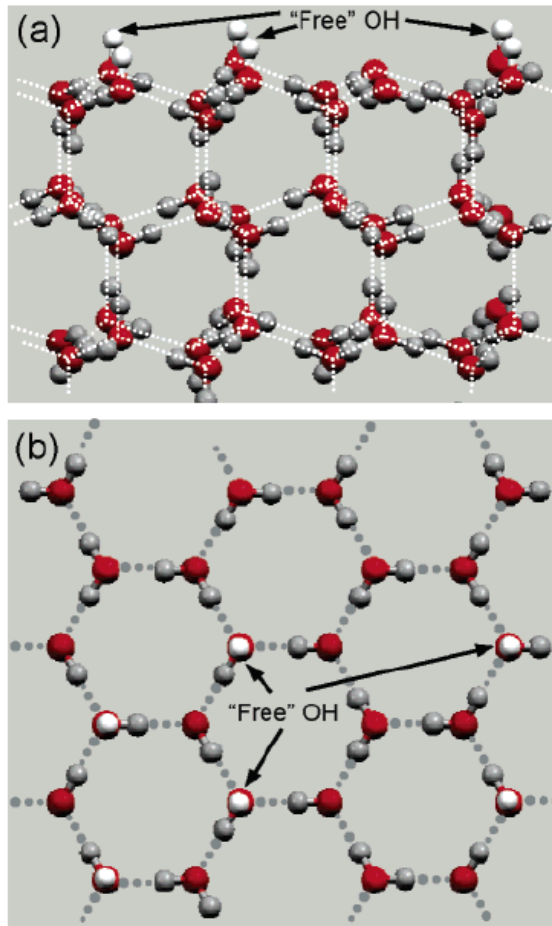
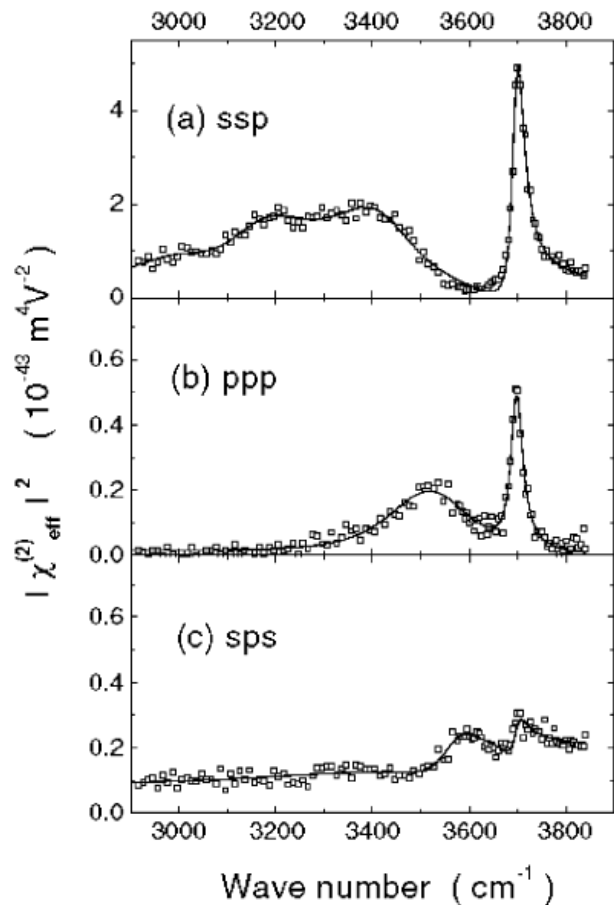


Figure 4. Molecular structure of hexagonal ice (I_h) crystal: (a) side view of the bulk near the (0001) surface; (b) top view of the (0001) plane. Red spheres represent O atoms (dark and light shades highlight higher and lower submonolayers in a single ice monolayer); gray and white spheres represent H atoms that are hydrogen-bonded to neighboring molecules and free-dangling nonbonded surface species, respectively. Dotted lines indicate hydrogen bonds.

□ Sum-Frequency Vibrational Spectra of water

- Vapor/Water Interfaces



The 3600cm⁻¹ peak can be assigned mainly to the bonded OH stretch mode of surface water molecules with one bonded OH and one dangling OH.

Figure 5. SFG vibrational spectra of water/vapor interface taken with (a) SSP, (b) PPP, and (c) SPS polarization combinations. Reprinted Figure 2 with permission from ref 62. Copyright 2001 by the American Physical Society. <http://link.aps.org/abstract/PRL/v86/p4799>.

□ Sum-Frequency Vibrational Spectra of water

- Vapor/Water Interfaces

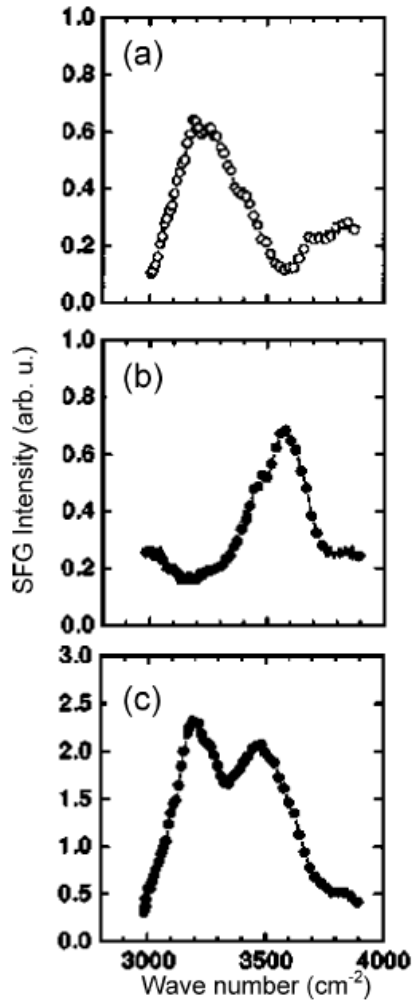
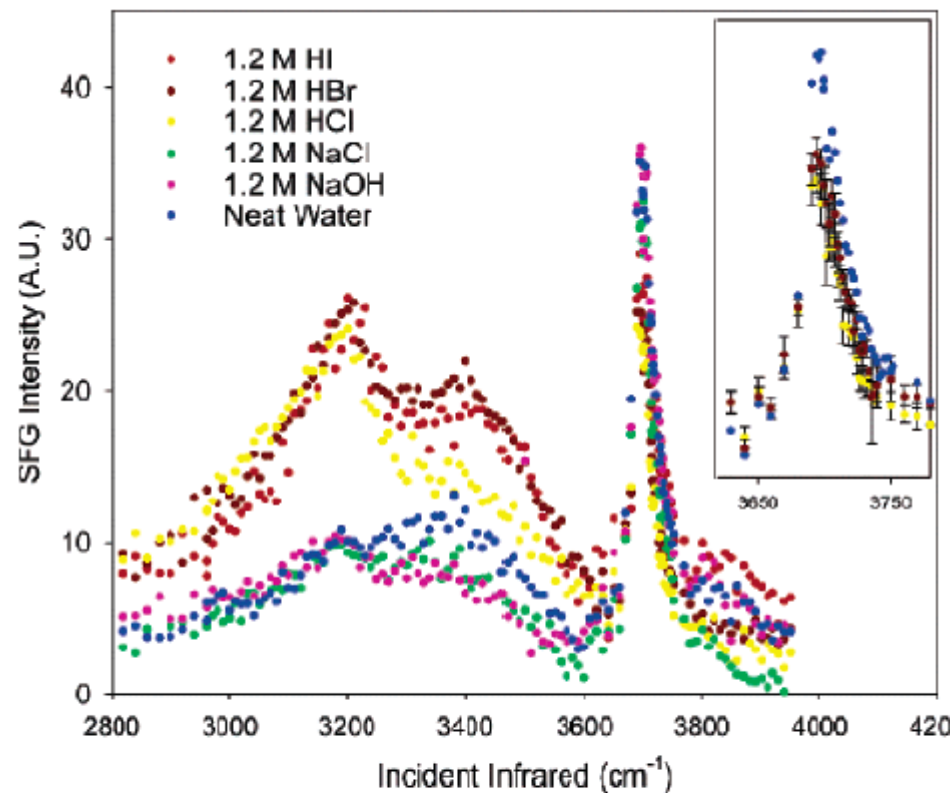


Figure 6. SFG spectra of water interfaces with (a) an octadecanol monolayer on water and (b,c) a hexacosanoic acid monolayer on water at (b) pH = 3.9 and (c) pH = 8.0. Reprinted from ref 84, Copyright 1998, with permission from Elsevier.

□ Sum-Frequency Vibrational Spectra of water

- Vapor/Water Interfaces



For solution of HBr and HI, both icelike and liquidlike peaks show significant enhanced.

Surface field created by excess negative ions at the interface.

The free OH peaks for the acidic solutions are weaker due to hydronium ions at the interface.

Figure 7. SFG spectra of water/vapor interfaces for neat water and several acid, base, and salt solutions. The inset shows an extended view of the dangling OH peak on neat water (blue), 1.2 M HCl (yellow), and 1.2 M HBr (brown). Reprinted with permission from ref 80. Copyright 2005 American Chemical Society.

□ Sum-Frequency Vibrational Spectra of water

- Hydrophilic Solid/Water interfaces

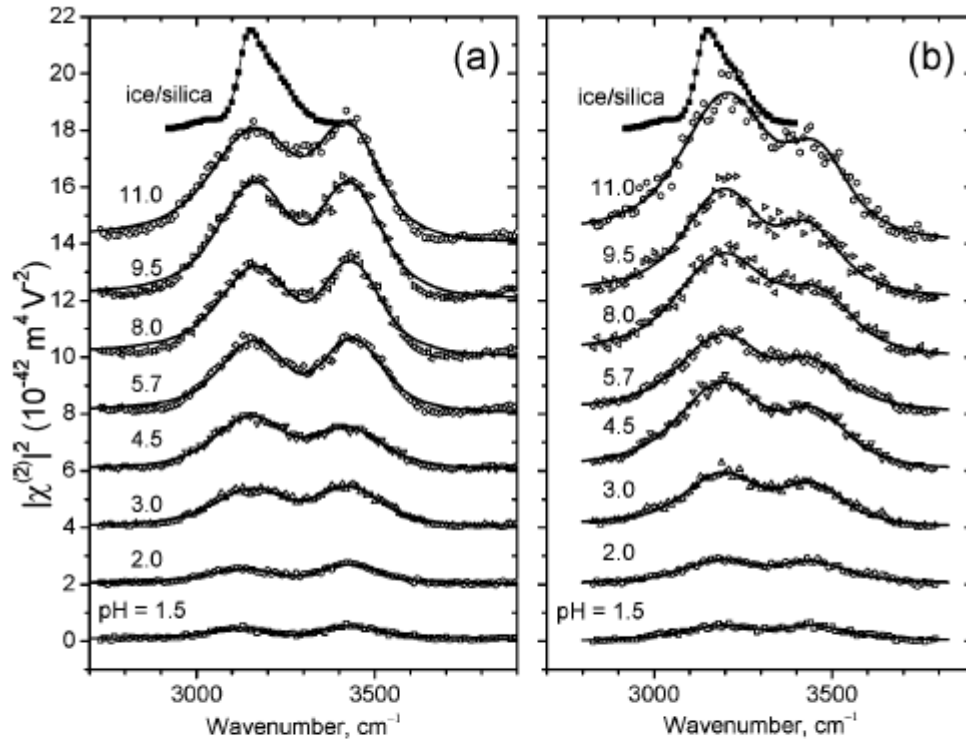


Figure 8. SFG spectra of interfaces of water with (a) the (0001) plane of α -quartz and (b) fused silica as a function of pH. Polarization combination is SSP. A spectrum of the ice/fused silica interface is shown for comparison (filled squares). The spectra are offset vertically by 2 units for clarity. Reprinted from ref 100, Copyright 2004, with permission from Elsevier.



The free OH peak is missing

The high pH is better polar ordered network at high pH.

It is phase changed by 180 deg. if the net polar orientation of interfacial water molecules when the bulk pH switches from low to high value.

It need an interference measurement on the SF output.

□ Sum-Frequency Vibrational Spectra of water

- Hydrophilic Solid/Water interfaces

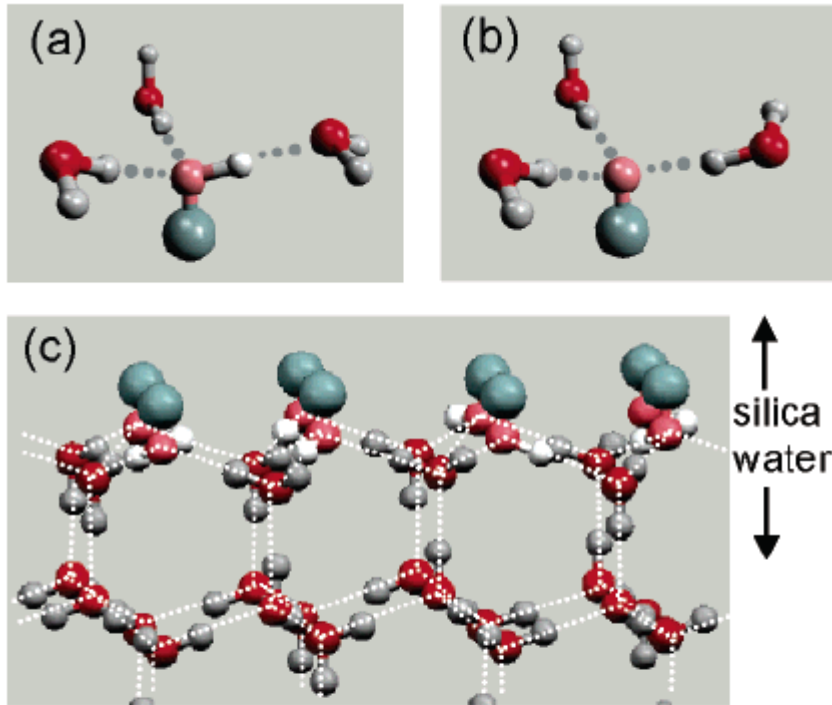
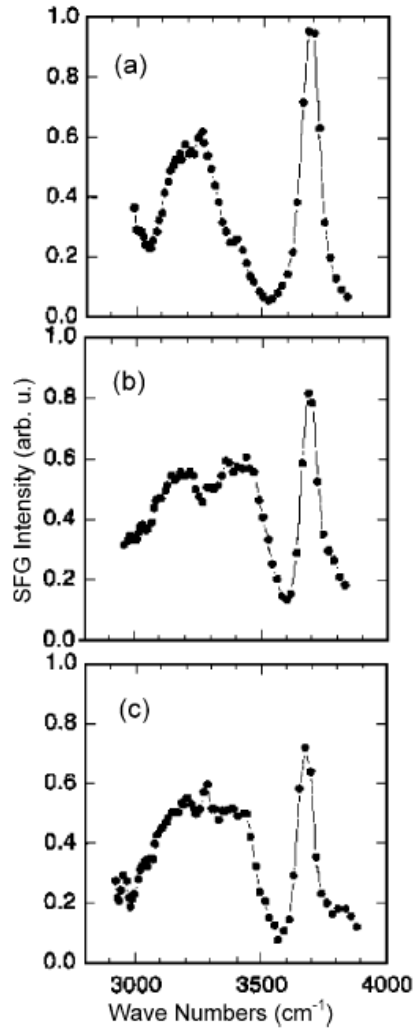


Figure 9. Possible hydrogen-bonding configuration of water molecules on hydrophilic silica surface: (a) protonated (SiOH) surface sites, low pH; (b) deprotonated (SiO⁻) surface sites, high pH; (c) structure of water/silica interface at low pH. Red and gray spheres represent O and H atoms of water molecules; large gray-green, pink, and white spheres represent Si, O, and H atoms of SiOH groups at silica surface. Dotted lines indicate hydrogen bonds.

□ Sum-Frequency Vibrational Spectra of water

- Hydrophobic Interfaces



Rigid wall could force the interfacial water molecules to form a more ordered bonding network.

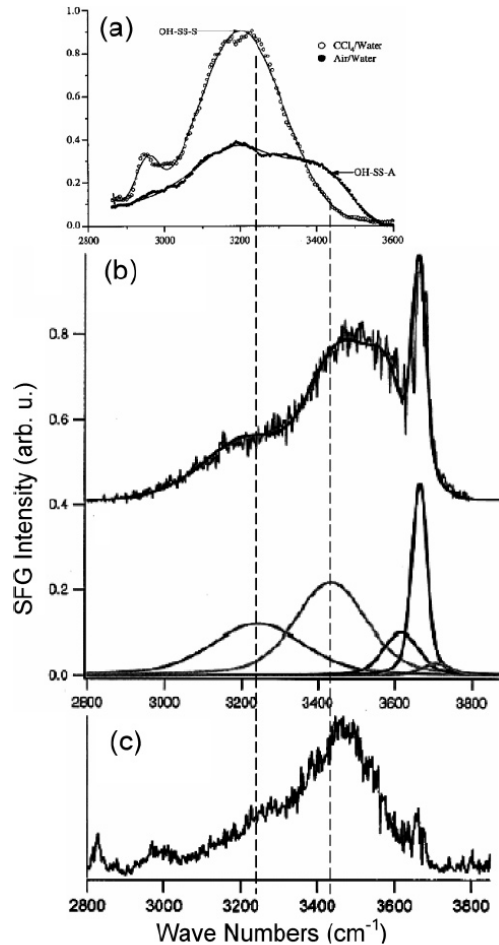
The water interfacial is not rigid.

Figure 10. SFG spectra of water on solid and liquid hydrophobic interfaces: (a) water/octadecyltrichlorosilane (OTS)/fused silica interface; (b) water/vapor interface; (c) water/hexane interface. Reprinted with permission from *Science* (<http://www.aaas.org>), 24. Copyright 1994 AAAS.

□ Sum-Frequency Vibrational Spectra of water

- Hydrophobic Interfaces

Rigid wall could force the interfacial water molecules to form a more ordered bonding network.



The water interfacial is not rigid.

Figure 11. SFG spectra of water–oil interfaces: (a) spectra of water/vapor and water/ CCl_4 interfaces from an earlier work (Reprinted with permission from ref 65. Copyright 1998 American Chemical Society); (b) spectrum of water/ CCl_4 interface from Brown et al. (Reprinted with permission from ref 66. Copyright 2000 American Chemical Society)—the solid line is a fit using the modes described by the bottom curves; (c) spectrum of water/hexane interface (Reprinted with permission from ref 110. Copyright 2001 American Chemical Society). Vertical lines are guide to the eye for the positions of icelike and liquidlike peaks of decomposition in panel b.

Phase-Sensitive Sum-Frequency vibrational Spectroscopy

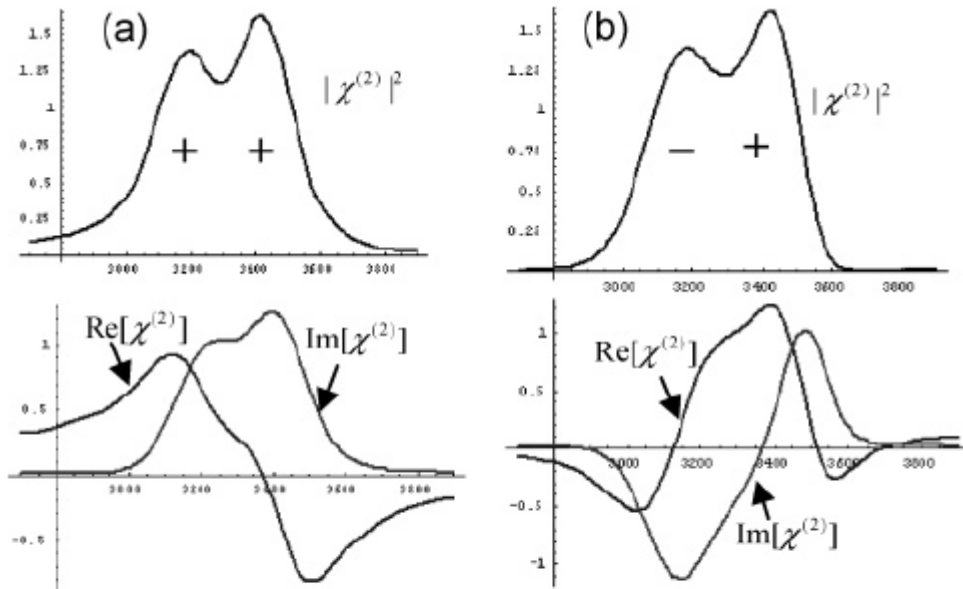


Figure 12. Simulated spectra of two overlapping spectral peaks with amplitudes having (a) the same relative sign and (b) the opposite signs. The $|\chi^{(2)}|^2$ spectra are generated from the corresponding spectra of $\text{Re}[\chi^{(2)}]$ and $\text{Im}[\chi^{(2)}]$.

The phase measurement can be achieved by an interference method.

□ Phase-Sensitive Sum-Frequency vibrational Spectroscopy

$$\overleftarrow{\chi}_{eff}^{(2)} = \chi_s^{(2)} + \chi_b^{(2)} / (i\Delta k)$$

$\Delta k = |k_{vis,z} + k_{IR,z} - k_z|$ is the wave-vector mismatch of SFG along the surface normal direction.

$$S(\omega) \propto \left| \chi_s^{(2)} + \chi_b^{(2)} / (i\Delta k) \right|^2 = \left| \chi_s^{(2)} \right|^2 + \left| \chi_b^{(2)} / (i\Delta k) \right|^2 - 2 \left| \chi_s^{(2)} \chi_b^{(2)} / (\Delta k) \right| \sin \Phi(\omega)$$

$\Phi(\omega)$ is the relative phase of $\chi_s^{(2)}$ with respect to $\chi_b^{(2)}$

$$\Phi(\omega) = \sin^{-1} \left\{ \frac{S_{SB}(\omega) - S_S(\omega) - S_B(\omega)}{2[S_S(\omega)S_B(\omega)]^{1/2}} \right\}$$

Phase-Sensitive Sum-Frequency vibrational Spectroscopy

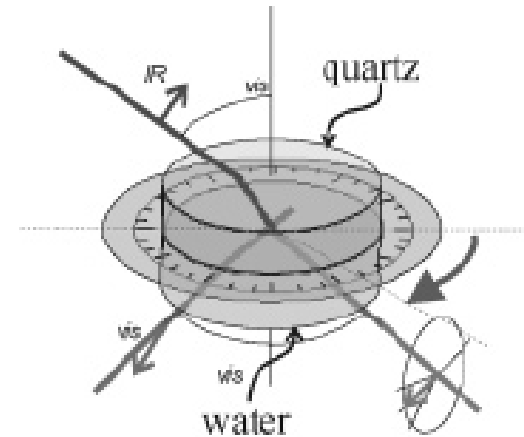
Using 3-fold symmetry of quartz, small angle $\pm\gamma$ from S polarization.

$$\chi_b^{(2)}(S_{\pm\gamma}SP) = \mp\gamma\chi_{B,XXX}^{(2)} \cos\theta_{IR} \cos\theta_{SF}, \chi_s^{(2)}(S_{\pm\gamma}SP) = \chi_{s,xxz}^{(2)} \cos\gamma$$

$$\Phi(\omega) = \sin^{-1} \left\{ -\frac{S_{SB}(\omega, \gamma) - S_{SB}(\omega, -\gamma)}{4[S_S(\omega)S_B(\gamma)]^{1/2} \cos\gamma} \right\}$$

NOTE!

$$\chi_s^{(2)}(\omega) = |\chi_s^{(2)}(\omega)|^2 \exp[i\Phi(\omega)] = \text{Re}[\chi_s^{(2)}(\omega)] + i \text{Im}[\chi_s^{(2)}(\omega)]$$



Phase-Sensitive Sum-Frequency vibrational Spectroscopy on Quartz/water Interface

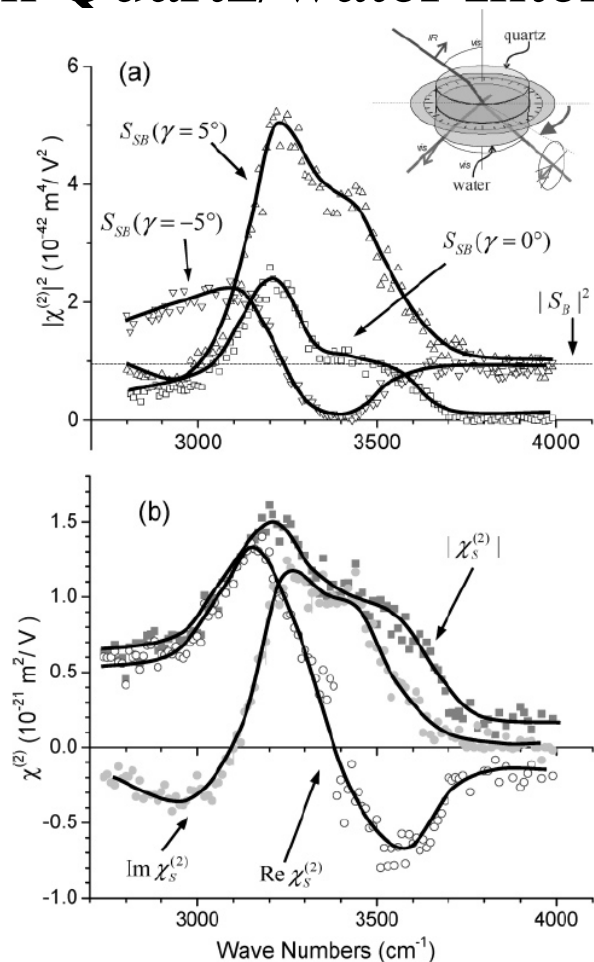


Figure 13. An example of phase-sensitive SFG spectroscopic measurement for a quartz/water interface at pH = 6.5: (a) measured spectra of $S_{SB}(\gamma = +5^\circ)$, $S_{SB}(\gamma = -5^\circ)$, $S_{SB}(\gamma = 0^\circ)$, and $|S_B^{(2)}|^2$; (b) deduced spectra of $|\chi_S^{(2)}|^2$, $\text{Re}(\chi_S^{(2)})$, and $\text{Im}(\chi_S^{(2)})$. The inset shows the experimental arrangement. The azimuthal angle ϕ of the quartz crystal is adjusted to suppress SFG in the SSP polarization combination. The analyzer of the SF output is set either for precise S polarization or at $\pm\gamma$ angle away from S-polarization. Adapted figure with permission from ref 30. Copyright 2005 by the American Physical Society. <http://link.aps.org/abstract/PRL/v94/e046102>.

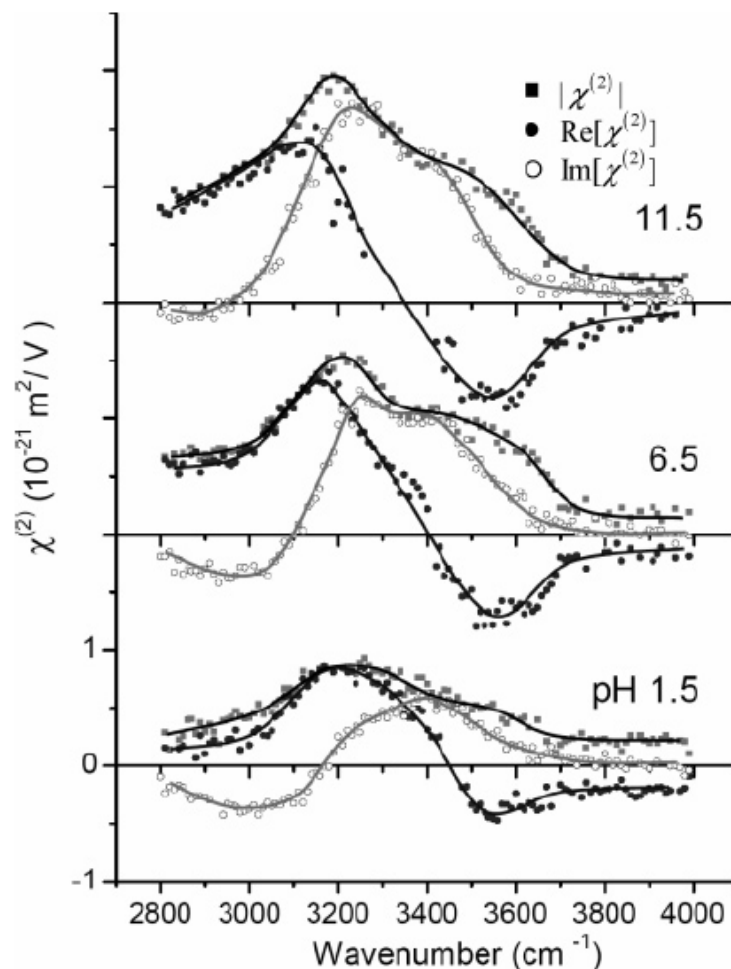


Figure 14. Spectra of $|\chi_S^{(2)}|^2$, $\text{Re}(\chi_S^{(2)})$, and $\text{Im}(\chi_S^{(2)})$ for water/ α -quartz interface at several pH values of water. Reprinted figure with permission from ref 30. Copyright 2005 by the American Physical Society. <http://link.aps.org/abstract/PRL/v94/e046102>.

Phase-Sensitive Sum-Frequency vibrational Spectroscopy on Quartz/water Interface

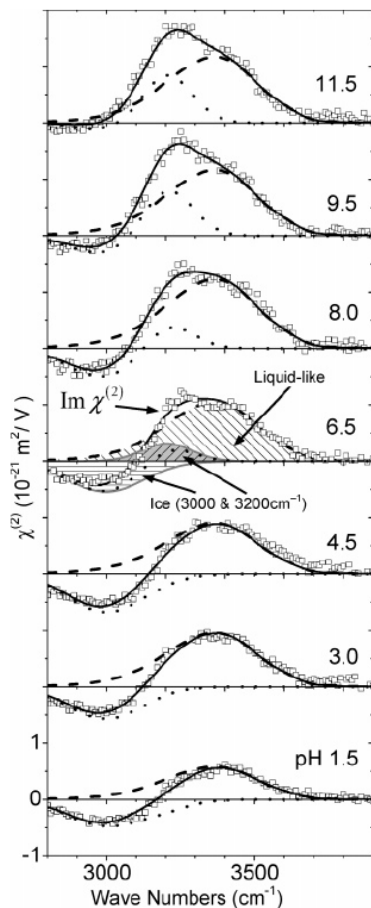


Figure 15. A series of $\text{Im}[\chi^{(2)}]$ spectra of the water/ α -quartz interface at different values of pH. In each spectrum, the solid curve is a fit to the data that comprises a liquidlike peak (dashed curve) and an icelike peak (dotted curves). The liquidlike peak profile is borrowed from the linear absorption spectrum of bulk water, and the icelike component is further decomposed into two subpeaks: a negative and a positive subpeak centered at ~ 3000 and 3200 cm^{-1} and having fwhm of 250 and 170 cm^{-1} , respectively. The graph for $\text{pH} = 6.5$ explicitly shows the two icelike components (hatched peaks) obtained in the decomposition. Adapted figure with permission from ref 30. Copyright 2005 by the American Physical Society. <http://link.aps.org/abstract/PRL/v94/e046102>.

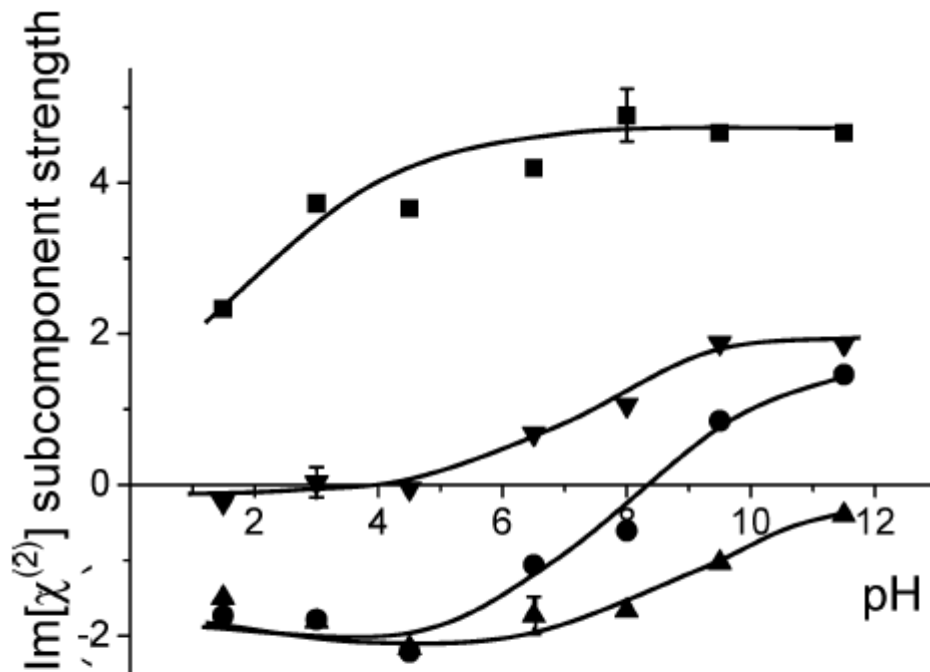


Figure 16. Strengths of various components obtained from decomposition of the spectra in Figure 15 as functions of pH: (■) liquidlike peak; (▲) 3000 cm^{-1} icelike component; (▼) 3200 cm^{-1} icelike component; (●) combined strength of the two icelike components. Reprinted figure with permission from ref 30. Copyright 2005 by the American Physical Society. <http://link.aps.org/abstract/PRL/v94/e046102>.

□ Phase-Sensitive Sum-Frequency vibrational Spectroscopy on Quartz/water Interface

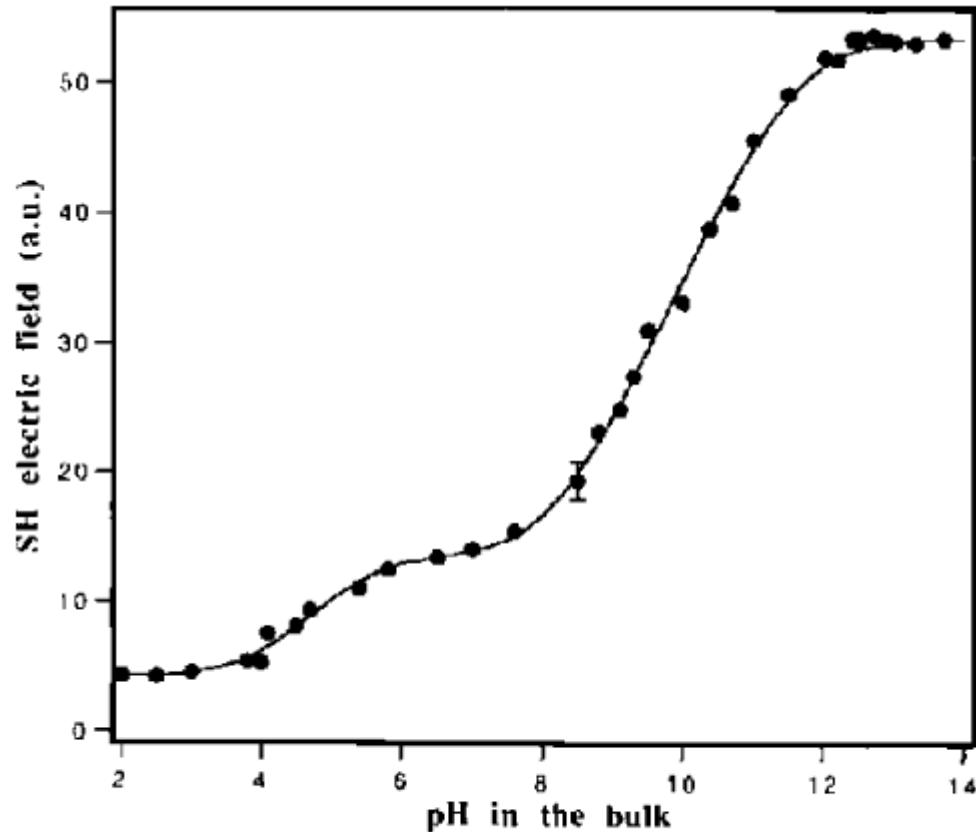


Figure 17. Second harmonic output field from a water/fused silica interface as a function of pH. Reprinted from ref 122, Copyright 1992, with permission from Elsevier.