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Water Structure at Superhydrophobic Quartz/Water Interfaces: A Vibrational Sum Frequency Generation Spectroscopy Study

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The water structure at superhydrophobic solid/bulk water interfaces has been investigated by vibrational sum frequency generation (SFG) spectroscopy. We have adapted a simple and facile chemical modification procedure (methyltrichlorosilane/toluene treatment followed by extraction with ethanol) to prepare transparent quartz crystal surfaces with varied wetting properties, from hydrophilic to hydrophobic and superhydrophobic. In comparison with those obtained on bare quartz, the SFG spectra on polymethylsiloxane-modified surfaces showed significant changes of the relative intensities of the two broad OH stretching modes of hydrogen-bonded water at ~ 3200 and ~ 3450 cm^{-1} , which can be correlated with surface morphology and molecular variations. Intriguingly, on superhydrophobic quartz these bands are very weak and replaced by a characteristic “free OH” (not hydrogen-bonded) stretching (> 3600 cm^{-1}) band that is typically observed at water/air interfaces. These results suggest that hydrogen bonding between water molecules weakens as hydrophobicity increases on rough heterogeneous solid surfaces. More importantly, this study provides direct evidence for the existence of stable solid/air/water three-phase interfaces when a superhydrophobic solid is in contact with bulk water.

1. Introduction

Superhydrophobicity, a property of surfaces that exhibit extremely high water contact angles ($CA > 150^\circ$), is commonly observed in nature: lotus leaves,^{1,2} water strider's legs,^{3,4} butterfly wings,⁵ and insects capable of plastron respiration⁶ are typical examples. Superhydrophobic materials can inhibit snow adhesion,⁷ oxidation, and current conduction;⁸ some of them also have self-cleaning properties.⁹ Research on this industrially important topic has mainly focused on new fabrication protocols (preparation of water-repellent micro/nanostructured surfaces) and is summarized in several recent review articles.^{10–12}

It has been experimentally demonstrated that superhydrophobicity is directly related to surface roughness.¹¹ Two classical models have been proposed to explain the observed ultralarge water contact angles on solids. Wenzel's theory predicts that water completely fills the grooves of a rough surface,¹³ while according to Cassie/Baxter air pockets are trapped underneath the water and thereby generate a water/air and water/solid composite interface.¹⁴ Besides these models of the micro/nanoscale architecture of hydrophobic surfaces,^{15,16} few experimental data about the correlation/transition between the two “wetting states” (the existence of a water/air/solid three-phase interface and the stability of trapped air pockets) are available.^{16–18} Bhushan and co-workers monitored by environmental scanning electron microscopy (SEM) the contact angle and the Wenzel–Cassie transition (existence and disappearance of air pockets) during the evaporation/condensation of water microdroplets on a patterned silicon surface.¹⁷ More recently, Chen et al. introduced a droplet-inside-view method based on MAC-mode

atomic force microscopy (AFM) and on a force-volume function to characterize such composite interfaces.¹⁸

Although surfaces can be imaged routinely by AFM and SEM, noninvasive techniques are required to investigate a buried superhydrophobic solid/bulk water interface. A neutron reflectivity (NR) study by Doshi et al. has shown that the superhydrophobic nature of the surface prevents infiltration of water into the rough, highly porous aerogel-like film (spin-coated on silicon).¹⁹ Herein we have explored vibrational sum frequency generation (SFG) spectroscopy as an alternate method for studying the water structure at chemically modified quartz crystal surfaces, for which the wetting properties were tuned from hydrophilic to superhydrophobic by simple silanization as originally reported by Gao and McCarthy.²⁰

Water can exhibit numerous structures depending on the degree of hydrogen bonding,²¹ and it is difficult to differentiate between interfacial and bulk water. Because SFG spectroscopy is based on a second-order nonlinear optical process that is forbidden in media with inversion symmetry,²² it is highly interface-sensitive and particularly suitable for above task.^{23–30} Shen and co-workers pioneered this technique for the study of air/water,²³ quartz/water,²⁴ and OTS (octadecyltrichlorosilane)-monolayer/water interfaces.²⁵ Scatena et al. evaluated the water structure at $\text{CCl}_4/\text{H}_2\text{O}$ and hydrocarbon/ H_2O interfaces and showed that hydrogen bonding is rather weak.²⁶ Our studies of the water structure on fused quartz surfaces modified with OTS monolayers revealed unique conformational changes upon shifting the pH from neutral to acidic.²⁷ Shultz et al.²⁸ and Liu et al.²⁹ extended the application of SFG spectroscopy to interfaces between aqueous solutions and air.

2. Experimental Section

2.1. Materials. All chemicals were of reagent-grade quality. Deionized water (>18.3 $\text{M}\Omega \cdot \text{cm}$) from a Milli-Q system was

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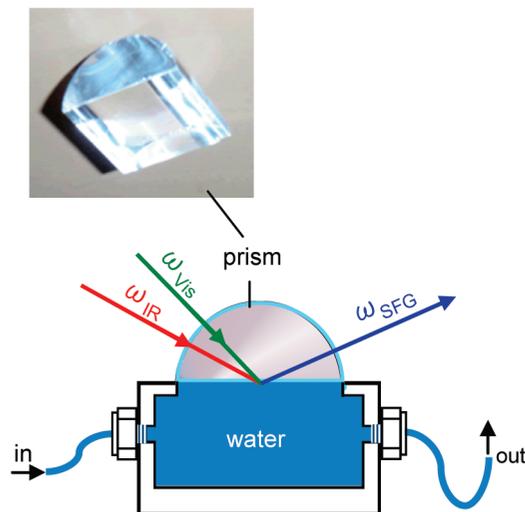


Figure 1. Experimental setup for SFG studies of water structure at a chemically modified quartz prism/water interface using a flow cell. The inset shows the superhydrophobic quartz prism which remains transparent upon treatment with methyltrichlorosilane/toluene.

used throughout the experiments. Methyltrichlorosilane (99%) was purchased from Aldrich, toluene (99.5%), ethanol (99.0%), sulfuric acid (96%), and hydrogen peroxide (30%) from Wako Chemicals.

2.2. Surface Preparation. A hemicylindrical fused quartz prism was cleaned in “piranha” solution (3:1 v/v concentrated H_2SO_4 /30% H_2O_2 ; caution, *extremely oxidative and should be handled carefully*) for 30 min and then rinsed thoroughly with deionized water. It was then dried at 110 °C for 5 min and irradiated in a UV/ozone cleaner for 30 min. After this treatment the flat side was covered with a thin film of 1.0 M methyltrichlorosilane in toluene. The silanization reaction was carried out at ambient conditions (18–22 °C, 30–40% relative humidity). The functionalized quartz surface was rinsed with 5–15 mL of ethanol/water (1:1 v/v) and dried at 110 °C for 5 min. To prepare samples for surface characterization, quartz plates and glass slides were modified in the same manner. The hydrophobicity of the modified surface was tuned by varying the reaction time (from 15 min to 12 h; hydrophobicity increases with time) and the number of washes with 50% ethanol (2–5 times).

2.3. SFG Spectroscopy. A picosecond Nd:YAG laser (PL2143B, Ekspla) was used to pump an optical parametric generation/optical parametric amplification/difference frequency generation (OPG/OPA/DFG) system to generate tunable infrared radiation in the 2.3–8.5 μm range. The second harmonic output of the YAG (yttrium–aluminum–garnet) laser (532 nm) was the source of the visible beam. These two beams were introduced from the quartz prism side and focused on the same point of the quartz/water interface (Figure 1). Deionized water (pH 5.7 \pm 0.5) was obtained immediately prior to the SFG measurement and used as it is. As mentioned above, the flat side of the quartz prism was treated with methyltrichlorosilane/toluene solution to achieve different wetting properties while keeping it transparent (Figure 1 inset). The incident angles of visible and infrared light were 70 and 50°, respectively, from the surface normal. The produced SFG beam was filtered through irises and a monochromator (Oriel Instruments, MS257) and detected by a photomultiplier tube (Hamamatsu, R3896). The SFG signals were normalized to the intensities of the visible and the infrared beam. The SFG, visible, and IR beams were either s, s, and p-polarized (ssp) or all p-polarized (ppp). All measurements were carried out at room temperature (22 \pm 2 °C).

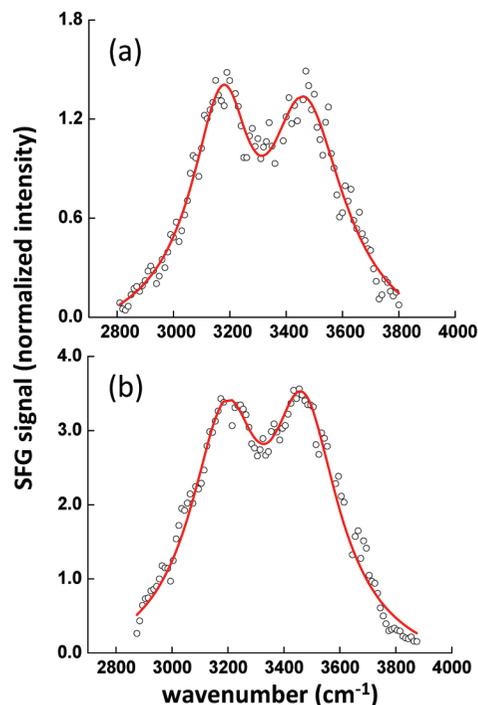


Figure 2. SFG spectra of unmodified quartz/ H_2O interfaces obtained with (a) ssp and (b) ppp polarization. The water contact angle is below 20°. The solid lines represent the best fits based on eqs 1 and 2.

The following equations express the SFG intensity (I_{SFG})

$$I_{\text{SFG}}(\omega_{\text{SFG}} = \omega_{\text{IR}} + \omega_{\text{VIS}}) \propto |\chi_{\text{eff}}^{(2)} \cdot E(\omega_{\text{IR}})E(\omega_{\text{VIS}})|^2 \quad (1)$$

$$\chi_{\text{eff}}^{(2)} = |\chi_{\text{NR}}^{(2)}| + \sum \left| \frac{A_n}{\omega_{\text{IR}} - \omega_n + i\Gamma_n} e^{i\phi_n} \right| \quad (2)$$

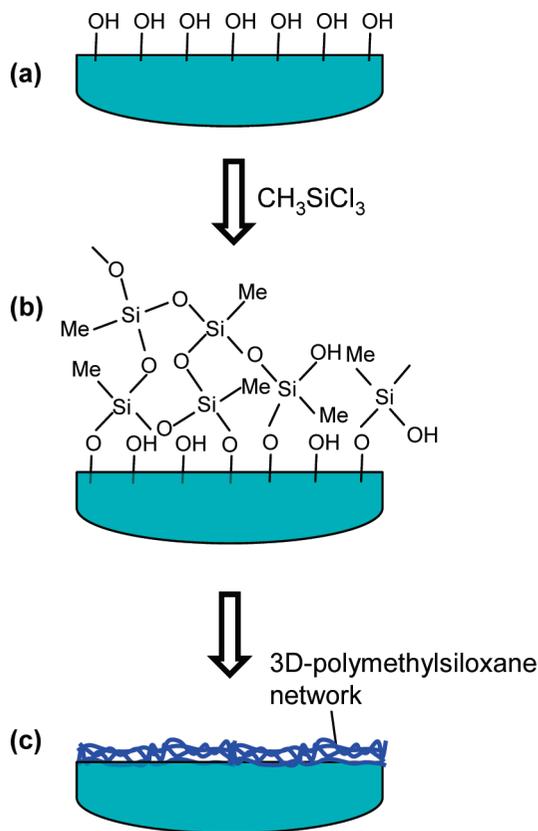
where $\chi_{\text{eff}}^{(2)}$ and $\chi_{\text{NR}}^{(2)}$ are the effective second-order nonlinear susceptibilities of the resonant and the nonresonant component, respectively, ϕ_n is the relative phase angle of the vibrational mode (n) with respect to the nonresonant background, A_n , and Γ_n are the amplitude and the homogeneous width, respectively, of the surface vibration mode (n) corresponding to frequency ω_n . A nonlinear least-squares routine was used to fit the SFG spectra.²⁷ The quality of the fit was judged by r^2 values (>0.900); the best fits are shown as solid lines in the SFG spectra presented below.

2.4. Surface Characterization. Wetting measurements were performed with an AST Optima contact angle system at ambient conditions (18–22 °C, 30–35% relative humidity) using a horizontal light beam to illuminate the 2.0- μL water droplet.

SEM images were obtained from a FEI DualBeam Strata 235 system (Hillsboro, OR). Samples were imaged using secondary electron imaging (SEI) and grounded using carbon paste to avert charging. The accelerating voltage was typically 10 kV and the magnification \times 5000.

3. Results and Discussion

We first examined the water structure on an unmodified, hydrophilic quartz surface which has a water contact angle of <20°. As shown in Figure 2, two broad bands of comparable intensities are centered at 3180 and 3460 cm^{-1} in the SFG spectra with either ssp or ppp polarization. The positions of the two bands, their relative intensities, and the insensitivity to the polarization combination are in good agreement with the results

SCHEME 1: Preparation of a Polymethylsiloxane-Modified Quartz/Glass Surface^a


^a Incubation of bare quartz (a) with dilute solution of methyltrichlorosilane in toluene (with trace of water) results in vertical polymerization (b). Upon extraction of toluene with ethanol, the polymethylsiloxane network collapses to a hierarchical structure (c).

reported by Qu et al. for a water/quartz interface at $\text{pH} > 5.6$.²⁴ The former band corresponds to the well-ordered, tetrahedrally coordinated, symmetric O–H stretching mode (“ice-like” hydrogen-bonding network), which is characteristic of the perfect hexagonal arrangement found in the SFG spectrum of an ice/air interface.³¹ The assignment of the latter band has been questioned³² but is generally attributed to more randomly oriented (“asymmetric”) O–H stretching vibrations (“liquidlike” hydrogen-bonding network). This is supported by the fact that as the temperature rises and the hexagonal ice structure distorts the intensity of this band increases significantly.³¹ Shen and co-workers have proposed that at a hydrophilic quartz surface (terminated with a uniform layer of hydroxyl groups as shown in Scheme 1a), water molecules are well oriented and arranged in an ordered “ice-like” hydrogen-bonded network that contributes to the strong band around 3200 cm^{-1} ; on progressively moving away from the surface, the molecules become less oriented and give rise to the “liquidlike” band at $\sim 3450\text{ cm}^{-1}$.^{23,25} The assignments of these two water bands are further supported by new phase-sensitive SFG studies³³ that have revealed the water structure at water/quartz and water/air interfaces with unprecedented detail (e.g., pH-dependent orientation changes). On the other hand, on the basis of isotopic dilution experiments, Sovago et al. have suggested that the double-peaked structure in the SFG spectrum of hydrogen-bonded interfacial water molecules originates from vibrational coupling between the stretching and bending overtones.³⁴ Nevertheless, this disagreement regarding the water band assignments will not influence our discussion of the correlation between the water

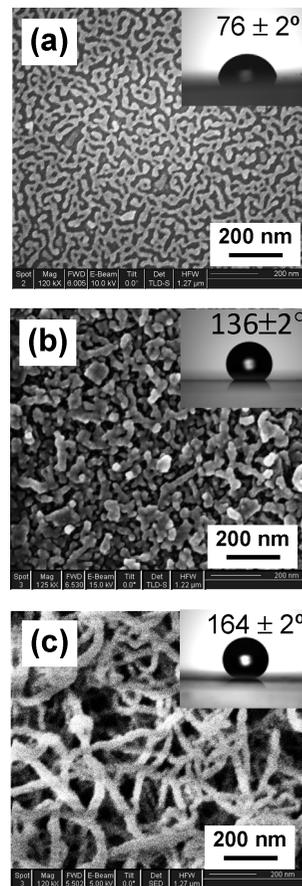


Figure 3. SEM images of quartz/glass surfaces modified with (a) hydrophilic, (b) hydrophobic, and (c) superhydrophobic polymethylsiloxane film. The insets show the corresponding water drop images and contact angles.

structure and interfacial morphological/molecular properties detailed below.

To systematically study the water structure at solid surfaces with different wettabilities, we have chemically modified the quartz surface (Scheme 1) by a simple silanization procedure, similar to the reaction employed by Gao and McCarthy to make perfectly hydrophobic ($\theta_A/\theta_R = 180^\circ/180^\circ$) silicon wafers.²⁰ The experimental challenge was to keep the modified quartz crystals transparent, which is essential for SFG investigations. As shown in Scheme 1, the quartz crystals were treated briefly with a dilute solution of methyltrichlorosilane in toluene and rinsed with ethanol/water. Condensation and hydrolysis of methyltrichlorosilanes generate a swollen polymeric 3-D polymethylsiloxane network and rapid “extraction” of toluene by washing with ethanol/water induces a phase separation. We have found that by carefully controlling the reaction time, temperature, and the number of washes the quartz/glass surface can be tuned from hydrophilic ($\theta_A < 90^\circ$) to superhydrophobic ($\theta_A > 150^\circ$). Artus et al. have shown that the wetting properties of a number of materials can be tuned similarly by growing silicone “nanofilaments” on the surface via chemical vapor deposition.³⁵ SEM images (Figure 3) indicate that the surface wettability of the modified quartz surface is associated with microscopic morphological changes. In the hydrophilic ($\theta_A = 76 \pm 2^\circ$) sample “worm-like” methylsiloxane aggregates are networked together and cover 60–70% of the surface (in two dimensions). The hydrophobic surface ($\theta_A = 136 \pm 2^\circ$) is more “particulate”, i.e., it contains well-separated “rods” and “islands” that make it rougher. The superhydrophobic surface ($\theta_A = 164 \pm 2^\circ$)

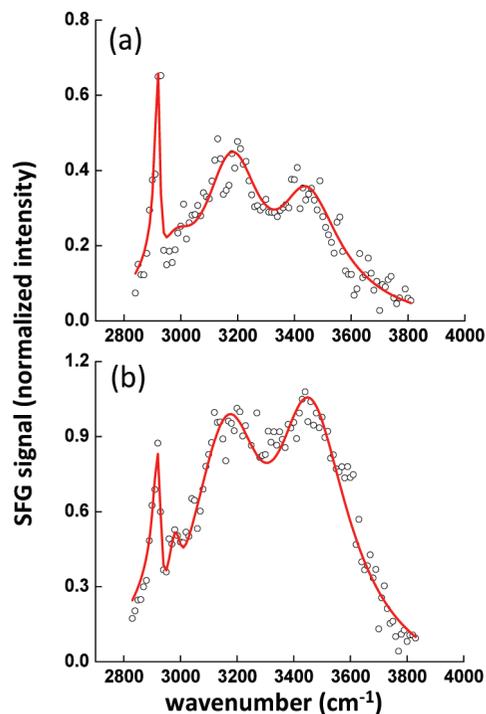


Figure 4. SFG spectra of hydrophilic polymethylsiloxane-modified quartz/water interface obtained with (a) ssp and (b) ppp polarization. The water contact angle is $76 \pm 2^\circ$.

consists of a unique 3D-network of “nanofabric” structure, with methylsiloxane “nanofibers” of about 20 nm diameter tangled together, which is similar to what has been observed on silicon.²⁰ Most importantly, in all cases the quartz prism remains transparent (inset of Figure 1), which enabled us to systematically characterize its interface with bulk water by SFG spectroscopy.

Figure 4 shows the spectra of hydrophilic quartz ($\theta_A = 76 \pm 2^\circ$) modified with a polymethylsiloxane film in contact with bulk water. The sharp peak at 2920 cm^{-1} and the shoulder band at 2979 cm^{-1} appearing in both ssp and ppp spectra probably arise from the methylsiloxane film as they are not present at the unmodified quartz/water interface (Figure 2). On the basis of our IR characterization of the film and previous vibrational spectroscopic studies of methyltrichlorosilane,³⁶ we assign these two new peaks to the symmetric and asymmetric C–H stretching modes of the terminal methyl groups of polymethylsiloxane (Scheme 1b). The peak at 2920 cm^{-1} may also include contributions from the symmetric C–H stretching mode of the methyl groups of residual toluene, as this band is predominant in the SFG spectrum of the toluene/air interface.³⁷ These two bands have also been observed in the SFG spectra of “dry samples” (data not shown), however much weaker and broader.

In the range of $3000\text{--}3800 \text{ cm}^{-1}$, the SFG spectra basically resemble those of unmodified quartz (Figure 2), i.e., two broad bands centered at 3180 and 3430 cm^{-1} , represent different degrees of hydrogen-bonding of interfacial water molecules. Although this surface is much less hydrophilic than unmodified quartz ($\theta_A < 20^\circ$), the water molecules appear to maintain similar conformations at the interface: neither the peak positions nor the relative intensities have changed significantly (compare to Figure 2). As indicated in the SEM image (Figure 3a), a portion of the surface (30–40%) remains bare (“flat”). We believe that the hydroxyl groups (mostly deprotonated) on this unmodified

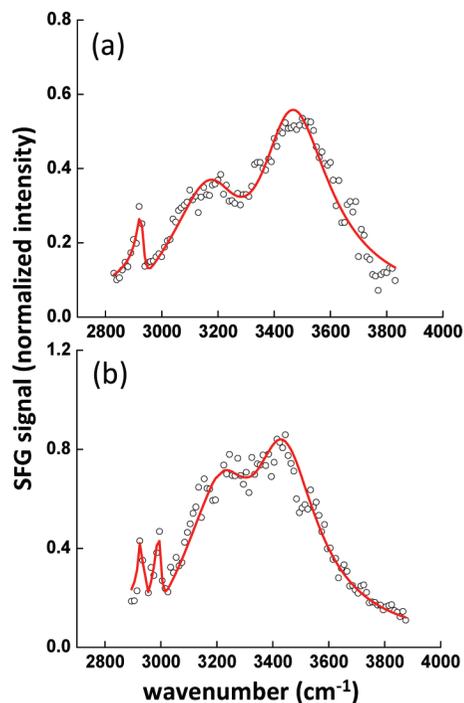


Figure 5. SFG spectra of hydrophobic polymethylsiloxane-modified quartz/H₂O interface obtained with (a) ssp and (b) ppp polarization. The water contact angle is $136 \pm 2^\circ$.

portion of the quartz surface form hydrogen bonds with water molecules at the interface and induce adjacent molecules to establish a well-extended hydrogen-bonding network in the aqueous phase. It should also be noted that unreacted hydroxyl groups and relatively polar Si–O–Si moieties coexist with hydrophobic methyl groups at the surface of methylsiloxane aggregates (Scheme 1b).

In the SFG spectra of the hydrophobic quartz surface ($\theta_A = 136 \pm 2^\circ$), the band intensity at 3220 cm^{-1} is decreased significantly relative to that centered at 3430 cm^{-1} (Figure 5a). This indicates that water molecules are more randomly oriented (imperfect tetrahedral coordination), i.e., the hydrogen bonding network is substantially weaker than on a hydrophilic surface. Such weakened hydrogen bonding among water molecules has also been reported for organic liquid (CCl₄ or hexane)/water interfaces by Scatena et al.,²⁶ for which the SFG spectra were dominated by the band around 3450 cm^{-1} . They also observed a sharp peak at $\sim 3670 \text{ cm}^{-1}$ (free OH). The spectra shown in Figure 5 also differ from those obtained on quartz surfaces modified with *n*-octadecyltrichlorosilane (OTS) monolayers,^{25,27} which are also hydrophobic ($\theta_A \approx 110^\circ$). The main differences in the water bands between 3200 and 3800 cm^{-1} include the strong $\sim 3200 \text{ cm}^{-1}$ band and the free OH peak (3690 cm^{-1}).^{25,27} It is known that OTS forms a highly oriented and closely packed self-assembled monolayer (SAM) on a hydroxylated surface, as evidenced by the strong methyl bands observed in our previous SFG investigation of water/OTS SAM interfaces.²⁷ Although the detailed “pictures” may differ from those shown in earlier studies of water/OTS SAM interfaces,^{25,27} the general understanding is that water molecules do not adhere to highly oriented alkyl chains (terminated with hydrophobic $-\text{CH}_3$ groups) and hence those residing adjacent to the surface possess free OH groups. Similarly, Du et al. attributed the ordering of water molecules into an “icelike” structure on OTS SAM surfaces to physical restrictions (forming packed conformations against rigid walls).²⁵

The differences observed between the SFG spectra of hydrophobic methylsiloxane-modified quartz/water interfaces (Figure 5) and those reported for organic liquid/water and OTS SAM/water interfaces clearly relate to the rough surface morphology and the heterogeneous chemical composition (Scheme 1b and Figure 3b). In the present system, the hydrophobicity is largely induced by the morphological roughness, as described by Wentzel's equation¹³

$$\cos \theta' = r \cos \theta \quad (3)$$

where θ' is the apparent water contact angle, r is the ratio of the true wetted area to the apparent area (which is essentially the surface roughness factor), and θ is the contact angle exhibited by a flat surface of the same chemical nature. As mentioned above, unreacted hydroxyl groups and relatively polar Si–O–Si moieties coexist with the hydrophobic methyl groups at the surface of methylsiloxane aggregates (Scheme 1b). The ordering of interfacial water molecules on such a “heterogeneous” solid surface cannot be compared with that on uniform hydrophobic interfaces (e.g., organic liquids or OTS SAMs).^{25,27} We have previously discovered that the intensity of the free OH band at a *partial* OTS monolayer surface is indeed much weaker than that at an OTS SAM of *full* coverage.²⁷

It is important to note that the relative intensities of the C–H stretching peaks at 2920 and 2979 cm^{-1} in Figure 5 are lower than those of the water bands at 3000–3800 cm^{-1} . The fact that we have observed much weaker methyl bands than those on an OTS-SAM-modified quartz surface indicates that the terminal methyl groups in the present system are not oriented.²⁷ This is in good agreement with the increased surface roughness of the polymethylsiloxane film-modified surface (leading to the coexistence of methyl, hydroxyl and other hydrophilic moieties). In theory, it is possible to deduce the molecular tilt angles of methyl groups; however, the methyl groups on topologically rough polymeric films exhibit a large range of orientations. The ratio between signal amplitudes of r^+ (symmetric methyl stretch) under ssp polarization and r^- (asymmetric methyl stretch) under ppp polarization decreases for a more hydrophobic system (Figure 5). The smaller ratio indicates that the tilt angle of methyl groups, on average, becomes bigger (away from surface normal).³⁸ It is evident from the SEM images that the surface coverage of a polymethylsiloxane film is much higher for the hydrophobic system (Figure 3b) than for the hydrophilic system (Figure 3a). The greater degree of polymerization (for a hydrophobic film) would involve more methyl groups extending parallel to the surface, i.e., more methyl groups are lying down, and thus the average tilt angle increases.

In accordance with the SFG spectroscopic changes from a hydrophilic to a hydrophobic surface, we expected to observe in the SFG spectra of the superhydrophobic quartz surface a further diminished contribution of the $\sim 3200 \text{ cm}^{-1}$ peak relative to that at $\sim 3400 \text{ cm}^{-1}$. Surprisingly, the results were more drastic: both bands virtually disappeared, and a new, relatively sharp peak was observed at 3730 cm^{-1} (ssp polarization) (Figure 6A); the same peak was observed with a lower intensity in the ppp spectrum. As mentioned above, this peak represents the hydrogen-bonding-free stretching mode of OH groups, which has been observed previously at several other interfaces.^{23–27} This peak appears much stronger under ssp polarization which can be explained by considering the effect of the rotation of O–H groups. Wei and Shen have theoretically shown that the oscillation amplitudes of free OH bonds are approximately four times larger under ssp than under ppp polarization.³⁹

One of the plausible explanations for superhydrophobicity suggests that air bubbles are trapped in the solid/water inter-

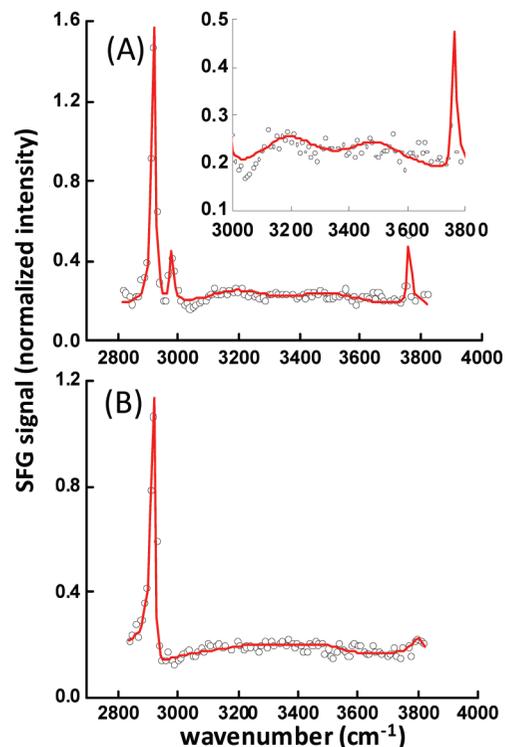
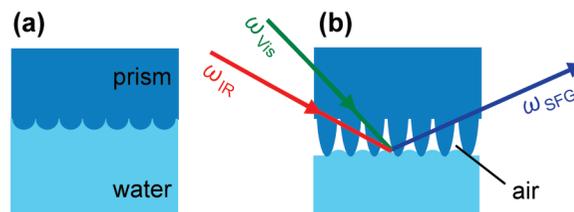


Figure 6. SFG spectra of superhydrophobic polymethylsiloxane-modified quartz/water interface taken with (a) ssp and (b) ppp polarization. The water contact angle is $164 \pm 2^\circ$.

SCHEME 2: Schematic Representation of Modified Quartz/Water Interfaces Probed by vSFG Spectroscopy: (a) Hydrophilic/Hydrophobic Surface; (b) Superhydrophobic Surface



face;¹⁴ we believe that the –OH groups of water molecules protruding into these air pockets are not hydrogen bonded. In fact, we can estimate the fraction of interfacial water molecules in contact with the polymethylsiloxane film from the Cassie–Baxter model¹⁴

$$\cos \theta' = -1 + f(1 + \cos \theta) \quad (4)$$

where θ' and θ are the same as in eq 3 and f is the fraction of solid in contact with water. Here we have assumed $\theta = 110^\circ$, which is the static contact angle of water on OTS monolayers.⁴⁰ The value determined for f in this case is as low as 6%, which indicates that most water molecules are interfacing with air, and only a small portion is in physical contact with the solid surface (Scheme 2b). This is in sharp contrast to the hydrophilic and hydrophobic surfaces investigated above, where the interfacial water is in direct contact with the solid surface (Scheme 2a). We are essentially providing spectroscopic evidence for the existence of a stable water/air/solid three-phase interface even though the sample is completely immersed in water. Our observation also supports the results of the earlier neutron reflectivity studies by Doshi et al.:¹⁹ only a small portion of the superhydrophobic surface, essentially at the apex of spikes, is in contact with water.

The high intensities of the sharp C–H stretching peaks (2918 and 2980 cm^{-1}) relative to those of the water bands (Figure 6) are particularly noteworthy. The superhydrophobicity arises from an intricate network of polymethylsiloxane “nanofibers”, as shown on the SEM image (Figure 3c), which suggests that large numbers of $-\text{CH}_3$ groups may be oriented on the surface. The features of the C–H stretching peaks (relative peak intensities of symmetric and asymmetric modes) on a hydrophobic and a superhydrophobic surface are significantly different. The contribution from the asymmetric methyl stretch is negligible in the ssp spectrum of a hydrophobic surface (Figure 5a); on a superhydrophobic surface both vibrational modes are discernible in the ssp spectrum (Figure 6a). This trend is reversed in the ppp-polarized spectra. We believe that this is a consequence of the orientation difference of CH_3 groups on the two samples: at a water/superhydrophobic interface, the amplitude ratio r^- (ssp)/ r^- (ppp) is bigger, indicative of a smaller methyl tilt angle.⁴¹ The ratio r^+ (ssp)/ r^- (ppp), which has been used to qualitatively analyze the orientation of methyl groups previously, supports this hypothesis.³⁸ At a water/hydrophobic interface, the repulsive force between water and the polymethylsiloxane film directs the methyl groups toward the surface, similar to the effect reported previously by Chen et al. at the poly(*n*-butyl methacrylate)/water interface.⁴² On the other hand, with a superhydrophobic film, only the apex of spikes is in contact with water (6% of the total area). The majority of methyl groups are interfacing with air; the tilt angle of methyl groups remains small.

As shown in the inset of Figure 6a, the intensities of the hydrogen-bonded water bands relative to those of free OH are substantially lower than those observed at a conventional air/water interface.²³ This intensity difference is difficult to interpret but it may be related to the limited propagation of electromagnetic fields at the interface (due to the reflectance setup for SFG measurements shown in Scheme 2b). Additionally, the decrease of hydrogen-bonded water bands may be due to water not being able to penetrate the polymethylsiloxane film and deprotonate the quartz substrate. Another unusual observation is the slightly higher wavenumber of the free OH band in comparison with a conventional air/water interface.²⁵ Nevertheless, substantial weakening of the hydrogen-bonding network, i.e., the disordering of interfacial water structures, is evident from our systematic study of solid surfaces with varied hydrophobicities. In addition, we were able to obtain SFG spectra with comparable intensities for both ssp and ppp polarization combinations (in Figure 4, the ppp spectrum is even stronger), suggesting that in our cases the interfacial water structure was not as well oriented as that at air/water interfaces; in contrast, the ssp combination produces about ten times stronger signals than ppp at air/water interfaces.²³ The average OH and CH_3 orientations could be estimated from that polarization combination dependence, which is beyond the scope of this study.

4. Conclusion

Weakening of the hydrogen bonding network of interfacial water molecules is evident upon increasing the hydrophobicity of chemically modified quartz surfaces. Unlike the SFG spectra reported for highly oriented OTS SAM surfaces, those of water on a polymethylsiloxane-modified quartz surface neither show a predominant “ice-like” water peak ($\sim 3200 \text{ cm}^{-1}$) nor the typical hydrogen-bonding free OH peak ($>3600 \text{ cm}^{-1}$). In the extreme case, at the water/superhydrophobic interface, the SFG spectrum resembles that of an air/water interface. This constitutes the first spectroscopic evidence for the existence of a stable

water/air/solid three-phase interface.⁴³ We are currently probing/analyzing the effects of different polarization combinations, phase dependences, and isotope substitutions on interfacial water structures.

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References and Notes

- Otten, A.; Herminghaus, S. *Langmuir* **2004**, *20*, 2405.
- Koch, K.; Neinhuis, C.; Enskat, H. J.; Barthlott, W. *J. Exp. Bot.* **2004**, *55*, 711.
- Hu, D. L.; Chan, B.; Bush, J. W. M. *Nature* **2003**, *424*, 663.
- Gao, X.; Jiang, L. *Nature* **2004**, *432*, 36.
- Zheng, Y.; Gao, X.; Jiang, L. *Soft Matter* **2007**, *3*, 178.
- Shircliffe, N. J.; McHale, G.; Newton, M. I.; Perry, C. C.; Pyatt, F. B. *Appl. Phys. Lett.* **2006**, *89*, 104106.
- Kako, T.; Nakajima, A.; Irie, H.; Kato, Z.; Uematsu, K.; Watanabe, T.; Hashimoto, K. *J. Mater. Sci.* **2004**, *39*, 547.
- Nakajima, A.; Hashimoto, K.; Watanabe, T. *Monatsh. Chem.* **2001**, *132*, 31.
- Blossey, R. *Nat. Mater.* **2003**, *2*, 301.
- (a) Sun, T.; Feng, L.; Gao, X.; Jiang, L. *Acc. Chem. Res.* **2005**, *38*, 644. (b) Feng, X.; Jiang, L. *Adv. Mater.* **2006**, *18*, 3063.
- Li, X.-M.; Reinhoudt, D.; Crego-Calama, M. *Chem. Soc. Rev.* **2007**, *36*, 1350.
- Zhang, X.; Shi, F.; Niu, J.; Jiang, Y.; Wang, Z. *J. Mater. Chem.* **2008**, *18*, 621.
- Wenzel, R. *Ind. Eng. Chem.* **1936**, *28*, 988.
- Cassie, A. B. D.; Baxter, S. *Trans. Faraday Soc.* **1944**, *40*, 546.
- (a) Lafuma, A.; Quéré, D. *Nat. Mater.* **2003**, *2*, 457. (b) Bico, J.; Marzolin, C.; Quéré, D. *Europhys. Lett.* **1999**, *47*, 220.
- (a) Nosonovsky, M.; Bhushan, B. *Langmuir* **2008**, *24*, 1525. (b) Jung, Y. C.; Bhushan, B. *Scripta Mater.* **2007**, *57*, 1057.
- Jung, Y. C.; Bhusahn, B. *J. Microsc.* **2008**, *229*, 127.
- Chen, P.; Chen, L.; Han, D.; Zhai, J.; Zheng, Y.; Jiang, L. *Small* **2009**, *5*, 908.
- Doshi, D. A.; Shah, P. B.; Singh, S.; Branson, E. D.; Malanoski, A. P.; Watkins, E. B.; Majewski, J.; van Swol, F.; Brinker, C. J. *Langmuir* **2005**, *21*, 7805.
- Gao, L.; McCarthy, T. J. *J. Am. Chem. Soc.* **2006**, *128*, 9052.
- Walrafen, G. E. *J. Chem. Phys.* **1967**, *47*, 114.
- Shen, Y. R. *Nature* **1989**, *337*, 519.
- Du, Q.; Superfine, R.; Freysz, E.; Shen, Y. R. *Phys. Rev. Lett.* **1993**, *70*, 2313.
- Du, Q.; Freysz, E.; Shen, Y. R. *Phys. Rev. Lett.* **1994**, *72*, 238.
- Du, Q.; Freysz, E.; Shen, Y. R. *Science* **1994**, *264*, 826.
- Scatena, L. F.; Brown, M. G.; Richmond, G. L. *Science* **2001**, *292*, 908.
- Ye, S.; Nihonyanagi, S.; Uosaki, K. *Phys. Chem. Chem. Phys.* **2001**, *3*, 3463.
- Shultz, M. J.; Baldelli, S.; Schnitzer, C.; Simonelli, D. *J. Phys. Chem. B* **2002**, *106*, 5313.
- Liu, D. F.; Ma, G.; Levering, L. M.; Allen, H. C. *J. Phys. Chem. B* **2004**, *108*, 2252.
- Kim, G.; Gurau, M.; Kim, J.; Cremer, P. S. *Langmuir* **2002**, *18*, 2807.
- Wei, X.; Miranda, P. B.; Zhang, C.; Shen, Y. R. *Phys. Rev. B* **2002**, *66*, 085401.
- (a) Scherer, J. R. *Advances in Infrared and Raman Spectroscopy*; Clark, R. J. H.; Hester, R. E., Eds.; Heyden: Philadelphia, PA, 1978; Vol. 5, p 149. (b) Gignere, P. A. *J. Raman Spectrosc.* **1984**, *15*, 354.
- (a) Ostroverkhov, V.; Waychunas, G. A.; Shen, Y. R. *Phys. Rev. Lett.* **2005**, *94*, 046102. (b) Ji, N.; Ostroverkhov, Tian, C. S.; Shen, Y. R. *Phys. Rev. Lett.* **2008**, *100*, 096102.
- (a) Sovago, M.; Campen, R. K.; Wurlpel, G. W. H.; Müller, M.; Bakker, H. J.; Bonn, M. *Phys. Rev. Lett.* **2008**, *100*, 173901. (b) Tian, C. S.;

Shen, Y. R. *Phys. Rev. Lett.* **2008**, *101*, 139401. (c) Sovago, M.; Campen, R. K.; Wurpel, G. W. H.; Müller, M.; Bakker, H. J.; Bonn, M. *Phys. Rev. Lett.* **2008**, *101*, 139402.

(35) Artus, G. R.; Jung, S.; Zimmermann, J.; Gautschi, H.-P.; Marquardt, K.; Seeger, S. *Adv. Mater.* **2006**, *18*, 2758.

(36) (a) Shimizu, K.; Murata, H. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 46.

(b) Hard, A. P.; Parker, S. F.; Jayasooriya, U. A. *Appl. Spectrosc.* **2007**, *61*, 314.

(37) Hommel, E. L.; Allen, H. C. *Analyst* **2003**, *128*, 750.

(38) Romero, C.; Baldelli, S. *J. Phys. Chem. B* **2006**, *110*, 6213.

(39) Johansson, T. *Sum frequency generation studies on the structure and dynamics of Langmuir Blodgett films*, Ph.D. Thesis, Simon Fraser University, Burnaby, April 2008.

(40) Tillman, N.; Ulman, A.; Schildkraut, J. S.; Penner, T. L. *J. Am. Chem. Soc.* **1988**, *110*, 6136.

(41) Wei, X.; Shen, Y. R. *Phys. Rev. Lett.* **2001**, *86*, 4799.

(42) Chen, C.; Wang, J.; Even, M. A.; Chen, Z. *Macromolecules* **2002**, *35*, 8093.

(43) At the time of this manuscript being reviewed, Zhang et al. reported a vibrational sum-frequency spectroscopy study of nanoporous silica-water interfaces. They studied a different system (periodic and fractal nanoporous silica films), but their results support our interpretation. (Zhang, L.; Singh, S.; Tian, C.; Shen, Y. R.; Wu, Y.; Shannon, M. A.; Brinker, C. J. *J. Chem. Phys.* **2009**, *130*, 154702.

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