# Hydrophobicity of Hydroxylated Amorphous Fused Silica Surfaces

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ABSTRACT: Understanding the mechanism of water adsorption on silica is important in many fields of science and technology, such as geo- and atmospheric chemistry. Vibrational IR−visible sum-frequency generation (SFG) spectroscopy of hydroxyls ($\sim$3100−3800 cm^{-1}) at the amorphous SiO$_2$ surface in contact with air of varying relative humidity provides information about the adsorption sites and orientation of water molecules. The similar magnitudes of the resonant and nonresonant contributions to the interfacial second-order susceptibility, $\chi^{(2)}$, allow the phases of the various hydroxyls (SiOH; HOH), and thus their orientations with respect to the surface, to be determined. The surface silanols (SiOH) appear to interact weakly with adsorbed water as indicated by the persistence of the narrow surface silanol (SiOH) peak at $\sim$3750 cm^{-1} as the relative humidity of ambient air increases from <5% to >95%. Adsorbed water molecules are represented by two oppositely oriented hydroxyl modes, at $\sim$3350−3400 and $\sim$3650 cm^{-1}, respectively. The weakly hydrogen-bonded water hydroxyls ($\sim$3650 cm^{-1}) are oriented toward the silica substrate and are assigned to water molecules that aggregate over the hydrophobic silica areas with exposed siloxane bridges. We believe that this is the first experimental identification of water molecules in contact with siloxane network whose hydrophobic nature has been predicted by molecular dynamics simulations for tetrahedral (SiO$_4$) surface of kaolinite. The SFG data suggest that, at the molecular level, hydroxylated amorphous fused silica has hydrophobic character.
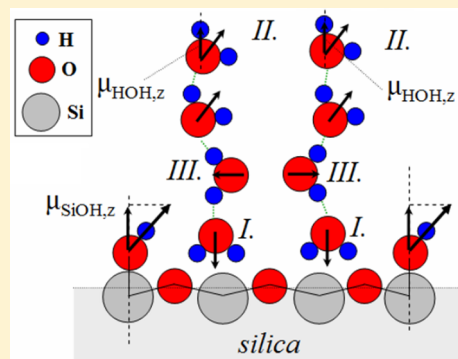
1. INTRODUCTION

The silica/air interface is of importance in various environmental and industrial processes such as the transport of organic molecules in the atmosphere and in groundwater by silica colloids, heterogeneous catalysis, and petroleum extraction.[1] Since water appears to be present on the surfaces of practically all solid minerals, including various forms of SiO$_2$ at even low relative humidity,[2] the adsorbed water molecules, together with the surface-bound hydroxyls (in the case of SiO$_2$, various forms of silanols, e.g., $\equiv$SiOH, $=$Si(OH)$_2$, etc.), influence the adsorption of organic substances on natural forms of silica.[3,4] The investigations of the latter phenomenon will be, in particular, useful in the understanding of organic molecular transport in the atmosphere as well as for the improvement of oil extraction from sands. However, in order to further the knowledge of such processes, one needs to approach a full description of the interaction of water molecules with the silica surfaces at the molecular level.

The surface of silica and its modifications, e.g., zeolites and kaolinites, have been studied extensively by various spectroscopic techniques such as Fourier-transform infrared (FTIR) absorption spectroscopy,[5−11] FTIR diffuse reflectance,[12] Raman spectroscopy,[13] inelastic neutron scattering,[14,15] and nuclear magnetic resonance.[16,17] To access the response of the silica interface, evacuation of the atmosphere around the silica is used typically, mostly for the purpose of removing the interference of adsorbed water vapor from the observed signal. However, such measurements place the silica surface in conditions that may not be relevant. In parallel, computational investigations have been extensively carried out for adsorption of water vapor on

silica and SiO$_2$-containing minerals.[18−24] However, the simulations frequently model the amorphous silica surfaces as combinations of various crystalline (ordered) planes of SiO$_2$.

Sum-frequency generation (SFG) spectroscopy is an experimental technique that can provide a truly molecular level description of interfaces under naturally relevant conditions. SFG avoids contributions from adjoining bulk isotropic phases as, in the dipole approximation, the second-order nonlinearity $\chi^{(2)}$ of centrosymmetric media equals zero rendering SFG truly surface specific.[25] The latter property makes SFG spectroscopy a useful probe of the surfaces of amorphous solids. The technique of vibrational SFG (vSFG) spectroscopy has been around for more than 20 years,[25] and recently it has seen the growth in the applications to bare mineral surfaces.[2−4,26,27] The first surface-specific SFG studies of hydroxyl vibrations on bare flat silica in ambient conditions were performed by the Allen group.[2,3] A particularly interesting finding was that at low to moderate relative humidity (RH) values ($\sim$0−54%) water adsorbs on the amorphous SiO$_2$ surfaces in clusters while leaving the surface-bound silanols ($\equiv$Si−O−H) non-hydrogen bonded.[2] The latter conclusion was made based on the persistence of the characteristic narrow-band peak at $\sim$3750 cm^{-1}, known from the FTIR spectroscopy of silicates as the hydroxyl stretch vibrations of the isolated silanols.[5] In addition, the authors found that prolonged exposure of the silica surface to water vapors (RH $\sim$ 40%)

led to the growth of disordered water molecular layers with strong hydrogen bonding[3] as manifested by the increase of the broad peak at ~3400 cm^{-1} with time.

A question that has not been fully explored in these and other similar studies[4] is the potential of vibrational SFG spectroscopy to probe the orientations of the interfacial oscillators. Because of the coherent nature of the nonlinear-optical SFG process, the surface-specific SFG spectra are sensitive not only to the intensities of the oscillators but also to their relative phases (i.e., sign of dynamic dipoles, see below). The latter correspond to the mutual orientations of the oscillators with respect to the probed interface.[25] While phase-sensitive SFG spectroscopy has been successfully applied to water/mineral[25] and water/air interfaces,[28,29] its use for bare mineral surfaces has been rather limited (e.g., sapphire surfaces in an evacuated atmosphere[27]).

In addition to the elucidation of the states of adsorbed water molecules, it is of particular interest to apply the surface specificity of SFG to investigate the affinity of the amorphous silica surfaces to water and organic molecules (hydrophilicity vs hydrophobicity of silica). The bare surfaces of hydroxylated silica and glasses have been traditionally considered as hydrophilic as they are highly wettable. This is ascribed to the affinity of water molecules to the surface hydroxyl groups which, in the case of silica, are increasingly deprotonated as the pH of the aqueous phase increases above pH ~ 3,[30] which further promotes the interaction of the charged surface with polar water molecules. On the other hand, the siloxane bridge structure Si−O−Si has been known to be hydrophobic due to the low polarity of this moiety.[31,32] For example, the hydrophobicity of tetrahedrally coordinated silica surfaces has been utilized in dealuminated zeolites to selectively adsorb volatile organic compounds[20,32] and has been predicted by molecular dynamics simulations for tetrahedral (SiO_4) surface of kaolinite.[22,24] In their SFG investigations of the vapor/silica interface, the Allen group briefly discussed hydrophobic nature of amorphous silica surface (mainly in the context of adsorption of organic molecules).[2,3]

In this work, we report a vibrational sum-frequency investigation of water adsorption on planar hydroxylated fused silica in ambient conditions. The phase sensitivity of the SFG measurements and thus the ability to extract the absolute orientations of hydroxyls follow from the high sensitivity of the SFG spectroscopic setup[33] which enables observation of the interference between the resonant and nonresonant nonlinearities directly in the intensity ($|\chi^{(2)}|^2$) spectra. Our "quasi-phase sensitive" SFG spectra from silica in contact with air of varying relative humidity (RH) provide strong evidence that there are at least two types of water molecules adsorbed on the surface: one with hydrogen atoms oriented toward the silica surface and the other with hydrogen atoms away from the surface. At lower humidity (RH ~ 20%), water molecules mostly adsorb in weakly hydrogen bonded states with their hydrogen atoms pointing toward the silica substrate. At high humidity (RH ~ 95% or more), the incoming water molecules adsorb into multilayered structures characterized by stronger hydrogen bonding and hydrogen-bonded atoms pointing away from the silica substrate. The SFG signal from the isolated silanols remains almost unperturbed over the entire humidity range investigated, suggesting that planar amorphous silica surface has a hydrophobic character at the molecular level, even though macroscopically silica appears as hydrophilic (e.g., displaying high wettability). We report a previously unobserved mode that we assign to surface water molecules that aggregate over the silica areas with exposed siloxane bridges and are oriented with their hydrogen atoms toward silica. Finally, we demonstrate quenching of non-hydrogen-bonded silanol signal in the presence of hexane vapors and assign it to be the result of preferential adsorption of nonpolar hexane molecules on the predominantly hydrophobic siloxane network which displace adsorbed water molecules to hydrogen-bond with SiOH.

2. EXPERIMENTAL SECTION

SFG spectroscopic measurements employed an ultra-broadband SFG system based on an infrared noncollinear optical parametric amplifier (NOPA), described in more detail elsewhere.[33] The broadband IR pulses were tuned to ~3400−3600 cm^{-1}; the bandwidth of the pulses provided coverage in the range ~3200−3800 cm^{-1} where the surface hydroxyl vibrations occur. The IR pulse energy was ~1−1.5 μJ, while the energy of the 800 nm pulses (narrowed with an interference filter to ~30 cm^{-1}) at the sample was ~15 μJ.[33]

The silica/air interface was created by using an infrared grade fused silica hemicylinder placed onto a Teflon holder.[33] The IR beam was tightly focused at the probed interface while the visible beam was loosely focused to cover the entire IR beam spot. The beams were incident at the interface at angles ~67° for the visible and ~75° for the IR beam, above the critical angles for both wavelengths (the setup was optimized for SFG spectroscopy of silica/water interfaces[33]). The polarization of the IR beam at the probed interface was set to p-, while that of the visible beam could be rotated with a halfwave plate. For normalization of the SFG spectra to the IR intensity profile, broadband reference SFG spectra were acquired from an IR-grade fused silica prism of the same dimensions as the sample prisms with its flat side coated with ~100 nm thick gold layer. The broadband SFG signal (peaked near ~620 nm) was coupled into an Andor integrated spectrograph + CCD detection system via a nonpolarization-maintaining fiber.[33] The polarization of SFG signal from the interface was selected with a polarizer in front of the fiber input. The sum-frequency scale was calibrated by measuring SFG spectra from the reference sample when a quartz plate (bulk peak at ~3672 cm^{-1}) was placed in the IR beam path.

Before each series of SFG measurements, the fused silica prism samples were cleaned with either freshly prepared "piranha" solution (1 vol conc H_2O_2:3 vol conc H_2SO_4, self-heated to ~90−100 °C; immersion for ~40−60 min) or by heating in SC1 mixture (1 vol conc NH_4OH:1 vol conc H_2O_2:4 vol H_2O; heating for ~30 min at ~80 °C); both methods lead to practically the same spectroscopic results. (*CAUTION: "piranha" and SC1 solutions are very reactive mixtures! They must be handled with great care; use of protective equipment, such as gloves, goggles, and lab coat, is necessary.*) After etching and cooling of the cleaning mixture, the cooled-down prism was rinsed with copious amounts of deionized H_2O and let dry in the ambient air in a covered precleaned glass container. The Teflon prism holder was precleaned prior to each series of measurements as well ("piranha" cleaning followed by rinsing and drying). The deionized water was obtained from a Thermoscientific Barnstead Easypure II purification system equipped with a UV lamp (water resistivity 18 MOhm·cm). Liquid D_2O (99.9% D, Cambridge Isotope Laboratories) was used as received. Liquid hexanes (Mallinckrodt Chemicals, content: mixture of isomers, >60% *n*-hexane) were used as received.

For SFG measurements from the silica surface in contact with air of humidity different from the ambient values (~20%), the experiments were carried out in the following way (Figure 1):

(1) The relative humidity of air in contact with the silica surface was increased to saturation level by placing liquid H_2O into the Teflon prism holder beneath the silica prism.

(2) To decrease the relative humidity of air in contact with silica close to zero, a hygroscopic material, i.e., concentrated sulfuric acid, was placed in the reservoir underneath but not in direct contact with the fused silica prism. The static RH values were verified by ex-situ
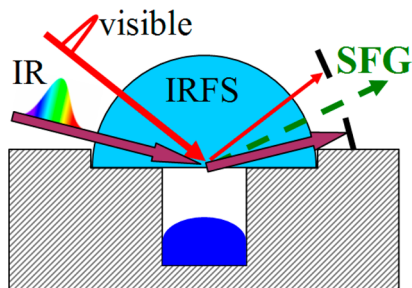
Figure 1. Experimental setup for vibrational SFG spectroscopy of the silica/vapor interface (side view). Fused silica hemisphere ("IRFS") is placed on top of the Teflon holder (shaded section). The reservoir of the holder contains ~1–2 mL of liquid (e.g., H_2O; conc H_2SO_4; D_2O; blue) to control humidity or exchange H with deuterons. In the case of silica/ambient air, no liquid was added to the reservoir.

measurements of humidity in a ~20 × 20 × 20 cm^3 chamber containing a 40 mL flask filled with either liquid water or concentrated sulfuric acid.

To assess the value of the nonresonant nonlinearity (see analysis below), liquid D_2O was placed in the Teflon holder underneath the silica prism sample.

The laser heating was not expected to cause considerable effects on the SFG spectra[34] based on the estimated fluence of the IR beam at the probed surface (~2.4 mJ/cm^2 [33]).

3. RESULTS

SFG spectra in both ppp (SFG = p, vis = p, IR = p) and ssp (SFG = s, vis = s, IR = p) polarization combinations were measured initially. Because of the low pulse energies and weak coupling of the visible evanescent wave into the interfacial vapor phase in s-polarization, the absolute signal levels measured in ssp polarization scheme were much lower than in ppp (~0.1 counts/s in ssp vs ~1–2 counts/s in ppp) which lead to much noisier spectra in the ssp configuration (Figure 2). Thus, the spectra presented and analyzed here were measured in the ppp polarization scheme. The normalization of spectra was done by dividing the raw SFG spectra from silica/vapor interface at different humidity levels by the corresponding reference SFG spectra from the silica−gold interface reflecting the IR pulse profile (gray dotted lines in Figure 3a−c). Normalization to the Fresnel factors was not done as the index of refraction of silica was assumed to be insensitive to wavelength in the probed wavelength range (the absorption in the IR-grade fused silica starts to onset at ~2800 cm^{-1}, while the water layer thickness can be considered too small (≤100 nm) from ellipsometric measurements[35] to influence the

Fresnel factors between silica and air). The reference SFG spectra of the IR pulses appeared narrower (half-maximum width) than the frequency range of the hydroxyls as temporal compression of the broadband IR pulses at the probed interface was not optimized; thus, tuning of the IR−vis interpulse delay was needed to measure spectra at lower frequencies (<3200 cm^{-1}).[33]

SFG spectra at typically encountered ambient values of relative humidity (~20%) display several features (Figure 3b) including (1) broad structure at ~3400 cm^{-1} and (2) relatively narrow peak at ~3750 cm^{-1}. The narrow peak at ~3750 cm^{-1} persists in the SFG spectra when RH < 5%, while the broad peak at ~3400 cm^{-1} disappears (Figure 3a). After exposing the silica surface to saturated D_2O vapor, the narrow peak at 3750 cm^{-1} is significantly suppressed, and the SFG spectrum becomes almost flat (Figure 3a). On the basis of the positions of the peaks in SFG spectra and their response to changes of RH, we assigned the peak at ~3750 cm^{-1} to non-hydrogen-bonded silanols, while the broad structure at lower frequencies (3200−3600 cm^{-1}) was assigned to hydroxyl stretches of water molecules adsorbed on the silica surface. Obviously, the bandwidth of the silanol peak in our measurements (~50 cm^{-1}) was limited by the resolution of the visible pulse (observed line widths <10 cm^{-1} in FTIR[5]).

In a series of control experiments, a silica prism sample was cleaned, heated in liquid D_2O for >1 h, and then the SFG spectrum was measured from the silica surface in contact with ambient air (20% H_2O vapor). The SFG spectrum displayed all the features of a silica surface in contact with the ambient air measured promptly after cleaning. These control experiments indicated that on the time scale of the SFG spectral acquisition (at least 1−2 min, if integrating a SFG spectrum at a single IR−vis delay), the exchange of vapor molecules with the amorphous silica surface occurs practically immediately.

The free-silanol peak disappeared after exposure of the silica prism surface to ambient air for prolonged periods of time (~1−2 days) which was assigned to adsorption of hydro-carbon-like contaminants, based on similar observations of a gradual increase of water contact angle on quartz.[36] Additionally, water was observed to spread to form of a thin film on the freshly cleaned silica surface (interference fringes could clearly be observed and contact angles were <5 degrees), thus facilitating quick drying of the silica prism sample in ambient air. For this reason, simple drying of the prism samples in air was preferred to drying with a flow of dry nitrogen, since the latter could potentially introduce organic contaminants.
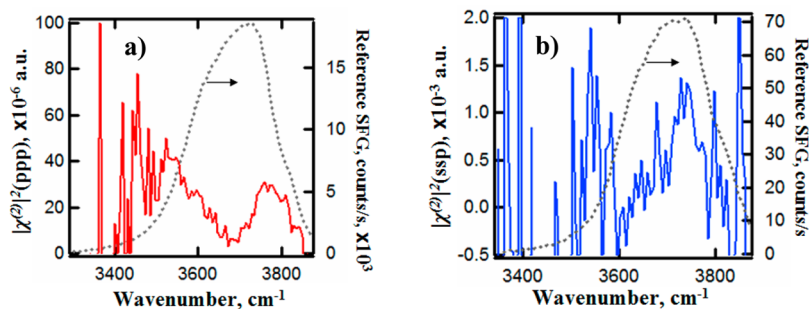

Figure 2. Intensities of SFG spectra (solid lines) measured from silica/ambient air (RH ~ 20%) surface in ppp (a) and ssp (b) polarization combinations, in the frequency range of free silanols. The SFG spectra were obtained by normalizing the raw SFG spectra to the corresponding reference SFG spectra (gray dotted lines).
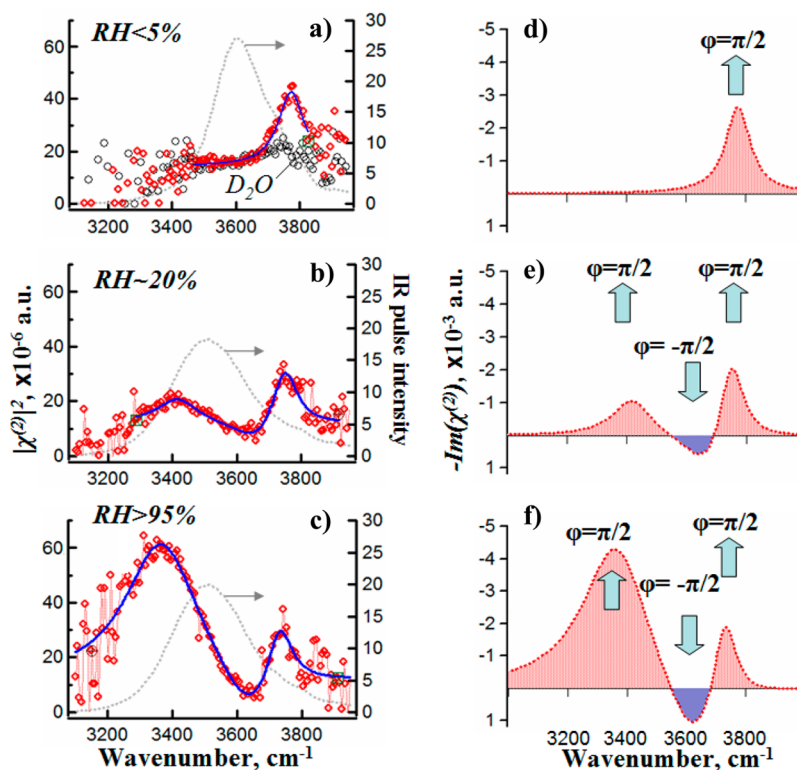
Figure 3. SFG spectroscopy of amorphous silica exposed to air of varying relative humidity. (a−c) Blue lines, three-peak fits to eq 1, of SFG spectra (red diamonds). Gray dotted lines: reference spectra of IR pulses. Black circles in (a): SFG spectrum from silica exposed to saturated D_2O vapor. Spectra of silica/vapor interface in (a−c) were obtained by normalizing the raw SFG spectra by the reference SFG spectra (gray dotted lines). (d−f) Imaginary parts of the surface second-order nonlinear spectra for silica exposed to the three corresponding relative humidity values, reconstructed from the fit results of the $|\chi^{(2)}|^2$ spectra. Blue arrows indicate relative orientations of corresponding oscillators.

4. ANALYSIS

Similar to the previously published studies,[2] our measurements show (Figure 3) that the intensity of the free silanols changes only slightly when the relative humidity of air increases from the ambient value (∼20%) to the saturation value (∼95%), whereas the intensity of the H-bonded peak in the ∼3300−3400 cm^{-1} region increases substantially. At the same time, the decrease of the relative humidity of the air in contact with silica leads to the suppression of the response of the hydrogen-bonded hydroxyls and to an increase of the isolated hydroxyl response at ∼3750 cm^{-1}. This supports the conclusion of the Allen group on the mechanism of water adsorption on flat silica surface that the water molecules adsorb on flat silica in "islands", covering a relatively small fraction of the surface and leaving most of isolated silanols unperturbed.[2] Interestingly, the silica surface preparation conditions used in the current study (wet etching of the silica surface followed by passive drying in air) lead to essentially the same observation of the isolated surface silanols in ambient atmosphere as the SFG spectra obtained by the Allen group, who, however, used annealing of silica (in a muffle oven at 900 °C for 12 h for removal of possible organic contaminants, followed by cooling at room temperature and equilibrating with the ambient conditions[2]). Control SFG measurements from a silica surface in contact with hexane vapors (section 5.3) show that the free silanol signal from silica/water vapor interface was not due to water in contact with a contaminated hydrophobic surface of the silica prism.

The vSFG spectra obtained previously from the silica/air interface were mainly discussed in terms of the intensities of the

isolated and hydrogen-bonded hydroxyl signals.[2,3] What we believe was not fully recognized in these studies is that the sum-frequency measurements can provide the information on the relative orientation of the observed oscillators via their relative phases (eq 1). Depending on the value of phase, 0 or π (+π/2 or −π/2), the oscillators will be oriented either toward or away from the surface. A change of orientation of water molecules was found previously by fitting the homodyne-SFG spectra, yielding a π phase change for water molecules at alumina surfaces as the charge went from positive to negative.[37] More recently, the phase of the sum-frequency signal has been used to directly determine the orientations of the OH oscillators at the air/water interface,[28] as well as the silica/water interface,[25] via phase-sensitive (heterodyne-detected) vibrational SFG spectroscopy. The Tahara group used heterodyne SFG to demonstrate a 180° change in orientation of water molecules at the surfactant-covered water surface when the surfactant charge was reversed.[28] In this respect, the ability to measure the $Im(\chi^{(2)}_{eff})$ spectrum becomes more valuable than only $|\chi^{(2)}_{eff}|^2$ since the signs of various peaks in $Im(\chi^{(2)}_{eff})$ spectrum directly reflect the relative orientations of the associated oscillators:

$$|\chi_{eff}^{(2)}|^2 = \left| \chi^{(2)}_{NR} \exp(-i\varphi_{NR}) + \sum_j \frac{B_j}{\omega - \omega_j + i\Gamma_j} \right|^2$$

(1)

where $\chi^{(2)}_{NR}$ is the nonresonant second-order susceptibility (typically caused by the electronic response), φ_{NR} is the relative phase of the surface nonresonant nonlinearity, B_j is the effective amplitude of the jth vibrational mode, and Γ_j and ω_j are the

Table 1. Fit Results for SFG Spectra of the Silica/Air Interface at Three Humidity Levels (Figure 3a–c)[a]

spectrum	χ_{NR}, au	oscillator strengths B_j, (au)	center freq ω_{j0} (cm^{-1})	line widths Γ_j (cm^{-1})
SiO$_2$/dry air	$0.00376 \pm 5 \times 10^{-5}$	0.139 ± 0.007	3774 ± 1	50 ± 3
SiO$_2$/ambient air (RH ~ 20%)	0.0035 ± 0.0002	0.092 ± 0.017	3418 ± 8	80 ± 15
		-0.12 ± 0.03	3670 ± 17	94 ± 22
		0.135 ± 0.017	3750 ± 3	50 ± 0
SiO$_2$/humid air (RH > 95%)	0.0035 ± 0.0005	0.67 ± 0.08	3364 ± 7	140 ± 12
		-0.36 ± 0.11	3630 ± 23	135 ± 38
		0.15 ± 0.03	3729 ± 6	50 ± 0

[a]The relative nonresonant phase value is $\varphi_{NR} = \pi/2$. The errors are fit parameter uncertainties; absolute uncertainty, including spectrometer accuracy and visible pulse bandwidth, will be greater.

natural line width and central frequency of the jth vibrational mode. According to eq 1, two oscillators with oppositely orientated oscillating dipoles will have opposite signs of their amplitudes, B_j.

Even though the current SFG setup does not measure directly the real and imaginary parts of $\chi^{(2)}_{eff}$, the changes in SFG spectra from silica/air surface at different levels of humidity provide strong evidence for the relative orientations of the hydrogen-bonded and free OH oscillators at this surface, namely, there is at least one type of adsorbed water molecules oriented in a direction opposite to the surface silanols (i.e., the OH groups of those water molecules point toward silica). This determination is possible because the SFG signal from the silica/air has a relatively high nonresonant signal ($\chi^{(2)}_{NR}$ in eq 1) compared to resonant features, e.g., free SiOH. When the nonresonant signal becomes of the same order as the resonant contributions $\chi^{(2)}(\omega_j)$, the destructive/constructive interference between these components can considerably change the shape of the homodyne-measured spectrum $|\chi^{(2)}|^2$. This feature of the vSFG spectra was recently employed to extract the relative phases of various oscillators with respect to the nonresonant nonlinearity in a study of the weak near-IR combination bands of water molecules (~5000–5300 cm^{-1}) at charged silica surfaces.[38]

We have observed that the spectra corresponding to the silica surface in contact with dry air (RH < 5%) have a very different shape from the SFG spectra when the silica is in contact with ambient or humid air (Figure 3). In particular, the signal at lower frequencies decreases when the air is dry, suggesting the removal of physically adsorbed water (similar to earlier observations[2]). The adsorption of sulfuric acid molecules from vapor was excluded since the vapor pressure of 95% H$_2$SO$_4$ (≪0.001 mmHg at ~25 °C; 1 mm at ~145 °C) is several orders of magnitude lower than that of water (~20 mmHg at room temperature). At the same time, the signal of the free silanols remains in spectra (which again supports the assignment of the peak at ~3750 cm^{-1} to surface-bound hydroxyls) and seemingly increases in intensity compared to the signal of free silanols in contact with humid air. We believe that the increase of the free-silanol signal in the $|\chi^{(2)}_{eff}|^2$ spectra upon placing silica in contact with dry air is caused by the disappearance of the destructive interference from signal of water molecules which vibrate out-of-phase with the surface silanols. Further supporting evidence of such a mechanism of water adsorption is the "dip" in the $|\chi^{(2)}_{eff}|^2$ signal at ~3600–3700 cm^{-1} from silica in contact with humid air, which suggests that the signs of contributions from water and silanols are 180° out of phase (opposite signs). The "dip" in the spectrum at ~3600–3700 cm^{-1} disappears upon desorption of water (Figure 2a–c), which is consistent with the picture that the

remaining silanols oscillate in phase since they all are presumably oriented in the same direction (pointing away from the silica into air). The detailed and quantitative analysis of the spectra, fit to eq 1, at different humidity levels, supports the proposed model of water adsorption on the silica surface, as is described below.

4.1. Fitting the Sum-Frequency Spectra from Silica/Air Interfaces. We start by fitting the SFG spectrum from the silica in contact with dry air (Figure 3a). To assess the value of the nonresonant signal $\chi^{(2)}_{NR}$, we measured the sum-frequency spectrum from the same interface with ~1–2 mL of liquid D$_2$O placed into the Teflon holder underneath the prism (Figure 3a, black circles). We found that this is a necessary step in the data analysis; otherwise, there is an ambiguity in the values of the silanol peak height. The correspondence between the average level of the signal in case of the silica/D$_2$O vapor interface and the silica/dry air interface indicates that the peak at ~3750 cm^{-1} in the latter case corresponds solely to the silanols.[2] Note that there is a small residual signal at ~3700–3750 cm^{-1} for the SiO$_2$/D$_2$O vapor interface which may indicate incomplete exchange of silanol protons with deuterons.[39]

The fits of the silica/dry air spectra suggest the relative phase offset between the nonresonant nonlinearity and the surface silanols is $\varphi_{NR} = \pi/2$ (Figure 3a), assuming positive $\chi^{(2)}_{NR}$. This was required mathematically since in the case of $\varphi = 0$ or π, the shape of the simulated $|\chi^{(2)}|^2$ spectrum does not correspond to the experimentally observed single-peak spectrum $|\chi^{(2)}|^2$. The $\pm\pi/2$ phase offset of interfacial resonant oscillations from the nonresonant signal was experimentally shown in the early work of Shen and colleagues.[40] In our case, however, the ability to define the relative signs of the oscillator amplitudes is more important than the exact value of φ_{NR}, since the SiOH hydroxyls provide the "reference" orientation at the interface. For the fitting of the sum-frequency spectra from silica in contact with ambient air and humid air, we used three oscillators (eq 1). In order to compare the oscillator strengths of the free silanol peak for the three values of relative humidity, the bandwidth and the sign of the free−OH groups were kept equal to those obtained from the fits for the silica/dry air surface. (We could also fit the spectra with "released" bandwidth of SiOH peak, which yielded $\Gamma \sim 37 \pm 15$ cm^{-1}. However, in this case it would not be possible to compare the SiOH peak heights among different relative humidity levels.) The results of the fits for the three values of relative humidity are plotted in Figure 3, and the best fit parameters are indicated in Table 1.

To compare the results of fits for the three cases of air humidity and to visualize the orientations of the H-bonded and free-OH oscillators, we plot the imaginary part of the resonant nonlinearity $\chi^{(2)}_R(\omega)$ (Figure 3d–f). The Im($\chi^{(2)}$) spectrum is
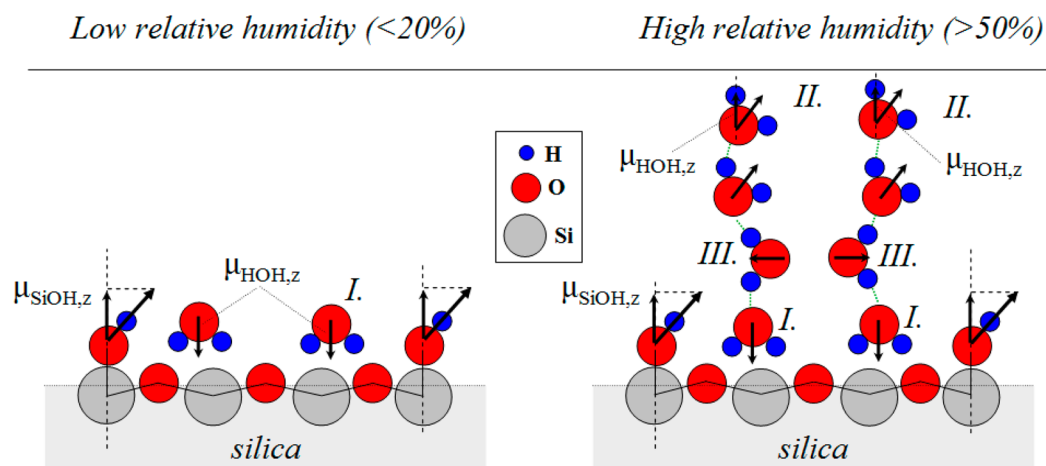
Figure 4. Suggested model for water adsorption on a silica surface from the vapor. Notations for hydrogen, oxygen, and silicon atoms are shown in the inset. Left: adsorption of water molecules at low RH. Water initially adsorbs into type I (weakly hydrogen bonded, $\omega \sim 3650$ cm^{-1}). Right: adsorption of water at high RH. Type I (weak H-bonding) water molecules are still present in direct contact with the silica surface; excess water molecules adsorb into multilayers with their dipole moments preferentially oriented away from silica (type II). Water molecules with their dipole moments parallel to the silica surface (type III) may be present to facilitate hydrogen bonding between type I and type II. However, vibrations of these molecules may not be visible in SFG spectra as they mutually compensate each other on average. $\mu_{SiOH,z}$ and $\mu_{HOH,z}$ denote the projections of the dipole moments of the hydroxyl groups in silanols and water molecules, respectively, onto the z-axis normal to the silica surface. Hydrogen bonding between water molecules is shown in the case of silica/humid air with thin dotted green lines.

equivalent to the FTIR absorption spectrum Im($\varepsilon^{(1)}$); however, due to the coherent nature of SFG process, the Im($\chi^{(2)}$) spectrum also visualizes the relative amplitude signs, and thus the orientations of the oscillators present at the silica/vapor interface.[41]

5. DISCUSSION

5.1. Mechanism of Water Adsorption on Silica Based on Sum-Frequency Spectroscopy Results. The SFG spectra from the silica/vapor interface are best described by three peaks: a negative peak at ~3750 cm^{-1} (corresponding to free silanols), a positive peak at ~3600 cm^{-1}, and a negative peak at ~3350−3400 cm^{-1} (both assigned to adsorbed water hydroxyls). The positive peak at ~3650 cm^{-1} is comparable in intensity to the peak at ~3400 cm^{-1} for the case of ambient air (RH ~ 20%, Figure 3b). As the RH value increases to ~95%, the peak amplitude at 3650 cm^{-1} changes slightly, while the negative peak at ~3400 cm^{-1} increases significantly in intensity (Figure 3c). The presence of a peak at ~3690−3700 cm^{-1} might have been expected at high humidity, corresponding to the "dangling" OH of water molecules at the multilayer-water/vapor interface (similar to the observation of free OD at mica/D$_2$O vapor[42] or at an octadecylsilane-modified silica/water interface[39]). However, the sign of this peak would be expected to coincide with that of the SiO−H peak, resulting in a double peak in the 3700−3750 cm^{-1} range which was not observed. This is consistent with other studies.[2,3]

The vSFG spectra of the silica/air interface described above suggest the following model of water adsorption on silica. At low humidity levels (relative humidity <20%), the initial water molecules adsorb preferentially in an orientation opposite to the surface silanols (Figure 4, water type I), as suggested by the phase difference of the peaks at ~3750 and ~3650 cm^{-1}. There may be a certain tilt of the molecular dipole with respect to the surface normal, but we do not determine it in our study. The preferential orientation is nevertheless suggested by the opposite phases of the OH oscillators of H$_2$O and SiOH. To our knowledge, this is the first observation of weakly hydrogen-

bonded water molecules (~3650 cm^{-1}), as characterized by a red-shift that is significantly less than liquid water, on flat silica surfaces in ambient conditions oriented toward the substrate (Si−O−Si network).

As the humidity of the air increases, so does water adsorption. Since the free-SiOH peak remains in the SFG spectrum at high humidity, it suggests that water molecules are more likely to gather in "patches" on the silica surface.[2] Water does not seem to adsorb in a layer by layer fashion, where one monolayer must be complete before another starts to form. Formation of water multilayers, before completion of monolayer and bilayer, etc., is most likely (since the free silanols are observed at about the same intensity even at RH ~ 95%); as a result, the strength of hydrogen bonding between water molecules in multilayers increases, leading to a red-shift of the hydrogen-bonded peak closer to the bulk values (~3400 cm^{-1}; water type II in Figure 4, right). Those hydrogen-bonded water molecules that contribute to the vSFG spectra have their dipole moment preferentially oriented away from the silica surface, as they have the same phase as the SiOH. At the same time, a large portion of water molecules remain in the geometry of adsorption at low humidity (permitting less hydrogen bonding) as revealed by the constancy of the spectral feature at ~3650 cm^{-1}. Such a model explains the behavior of the Im($\chi^{(2)}$) spectra when the RH value increases from 20% to 95% (Figure 3b,c). There may be also water molecules that have their dipole moment oriented parallel to the silica surface (type III in Figure 4); their presence is very likely since the multilayer structure has to be stabilized via a hydrogen-bonding network. However, such molecules would not be visible in the sum-frequency spectra as their transition dipole moments would cancel out on average. Additional evidence supporting the symmetric nature of the vibrations of water hydroxyls in vSFG spectra is the much higher normalized intensity of SFG spectra in the ssp configuration than in ppp (~10−20 times, Figure 2).[41]

The existence of non-hydrogen-bonded silanols can be explained by the relatively low surface concentration of the
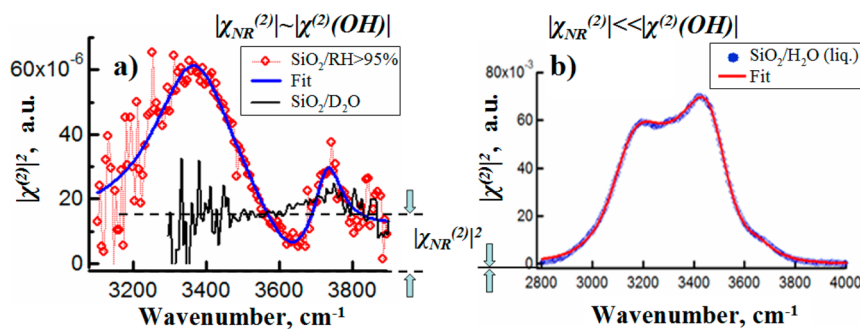
Figure 5. Relative contributions of the resonant and nonresonant nonlinearities in SFG spectra from silica/humid air (a) and silica/neutral water (b) interfaces. In (a), the dashed line corresponds to the level of $|\chi^{(2)}_{NR}|^2$ deduced from fits of spectra in Figure 2. In (b), the red line is a three-peak fit of the spectrum.[38] The water/silica SFG spectrum in (b) was obtained by normalizing the raw SFG spectra by the reference SFG spectra and the Fresnel factor for the silica/water interface.[38] The magnitudes of the nonresonant nonlinearity $\chi^{(2)}_{NR}$ contribution are indicated by the dashed line in (a) and the baseline in (b) as deduced from experiments with D_2O.

silanol groups (<5 nm^{-2}),[25] compared to that of water molecules at the surface (∼20 nm^{-2}) based on bulk density. In this adsorption mechanism, the low SiOH surface density can give adsorbing water molecules the ability to gather into islands atop the Si−O−Si two-dimensional network. As we discuss below, an additional factor that may contribute to low hydrogen bonding between surface silanols and water molecules is the irregularity of SiOH groups which likely do not match the lattice of ice (as opposed to crystalline mica and kaolinite surfaces). Still, partial hydrogen bonding of silanols to adsorbed water molecules seems to occur as the free-silanol peak undergoes ∼30−40 cm^{-1} red-shift when RH changes from <5% to >95%.[5] While the largely blue-shifted peak position for the free silanols in the case of dry air/silica surface (>3770 cm^{-1}) remains to be confirmed in additional studies, it may be indicative of silanols with reduced anharmonicity[43] due to further decreased perturbation of the O−H oscillator potential energy curve as the water molecules are removed from the surface.

Our results are in contrast to a recent attenuated total reflection (ATR) FTIR study of water adsorption on silicon oxide layer formed on a silicon surface.[44] On the basis of the dichroic ratio analysis, the authors concluded that water has a preferential orientation of the dipole moment (∼35° tilted from the surface normal) at lower humidity (∼20%); however, at higher humidity (>50%) water in the multilayers was suggested to have absolutely no preferential orientation.[44] In contrast, our data clearly show constructive and destructive interferences between the OH stretches of water and SiOH groups even in the case of RH ∼ 95% (Figure 3c), suggesting that the water dipole alignment is preserved even at high RH. It should be noted that the spectra shown in ref 44 only go up to 3650 cm^{-1}, and there is only a brief mention of a weakly hydrogen bonded hydroxyl peak at ∼3600 cm^{-1} which, however, was not considered further. A possible explanation for such discrepancy is that the ATR technique probes all of the adsorbed water layers, thus showing disorder at high humidities, while the SFG technique probes only the first few water layers where $\chi^{(2)} \neq 0$. Various reports on studies of silica/vapor interfaces indicate ∼10−20 nm water layer thickness[35,45] corresponding to ∼30−50 molecular layers when relative humidity is close to saturation levels. At the moderate humidity, the adsorbed water layer thickness has been reported ∼2−3 nm corresponding to <10 layers.[35] Thus, we believe we are able to investigate in situ the interactions among various hydroxyl species on the silica/vapor surface at the level of few molecular layers.

Lastly, we note that the contributions of nonresonant and resonant hydroxyl signals into the homodyne SFG spectra of silica/vapor interface are comparable (Figure 5a). On the other hand, the resonant contribution of the water hydroxyls in the SFG spectra of silica/water (pH ∼ 6) interface is at least 2 orders of magnitude higher in the $|\chi^{(2)}|^2$ spectra than that of $\chi^{(2)}_{NR}$ (Figure 5b). The comparison between these two situations suggests that in the case of the silica/water interface mutlilayers of water molecules must be contributing via $\chi^{(3)}$:E_{DC}, where E_{DC} is the static electric field created by the charged silica surface. Thus, we believe that the SFG spectroscopy of the silica/vapor interface may provide an insight into the debate over the extent of contributions of $\chi^{(2)}$ and $\chi^{(3)}$:E_{DC} nonlinearities of water molecules at charged silica/water interfaces to the observed SFG spectra.[46−48]

5.2. Hydrophobic Nature of Flat Amorphous Hydroxylated Silica Surfaces. It is interesting to compare our results of water adsorption on amorphous silica with investigations of other naturally occurring crystalline modifications of silica. For water (D_2O) adsorption on mica, a crystalline composite of aluminum and silicon oxides with admixtures of sodium or potassium oxide, the non-hydrogen-bonded peak at ∼2740 cm^{-1} appeared in the SFG spectra only at relative humidity >97% and was assigned to the free-OD peak formed at water/vapor interface of D_2O multilayers.[42] The spectra in the humidity range 53−97% contained the broad peak at ∼2300−2500 cm^{-1} for hydrogen bonded OD stretches (which would correspond to ∼3200−3400 cm^{-1} for OH oscillators). As the peak position was close to the maximum of the IR absorption spectrum of ice, the presence of "ice-like" water on the mica surface was concluded.[42] The authors suggested that the formation of "ice-like" structures of adsorbed water may be favored by the approximate lattice matching of the mica surface and the hexagonal ice basal plane,[42] so that the creation of strongly hydrogen-bonded water molecular network (as in ice) is likely. Such interaction of water with the mica surface is very similar to the enhanced nucleation of ice on the surface of a clay mineral kaolinite ($Al_2Si_2O_5(OH)_4$) reported by experimental[49] and theoretical[22] investigations. Field studies have shown the presence of kaolinite in ice crystals.[50] This action of kaolinite has been explained by the large surface density of hydroxyl groups available for hydrogen bonding with adsorbed water molecules on kaolinite's octahedral faces.[22] Properly spaced hydroxyl groups can provide a match to the ice lattice, thus encouraging strong hydrogen bonding of water molecules to the substrate and formation of "ice-like" water
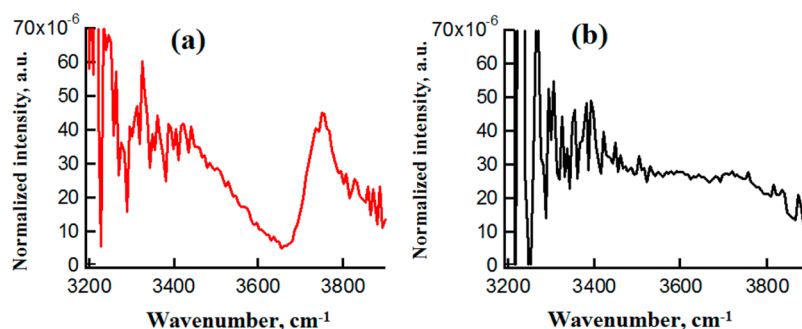
Figure 6. Quenching of the free SiOH response from silica upon exposure to hexane vapors. (a) SFG spectrum from a silica/air interface after SC1 cleaning of the prism, ambient air. (b) SFG spectrum from the same silica prism with ~1−2 mL of hexane present in the Teflon holder beneath the prism sample, at ambient relative humidity (~20%). The hexane adsorption was nonreversible, i.e., spectrum in (a) could not be restored by replacing the hexane vapor with water vapor. The spectra are noisy at <3300 cm^{-1} since the main focus of these measurements was on the frequency range around the free-silanol peaks.

structure. An additional factor that may increase hydrogen bonding among adsorbed water molecules, as well as of water molecules to the surface, is the presence of ions in the crystalline structures of mica and kaolinite,[51] which are absent in amorphous fused-silica surfaces. Recent theoretical investigations suggest that the amphoterism of the surface hydroxyl groups (i.e., their ability to accept and donate protons) also plays a significant role in two-dimensional ice formation.[50,52]

In contrast to crystalline mica and kaolinite surfaces, we find that initial water adsorption on silica at low humidity results in weakly hydrogen-bonded (~3650 cm^{-1}) species. Increased hydrogen bonding between molecules starts to appear at higher humidity. Even in the case of air at saturated humidity (RH~95%), no "ice-like" OH peak is observed in SFG of silica/air either here or in other investigations.[2] By combining the observation of the free-SiOH peak in the SFG spectra of silica in the presence of adsorbed water (Figure 3b,c) with the knowledge that the density of surface silanol groups on amorphous silicas is relatively low (<5/nm^2)[25] compared to OH groups of liquid water, and the orientation of what is likely the first adsorbing water molecular layers observed by SFG (Figure 3), it is logical to conclude that water molecules do not strongly hydrogen-bond to the basal oxygen atoms of the siloxane bridges Si−O−Si (Figure 4, water type I). Interestingly, the orientation of these weakly hydrogen-bonded molecules deduced from our SFG measurements is in good agreement with the predictions of weak H-bonding and the orientation of water on the tetrahedral plane of kaolinite which does not have surface hydroxyl groups.[22]

Summarizing the data presented here, and the experimental and theoretical data available for water adsorption on crystalline forms of silica, we conclude that the flat freshly prepared surface of amorphous silica is essentially hydrophobic. The high wettability (and thus hydrophilicity) of hydroxylated silica surfaces (as observed, for example, by low contact angles in our cleaning procedures) most likely is due to deprotonation of surface silanols when in contact with bulk liquid water. The hydrophobicity is the result of several factors, mainly (i) the low surface density of silanols and (ii) the preferential hydrogen bonding of water molecules to each other rather than to the oxygen atoms in surface siloxane bridges.

The hydrophobic character of the silica surface has been suggested previously by molecular dynamics simulations of the interaction of water with the "dense" (0001) surface of quartz which is characterized by 3- and 6-membered rings with siloxane bonds at the top.[53] The hydrophobicity of the silica

surface was also suggested in the previous SFG studies[2,3] as well as in near-IR investigations of water adsorption on silica, alumina, and titania.[54] Our SFG data support the notion of the hydrophobic character of neat hydroxylated SiO$_2$ surfaces; in addition, we are able to clearly distinguish at least two types of water molecules with various strengths of hydrogen bonding and orientations with respect to the substrate.

5.3. Quenching of Free SiOH with Alkane (Hexane) Vapor. The surface sensitivity of SFG spectroscopy can help understand the interaction of silica surfaces with vapors of various nonpolar molecules such as hydrocarbons, as a complement to studies of silica in contact with nonpolar liquids.[55−57] Such measurements would be particularly useful in the context of investigations of the microscopic hydrophobicity of silica surfaces as well as provide additional insight into interaction of silica-based minerals with paraffins and other nonpolar molecules. After placing liquid hexane into the Teflon prism holder (but not into direct contact with the prism surface), we observed quenching of the free-silanol peak at 3750 cm^{-1} (Figure 6). This observation suggests that adsorption of hexane(s) vapors onto silica leads to an increased role of hydrogen bonding between either (1) isolated silanols, though these may be too far apart on average or (2) between adsorbed water molecules and the isolated silanols. Additional mechanisms responsible for the observed SFG spectrum change could be (3) adsorption of hexane molecules on top of water layers and (4) complete displacement of water molecules at the silica surface by the hexane molecules. Mechanism 3 seems unlikely since the SFG spectral change is irreversible upon exposure of SiO$_2$ to hexane vapors (see below). On the other hand, it would be interesting to confirm mechanism 4 as it would suggest the possibility for a direct hydrogen bonding between hexane molecules and surface silanols. Based on our current understanding of the silica surface, mechanism 2 seems most likely due to the relatively low SiOH surface density and would support the notion of affinity between nonpolar hexane molecules and the low-polarity siloxane bridge networks.[36] As the result of hexane adsorption, water molecules would no longer have the access to exposed siloxanes and thus would be forced to hydrogen bond with silanols. An additional factor in favor of this mechanism is the disappearance of the mode at 3650 cm^{-1}. Note that contrary to the full reversibility of the SFG spectra from SiO$_2$ surface in contact with H$_2$O and D$_2$O vapors, the change in SFG spectra depicted in Figure 6 was irreversible. Namely, after exposing the silica surface to hexane vapor, the spectrum from silica surface in contact with pure

water vapors (e.g., free silanol peak, Figure 6a) could not be restored. The silica prism had to undergo the wet cleaning procedure to obtain a spectrum such as in Figure 6a.

The disappearance of the free-silanol peak in sum-frequency spectra of the silica/air interface in the presence of hexane vapors suggests a possible mechanism for the observation that silica prisms exposed to ambient air for prolonged times (several days) also showed disappearance of free-silanol peak (section 3). Namely, it is possible that hydrocarbon-like contaminants adsorb onto silica surfaces exposed to ambient air over days or weeks, which in turn suppress the isolated silanol response, similar to the action of hexane vapors.

The observation of the quenching of the free-OH response in the presence of hexane is in contrast to the SFG of water/hexane interfaces,[25,58] where the free-OH signal from interfacial water molecules is preserved, even though the band intensity is weaker than at the water/air interface. In addition, we note in our observations that the contact angle of hexane on silica approaches zero (hexane easily spreads on silica surface, before it completely evaporates), suggesting that there is a considerable interaction between this small-molecule alkane and the silica surface.[59] We hope that these initial results will stimulate further applications of the surface sensitivity of SFG toward investigations of alkane vapor adsorption on silica and its various forms, as they are of great importance for environmental chemistry as well as industrial applications such as catalysis on solid oxides and enhanced oil extraction.

6. CONCLUSIONS

In summary, we have investigated the adsorption of the few first water molecular layers on flat amorphous silica surfaces under ambient conditions of various relative humidity. The similar magnitudes of the resonant and nonresonant surface non-linearities make it possible to observe interferences between the various contributing oscillators and the nonresonant susceptibility directly in homodyne SFG spectra which renders the measurement in some respects "quasi-phase-sensitive". This phase-sensitivity provides access to the orientation of adsorbed water molecules relative to the silanol hydroxyls. The spectra in $3100-3700$ cm^{-1} range suggest that there are at least two types of water molecules adsorbed on the silica surface: (1) weakly hydrogen-bonded water molecules ($\tilde{\nu} \sim 3650$ cm^{-1}) with their hydrogen atoms oriented toward the silica substrate; (2) bulk-like, stronger hydrogen-bonded water molecules ($\tilde{\nu} \sim 3400$ cm^{-1}) preferentially oriented with their hydrogen atoms away from silica. At low humidity, water molecules preferentially adsorb into a weakly hydrogen bonded state; at high humidity, the new incoming water molecules adsorb in multilayers with stronger hydrogen bonding. We believe that this is the first experimental report of weakly hydrogen bonded water molecules (~ 3650 cm^{-1}) that were predicted by earlier theoretical investigations of kaolinite. The observation of this mode, as well as small changes in the intensity of the isolated silanols, indicates that, surprisingly, the water in thin films does not interact with the surface-bound hydroxyls, thus supporting the conclusion that the amorphous hydroxylated silica has a largely hydrophobic character. This may be due to the absence of charged silanol groups on silica surfaces in contact with water vapors. A comparison of the vSFG data for the silica/air interface obtained in this work to the FTIR data from silica gels indicates that flat silica surfaces are fundamentally different from the curved surfaces of silica gels and colloid silicas. In the case of flat silica, we can observe the sum-frequency spectrum

of free silanols at ambient conditions; in the case of silica gels, evacuation at elevated temperatures is required to drive off adsorbed water and obtain the FTIR spectrum of isolated silanols. It is possible that the porous structure of the silica gels can bring the silanol groups much closer and thus enhance hydrogen bonding between them as well as with the adsorbed water molecules. Hence, the extension of conclusions from the FTIR data obtained on high surface area colloid systems to flat surfaces has to be made with caution.

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Notes

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