Hydrogen-bonding structure in self-formed nanodroplets of water adsorbed on amorphous silica revealed by surface-selective vibrational spectroscopy

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Water adsorption onto materials surface is known to change macroscopic surface properties such as wettability and friction coefficient. While the role of the adsorbed water has been discussed for a long time, the interfacial structure of the adsorbed water is not fully recognized in many cases. In this study, hydration structure of water adsorbed on vapor/silica interface at room temperature was studied by heterodyne-detected vibrational sum-frequency generation spectroscopy. The vibrational spectra of the interfacial molecules obtained here were different from those estimated by conventional sum-frequency generation spectroscopy. Interestingly, our results suggest that, at low humidity, the adsorbed water on silica forms nanodroplets instead of uniform film. Because no silanol group was found to be hydrogen-bonding free, it was concluded that water molecules gather around the silanol group to form strongly hydrogen-bonded droplets. At high humidity, while the adsorbed water partially behaves like bulk liquid, deprotonation of silanol was not observed unlike silica surfaces in contact with bulk liquid water.

Introduction

Macroscopic surface properties, such as wettability and friction coefficient, are known to depend on the humidity of the environment. 1, 2 This dependence originates from water adsorption onto the material surfaces. While the mechanism how the adsorbed molecules change the macroscopic properties has not been fully understood yet, several groups have tried to rationalize the humidity-dependence from the viewpoint of hydration structure of the adsorbed water. For example, attenuated total reflection infrared (ATR-IR) spectra of silica/air interface suggested that the adsorbed water undergoes phase transition from ice-like to liquid-like depending on its thickness, and humidity dependence of friction force at silica/silica system was discussed on the basis of the transition. 3, 4 Molecular dynamics (MD) simulation implied that the adsorbed water affects tribochemical formation of covalent bond between two surfaces of α-SiO₂ and oxidized Si. 5

Despite such the effort, water structure on solid substrate is still far from rigid understanding even at solid/air interfaces. For example, it is unclear whether the adsorbate forms uniform “film” growing layer-by-layer upon increase of humidity or forms “nanodroplets” without covering the whole surface. Because physical theories for wettability and friction forces generally assume that the surfaces are flat and chemically homogeneous, it must be clarified whether the surface water uniformly spreads or forms multiple domains. For mica surface, scanning polarization force microscopy and vibrational sum-frequency generation spectroscopy revealed that the adsorbed water forms uniform film with ice-like hydration structure. 6-8 First coverage of full-monolayer of water was first thought to be achieved at relative humidity (RH) of around 20%, but it was revisited to be 90%. 9 In contrast to the quite thin water layer on mica, Asay and Kim reported that silica possesses about two monolayers of water even at ~20% and the water layer further grows at higher RH. 4 This thickness was determined by signal intensity of water bending mode of ATR-IR spectra observed for native oxide layer of silicon prism, and hence the thickness evaluated in the study was only “average thickness” with an assumption with uniform film model. Because silicon oxide (silica) is one of the most abundant materials and often used as a model substrate for examining surface properties such as wettability, 8, 10 the hydration manner on silica is especially important. However, despite of such importance, the homogeneity of adsorbed layer on silica surface had been very rarely discussed. The rare study is one performed by Isaienko and Borguet. 11 They observed vibrational spectra of adsorbed water on silica with vibrational sum-frequency generation (VSFG) spectroscopy. According to this literature, some portion of surface silanol (SiOH) group remains water-free even at RH
higher than 90%, indicating water does not cover the whole surface. They also observed water molecules which weakly interact with oxygen atom of siloxane (Si-O-Si) group. These results let them conclude that silica is microscopically hydrophobic, presumably due to absence of charged silanol (SiO) groups at vapor/silica interface. However, this model has serious unnaturalness that water more prefers siloxane to silanol. As clarified for silica/acidic aqueous solution interface by Myalitsin et al, hydrogen-bonding between water and protonated silanol (SiOH) group is stronger than that between water and siloxane bridge.  

Furthermore, the hydrogen-bonding structure inside the film (or domains) is not consistently understood. The ATR-IR spectra indicated that the adsorbed water forms anisotropically oriented ice-like structure at RH below 50 % while randomly oriented liquid-like structure gets dominant at higher RH. The VSFG spectra were significantly different from those obtained by ATR-IR spectroscopy and noticeable molecular alignment was observed even at ideally saturated humidity. VSFG spectra also suggested that very weakly and moderately hydrogen-bonded water species exist at low RH. This is clearly inconsistent to the model proposed by ATR-IR, in which water forms ice-like structure. While the spectral discrepancy can be attributed to the different surface selectivity of these spectroscopies as previously mentioned, it does not make any rationalization for the models proposed by ATR-IR and VSFG techniques remaining totally different.

What is making the comprehensive discussion difficult is spectral distortion, which is generally found in conventionally obtained VSFG spectra. The spectral distortion arises because only the intensity (i.e., magnitude square of electric field; |E|^2) of the signal light is probed in the traditional VSFG spectroscopy although the spectroscopic information is in fact included in complex electric field itself (E). The complexity of the electric field physically corresponds to the phase of the light, and hence it is lost if only the intensity is probed. The spectra obtained by the conventional VSFG technique are sometimes analyzed by fitting with theoretical equation in order to obtain the phase information, but such analysis should be with special care especially for water system. This is because the fitting analysis needs to assume the spectra consisting with a couple of Lorentzian peaks while vibrational spectra of water are often composed of multiple and/ or asymmetric peaks mainly due to complicated vibrational coupling and inhomogeneous broadening.  

In the present study, we applied heterodyne-detected (HD-) VSFG spectroscopy to vapor/silica interface at several RH. HD-VSFG spectroscopy simultaneously probes the intensity and phase of the signal light, and hence the vibrational spectra with no spectral distortion can be experimentally obtained as imaginary part of second-order nonlinear susceptibility (Im χ^(2)). The spectra obtained here were different from those previously estimated by fitting of conventional (homodyne-detected) VSFG data, allowing us to propose consistent model of hydration manner on the silica surface at ambient environment.

**Experimental**

**Sample**

The sample substrate (IR-grade fused silica purchased from Pier-optics) was immersed in sulfuric acid overnight prior to the measurements. After thoroughly rinsed by copious amount of water, it was dried in a clean-bench (AIRTech, L-VS-10011; class 100) without using gas blow as suggested in literature. UV/ozone cleaner (SEN Lights Corporation, PL10-110) was then used for 30 minutes. Note that UV/ozone cleaner was used also in the ATR-IR studies so that surface properties (such as surface silanol density) is expected to be essentially the same.

**HD-VSFG Apparatus**

Experimental setup for HD-VSFG measurement was built according to literature. Briefly, output of regenerative amplified femtosecond laser (Coherent, Astrella; average power: 7 W, pulse duration: 30 fs, and repetition rate: 1 kHz) was split into two. One (∼2.5 W) was passed through a bandpass filter (band width: 1.5 nm (∼25 cm^-1) of full width of half maximum, center wavelength: 795 nm) and neutral density filter to make a narrow band pulse having frequency of ω_1 with energy of ∼5 μJ/pulse. The other was used to pump OPA/DFG system (Coherent, OPerA solo) to generate broadband IR having frequency of ω_2 (2800-3800 cm^-1, ∼4-8 μJ/pulse). The two lasers were first focused onto y-cut quartz to generate sum-frequency (SF) light, which was used as local oscillator (LO) for heterodyne detection. Then the three beams of ω_1, ω_2, and LO were again focused onto the sample substrate with LO passing a thin glass plate to make optical delay. The SF lights generated from the sample and delayed LO were interfered and detected by a charge coupled device (Princeton Instruments, Spec10-400BR-M) combined with a polychromator (Princeton Instruments, Acton SP 2300). Incident angles of the two lasers of ω_1 and ω_2 are ca. 45 and 50 degrees from the surface normal, respectively. Polarizations of the detected and incident lights were set to s-, s-, and p-polarization for SF, ω_1, and ω_2, respectively (ssp polarization). Focus size at the sample was 200-300 μm. Intensity and phase of the SF light were normalized by those obtained with SF from z-cut quartz. The sample substrate was covered with half-open cell to control humidity from 20 to 90%RH. The humidity was controlled by introducing dry or hot water-bubbled air into the cell. Fluxuation of the humidity was mostly less than ± 5%RH. While sometimes the humidity suddenly changed more than 5%RH, we did not find any spectral change due to this spike-like fluctuation. Temperature inside the cell was kept at 22.0-23.0 degree. Note that it takes typically about 20 minutes to stabilize humidity inside the cell and the sample had been exposed to lab air until the humidity got stable.

**Results and Discussion**

Figure 1 shows Im χ^(2) spectra of the vapor/silica interface at 20, 50 and 90%RH. As shown in Figure S1 in the Supporting Information (SI), potential phase error of ±15° did not alter
In hydrogen-bonded OH stretching region (3000-3650 cm\(^{-1}\)), it is noted that no negative band appeared at any RH, which was estimated by fitting of traditional VSFG spectra measured with ppp-polarization\(^{11}\) and ssp-polarization\(^{15,16}\) (see Figure S2 in the SI). Observation of so-called free-OH band at high frequency (ca. 3700 cm\(^{-1}\)) also indicates that our substrate was not heavily contaminated. This is because the free-OH is known to be absent if silica surface densely collects organic molecules.\(^{11}\) The cleanliness of the silica surface was further confirmed by measuring contact angle. While hydrophilicity of silica does not directly mean its cleanliness, it may be possible to be used as a qualitative indicator of contamination. It was about 13° even four hours after the cleaning (Figure S3 in the SI), suggesting the silica kept hydrophilic in our measurement duration.

In hydrogen-bonded OH stretching region (3000-3650 cm\(^{-1}\)), both positive and negative peaks appear at low and high frequency region, respectively. Since \(\text{Im}\chi^{(2)}\) spectra consist of information of intensity and phase of the SF light, the sign of the band is directly related to the surface molecular orientation: positive band corresponds to water molecules which orient their hydrogen atoms toward the air (hereafter called “air-oriented” for short) and negative band corresponds to those orienting their hydrogen atoms toward the silica substrate (“silica-oriented”). The fact that both positive and negative bands grew with increasing RH indicates that at least two types of water (having different orientation) coexist at the silica surface. The “air-oriented” water should form hydrogen-bond between water O and the silica substrate. Because surface silanol (SiOH) is the only candidate to be hydrogen-bond donor, the “air-oriented” water is considered to be trapped at surface-silanol sites of silica. This is consistent to the fact that no free silanol groups was observed in our spectra. Note that the high frequency band in our spectra appeared at 3700 cm\(^{-1}\), and hence it should be assigned to free-OH of water\(^{22,24}\), not of silanol (3750 cm\(^{-1}\))\(^{14,16}\). As for the air-oriented water, its peak frequency (around 3250 cm\(^{-1}\) at 20%RH) indicates that the OH moieties of these water molecules also form hydrogen-bond with something on it. Because this water is “air-oriented”, the only candidate for the hydrogen acceptor is other water molecules. This is consistent to previous study which reported that the water layer at 20%RH is as thick as two monolayers in average. Structural assignment of the negative band is more difficult, but the fact that the negative band appears only at higher RH (> 50%RH) implies that the “silica-oriented” water is interacted with other water molecules below it. Very roughly speaking, the “air-oriented” water is attributable to water molecules at water/silica interface while “silica-oriented” water mainly corresponds to molecules at air/water interface. The details will be discussed later. One might worry about phase shift between water/silica interface and air/water interface, but it is negligible. This is because the water layer is no thicker than 3 nm even at 99%RH so that the phase shift is expected to be <2.5°. In our spectra, it is noteworthy that no negative band appears at around 3650 cm\(^{-1}\) at any RH, which was estimated by fitting of traditional VSFG spectra measured with ppp-polarization (note that sign of Im\(\chi^{(2)}\) in reference 11 is opposite from ours because they irradiated lasers to the surface through the silica whereas we focused them from the air).\(^{11}\) Polarization in our measurement is different from the previous study (at RH of 20%), but we cannot reasonably explain the reason of absence of the negative peak in ssp polarization if such species does exist. We observed a negative band at 90%RH, but its frequency is at around 3500 cm\(^{-1}\), not 3650 cm\(^{-1}\). It might be possible that a weak, negative band at 3650 cm\(^{-1}\) band at high RH, but no negative feature appeared at <50%RH. Our results, thus, do not support the existence of the water molecules which very weakly interact with siloxane bridge (Si-O-Si) oxygen of the silica surface, at least at low RH and at our experimental condition. Furthermore, we did not observe any free silanol groups as written above. This is also an important difference from the results obtained from the fitting of conventional VSFG spectra.\(^{11}\) Note that this discrepancy cannot be assigned to spectral distortion owing to Fresnel factor (see Figure S4 in the SI).
monolayers at 20%RH, there is no contradiction. However, the IR study estimated the hydration layer to be as thick as 2
slowly but clearly
water/silica interfaces). The agreement between HD-VSFG and
ATR-IR at 20%RH indicates the water layer is thin enough for
region in-between the two interfaces (hydration layer is sensitively detected while HD-VSFG only
obtained here did not drastically get stronger. This is because
monotonically grew upon increase of RH, HD-VSFG spectra
probes the interfaces regardless of presence of the thick “bulk”
agreement between HD-VSFG and ATR-IR spectra at
20%RH suggests that water molecules in the nanodroplet are
anisotropically oriented while each droplet is thicker than 2
monolayers. This low-frequency band was traditionally assigned
to “ice-like” water, but currently the term “ice-like” should be
more carefully used. This is because vibrational spectra of water
are generally distorted by intra/intermolecular vibrational
couplings, so that the low frequency does not always
mean strong hydrogen-bonding. Furthermore, even if the
hydrogen-bonding is indeed strong, it does not mean water forms tetrahedral structure. To unambiguously interpret the
spectra, it is necessary to measure the spectra with using
isotopically diluted water (H\(_2\)O:D\(_2\)O mixture). However, because
the signal from diluted water is very weak, here we interpret
the H\(_2\)O spectra by comparing them with those obtained for
silica/liquid water, air/ice, and silica/ice interfaces. First of all, band widths of H\(_2\)O ice surface are about 250 cm\(^{-1}\)
and 50 cm\(^{-1}\) for silica/ice and air/ice, respectively. Because the positive band obtained in the present study is as broad as 350
cm\(^{-1}\), it is unlikely that the water molecules form ice-like
tetrahedral structure. Broad low-frequency band similar to that
of present study was also observed at silica/acidic solution
interfaces. For this interface, the peak frequency was still around 3200 cm\(^{-1}\) even for isotopically diluted solution,
suggesting that the interfacial water forms strongly hydrogen-
ond (but not tetrahedral) structure. Because this band was
assigned to water molecules which interact with hydrogen atom
of silanol groups, origin of this band is essentially the same as
that of “air-oriented” positive band observed in the present
study. Therefore, while direct comparison of silica/liquid water
and silica/adsorbed water is difficult, the positive peak obtained
here is also assignable to water molecules which form strongly
hydrogen-bonded (but not tetrahedral) structure. Note that this
band is “air-oriented”, \textit{i.e.}, the strong hydrogen-bond is formed
between water molecules, not water and silanol groups.

At higher RH, the HD-VSFG spectra exhibited a negative
band around 3500 cm\(^{-1}\) (Figure 1). While assignment of this
band to a specific structure is difficult, this band is mainly

The spectrum obtained here at 20%RH were essentially the
same with those obtained by ATR-IR in the literature. While they are different at higher humidity, this discrepancy is
attributable to difference of surface selectivity between ATR-IR
and VSFG technique as mentioned in the early VSFG study. In
fact, while signal intensity of the ATR-IR spectra in the literature
monotonically grew upon increase of RH, HD-VSFG spectra
obtained here did not drastically get stronger. This is because
ATR-IR probes all adsorbed molecules and hence growth of the
hydration layer is sensitively detected while HD-VSFG only
probes the interfaces regardless of presence of the thick “bulk”
region in-between the two interfaces (\textit{i.e.}, air/water and
water/silica interfaces). The agreement between HD-VSFG and
ATR-IR at 20%RH indicates the water layer is thin enough for
VSFG to probe all molecules. Because VSFG technique generally
probes molecules in 2-3 layers of interfacial region and the ATR-
IR study estimated the hydration layer to be as thick as 2
monolayers at 20%RH, there is no contradiction. However, the
2 monolayer-thick film model is not enough to fully interpret
the origin of the positive peak. This is because the positive band
slowly but clearly grew with the humidity. While the relative
intensity of each spectrum sometimes fluctuates as written
above, this trend never changed. Because the intensity increase
is not as drastic as that of ATR-IR, it is unlikely that thickness of the
adsorbed directly contributed to the signal intensity. Besides the contribution of thickness, there are two possibilities
left for the mechanism of signal increase: (1) molecular
orientation of the interfacial water changed, or (2) area of the
water/silica interface increased. The former is possible because
not only the number of probed molecules but also their
orientation affects the signal intensity of VSFG spectra. However, polarization-dependent ATR-IR spectra revealed that
the molecular anisotropy of the water on silica does not
increase from 50 to 85%RH. The orientational change may
somewhat contribute to the signal increase from 20 to 50%RH,
but it cannot explain the general trend that the positive peak
gradually grows with humidity increase. Therefore, we
concluded that the area of water/silica interface increased at
higher RH. In other word, the interfacial water was concluded to
form nanodroplets instead of covering whole surface of the
substrate, at least at <50%RH. It is noteworthy that the multi
domain model was previously proposed, but the hydrogen-
bonding sites of silica were totally updated. In the previous
assignment, water molecules were estimated to interact with
siloxane bridges with some portion of silanol groups remaining
bare. In our model, water-siloxane interaction has negligible
coupling contribution and silanol groups are the most favored
interaction sites. Because siloxane bridges are weaker
hydrogen-bonding sites than silanol groups, our model is more
natural. From the facts that (1) free silanol group was absent
even at 20%RH, (2) water molecules are net “air-oriented”, and
(3) no “silica-oriented” water which interacts with siloxane
bridge was observed, we concluded that the water droplet
formed around silanol groups (Figure 2). It is possible that some
of silanol groups were consumed by the contaminants, but the
slight consumption cannot rationalize the absence of the “silica-
oriented” water if water molecules indeed prefer siloxane
bridges. Therefore, the model depicted in Figure 2 is considered
to be essentially unaffected by the contamination.

The agreement between HD-VSFG and ATR-IR spectra at
20%RH suggests that water molecules in the nanodroplet are
anisotropically oriented while each droplet is thicker than 2
monolayers. This low-frequency band was traditionally assigned
to “ice-like” water, but currently the term “ice-like” should be
more carefully used. This is because vibrational spectra of water
are generally distorted by intra/intermolecular vibrational
couplings, so that the low frequency does not always
mean strong hydrogen-bonding. Furthermore, even if the
hydrogen-bonding is indeed strong, it does not mean water forms tetrahedral structure. To unambiguously interpret the
spectra, it is necessary to measure the spectra with using
isotopically diluted water (H\(_2\)O:D\(_2\)O mixture). However, because
the signal from diluted water is very weak, here we interpret
the H\(_2\)O spectra by comparing them with those obtained for
silica/liquid water, air/ice, and silica/ice interfaces. First of all, band widths of H\(_2\)O ice surface are about 250 cm\(^{-1}\) and 50

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while it is expected that the surface negative charge makes water molecules be “silica-oriented” (hydrogen atoms toward the silica) owing to electrostatic interaction, our spectra indicate that water molecules are mainly air-oriented even at 90%RH. Furthermore, the spectrum measured at 90%RH is more like that obtained for silica/acidic (pH≈2) aqueous interface than that of silica/basic (pH 12) solution interface (Note that the complex phase of the spectra in these references should be inverted for comparison with ours because optical configuration around the sample was upside-down). These comparisons clearly indicate that the surface silanol groups are protonated and no negative charge was induced. This is presumably because the hydration layer is too thin (~6 monolayers at 90%RH) for protons to escape into the “bulk”.

We summarize the model for water adsorption onto silica surface. At very low RH, water in the gas phase start to adsorb around silanol groups (Figure 3a). When RH increases to ~20%RH, additional water molecules gather around the “nucleus” composed of water and silanol groups to form the nanodroplets (Figures 2 and 3b). The size of the nanodroplets grows upon increase of RH, and liquid-like water starts to appear at vapor/water interfaces at around 50%RH (Figure 3c). The nanodroplets may finally get together to form hydration “film”, presumably at ~90%RH. Once the whole surface is covered by the water film, the uniform film may accept additional water molecules without changing surface energy, which rationalizes the previous observation that water adsorption suddenly increased at RH higher than 90%RH.

Conclusions

In this study, we measured vibrational spectra of vapor/silica interface by HD-VSFG spectroscopy. The observed spectra were different from those estimated by conventional VSFG spectroscopy. The results suggest existence of “nanodroplets” around silanol groups on the surface at RH lower than about 90%RH. The innermost water at the droplet/silica interface was found to form strong hydrogen-bond with other water molecules, but formation of ice-like (or tetrahedral) structure was not supported. Weak hydrogen bonding between the innermost water and siloxane, which was estimated by the conventional VSFG spectroscopy, was not observed at least at low RH. At RH higher than about 50%, the nanodroplets grow to have bulk liquid-like water at the vapor/droplet interface as previously proposed from ATR-IR results. Despite of the existence of liquid-like water, the surface silanol groups are not deprotonated at whole RH range studied. This study will help further investigation clarify how the adsorbed water perturbs macroscopic surface properties.

Conflicts of interest

There are no conflicts of interest to declare.
Acknowledgments

This work was supported by JSPS KAKENHI, Grant Numbers JP19K05200 and JP20K15234.

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