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Understanding Rubber Friction in the Presence of Water Using Sum-Frequency Generation Spectroscopy

Kumar Nanjundiah

Ping Yuan Hsu

Ali Dhinojwala
University of Akron Main Campus, ali4@uakron.edu

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Kumar Nanjundiah, Ping Yuan Hsu, and Ali Dhinojwala[a]
Department of Polymer Science, The University of Akron, Akron, Ohio 44325-3909, USA

Infrared-visible sum-frequency-generation spectroscopy (SFG) was used to study the molecular structure of water between a poly(dimethylsiloxane) (PDMS) and a sapphire substrate. The observation of SFG peaks associated with the dangling surface hydroxyl groups (3690 cm^{-1}) and water bands (3000–3400 cm^{-1}) indicates that the contact spot between the PDMS lens and the sapphire substrate is heterogeneous. Within the contact spot there are regions where the methyl groups of the PDMS chains are in direct contact with the surface hydroxyl groups on the sapphire substrate. In the other regions, a thin water layer is trapped between the two surfaces with spectral features that are different from that of the unconfined water next to the sapphire or the PDMS surface. The higher adhesion and friction values observed in these experiments, compared to those expected for a uniform thin layer of water trapped between the PDMS and the sapphire substrate, are consistent with the hypothesis that the contact spot is heterogeneous. These results have important implications in understanding the sliding behavior of wet, deformable hydrophobic materials on hydrophilic substrates. © *2009 American Institute of Physics.*
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I. INTRODUCTION

Sliding two surfaces is considerably easy in the presence of a thin layer of water.[1–6] The Egyptians in $\approx$2400 B.C used water to lubricate wooden sledges that transported large stones used to build pyramids.[7] Interestingly, nature has selected water as a biological lubricant, which is far superior to manmade oil-based lubricants.[8] Roberts and Tabor[1] conducted systematic studies of an elastomeric rubber sliding on solid surfaces in the presence of water and other lubricants. Roberts and Tabor measured the time it took to drain the water from a gap between the rubber and the solid surface. They noticed that the effective viscosity to drain the liquid increased dramatically when the gap was nanometer thin. They concluded that it is likely that the increase in effective viscosity was due to asperity contacts rather than actual changes in the viscosity of the liquid. Since then the use of surface force apparatus has revealed several interesting properties of water confined between two atomically smooth mica surfaces.[9] For example, oscillatory force profiles were observed for water confined between two hydrophilic mica surfaces, which indicated layering of water molecules.[9] In comparison, long-range attractive hydrophobic forces were observed for water confined between two hydrophobic surfaces.[10] However, the experimental results between two mica surfaces cannot directly explain the friction results for a wet elastomeric rubber sliding on a solid surface. To relate the friction results to the molecular structure of the confined liquid between two surfaces is difficult due to the influence of dissipation in the bulk, asperity contact, and the changes in viscosity on the measurements of shear forces. The sliding of wet soft materials is encountered in many areas of our daily lives, which includes the use of wind shield wipers in the rain, and driving or walking on wet roads. To understand friction and adhesion, we need to develop experimental approaches to directly study the interfacial structure between two surfaces.

The direct measurements of the structure of water confined between two solid surfaces were not possible because of the difficulty in positioning two large macroscopic surfaces at nanometer separations. In the design of the surface force apparatus, this difficulty of using two macroscopic flat surfaces was overcome by using a cross-cylinder geometry with atomically smooth mica layers. However, the cross-cylindrical geometry made it difficult to couple the force measurements with spectroscopic techniques to study the structure of confined liquids. Recently, some promising developments have been reported using Raman,[11] fluorescence,[12,13] and refractive index measurements.[14] Here, we have used a flexible elastomeric lens [hydrophobic poly-(dimethyl siloxane) (PDMS)], which deforms against a flat solid surface, to study confined liquids, which offsets the need to have perfectly parallel surfaces. The soft PDMS lens deforms and forms a large uniform contact area that is suitable for infrared (IR)-visible sum-frequency generation spectroscopy (SFG). SFG is a second order nonlinear optical process and is directly sensitive to the orientation and density of molecules at the interface. According to the dipole approximation, the generation of SFG photons is forbidden in centrosymmetric bulk and permitted only at interfaces where inversion symmetry is broken.[15] The surface selectivity of SFG is important in probing the interfacial structure without the measurements being swamped by the signals generated in the bulk, which is a common problem encountered in us-

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[a]Electronic mail: ali4@uakron.edu.

ing Raman and IR techniques. Additionally, the SFG conversion is resonantly enhanced when the IR frequency overlaps with the molecular-vibrational modes that are both Raman and IR active. The position and the magnitude of these resonance peaks provide chemical and orientation information on the molecules at the buried interface.

In this paper, we have specifically addressed three main questions. First, is there a layer of water left between these two dissimilar surfaces (PDMS and sapphire)? Second, if water is present, what is the structure of this confined water film? Third, what are the consequences of these results on understanding wet friction and adhesion?

II. EXPERIMENTAL

A. Sample preparation

The PDMS lenses were prepared by using Sylgard 184 monomer supplied by Dow Corning Inc. The recipe consisted of one part cross-linker to ten parts monomer. The monomer and the cross-linker were mixed together and the air bubbles removed. The lenses were made by placing a drop of this mixture on a fluorinated glass surface under water. The lenses used in these experiments were ≈ 5 mm in diameter. The lenses were cured under water at room temperature for 24 h. The water was removed and the lenses were dried using dry nitrogen. The lenses were further cured in a vacuum oven for 4 h at 60 °C. The cured lenses had some amount of uncross-linked PDMS oligomers that could potentially leach out during the experiments.[16,17] Therefore, the lenses were soaked in toluene to remove these uncross-linked chains. Toluene was replaced every 3 days for 2 weeks. The lenses were then removed from toluene and dried under vacuum for 4 h before use. The root-mean-square (rms) roughness determined by atomic force microscopy (AFM) measurements (Digital Instruments Nanoscope IIIa multimode AFM with tip of radius of curvature of ≤ 10 nm) of the surface of the PDMS film was $\approx 4-5$ Å.[16,17] The modulus of the PDMS lenses was 2–3 MPa. The static contact angle of water was 110° on PDMS film. The surface energy of the PDMS surface was determined using Johnson Kendall and Roberts (JKR) measurements to be $20-23$ mJ/m^2.[17]

The sapphire prisms were first wiped with toluene using a soft tissue and sonicated in toluene for 1 h. Subsequently, the lenses were washed with copious amounts of water and blow dried using dry nitrogen. Finally, the sapphire prisms were plasma cleaned using air plasma for a period of 5 min before the experiments. The SFG cell was washed in soap solution and sonicated in toluene for a period of 2 h. The cell was then washed with water and blow dried using dry nitrogen. The cell was heated in an air oven at 135 °C for 10 min and plasma cleaned before the experiments. The rms roughness of the sapphire prism was 10–15 nm measured using AFM (20×20 μm^2 scan area). Water wets the surface of the sapphire prisms after plasma cleaning, consistent with the hypothesis that sapphire is hydrophilic. Ultrapure water (18 MΩ/cm) was used from a Millipore filtration system (pH $\approx 5-6$). D$_2$O was purchased from Cambridge Isotopes (D 99.9%). For the SFG measurements, the chamber contain-
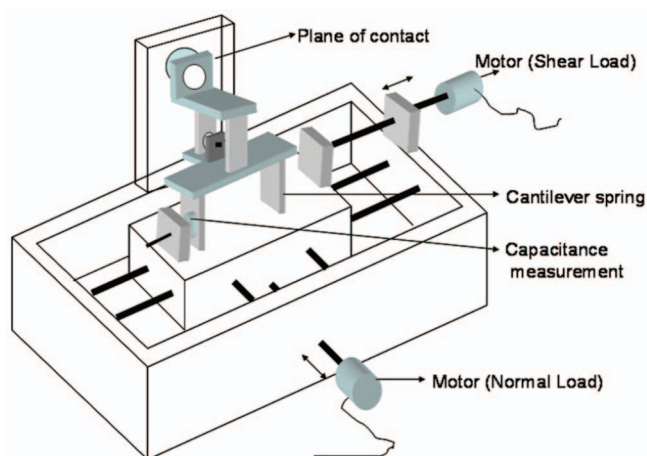

FIG. 1. (Color) Schematic of the friction cell developed in house to measure friction coefficient.

ing the lens was filled with water and the sapphire prism was pressed into contact with the PDMS lens, which resulted in the drainage of the excess water between the lens and the sapphire prism. The lens deformed under pressure (the pressure was estimated to be between 0.1 and 1 MPa based on the flattened contact area) creating a uniform contact area of 0.5–1 mm in diameter. No time dependent changes in spectral features were observed in the experimental time scale of 8–10 h.

B. Friction and adhesion measurements

The friction and adhesion measurements were conducted using a homebuilt instrument (schematic of the friction cell is shown in Fig. 1) based on the design of Barquins.[18] The instrument has two bridges perpendicular to each other, and we have used homebuilt capacitance sensors to measure displacement. The bridges were made of spring steel and the spring constants were calibrated by hanging known weights and recording the displacement. The perpendicular arrangement of the bridges permitted independent measurements of normal and shear forces. The PDMS lens was mounted, as shown in Fig. 1, and the sliding was conducted using high resolution picometer® motors. Water was introduced between the lens and the substrate by forming a capillary bridge between the lens and the sapphire substrate. Coefficients of friction (defined as shear force/normal force) for dry and wet PDMS lenses were measured using a velocity of 5 μm/s. For the adhesion measurements, the forces were recorded by moving the motors in and out of contact at constant speeds. We have used the procedure described by Roberts and Tabor[1] to measure the thickness of the water film between the lens and the sapphire substrate. The measurement was based on the interference of light and the thickness was determined by the changes in the intensity of the reflected light as the lenses were pressed into contact. Figure 2(b) shows the optical images of the contact area before contact, upon contact, and after applying pressure. We measured the thicknesses of 40 and 36 nm in the presence and absence of water, respectively. Because of scattering from the PDMS lenses, we estimated the gap thickness to be between 4 and
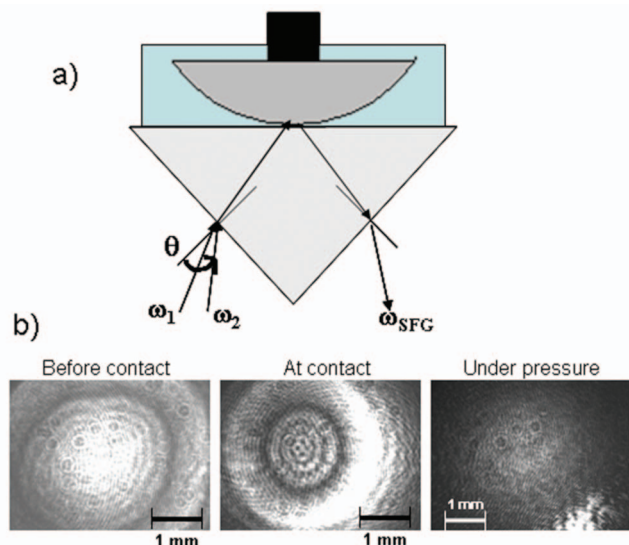
FIG. 2. (Color) A schematic (not to scale) of the total internal reflection setup used for the SFG measurements of confined water (a). θ is the incident angle. The thickness of the confined water was measured using optical interferometry (b). Some illustrative examples of optical images before contact, after contact and under pressure are shown in (b). The Newton rings are observed inside the contact region due to water being trapped in the center of the contact spot. The water layer is squeezed out under pressure indicated by the disappearance of the Newton rings. The SFG measurements were taken when the lens was under pressure.

40 nm. On further compression, we observed only the contact area increase without any further changes in the intensity, which indicates no further changes in the thickness of the water layer.

C. SFG measurements

The SFG measurements involve spatial and temporal overlap of a high-intensity visible laser (of frequency ω_1) with a tunable-IR laser (of frequency, ω_2). The SFG measurements were performed using a picosecond Spectra-Physics laser system with a tunable IR beam (2000–3800 cm^{-1}, 1 ps pulse width, 1 kHz repetition rate, and a diameter of 100–200 μm) and a visible beam (800 nm, 1 ps pulse width, 1 kHz repetition rate, and a diameter of 1 mm).[19] We have used sapphire prisms in these measurements because in total internal reflection geometry the SFG signals were a factor of 10–100 higher near critical angles.[20] The 60° sapphire prism was cut with the optical axis parallel to the polished sides and along the thickness direction to avoid any distortion of the incoming and outgoing polarized beams. All the results reported in this paper were conducted at room temperature. The SFG experiments for the blank sapphire prism were conducted with no humidity control. We estimated that humidity could vary between 20% and 50% during those experiments. The SFG signals were collected using a photomultiplier tube connected to a 0.5 m length spectrometer. The full width half maxima of the tunable IR pulse was $\approx$10 cm^{-1}. A typical SFG spectrum was collected between 2200 and 3800 cm^{-1}. It was possible for us to scan such a broad range in wavenumber because our calculations showed that the SFG intensity in internal reflection geometry does not change by more than 6% due to the changes in the

TABLE I. Relevant peak assignments for H$_2$O, D$_2$O and PDMS next to various interfaces (Refs. 16 and 22–24).

Origin	Peak position (cm^{-1})
Liquidlike water network[a]	3400[b,c]
Icelike water network[a]	3200 and 3000[b]
Dangling OH next to air	3700[b,d]
Dangling OH next to hydrophobic surface	$\approx$3690[c]
Liquidlike D$_2$O network[a]	2510[e]
Icelike D$_2$O network[a]	2375[e]
Dangling OD next to air	2740[e]
PDMS CH$_3$ symmetric	2910[f]
PDMS CH$_3$ asymmetric	2965[f]

[a]Both pairs (3200/3400 and 2375/2510) are associated with the symmetric vibration (Ref. 25).
[b]Reference 22.
[c]Reference 23.
[d]Reference 26.
[e]Reference 24.
[f]Reference 16.

critical angles at different wavenumbers. The SFG spectra for the sapphire/air, sapphire/water, PDMS/sapphire interfaces were measured at 42°, 16°, and 8° incident angles of the IR beam, respectively. The incident angle of the IR beam was 1°–2° higher than the visible beam [Fig. 2(a)]. The incident angles used for these three systems were near the values determined using refractive indices of the materials and Snell's law.[19–21]

In this paper, the ssp polarization refers to s-polarized SFG beam, s-polarized visible, and p-polarized IR beam. In the case of ppp polarization, all the beams are set to be p-polarized. Because the sps intensities are weak, we report the results using only ssp and ppp polarizations. Table I summarizes the various peak assignments for water and PDMS bands reported in literature. To obtain quantitative information the SFG spectra are fitted using the following Lorentzian equation,[20]

$$I(\text{SFG}) \propto \left| \chi_{\text{eff,NR}} + \sum_q \frac{A_q e^{i\phi_q}}{\omega_{\text{IR}} - \omega_q - i\Gamma_q} \right|^2, \qquad (1)$$

where A_q, Γ_q, ω_q, and ϕ_q are the strength, damping constant, angular frequency of a single resonant vibration, and phase, respectively. $\chi_{\text{eff,NR}}$ is the nonresonant part of the SFG signal. Because of broad overlapping vibration bands from 2900 to 3800 cm^{-1} for H$_2$O and the PDMS, it is difficult to obtain unique results from fitting the SFG data. The difficulty of fitting SFG water spectra without the phase information was discussed by Shen and Ostroverkhov.[22] Here, we have used the fitting results to only identify the peak positions. We did not make any quantitative conclusions based on the amplitude strengths from the fits.

III. RESULTS AND DISCUSSION

A. Friction and adhesion results

The values of the normal forces when the dry or wet lenses are brought in contact with and retracted from the
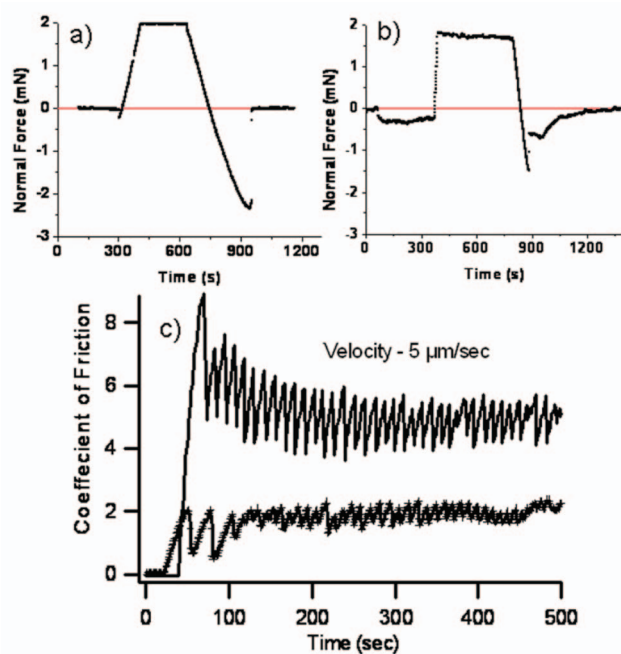
FIG. 3. (Color) Graphs showing loading and unloading forces as a function of time for a PDMS lens against a sapphire surface (dry contact) (a) and in the presence of water (b). (c) shows the coefficient of friction for the PDMS lens sliding on the sapphire substrate in the absence (top curve) and in the presence (bottom curve) of external water at a velocity of 5 μm/s.

FIG. 4. (Color) The SFG spectra for a sapphire/air interface (a) and a sapphire/water interface (b) collected using *ssp* ($\bigcirc$) and *ppp* (+) polarizations. The solid lines are fit to a Lorentzian equation.

sapphire substrate are shown in Figs. 3(a) and 3(b), respectively. For the dry lens, the normal load increases after the lens is pushed against the substrate, followed by a constant load when the pressure is held constant. On retraction, for both dry and wet lenses, we observe jump-outs indicating adhesive contacts. The jump-out for the wet lenses consists of two steps. The first jump-out is smaller than that observed for the dry lens, indicating reduction in adhesion due to the presence of water. The second jump-out is due to the breaking of the water capillary bridge formed between the lens and the sapphire substrate. The friction coefficients for dry and wet PDMS lenses sliding on the sapphire substrates are shown in Fig. 3(c). Initially, the shear forces increase due to stiction and then the lenses start sliding nonuniformly due to the stick-slip process.

Even though the friction coefficients for the wet PDMS lens (lower curve) are lower than the dry PDMS lens, these values are much higher than expected based on the bulk viscosity of water, thickness of the film, and the velocity. We estimated that the sliding of a flattened contact spot with a velocity of 5 μm/s in the presence of $\approx 4-40$ nm thick water layer of viscosity of 1 cP would require a shear stress of only 1.2–0.12 Pa. The measured frictional stress ($\approx 5-20$ kPa) is many orders of magnitude higher than our estimate for lubricated sliding. To understand the origin of these higher shear forces, we discuss next the SFG measurements of the PDMS/sapphire contact interface in the presence of water.

B. SFG results

1. Sapphire in contact with air and bulk water

Figure 4(a) shows the SFG spectra for sapphire/air interface in ssp and ppp polarizations. The SFG spectra show
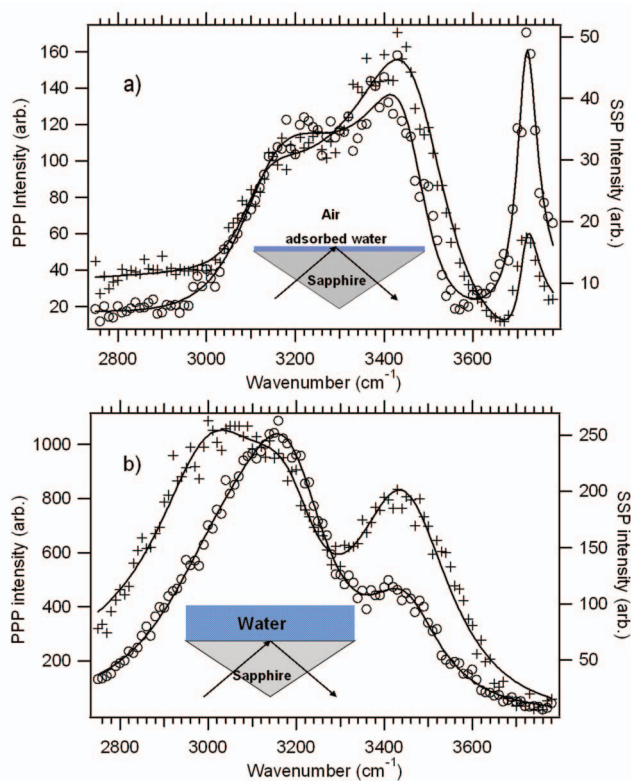
peaks at 3200 and 3400 cm^{-1}, which have been previously assigned to icelike and liquidlike water, respectively.[22,27] Additionally, we observe a peak at 3700–3720 cm^{-1} which is assigned to dangling OH groups[28] or surface hydroxyl groups on the sapphire surface.[29–31] From these results, it can be inferred that after the plasma treatment (the last step used in cleaning the prisms) the sapphire substrate is rapidly covered with adsorbed water. The features observed in the SFG spectra may resemble that of water/air, water/sapphire, or sapphire/air interfaces. Similar conclusions were drawn from the SFG measurements for the mica surface in the presence of D_2O vapor.[24]

Figure 4(b) shows the SFG spectra for sapphire substrate in contact with bulk water. The SFG spectra show an additional peak at 3000 cm^{-1}, previously assigned to icelike structure of water. In a recent review article by Ostroverkhov *et al.*,[32] the authors have suggested that the OH groups of water that are hydrogen bonded with surface OH groups of silica are responsible for the 3000 cm^{-1} peak. In high *p*H solutions, the surface OH groups are deprotonated to O$^-$ and the 3000 cm^{-1} peak decreases in intensity. The peak at 3700 cm^{-1} is not observed in the SFG spectra of sapphire/water interface, which suggest the absence of dangling OH (nonhydrogen bonded) groups at the water/sapphire interface.

Two papers published recently have raised several interesting points regarding the interpretation of the SFG spectra for water/sapphire interfaces. Here, we discuss the results that are pertinent for this paper. Experiments by Zhang *et al.*[33] showed that for water next to (0001) plane of sap-
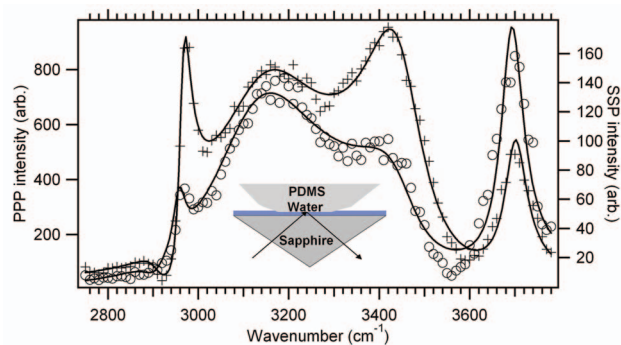
FIG. 5. (Color) The SFG spectra of water confined between the PDMS lens and the sapphire substrate collected using *ssp* (○) and *ppp* (+) polarizations. The solid lines are fit to a Lorentzian equation.

FIG. 6. (Color) The SFG spectra collected using *ssp* (○) and *ppp* (+) polarizations between 2700 and 3800 cm^{-1} for D$_2$O confined between the PDMS lens and the sapphire substrate. The solid lines are fit to a Lorentzian equation.

phire, the dangling OH peak observed at 3700 cm^{-1} does not disappear upon contact with water. The results of Zhang *et al.* are very different from what we have observed for the sapphire prism in contact with water and also previously reported in literature.[27] Zhang *et al.* suggested that the hydrogen atoms of the dangling OH of the sapphire surface are strongly bonded and do not participate in hydrogen bonding with adsorbed water molecules and are also not easily deprotonated. In comparison, the amorphous alumina particles in contact with water does not have a peak at 3700 cm^{-1}. Their explanation is that the ability of the surface hydroxyl groups on the sapphire to hydrogen bond with water depends on the crystallinity of the sapphire surface. Recently, Braunschweig *et al.*[34] also observed a peak at ≈3700 cm^{-1} for (0001) plane of sapphire in contact with water and they attribute this peak to hydroxyl groups in the hydrophobic nanopores that do not wet water and thus are not in contact with water. In Braunschweig *et al.* experiments, when the sapphire samples were annealed at 1400 K, the 3700 cm^{-1} peak was absent in the SFG spectra, which they attributed to the disappearance of the nanopores. In comparison, we did not observe a 3700 cm^{-1} peak for water in contact with the sapphire prism, which is an important point in the interpretation of the wet PDMS/sapphire contact interface as discussed later.

Traditionally, the SFG spectra of water have been interpreted based on icelike and liquidlike structure at 3200 and 3400 cm^{-1}, respectively. Recently Sovago *et al.*[25] suggested that both the 3200 and 3400 cm^{-1} peaks are due to the symmetric OH vibration. Because of the Fermi resonance with the overtone of the bending mode, the symmetric OH band is split into low and high frequency bands.[25] Keeping both these pictures in mind, we now discuss the results for PDMS lenses in contact with sapphire in the presence of water.

2. SFG spectra of wet contact interface in the presence of H$_2$O and D$_2$O

Figure 5 shows the SFG spectra for the PDMS/sapphire interface in the presence of H$_2$O using ssp and ppp polarizations. We observed both water and PDMS peaks in Fig. 5, which indicate the presence of water between the PDMS lens and the sapphire substrate. The assignments for the symmetric and asymmetric PDMS methyl peaks are 2905 and 2965 cm^{-1}, respectively. In addition to the standard water

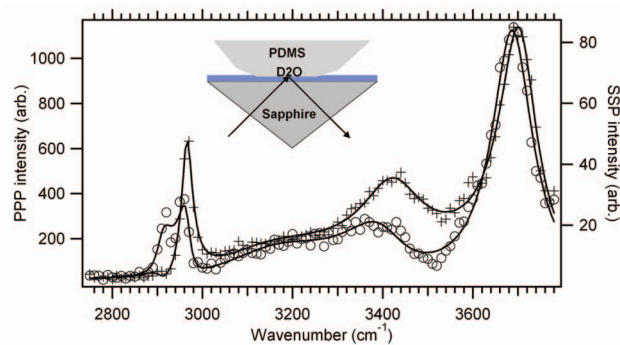peaks between 3000 and 3600 cm^{-1}, we also observed a strong narrower peak at ≈3690 cm^{-1}. This peak is slightly red shifted and can be due to nonhydrogen bonded OH groups in contact with hydrophobic methyl groups of PDMS chains, which has also been observed for water in contact with methyl groups of the self-assembled monolayers (octadecyltrichlorosilane).[23]

Besides the water bands between 3000 and 3700 cm^{-1}, there are also assignments for the surface hydroxyl groups of aluminum oxide surfaces in this range.[30,31] The peak assignments depend on the charge of the Al group on the surface. Therefore, the peak at 3690 cm^{-1} could also be assigned to the surface hydroxyl groups of the aluminum oxide.[29–31,33,34] To confirm that the peak at 3690 cm^{-1} in Fig. 5 is due to the surface hydroxyl groups and not due to OH groups of water in contact with PDMS, we also measured the SFG spectra of the PDMS/sapphire interface in the presence of D$_2$O.

Figure 6 shows the SFG spectra taken in ssp and ppp polarization for D$_2$O confined between the PDMS and the sapphire substrate. The spectra show methyl PDMS peaks and in addition, a strong peak at 3690 cm^{-1}. The presence of this peak in both H$_2$O and D$_2$O confirms that this peak is due to the surface hydroxyl groups on the sapphire substrate. Because the SFG spectra of sapphire in contact with water do not have a peak at 3690 cm^{-1} (Fig. 4), the surface hydroxyl peak observed for confined H$_2$O and D$_2$O has to be due to the surface hydroxyl in contact with the methyl groups of PDMS chains. The assignment of the 3690 cm^{-1} peak to the surface OH group in contact with methyl groups of PDMS chains is further substantiated by the observation of a strong peak at ≈3700 cm^{-1} in the SFG spectra at the contact interface between a dry PDMS lens and the sapphire substrate (data not shown). One could perhaps argue that there is a possibility of air trapped between the PDMS and sapphire substrate and the 3700 cm^{-1} peak could be due to surface hydroxyl groups in contact with air. There are two observations that do not support the argument that air is present within the contact spot. First, the peak assignment for sapphire OH in contact with air[29] is near 3710 cm^{-1} and not 3690 cm^{-1} as observed for confined H$_2$O and D$_2$O. Second, the friction coefficients observed for the wet PDMS lens sliding on the sapphire substrate are higher than expected for lubricated sliding in the presence of air pockets. Additionally,
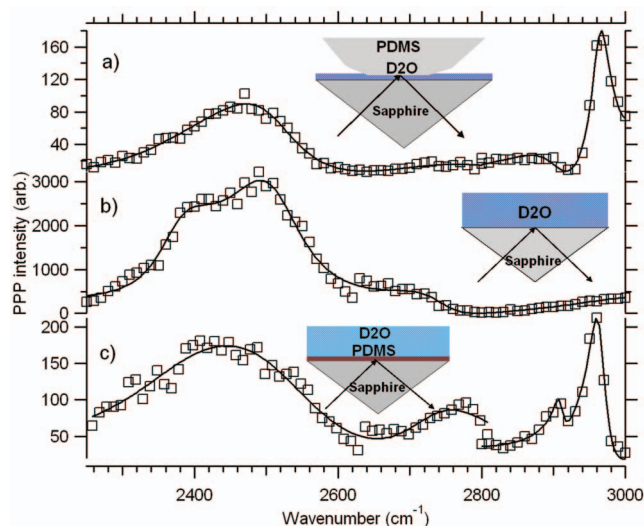
FIG. 7. (Color) The SFG spectra in the D_2O region in three different conditions. The SFG spectrum of D_2O confined between the PDMS lens and the sapphire substrate (a). The SFG spectrum of D_2O liquid next to the sapphire substrate (b). The SFG spectrum of D_2O liquid next to the PDMS film spin coated on the sapphire substrate (c). The spectra were collected in ppp polarization. The solid lines are fit to a Lorentzian equation.
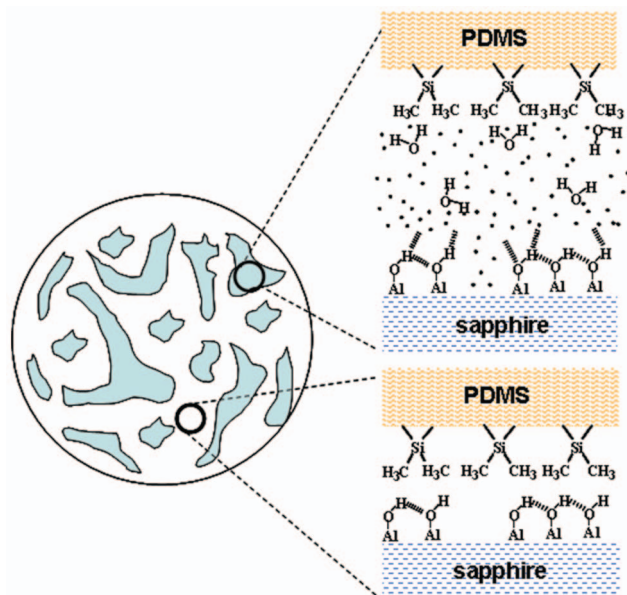

FIG. 8. (Color) A model illustrating the contact region formed between the PDMS lens and the sapphire surface in the presence of confined water. A tentative physical model of the molecular structure in these two types of contact regions is also shown in the panels on the right. The relative sizes of these two regions cannot be quantified from the SFG measurements, and the areas and sizes illustrated in the sketch are only for visual aid.

we observe H_2O peaks between 3200 and 3400 cm^{-1} due to trace amount of H_2O that may collect on the sapphire prim upon exposure to ambient air.

With the assignment of the surface hydroxyl peak, we can now interpret the SFG results for water confined between the PDMS lens and the sapphire substrate (Fig. 5). The peak at 3690 cm^{-1} is assigned to the surface hydroxyl groups in contact with the methyl groups of the PDMS surface chains. The peaks between 3000 and 3600 cm^{-1} are due to water between the PDMS lens and the sapphire substrate. Because of the presence of water and the surface hydroxyl groups in contact with the PDMS surface chains, the contact spot is heterogeneous. In some regions, the liquid water is squeezed out and as a result the PDMS methyl groups come in direct contact with the sapphire surface hydroxyl groups. The same conclusions can be reached for the D_2O confined between the PDMS and the sapphire substrate (Fig. 6). Because the size of the IR laser beam is of the order of 100 μm, the SFG signals are averaged over these heterogeneous patches inside the contact spot.

To understand the structure of confined water, we compare the SFG results for confined D_2O between the PDMS and the sapphire substrate, D_2O in contact with the sapphire and D_2O in contact with the PDMS film (Fig. 7). In the D_2O region, there is negligible interference from the PDMS peaks and that makes it easier to compare the changes in the structure of water molecules upon confinement. Because the contact region has potentially two interfaces, PDMS/water and water/sapphire, the D_2O experiments also eliminate the potential interference due to these two interfaces. The peaks at 2375, 2510, and 2740 cm^{-1} are assigned to icelike network, liquidlike network, and nonhydrogen bonded OD, respectively. The icelike water peak is weaker in the SFG spectra for confined D_2O compared to the SFG spectra for D_2O in contact with the sapphire surface. Additionally, the dangling

OD peak for confined D_2O is much weaker in comparison to the D_2O/PDMS interface. These results indicate that the structure of confined D_2O is more liquidlike upon confinement.

We can also interpret the SFG spectra based on the model suggested by Sovago et al.[25] recently. They reported that the primary symmetric OD resonance frequency is at 2510 cm^{-1}. For D_2O next to charged lipid surface, the peak is split into two due to the overlap of the symmetric vibration with the overtone of the bending mode. However, when the pure OD is replaced with a 1:1 mixture of OD and OH, a single peak corresponding to the primary OD resonance is observed at 2510 cm^{-1}.[25] Here, the SFG spectra for the D_2O trapped between PDMS and sapphire substrate have a dominant broad peak near 2510 cm^{-1}. These results can be explained by two possible reasons. First, there is a deuterium exchange between D_2O and the trace amount of H_2O on the prism or the PDMS lens. The presence of trace amount of water was inferred due to the presence of peaks between 3200 and 3400 cm^{-1} in the SFG spectra in Fig. 6. However, this mechanism is unlikely because there is a large volume of D_2O added in these measurements compared to the trace amount of H_2O present in the gap. The second and more probable hypothesis is that the there is an increase in liquidlike structure of water in these thin films. Based on the physical picture presented by Sovago et al.,[25] this would shift the D_2O peak to higher wavenumbers and as a consequence lead to decrease in the overlap of the symmetric vibration with the overtone of the bending mode. This mechanism can also explain the broad peak observed at 2510 cm^{-1}.

Finally, we discuss the consequences of the SFG results in understanding friction and adhesion data shown in Fig. 3.

The sliding of the PDMS lens in the presence of water shows lower friction than dry sliding. However, these friction coefficients for wet sliding are quite high compared to lubricated sliding. The patchy contact spot with regions where the PDMS methyl groups are in direct contact with the sapphire surface hydroxyl groups explains the higher friction coefficients than those expected for a contact spot with a uniform layer of water. Roberts and Tabor[1] also observed higher friction for a rubber lens sliding on a glass surface in the presence of water. They concluded that the higher friction was due to asperity contact rather than higher viscosity of confined water. The SFG results agree with the hypothesis of the PDMS sliding on wet sapphire surface with patchy adhesive contact. The asperity contacts are where the PDMS methyl groups come in direct contact with the surface hydroxyls on the sapphire substrate, which is also consistent with the jump-out observed in the adhesion experiments. However, these asperity contacts are not similar to those between two hard surfaces. The soft PDMS lens can deform under pressure and follow the surface topography.

IV. SUMMARY

We have summarized our main conclusions using a model showed in Fig. 8. The observation of a 3700 cm^{-1} peak in H$_2$O (Fig. 5) and D$_2$O (Fig. 6) proves that this peak is due to surface hydroxyl groups. Additionally, Fig. 4(b) provides the evidence that the 3700 cm^{-1} peak cannot be assigned to surface hydroxyl groups in contact with water. Therefore, the only plausible explanation is that the surface hydroxyl groups are in contact with the methyl groups of the PDMS chains. Furthermore, the presence of water bands between 3000 and 3400 cm^{-1} in Fig. 5 and surface hydroxyl groups in contact with PDMS support our hypothesis that the contact is heterogeneous, as shown in Fig. 8. The structure of PDMS sketched in Fig. 8 is also consistent with the SFG results for PDMS/water interface that show methyl groups facing the water molecules. The small number of O–H groups sketched facing the PDMS chains is also consistent with the observation of the free hydroxyl peak in Fig. 7(c) near 2750 cm^{-1}. The SFG results are in good agreement with the higher friction coefficient and jump-out during adhesion measurements.

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