

Icelike Water Monolayer Adsorbed on Mica at Room Temperature

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The structure of a water film formed on mica at room temperature, in equilibrium with water vapor at various relative humidities (RH), was studied using sum-frequency-generation (SFG) vibrational spectroscopy and scanning polarization force microscopy (SPFM). Analysis of the O-D stretch modes in the SFG spectra of D₂O on mica indicates that as RH increases, the submonolayer water structure evolves into a more ordered hydrogen-bonding network. At full monolayer coverage (~90% RH), the SFG spectrum suggests an icelike film with no dangling O-D groups, in agreement with a recent molecular dynamics simulation. [S0031-9007(98)08082-X]

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Hydrophilic surfaces of solid materials adsorb water when exposed to humid environments. These films are thought to play a key role in atmospheric and environmental chemistry, wetting, weathering, and biological phenomena [1–3]. Because of their small film thickness, which can vary from one to several molecular monolayers, the film structure can be strongly influenced by the boundary surfaces associated with the substrate and vapor on the two sides, respectively. Although adsorbed water films have been the object of extensive investigation for a long time [4–8], only recently have spectroscopy and microscopy techniques possessing the sensitivity and selectivity to the last surface atomic layers become available for a more microscopic study. Two such techniques have been developed in our laboratories: sum-frequency generation (SFG) vibrational spectroscopy [9,10] and scanning polarization force microscopy (SPFM) [11]. We have applied these techniques to probe the structure of a water film condensed on mica in equilibrium with a humid environment.

Recent SFG studies of bulk water interfaces have revealed that ~25% of the molecules at the liquid/vapor interface have free, non-hydrogen-bonded OH groups pointing towards the vapor phase [12]. This interface is considered hydrophobic because a similar behavior is found at water interfaces with hydrophobic materials [13]. On the other hand, the mica surface is hydrophilic. Thus, an adsorbed water film on mica is sandwiched between a hydrophilic and a hydrophobic interface.

Some hints to the structure of the water film on mica come from recent SPFM imaging studies [14]. The technique uses a noncontact operation mode of the atomic force microscope (the tip scans at a height of about 10 nm away from the surface) and relies on the attractive electrostatic force to map the surface topography and dielectric properties. It has a ~10 nm resolution in the surface plane, and 0.1 nm resolution in the perpendicular direction. Within this resolution, the film formed in equilibrium with the vapor was found to have a uniform structure. In order to gain more information on

this structure, the uniformity of the film was perturbed by a brief contact (of nanometer dimension) of the tip (~30 nm radius) with the film. This contact served to locally increase the surface water concentration through capillary action. After retraction of the tip and rapid evaporation of the excess water, metastable, two-dimensional islands (they slowly disappear) with polygonal shapes in angular epitaxial relationship with the mica lattice were left on the surface [14,15]. Based on these findings it was proposed that the water islands are crystalline and possess an icelike structure, as such structure could be stabilized by approximate lattice matching between the mica surface and the hexagonal ice basal plane [3]. This result triggered a molecular dynamics simulation by Odelius *et al.* [16], who concluded that indeed the stablest configuration of a water monolayer on mica should resemble a two-dimensional icelike water bilayer, but with no free OH groups. The present studies were conducted to ascertain the nature of such water films.

The experiments were conducted in two separate chambers, one for SFG measurements and the other for SPFM. The chamber used for SFG experiments was equipped with CaF₂ windows for optical input and output. The humidity in the chamber, measured with a hygrometer (model DH301, Pacer Instruments), was varied by adjusting the flow rate of N₂ gas bubbling through a container with water. The SPFM experiments [14,15] were performed in air, in a chamber that could maintain a controlled humidity level by circulating N₂ gas bubbling through water and/or by using desiccant material to lower the humidity. In both cases the mica sample was cleaved *in situ* prior to the measurement.

The SFG setup has been described elsewhere [17]. Briefly, a mode-locked Nd:YAG laser producing pulses of ~25 ps duration with a repetition rate of 20 Hz was used to pump an optical parametric system to generate picosecond infrared pulses tunable in the hydroxyl stretch region. A nonlinear crystal was used to generate picosecond green pulses at 532 nm. The infrared and green beams were overlapped on the vapor/mica interface and

the sum-frequency output was detected. Scanning the infrared frequency over the hydroxyl stretch resonances resulted in an SFG spectrum. To avoid interference, the back side of mica was roughened.

SFG spectra of adsorbed D_2O on mica under various degrees of humidity obtained using the *SSP* polarization (*S*, *S*, and *P* polarization for sum-frequency output, visible input and infrared input, respectively) are shown in Fig. 1. Deuterated water (D_2O) was used in the SFG experiments to avoid confusion of the hydroxyl stretch modes in the spectrum from both water and mica. This isotopic substitution should not change significantly the interfacial structure so that our conclusions based on the SFG spectra of D_2O can be extended to H_2O . Spectra were obtained as a function of humidity, from less than 5% relative humidity (RH) (the limit of our hygrometer sensitivity) to RH \sim 97% (the upper limit of our hygrometer). The hygrometer was calibrated for both D_2O

and H_2O vapor with an absolute accuracy of $\pm 5\%$ RH and a relative solution better than 1% RH. In Fig. 1, a spectrum of the bulk liquid D_2O /vapor interface is also shown (lowest spectrum) for comparison. It is very similar to that of the H_2O /vapor interface except that the peaks are shifted to lower frequencies. Following what we already know about the latter, we can assign the peaks in the D_2O /vapor spectrum accordingly [12,13]. The sharp peak at $\sim 2740\text{ cm}^{-1}$ corresponds to the O-D stretch of the non-hydrogen-bonded O-D groups ("free O-D" stretch), while the broad peaks at $\sim 2375\text{ cm}^{-1}$ and $\sim 2510\text{ cm}^{-1}$ are O-D stretch modes associated, respectively, with an ordered and disordered tetrahedrally coordinated hydrogen-bonding network. The peak positions agree roughly with those obtained from D_2O ice [18,19] and liquid [20,21] by Raman and infrared spectroscopy and with the free O-D stretch of thin ice films in UHV [22].

The SFG spectrum below 5% RH has hardly any discernible features above the noise background. At 23% RH, however, O-D stretch modes associated with the hydrogen-bonded O-D groups begin to emerge. At 40% RH, the bonded O-D peak corresponding to the ordered structure already appears to be stronger than the one connected with the more disordered structure. Further increase of the RH makes the "ordered" O-D peak relatively stronger and the spectrum closer to that of ice. In these spectra, the free O-D peak at $\sim 2740\text{ cm}^{-1}$ is rather weak, if present. We also note that the intensity of the spectrum increases appreciably with an increase of RH up to 90%. At 90% RH, the spectrum is completely dominated by the "ordered" O-D peak with the free O-D peak clearly absent. This suggests that the water coverage on mica has reached a full monolayer and formed an ordered icelike structure as predicted by a molecular dynamics simulation [16]. At even higher RH (see, for example, RH $> 97\%$ in Fig. 1), the spectrum changes only slightly, but the free O-D peak now appears clearly. The latter observation is an indication that a multilayer water film must have formed on mica because the free O-D groups can now exist at the water/vapor interface.

An early ellipsometry measurement [6] indicated that at RH $\sim 70\%$ the average water layer thickness reaches 0.4 nm which is roughly the thickness expected from one monolayer (often referred to as a buckled bilayer as it is composed of two stacked submonolayers). This is different from what we have found. To see whether laser heating of mica (which has a 70% transmission at 532 nm through a 200 μm thick sample) could cause the discrepancy, we have measured the temperature rise of the sample during laser irradiation and found that it was less than 1 K. This could lead to a humidity change of only 5% at 90% RH. We have also reduced the laser pulse repetition rate from 20 to 2 pulses/sec and found no noticeable change in the SFG spectra. Therefore the laser heating effect in our experiment certainly could be neglected. We believe that the discrepancy between

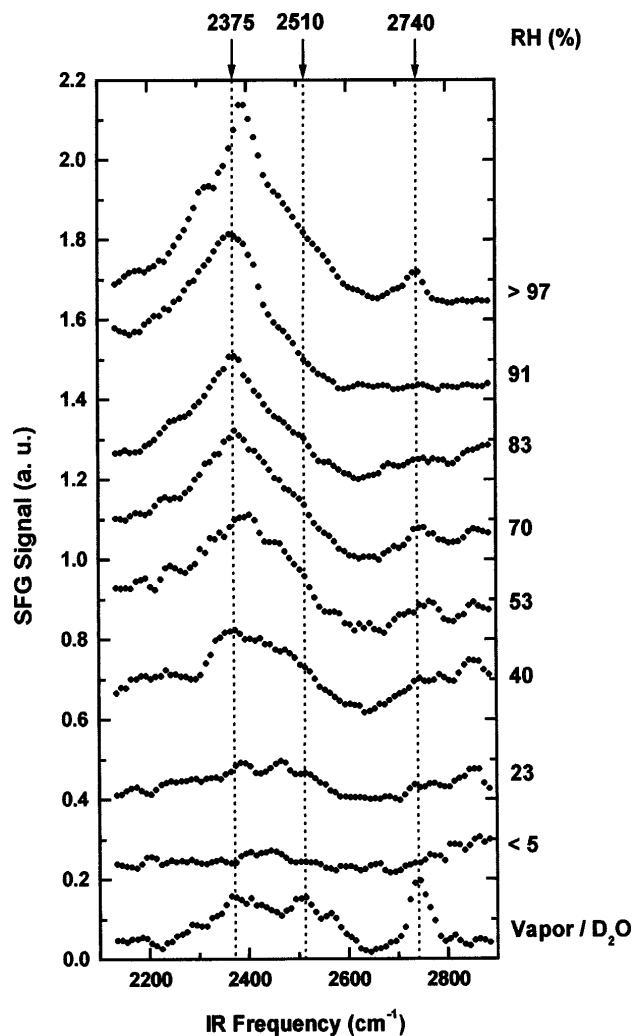


FIG. 1. SFG spectra in *SSP* polarization of a water (D_2O) film on mica as a function of the relative humidity (RH) at room temperature (296 K). The bottom trace corresponds to the spectrum of the bulk waver/vapor interface.

the ellipsometry findings and ours may have arisen from determination of absolute film thickness in the ellipsometry measurement.

The above SFG results shed light on the previous findings from SPFM. In that earlier study [15] the water (H_2O) coverage on mica was proposed to be one monolayer at 20% RH, based on the observations that only above this humidity, polygon-shaped islands appeared upon contact of the scanning tip with the water-covered mica and on the large increase of the adhesion force (pull-off force) of the tip to the surface due to capillary action. The SFG spectra now indicate that up to 20% RH, the water coverage is significantly below a monolayer and the water molecules do not form a well-ordered structure on the surface. It then appears that the "monolayer coverage" defined in the earlier SPFM study simply corresponds to a threshold water coverage above which the polygon-shaped islands can be nucleated and formed on mica by the capillary action of the tip. Water molecules adsorbed on mica may have aggregated into two-dimensional clusters, but they are too small for SPFM to resolve. The tip can pull the molecules or clusters together by capillary action to form a macroscopic monolayer film that has an icelike structure resulting from epitaxial interaction with the mica substrate. As the RH increases one expects that, even without the tip touching the surface, the coverage of these clusters will increase and eventually coalesce into a continuous icelike monolayer film when the RH approaches 90%. This picture is well corroborated by the observed SFG spectra.

We have performed new SPFM measurements (with H_2O) to confirm the above picture. The SPFM image should be uniform within an island because of its ordered monolayer structure, and also between islands because these regions are occupied by water molecules or two-dimensional water clusters of dimensions smaller than our SPFM resolution (a few tens of nanometers). If the above picture is correct, the icelike islands formed by tip contact with the surface should no longer be seen when the monolayer film becomes continuous.

In contrast to the previous SPFM experiment performed with a dc bias of the tip, an ac voltage (10 kHz, 10 V peak to peak) was used in the present experiment. By maintaining the second-harmonic amplitude of the lever oscillation constant using feedback control, topographic maps free of contact potential differences were produced [23]. Such contact potential differences due to solvated K ions would make separation of the topographic contrast difficult, as they will interfere with the topographic image in the dc imaging mode. The results of the new experiment are shown in Fig. 2 for four different humidity values.

The islands, which tend to exhibit polygonal shapes, were generated by tip contact with the surface and could be observed from 20% RH up to $\sim 70\%$ RH, but not at 80% RH and above. The height contrast of the image was

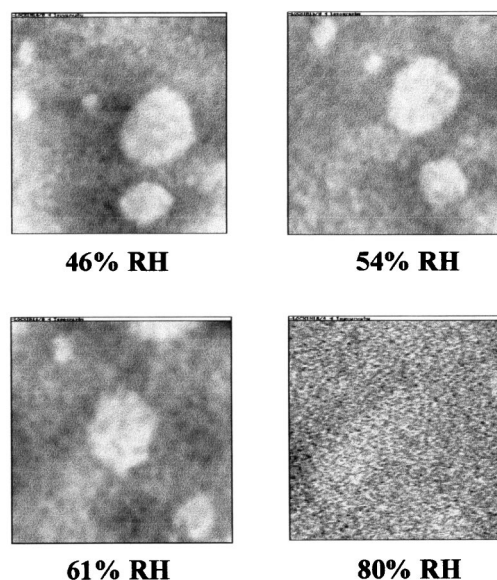


FIG. 2. Scanning polarization force microscopy images ($7.5 \mu\text{m} \times 7.5 \mu\text{m}$), showing 2-dimensional islands of water (bright patches) produced by a brief contact of the atomic force microscope tip near the center of the image, that induces capillary condensation around the contact point. At relative humidity values below 70%, the clusters show a contrast of $2.5 \pm 0.5 \text{ \AA}$. The contrast decreases down to the noise level at high humidity ($>80\%$). Notice the tendency of the clusters to exhibit polygonal boundaries.

$2.5 \pm 0.5 \text{ \AA}$ when the humidity was in the intermediate range of 20% to 60%, and decreased rapidly above this humidity so that they could not be distinguished from the noise level of the surrounding area. This is shown in the image acquired at 80% RH in Fig. 2. This behavior is precisely what is expected from the picture described above. With an increasing fraction of the surface covered by an icelike water film, it will become more difficult to observe an isolated icelike island (formed either by tip nucleation or coalescence of two-dimensional clusters) or holes in the film because of the limited resolution of SPFM.

In conclusion, the present SFG experiment has proven conclusively the existence of an icelike water layer on mica that saturates at room temperature (296 K) when the humidity becomes $\sim 90\%$. This layer does not contain free (non-hydrogen-bonded) OH (O-D) groups. At humidities below 20%, the surface water coverage is low, and the SFG spectra are hardly discernible from noise. Above 20% the water coverage increases with RH and the spectra show that an increasing portion of the adsorbed water has an icelike ordered structure. In this range of RH (up to $\sim 80\%$), large, contiguous icelike islands can be generated by perturbing the surface with a tip contact that will increase the local surface density of water via capillary action. Around 90% RH, the water coverage reaches a full monolayer and its structure is icelike. That the full water monolayer on mica has an

icelike ordered structure with, in particular, no free OH groups is in good agreement with the predictions of the molecular dynamics simulation [16].

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