6/4/06 revision

Water growth on metals and oxides: binding, dissociation and role of hydroxyl groups

M. Salmeron[1,2], H. Bluhm[1], M. Tatarkhanov[1,3], G. Ketteler[1], T.K. Shimizu[1,#], A. Mugarza[1,*], Xingyi Deng[1], T. Herranz[1], S. Yamamoto[4] and A. Nilsson[4]

[1] Lawrence Berkeley National Laboratory
[2] Materials Science and Engineering Department. University of California, Berkeley
[3] Physics Department, University of California, Berkeley. USA
[4] Stanford Synchrotron Radiation Laboratory, SLAC, 2575 Sand Hill Road, Menlo Park, CA94025, USA

We discuss the role of the presence of dangling H bonds from water or from surface hydroxyl species on the wetting behavior of surfaces. Using Scanning Tunneling and Atomic Force Microscopies, and Photoelectron Spectroscopy, we have examined a variety of surfaces, including mica, oxides, and pure metals. We find that in all cases, the availability of free, dangling H-bonds at the surface is crucial for the subsequent growth of wetting water films. In the case of mica electrostatic forces and H-bonding to surface O atoms determine the water orientation in the first layer and also in subsequent layers with a strong influence in its wetting characteristics. In the case of oxides like TiO_2, Cu_2O, SiO_2 and Al_2O_3, surface hydroxyls form readily on defects upon exposure to water vapor and help nucleate the subsequent growth of molecular water films. On pure metals, such as Pt, Pd, and Ru, the structure of the first water layer and whether or not it exhibits dangling H bonds is again crucial. Dangling H-bonds are provided by molecules with their plane oriented vertically, or by OH groups formed by the partial dissociation of water. By tying the two H atoms of the water molecules into strong H-bonds with pre-adsorbed O on Ru can also quench the wettability of the surface.

Understanding wetting at the molecular scale implies knowing the structure of water near interfaces. This is exceedingly important for a large number of applications, from atmospheric and environmental phenomena, to biology, catalysis and electrochemistry[1,2]. Only a good knowledge of the water structure at the molecular level can bring understanding and predictability to these important phenomena. The discussion in this paper will therefore be centered on the study of the adsorption, reactions and growth of water on surfaces. In our laboratory we have developed and applied Scanning Tunneling and Atomic Force Microscopies (STM, AFM) as well as photoelectron spectroscopy techniques (XPS and XAS) to study water adsorption on pure metals (Pd, Ru, Cu), oxides

---

[#] Current address: Surface Chemistry Laboratory, RIKEN (The Institute of Physical and Chemical Research), 2-1-1 Wako, Hirosawa, Saitama 351-0198, Japan.
[*] Current address: Centre d'Investigació en Nanociència i Nanotecnologia CIN2 (ICN-CSIC), Campus UAB, 08193 Bellaterra Spain

(mica, TiO_2, Cu_2O, SiO_2, Al_2O_3), and metal surfaces modified by pre-adsorbed oxygen (Ru). In all cases we find that the formation of structures that expose dangling H bonds from water or hydroxyl groups is crucial to the subsequent adsorption and 2-dimensional growth of water films.

Orientation and wetting properties of water on mica

Atomic force microscopy was used in the non-contact electrostatic force mode called Scanning Polarization Force Microscopy (SPFM), to image the structure of water in equilibrium with vapor.[3,4] We found that at room temperature water forms a complete monolayer when the relative humidity (RH) reaches between 70 and 80%, although the film is nearly complete at humidities as low as 30-40%. The SPFM images reveal that the first and second monolayers form hexagonal structures in good orientational epitaxy with the mica lattice.[4] Sum Frequency Generation Vibrational Spectra (SFG), shown in figure 1, revealed that the bonding and orientation of the water molecules is such that no free or dangling H bonds exist in the complete first monolayer[5], as shown by the absence of the characteristic O-H stretch vibration mode at 2740 cm^{-1} (for D_2O, 3600 cm^{-1} for H_2O). However, above the first monolayer the free or dangling H became visible, as shown in the figure. In these experiments, due to the small local heating from the laser beam, the ambient humidity is larger than on the surface. As we show later, in the absence of laser heating the monolayer is completed around 70% RH. This result indicates that in the second and subsequent layers, water molecules exhibit free dangling H at the vapor interface.

Supporting these findings, contact potential measurements of the mica surface as a function of RH with SPFM operating in the Kelvin Probe (KP) mode, revealed a decrease of surface potential, which indicate that on average the water dipole is pointing towards the surface[6]. After the monolayer was completed, additional water adsorption changed the potential to positive values, as shown in figure 2. These findings provide additional support for a model of the growth of water on mica at room temperature, where the molecular dipole points down on average and where no free H bonds are present in the first layer. Reversal of the average dipole direction occurs in the second and following layers.

Perhaps more surprising is the observation that, in contrast to the room temperature case, at temperatures below 0C the contact potential continues to decrease (i.e. becomes more negative) when the coverage of water goes beyond the first monolayer, as shown in figure 2. This observation suggests that at the lower temperatures water continues to grow with the average dipole moment pointing down, effectively forming a "ferroelectric" ice film. The downward orientation of the water dipole is probably related to the negative charge on the mica due to the presence of Al^{+3} ions substituting for Si^{+4} in the tetrahedral lattice, while the K ions are solvated on top of the monolayer. The electrostatic force however may not be strong enough to orient the water molecules beyond a few layers. In addition, oriented dipoles in successive layers store electrostatic energy, like a charged capacitor, offsetting the gains due to interaction with the surface. At sufficiently low temperatures however, metastable dipole oriented films might form.

The metastable nature of these films was manifested in our experiments by a sudden and spontaneous change of the contact potential, which went back to positive values (indicated by the arrow in figure 2), after the film reached a certain thickness. The wetting characteristics through these temperature and thickness changes was studied with SPFM[7,8]. Water deposited at -36C forms 3D islands on top of flat ice platelets, as shown in figure 3. The islands have a contact angle of ~2 degrees, as measured in non-contact SPFM mode images, while the ice platelets underneath were revealed by contact AFM imaging, performed immediately after. Contact imaging strongly perturbs the film and removes the 3D islands in the area scanned. Heating the surface from -36 C to -17 C dramatically changed the structure of the film, which now exhibits a flat wetting structure as a result of spreading of the 3D islands.

We propose that the hydrophyllicity of mica above 0C is related to the fact that dangling H from the water molecules are formed easily above the monolayer upon adsorption of additional water. The formation of 3D (i.e., non-wetting) structures at low temperature, with the water film in a ferroelectric state, may be the result of the difficulty of turning the orientation around, a process that might require activation. More detailed experiments using SFG are clearly necessary (now in preparation) to support this interpretation.

A recent result by Michaelides et al. is relevant and should be mentioned here. These authors concluded using DFT calculations that on Kaolinite, water does not form a stable layer on the basal plane termination that exposes O only, while a 2-dimensional film is stable on the opposite surface that exposes OH groups with dangling H bonds. The authors point out the relevant fact that these groups can reorient on that surface termination to expose the H bonds.[9]

Two-dimensional ice rules

We switch now to the behaviour of water on metal surfaces. Using low temperature STM we studied the adsorption of water on Pd(111) and Ru(0001), both surfaces have hexagonal symmetry and lattice parameters that are within a few percent of a good match with those of the basal plane of ice. At low coverage, water molecules form small clusters made of side sharing hexamer units of 6 water molecules. We found that the flat honeycomb structures formed by side sharing hexamers are limited laterally to no more than two or three hexagonal cells. This is shown if figure 4 for Pd. The surface temperature is 100 K and the honeycomb clusters can be seen to have widths of only a few cells[10]. A similar observation was made for Ru(0001), when the temperature is below 140 K, where water also forms limited size clusters with the molecule oriented flat and parallel to the surface maximizing in-plane H bonds and terminating with dangling H at the peripheries. In the example shown in figure 5, we can see a few hexamers with additional water molecules attached at the edges. Even at 50 K these molecules are moving along the periphery. When 2 or more molecules are attached to the edges they can occupy contiguous or opposed corners, with no observed change in the STM contrast of the hexamer ring. This indicates that the water molecules in the hexamer are equivalent, i.e. have the same bonding configuration with the metal atoms underneath.

These results can be interpreted by postulating a set of "2-D ice rules". According to these rules: (a) water molecules bind to metal atoms on a top position through their lone pair orbital in a flat lying geometry, as predicted theoretically[11,12]; (b) the water molecules form as many H bonds with other molecules as possible, i.e. 3 inside the cluster, two being donors and one acceptor; (c) cluster growth terminates when a H bond cannot be satisfied in this way. The unsatisfied or non-donor bond is therefore confined to the periphery of the cluster. It is obvious from geometrical considerations that the rules can only be satisfied when the cluster size is limited in at least one dimension. Our experiments indicate that the 2-D ice rules are followed remarkably well on both the Pd and Ru hexagonal planes at temperatures below 130 K, although they break down above that temperature where extensive honeycomb structure are formed. Clearly the 2-D ice rules describe a metastable growth pattern with an important local energy minimum. Growth beyond the limited size requires energy to overcome barriers, which trigger the formation of extended hexagonal structures where alternating molecules are flat, with 2 donor and 1 acceptor bonds, and vertical, with 2 acceptor and 1 donor H bonds. The other H is not involved in a H-bond and points either towards the surface in Pt[13] and Pd, or away towards the vacuum.

If the temperature is maintained below 100 K for Pd and Ru, the addition of more water to the surface results in the formation of 3D structures, even if the metal surface is not yet covered with a continuous film. The formation of a second layer before the 1st one is completed indicates again that the surface is hydrophobic. This result could be interpreted as due to the lack of dangling H atoms in the first water layer and to the difficulty of "turning around" the molecules in the first later to provide donating H-bonds to the 2nd layer. This process might be either energetically unfavorable or require and activation energy, as in the mica example discussed above. Interestingly, theoretical calculations by Michaelides et al.[14] indicate that the energy difference between H-up and H-down extended structures is very small, which would suggest that a second layer could favorably bond with a modified first layer. Experiments to explore the structure of the second layer of water are thus highly desirable and are being planned in our laboratory.

We should mention here the work of Kimmel et al.[15] on the growth of water Pt(111). In their experiments using thermal programmed desorption of Xe on the water films they observed that water grows in a 3D manner beyond the first monolayer after annealing to 135 K, a result that they interpret as due to the lack of dangling H bonds. Similarly observation were made by Hodgson et al.[16] on Ru(0001) where, according to these authors the strong binding of the first layer rendered the surface hydrophobic. We will show below that this behavior is also followed by a modified Ru(0001) surface by the preadsorption of 0.25 monolayers of oxygen.

Wetting in the presence of OH groups

We now turn our attention to oxide surfaces where hydroxyl groups can form easily. The experiments were performed using a special X-ray photoelectron spectrometer designed

in our laboratory that operates under ambient pressures of gases (a few Torr)[17], sufficient to reach humidities near 100% at temperatures close to the triple point of water. In this manner we can study surfaces in thermodynamic equilibrium with water vapor, which is extremely important in environmental studies[18].

We describe two experiments here involving single crystal $TiO_2(110)$ and a thin (≥ 1.5 nm) film of Cu_2O formed by thermal oxidation of a polycrystalline Cu foil. In both cases XPS reveals the surface composition clearly differentiating between lattice O in the oxide substrate, O in OH groups and H_2O. In addition a peak due to the gas phase above the surface can also observed. We follow the growth of water by measuring the areas under the peaks and after calibration of the XPS signals. Figure 6 shows the results for TiO_2. The results can be summarized as follows: after preparation of the TiO_2 surface by sputtering and annealing in O_2, the surface contains a number of O vacancies that previous investigations have identified as located in the bridge O-rows[19,20,21]. Under our conditions the concentration of these vacancies is ≤ 0.125 ML. Water adsorbs efficiently on these sites where it dissociates giving rise to 2 OH groups. Molecular water grows always after saturation of the vacancies, forming strong bonds with the OH groups[22].

Similarly, on Cu_2O the presence of a small amount of O vacancies gives rise to the formation of OH groups, which nucleate the subsequent adsorption of molecular water[23]. This is shown in figure 7.

The clean Cu metal is a particularly interesting case in our discussion. We found out that the (111) and (110) surfaces of this metal behave in surprisingly different ways. On the (111) face no water adsorption was observed using XPS in the presence of 1 Torr of water at room temperature. This clearly indicates that the clean metal surface is hydrophobic.[24] On the (110) surface of the same metal however, partial water dissociation into OH and H occurred readily, which was then followed by molecular water adsorption.

Although not shown here, similar results were obtained on two other oxide surfaces: SiO_2 that contain OH groups as a result of the etching and oxidation procedure[25], and Al_2O_3 films on Al foil[23]. Other examples, including Fe_2O_3 and MgO are currently being investigated in our laboratory.

Adsorption of water on an O-covered Ru(0001) surface

In this last example we explore the effect of blocking the formation of dangling H bonds on the wetting properties of a Ru(0001) surface. Such blocking can accomplished by pre-adsorbing 0.25 monolayer of oxygen on the surface. The oxygen atoms form a 2x2 structure on the Ru surface with each O atom sitting on an hcp site[26]. On this surface water adsorbs readily forming also a 2x2 structure and does not dissociate[27]. We found that water adsorbs on the top Ru site inside the 2x2 cell, forming a covalent bond with Ru through the lone pair orbital and two additional H-bonds with the chemisorbed O of the 2x2 structure. This is shown by the STM images acquired at 6 K, in figure 8. The

drawing on the right shows the DFT calculated structure by Cabrera-Sanfelix et al.[28] The result of interest for our discussion is that the H-bonds to the chemisorbed O atoms are strong enough to prevent H-bonding between water molecules, which then remain separated from each other in their 2x2 unit cells. As the coverage of water increases beyond 0.25 monolayers, the molecules in excess of 0.25 ML are weakly bound and are easily moved about by interaction with the tip, i.e. no stable second layer is formed. This result indicates that once the H atoms of the water molecule are tied strongly and prevented from presenting dangling free on the surface, the surface becomes hydrophobic. We found also that heating beyond 140 K results in desorption of the water with no dissociation, unless defects (missing O atoms) in the initial O(2x2) structure are present. These results are again in line with the previous results presented in this paper. This time we have shown that if water is prevented from reorienting to present dangling H atoms, no wetting takes place.

Conclusions and outlook

All the examples discussed here support a mechanism for the molecular scale wetting by water that is strongly dependent on the ability of the surface to produce dangling H bonds, from either molecular water (mica, Pd, Ru), or OH groups (oxides with defects). We have also shown how pre-adsorbed oxygen on Ru(0001) forms strong H-bonds with water, blocking the formation of new H-bonds with other water molecules, making the surface hydrophobic. Although a firmly established mechanism cannot yet be presented, the observations clearly point to the importance of dangling H-bonds. Several experiments are suggested, with some underway in our laboratory, to clarify some of the questions raised by the results and discussion presented in this paper. One is the study of water orientation on mica at temperatures below 0C using SFG beyond the first monolayer. Another is STM (and/or AFM) experiments to determine the molecular level structure of multilayer water films as a function of layer thickness at various temperatures. Finally, it would be important to explore the adsorption of water on perfect oxide surfaces, with no O-vacancy defects, to see if OH groups can still form and the effect on wetting.

Acknowledgments

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. A.M. was financed by the Marie Curie Outgoing International Foundation, Project No. 514412. T.H. acknowledges also the financial support from the Ramon Areces Foundation.

Updated

Figures captions

Figure 1.

Sum frequency generation spectra of water on mica as a function of relative humidity. The spectrum for neat water-air surface (deuterated) is shown at the bottom for reference. Due to a small local heating the ambient relative humidity (RH) is 91% when the monolayer is saturated, which under normal conditions occurs around 80% RH. The most important finding of this experiment is that at the completion of the monolayer the peak due to stretching of the free H bonds, at 2740 cm^{-1} is absent. The peak becomes visible when the water coverage exceeds 1 monolayer.

Figure 2.

Contact potential of mica as a function of relative humidity for different temperatures of the substrate. Above 10 C the contact potential reverses direction towards positive values, in agreement with the SFG findings that at RT the orientation of the water molecules is such that dangling H are present. Below 0C however, the contact potential, starts to decrease again, i.e., becoming more negative. We interpret this as evidence for the continued downward orientation of the molecules, with their dipoles pointing down on average towards the mica surface. This "ferroelectric" orientation however is metastable, and the film spontaneously reverts to a random orientation, except for the last layer, after accumulation of a few layers or by thermal fluctuations.

Figure 3.

Left: SPFM (non-contact) images of a water film on mica formed by exposure to water at -37C near 100% humidity. Three-dimensional droplets of ice are formed. The droplets sit on top of flat monolayers of ice that can be imaged in contact (right image). The 3D droplets are removed from the area scanned in contact mode, as shown in larger images acquired subsequently (not shown). Topographic profiles along the line shown on the right image allow for a comparison of the 3D and 2D structures of water.

Figure 4.

STM images of a partial monolayer of water on Pd(111) at 100 K. Hexagonal clusters of ice form in epitaxial relationship with the substrate, with $\sqrt{3}x\sqrt{3}$-R30 structure. The Pd atoms in the dark region are not visible due to their very week contrast (~2 pm), compared to that of the water clusters (~50 pm). The expanded views on the right show the limited size of the clusters, which are due to the saturation of the H bonding by the water molecules laying flat (molecular plane parallel to the surface). The clusters stop growing laterally when dangling H bonds form at the periphery.

Figure 5.

Hexagonal clusters of water on Ru(0001) formed by exposure of the sample to $2x10^{-8}$ torr of water at 50 K followed by heating to 130 K and cooling back to the imaging temperature of 50K. In this image 4 hexamers are visible that have additional water molecules attached to the edges (3, 5, 2 and 2). In subsequent images taken at 1 minute intervals the position of these molecules changes as they visit each periphery site without any preference. A larger cluster of 3 fused hexamers with one additional water molecule at the edges is also visible. The corners of the hexagons in the images are at the position of the water molecules and are located on top of Ru atoms. The Ru atoms are not visible due to their weak contrast of ~ 2 pm, as compared to the 40 pm of the water in the clusters, and 100 pm of the additional water molecules at the periphery.

Figure 6.

Left: X-ray photoelectron spectra of water on TiO_2(110) showing the peaks due to excitation of the O1s electrons by 690 eV photons. Various O species can be distinguished that correspond to lattice O in TiO_2 (lowest binding energy), hydroxyls, adsorbed molecular water (near 534 eV) and gas phase H_2O (536 eV). By measuring the areas under the peaks isotherms and isobars of the amount of surface water and hydroxyls can be determined, and are shown on the right. Isotherms and isobars collapse into a single curve when plotted against relative humidity. OH forms always first by dissociation of water on O-vacancies in the bridge O rows. Two OH groups form for every defect site. Subsequently water molecules bind to the OH groups forming several layers well before reaching the saturation humidity of 100%, i.e., with good wetting.

Figure 7.

Adsorption isobars and isotherms of water adsorption on polycrystalline Cu_2O measured from the areas under the XPS peaks of the corresponding O species, similar to those shown in figure 6 for TiO2. Both isobars and isotherms collapse into the same curve when plotted against relative humidity. As with TiO2, formation of OH precedes the formation of molecular water films.

Figure 8.

Experimental STM image (18 nm x 18 nm) of an O(2x2)-Ru(0001) surface with a water layer on top with a coverage of 0.18 ML, acquired at 6 K. The bright spots correspond to water molecules. The underlying 2x2 structure is from O that produce the dark spots in the image. The molecules adsorb as shown in the schematic drawing on the top, with the O of the water molecule on top of a Ru atom (green circles 1st layer, blue circles 2nd layer) and the 2 H atoms making H-bonds with the O atoms of the 2x2 cell. Image acquired at constant current of 95 pA and an applied bias voltage of -220 mV, after annealing to 140 K.

References:

[1] M. A. Henderson, *Surf. Sci. Rep.* **46**, 5 (2002) and references therein

[2] A.Verdaguer, G.M. Sacha, H. Bluhm, M. Salmeron. *Chem. Rev.* **106**, 1478-1510 (2006).

[3] J. Hu, X.-d. Xiao, D.F. Ogletree and M. Salmeron. *Science*. **268,** 267 (1995). Note: In this paper the water structures formed are due to contact with the tip and correspond to a second water layer, not the first (see ref. 4).

[4] L. Xu and M. Salmeron. *Nano-Surface Chemistry*, ed. M. Rosoff. **6**, 243-287 New York: Marcel Dekker, Nov. 1, 2001.

[5] P.B. Miranda, L. Xu, Y.R. Shen and M. Salmeron. *Phys. Rev. Lett.* **81,** 5876 (1998).

[6] H. Bluhm, T. Inoue and M. Salmeron. *Surf. Sci.* **462,** 1, L599 (2000).

[7] H. Bluhm and M. Salmeron. *J. Chem. Phys.* **111,** 6947 (1999).

[8] M. Salmeron and H. Bluhm. *Surf. Rev. Lett.* **6,** 1275 (1999).

[9] Xiao Liang Hu, Angelos Michaelides. *Surface Science*, **602**, 960 (2008).

[10] J. Cerda, A. Michaelides, M.L. Bocquet, P.J. Feibelman, T. Mitsui, M. Rose, E. Fomin, and M. Salmeron. *Phys. Rev. Lett.* **93,** 6101 (2004).

[11] A. Michaelides, V.A. Ranea, P.L. de Andres, and D.A. King, *Phys. Rev. Lett.* 2003, **90,** 216102.

[12] S. Meng, E.G. Wang, and S. Gao. *Phys. Rev. B* **2004**, *69*, 195404.

[13] Ogasawara, H.; Brena, B.; Nordlund, D.; Nyberg, M.; Pelmenschikov, A.; Petterson, L.G.M.; Nilsson, A. *Phys. Rev Lett.* **2002**, *89*, 276102

[14] A. Michaelides, A. Alavi, and D. A. King, *J. Am. Chem. Soc.* **125**, 2746 (2003).

[15] G.A. Kimmel, N.G. Petrik, Z. Dohna´lek, and B.D. Kay. *Phys. Rev. Lett.* **95,** 166102 (2005)

[16] S. Haq and A. Hodgson *J. Phys. Chem. C,* **111**, 5946 (2007)

[17] D. Frank Ogletree, H. Bluhm, G. Lebedev, C. Fadley, Z. Hussain and M. Salmeron. *Rev. Sci. Instr.* **73,** 3872 (2002).

[18] M. Salmeron and R. Schlögl. *Surf. Sci. Rep.* **63,** 169 (2008)

[19] S. Wendt, J. Matthiesen, R. Schaub, E.K. Vestergaard, E. Lægsgaard, F. Besenbacher, B. Hammer, *Phys. Rev. Lett.* **96**, 066107 (2006).

[20] S. Wendt, R. Schaub, J. Matthiesen, E.K. Vestergaard, E. Wahlstrom, M.D. Rasmussen, P. Thostrup, L.M. Molina, E. Lægsgaard, I. Stensgaard, B. Hammer, F. Besenbacher, Surf. Sci. 598, 226 (2005).

[21] O. Bikonda, C. L. Pang, R. Ithnin, C.A. Muryn, H. Onishi, G. Thornton, *Nature Mat.* **5**, 189 (2005).

[22] G. Ketteler, S. Yamamoto, H. Bluhm, K. Andersson, D.E. Starr, D.F. Ogletree, H. Ogasawara, A. Nilsson, M. Salmeron. *J. Phys. Chem. C.* **111,** 8278 (2007).

[23] Xingyi Deng, Tirma Herranz, Christoph Weis, Hendrik Bluhm and Miquel Salmeron. J. Phys. Chem C. In press (2008.)

[24] Susumu Yamamoto, Klas Andersson, Hendrik Bluhm, Guido Ketteler, David E. Starr, Theanne Schiros, Hirohito Ogasawara, Lars G.M. Pettersson, Miquel Salmeron, Anders Nilsson. *J. Phys. Chem. C.* **111**, 7848 (2007)

[25] A. Verdaguer, C. Weis, G. Oncins, G. Ketteler, H. Bluhm, M. Salmeron. *Langmuir* **23**, 9699 (2007).

[26] M. Lindroos, H. Pfnür, G. Held and D. Menzel, *Surf. Sci.* **222**, 451 (1989)

[27] Gladys, M. J.; Mikkelsen, A.; Andersen, J. N.; Held, G. *Chemical Physics Letters* 2005, **414**, 311.

[28] Pepa Cabrera-Sanfelix, Daniel Sanchez-Portal, Aitor Mugarza, Tomoko K. Shimizu, Miquel Salmeron, Andres Arnau. *Phy. Rev. B.* **76**, 205438 (2007).

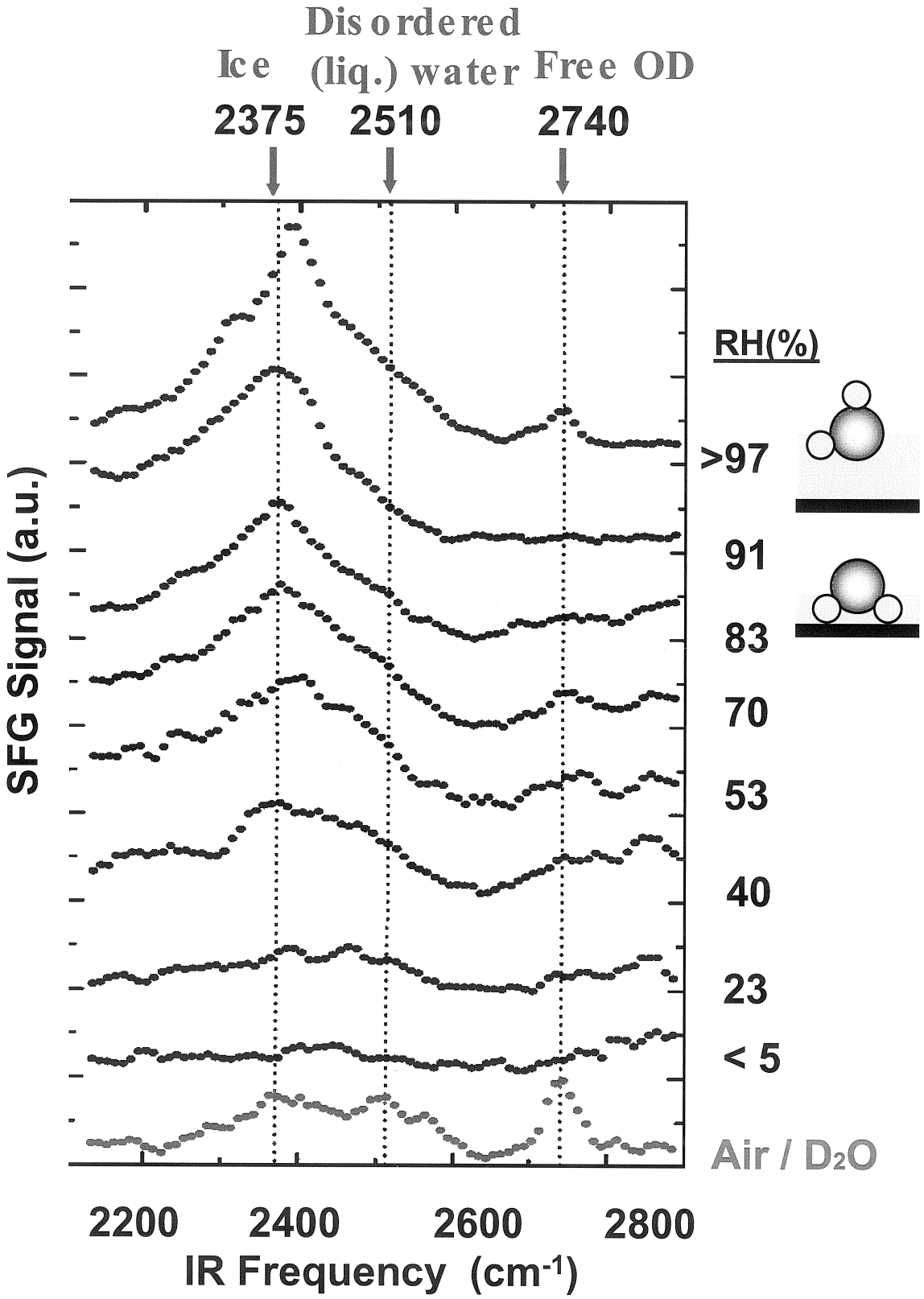
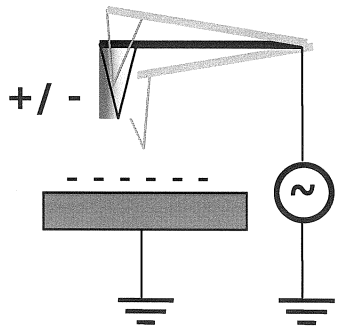

Disordered
Ice
(liq.) water
Free OD
2375
2510
2740
RH(%)
>97
91
83
70
53
40
23
< 5
Air / D2O
SFG Signal (a.u.)
2200
2400
2600
2800
IR Frequency (cm-1)

Figure 1



Kelvin Probe

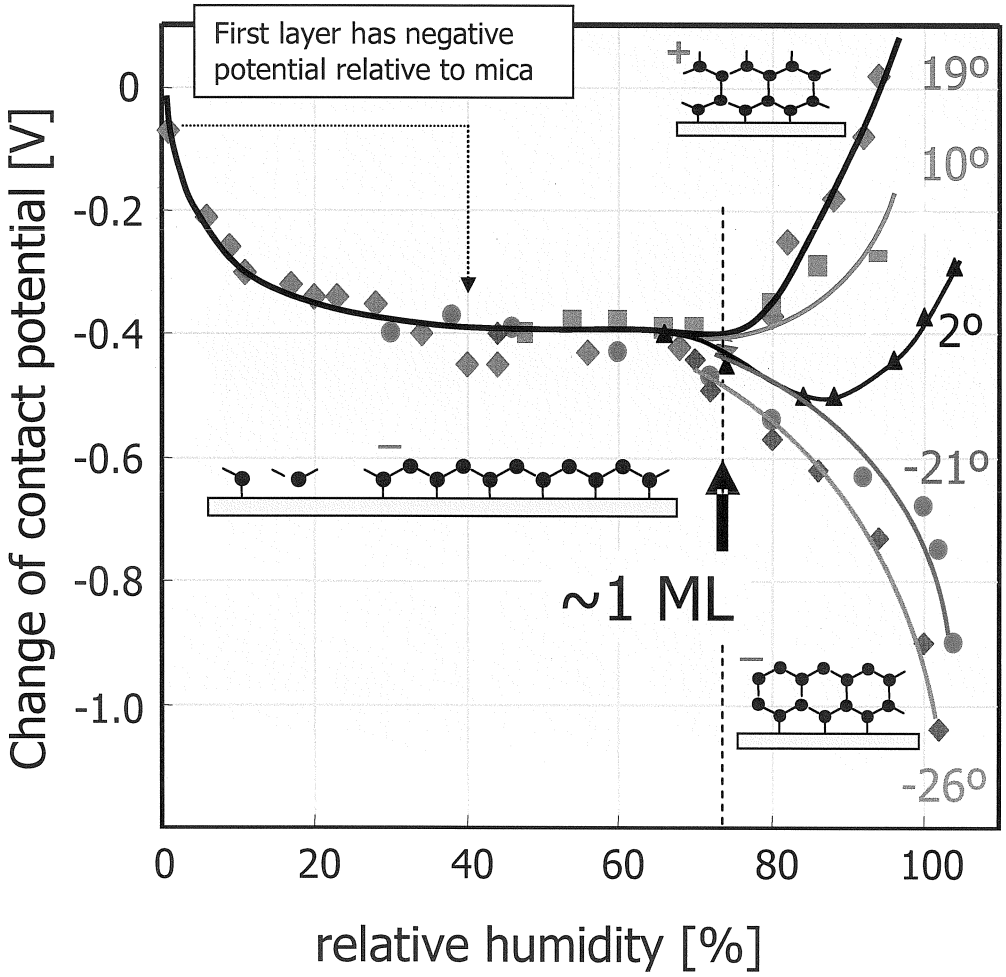


Figure 2

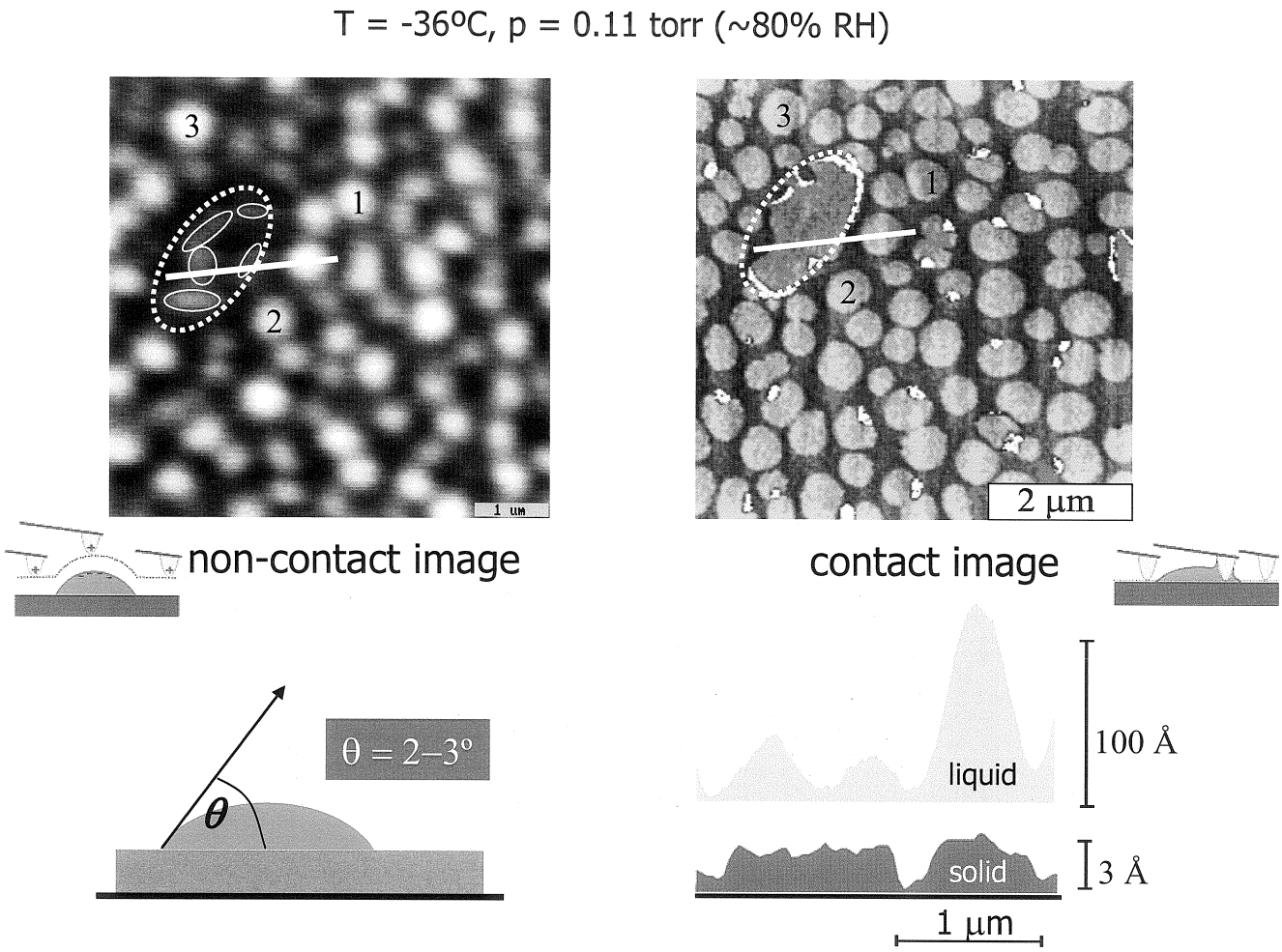

T = -36°C, p = 0.11 torr (~80% RH)
3
1
2
1 um
non-contact image
3
1
2
2 µm
contact image
θ = 2–3°
θ
liquid
100 Å
solid
3 Å
1 µm

Figure 3

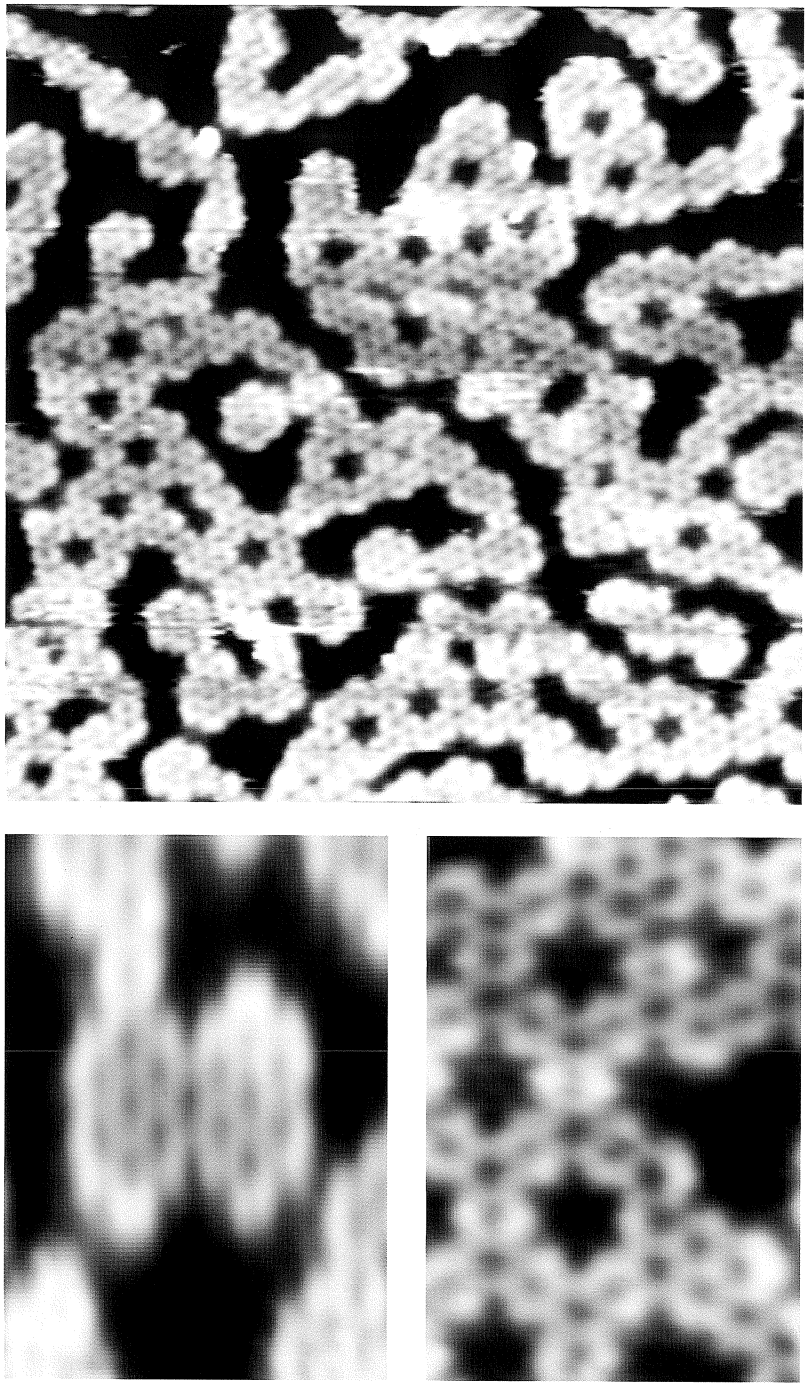


Figure 4

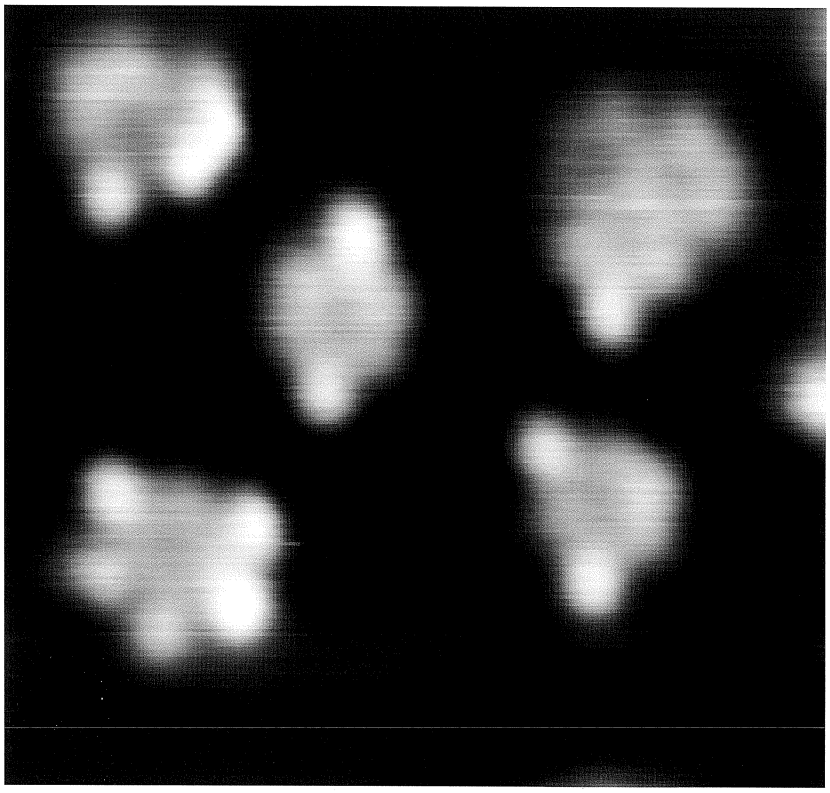


Figure 5

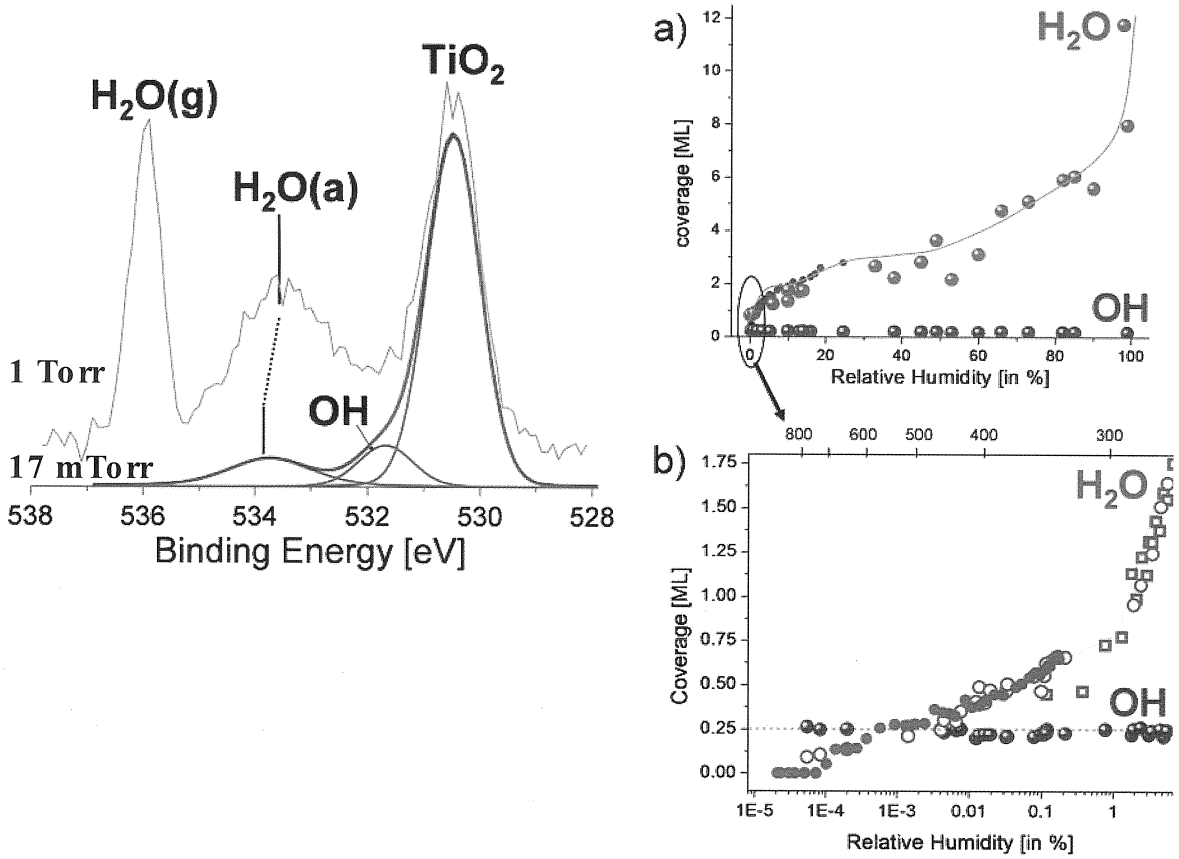

H2O(g)
H2O(a)
TiO2
OH
1 Torr
17 mTorr
538
536
534
532
530
528
Binding Energy [eV]
a)
H2O
OH
coverage [ML]
Relative Humidity [in %]
b)
H2O
OH
Coverage [ML]
Relative Humidity [in %]

Figure 6

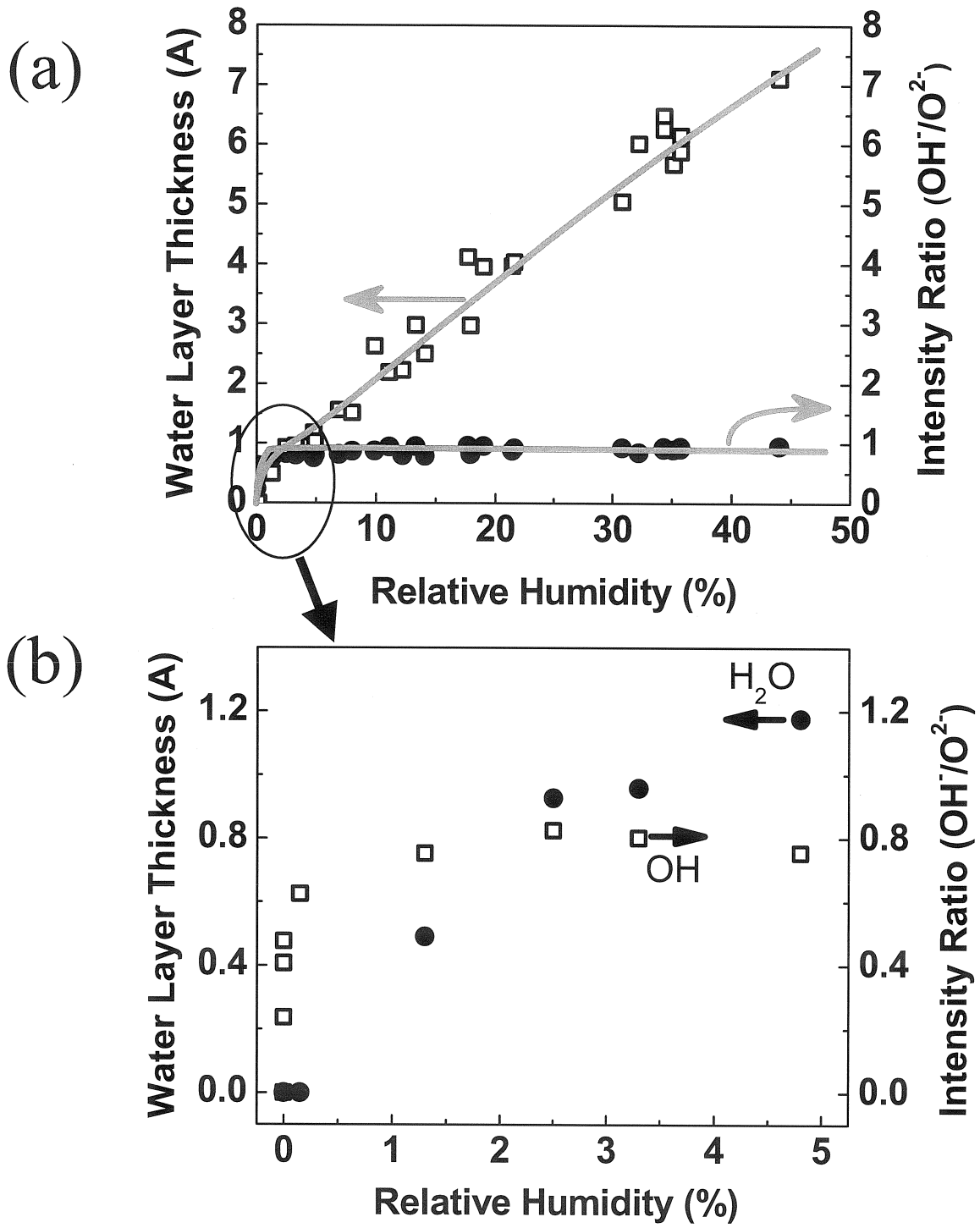
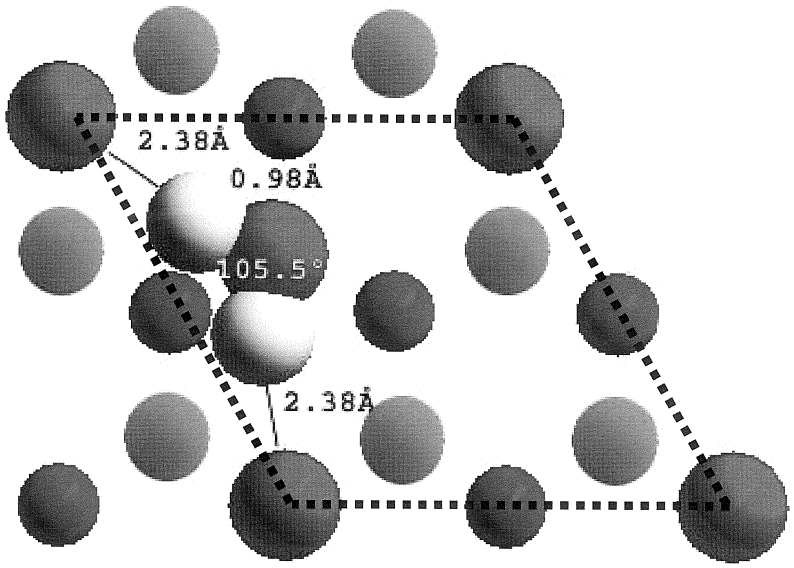

(a)
Water Layer Thickness (A)
Intensity Ratio (OH⁻/O²⁻)
Relative Humidity (%)
(b)
Water Layer Thickness (A)
Intensity Ratio (OH⁻/O²⁻)
H2O
OH
Relative Humidity (%)

Figure 7



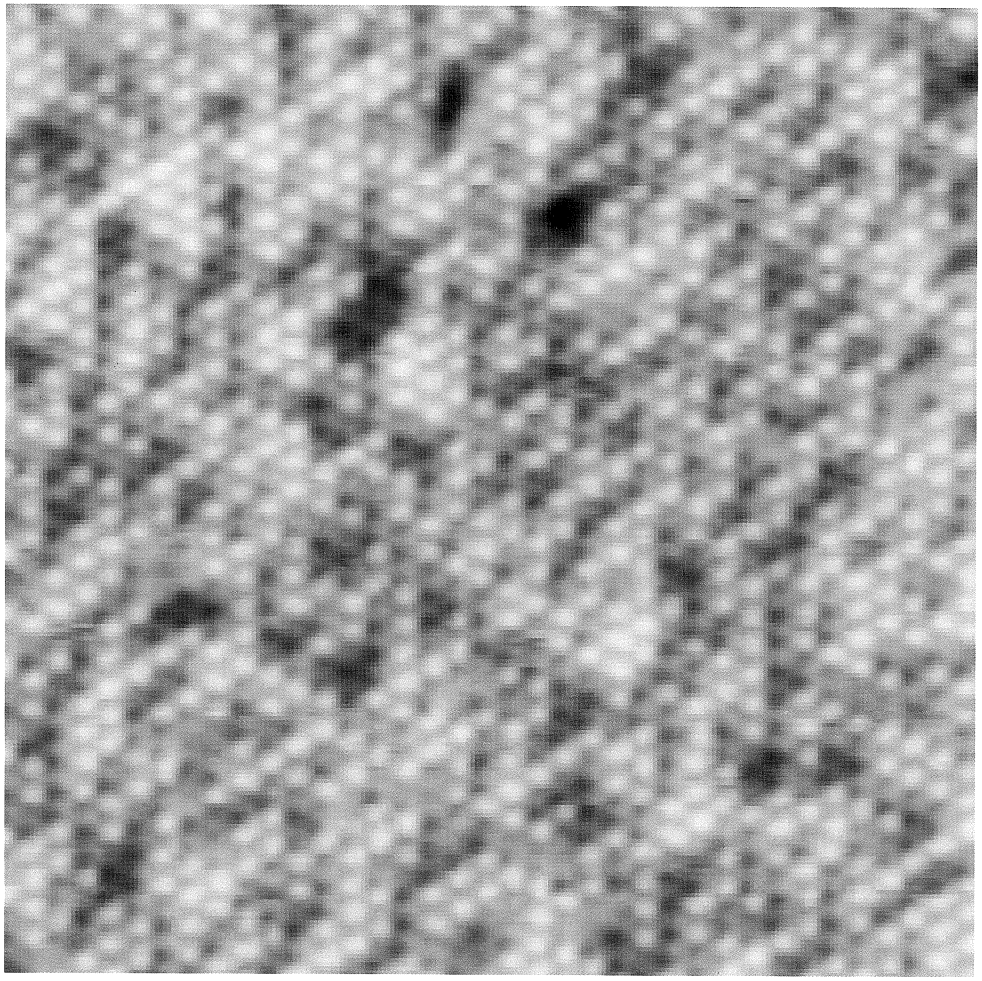


Figure 8