

SANDIA REPORT

SAND2014-17839

Unlimited Release

Printed September 2014

Deciphering Adsorption Structure on Insulators at the Atomic Scale

Konrad Thürmer and Peter J Feibelman

Prepared by
Sandia National Laboratories
Albuquerque, New Mexico 87185 and Livermore, California 94550

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Approved for public release; further dissemination unlimited.



Sandia National Laboratories

Issued by Sandia National Laboratories, operated for the United States Department of Energy by Sandia Corporation.

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government, nor any agency thereof, nor any of their employees, nor any of their contractors, subcontractors, or their employees, make any warranty, express or implied, or assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represent that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government, any agency thereof, or any of their contractors or subcontractors. The views and opinions expressed herein do not necessarily state or reflect those of the United States Government, any agency thereof, or any of their contractors.

Printed in the United States of America. This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-Mail: reports@adonis.osti.gov
Online ordering: <http://www.osti.gov/bridge>

Available to the public from

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Rd.
Springfield, VA 22161

Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-Mail: orders@ntis.fedworld.gov
Online order: <http://www.ntis.gov/help/ordermethods.asp?loc=7-4-0#online>



SANDIA Report

SAND2014-17839

Unlimited Release

Printed September 2014

Final Report for LDRD project #158823:

Deciphering Adsorption Structure on Insulators at the Atomic Scale

Konrad Thürmer
Materials Physics

Peter J Feibelman
Integrated Nanotechnologies

Sandia National Laboratories
P.O. Box 969
Livermore, California 94551-MS9161

Abstract

We applied Scanning Probe Microscopy and Density Functional Theory (DFT) to discover the basics of how adsorbates wet insulating substrates, addressing a key question in geochemistry. To allow experiments on insulating samples we added Atomic Force Microscopy (AFM) capability to our existing UHV Scanning Tunneling Microscope (STM). This was accomplished by integrating and debugging a commercial qPlus AFM upgrade. Examining up-to-40-nm-thick water films grown in vacuum we found that the exact nature of the growth spirals forming around dislocations determines what structure of ice, cubic or hexagonal, is formed at low temperature. DFT revealed that wetting of mica is controlled by how exactly a water layer wraps around (hydrates) the K^+ ions that protrude from the mica surface. DFT also sheds light on the experimentally observed extreme sensitivity of the mica surface to preparation conditions: K atoms can easily be rinsed off by water flowing past the mica surface.

ACKNOWLEDGMENTS

We wish to recognize Josh Whaley's contribution to the design of the sample holder needed for mica substrates. This work was funded under LDRD Project Number158823 and Title "Deciphering Adsorption Structure on Insulators at the Atomic Scale".

CONTENTS

1. Introduction.....	7
1.1. Project Purpose	7
1.2. Technical Approach	7
2. Accomplishments.....	8
2.1. SPM Experiments	8
2.2. DFT calculations.....	10
3. Conclusions.....	11
4. Publications supported by this project	12
5. References.....	12
Distribution	13

FIGURES

Figure 1. AFM image showing the rich surface topography of a 20-nm-thick film of ice grown onto Pt(111) at 140 K. (Image taken from Ref.[6].).....	8
Figure 2: (a) qPlus AFM image of a 40-nm thick film of ice. Red arrows mark double spirals, which allow the formation of hexagonal ice without nucleation. (b-e) Scenario leading to a double spiral (adapted from Ref.[6].)	9
Figure 3 AFM images of (a) the bare muscovite (mica) substrate, and (b) a 6 nm thick ice film on mica.....	10
Figure 4 (a)Top and (b) side view of the non-hydrating water layer of Ref. [8], (c) top and (d) side views of a hydrating water layer. The O atoms of the adsorbed water molecules are colored blue. Otherwise, spheres representing K, Si, Al, O, and H atoms are green, cyan, yellow, red, and white. (Adopted from Fig. 3 and 4 of Ref.[5])......	11
Figure 5: Snapshot of a molecular dynamics calculation simulating water flow in a narrow channel bounded by mica walls	11

NOMENCLATURE

DFT	Density Functional Theory
SPM	Scanning Probe Microscopy/Microscope
STM	Scanning Tunneling Microscopy/Microscope
AFM	Atomic Force Microscopy/Microscope (AFM)
UHV	Ultra-high Vacuum

1. Introduction

1.1. *Project Purpose*

Whether to understand ice-nucleation in clouds, lubricant degradation in micro-machines, or aqueous electrochemical kinetics, one wants a molecular-level knowledge of water-solid interactions. Water behavior at interfaces has therefore been the subject of hundreds of studies. Still, even the simplest issue, the structure of the first water layer on a solid surface, has been hard to resolve. E.g., for three decades, low-temperature, 2-dimensional wetting layers on close-packed precious metal surfaces were thought to be “ice-like” arrangements of water molecules, strained into registry. Recently, via STM imaging and DFT-supported interpretation, we overturned that idea, discovering the remarkably non-ice-like molecular arrangement adopted by water on Pt(111) [1]. That success offers the prospect of understanding how water binds to the more stable materials: oxides, sulfides, and salts, of which the world is largely comprised. The obstacle is that these materials are generally insulators, for which high-resolution microscopic techniques have been unavailable.

By exploiting an AFM breakthrough, we aimed to perform atomic-scale studies of adsorbates on insulating surfaces relevant to environmental and technological processes bearing on national needs. Unprecedented resolution has been achieved with a novel tuning-fork type sensor known as “Q-plus” [2]. Proof-of-principle of the Q-plus technique, atomic-resolution AFM of an adsorbed pentacene molecule [3], suggests breakthrough possibilities for molecules on oxides, assuming the technique proves robust enough to provide similarly high resolution images of delicately bonded, adsorbed water. Our project targets the wetting of muscovite and kaolinite, oxides ubiquitous in nature, implicated as cloud-seed materials, and subjects of many experimental and theoretical studies with no definitive conclusions. Making inroads into understanding the interaction of insulating materials with their surroundings will foster progress in understanding friction and lubrication, the role of oxide supports in surface chemistry, the stability of protective coatings, and a host of geochemistry problems.

1.2. *Technical Approach*

Our approach is to combine high-resolution SPM and DFT to discover the basic mechanisms that govern the properties of molecularly thin water layers on oxides and salts. Specifically, experimental images will provide clues about the structure of water layers. Structure models will be developed, and then tested and refined with DFT. The relaxed DFT structures will be used to simulate images, which through comparison with the experimental ones, will help eliminate or validate the tested structures. After investigating the first molecular layer we will address key questions concerning film growth at higher thicknesses.

1.2.1. **Experiment**

In a well-controlled UHV environment, we grow molecularly thin water layers onto atomically flat oxide and salt surfaces at low temperatures, and attempt to image them at high resolution. The difficulty here is that the technique that excels for water/metals, i.e., STM, cannot be used on insulators. One has to resort to AFM, which has proven quite useful for water layers, but, in its conventional implementation [4], lacks the high resolution of STM. Far better resolution is needed to decipher molecular structure. The recent invention of the “qPlus” AFM sensor by F.J. Giessibl [2] puts this goal within reach. Shortly before work on this LDRD project commenced we upgraded our variable temperature SPM with qPlus-AFM capability. The AFM capability

has to be tested and procedures developed that allow nondestructive imaging of the very delicate adsorbate layers to be examined in this project. After establishing qPlus-AFM imaging on ice/Pt subsequent experiments are conducted on muscovite (mica). The commercial sample holders, which had been developed for metals and semiconductors, might need modifications before using thin mica sheets as substrates.

1.2.2. Density Functional Theory

The DFT calculations focused on mica wetting because most studies of water transport under confinement at the nanoscale have been conducted in a Surface Forces Apparatus between mica sheets, and because low-resolution imaging implies that a periodic arrangement (in principle easier to interpret) forms. The first goal is to predict ground-state structures of the one-molecule thin wetting layer of water on mica. Computational details are given in section II of Ref.[5].

2. Accomplishments

The main results of this project are well documented in two peer-reviewed journal articles, Refs. [5] and [6]. We thus provide only brief summaries of those, supplemented by accomplishments not covered in Refs. [5] and [6].

2.1. SPM Experiments

2.1.1. Setting up AFM experiments

At the beginning of this project we installed and tested the previously purchased qPlus AFM upgrade module. Our Variable Temperature SPM system was the first instrument for which the vendor (Omicron) had sold this retrofit. It turned out that this module had various problems (1-3) initially preventing operation. (1) A software deficiency prevented the AFM-based tip-sample approach needed on insulating substrates. (2) A hardware bug prevented temperature measurement during AFM imaging. (3) The scanning hardware needed service (one electrical contact missing). Through extensive testing and interactions with the vendor we eliminated these problems. Molecular surface steps can now be resolved nondestructively with AFM using the qPlus sensor technique. An example AFM image is shown in Figure 1.

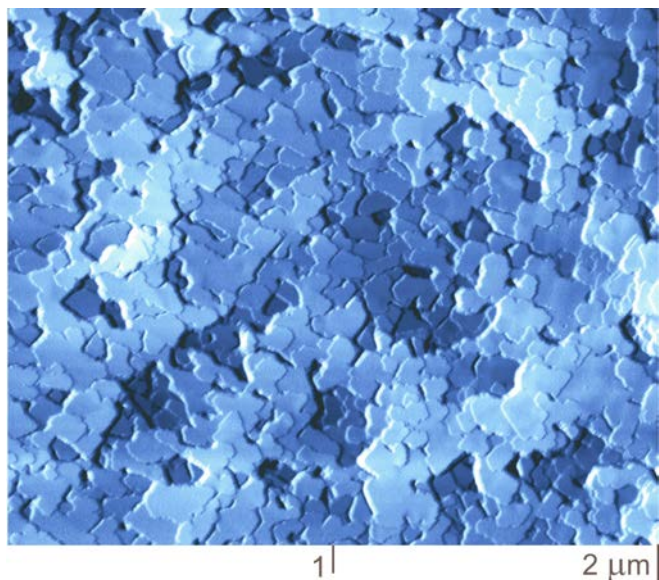


Figure 1. AFM image showing the rich surface topography of a 20-nm-thick film of ice grown onto Pt(111) at 140 K. (Image taken from Ref.[6].)

2.1.2. AFM study of the low temperature growth of ice

Establishing AFM's capability to routinely resolve molecular steps on ice surfaces positioned us to examine the growth morphology of ice films thicker than 10 nm, which are beyond the reach of STM. Our AFM experiments revealed that these thicker films grow via double spirals around screw dislocations with a double burgers vector, a mechanism that explains the nucleation-free formation of hexagonal ice at low temperature. The AFM image in Figure 2 (a) shows two double spirals and the schematics in Figure 2(b-e) illustrate a scenario leading to a double spiral.

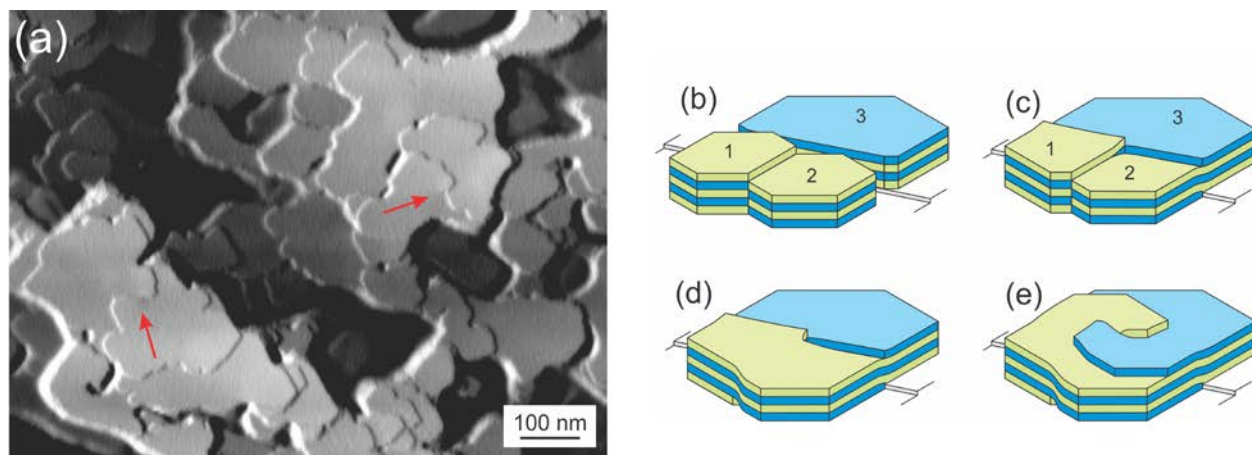


Figure 2: (a) qPlus AFM image of a 40-nm thick film of ice. Red arrows mark double spirals, which allow the formation of hexagonal ice without nucleation. (b-e) Scenario leading to a double spiral (adapted from Ref.[6].)

These AFM experiments combined with earlier STM experiments on thinner films allowed us to develop a comprehensive picture of the thickness-dependent growth of ice films at low temperature. We found that the crystal structure of ice, deposited at low temperatures ($\sim 140\text{K}$) onto Pt(111), switches twice as films grow thicker. Isolated 3D clusters, which can only grow via layer nucleation, consist of hexagonal ice. Following coalescence, cubic ice is produced in growth spirals created by screw dislocations above substrate steps. Eventually, at thicknesses of ~ 20 nm, a double growth spiral, generated by dislocations with a double Burgers vector, becomes dominant, causing the preferential formation of hexagonal ice. These results are extensively documented in Ref.[6].

2.1.3. AFM demonstration of ice on muscovite (mica)

Flat mica surfaces can be obtained rather straightforwardly by cleaving commercially available mica sheets in air. After resolving the AFM problems described in 2.1.1., imaging insulating substrates like mica did not pose any additional challenges. However, it turned out that the temperature control of insulating samples like mica is very poor when using the vendor-supplied sample holders, whereas a good temperature control is essential when studying water adsorption at a molecular scale. Several attempts to grow ice on mica using a modified commercial sample holder failed; and we thus decided to design a completely new sample holder suitable for working with mica substrates. This new sample holder finally allowed us to grow ice films on mica in UHV. Figure 3 shows AFM images documenting that our new sample holder has sufficient temperature control to allow growth and imaging of ice on mica. The clustered

topography of the 6 nm thick ice film in Figure 3(b) suggests that ice grows polycrystalline on mica at $T=140\text{K}$.

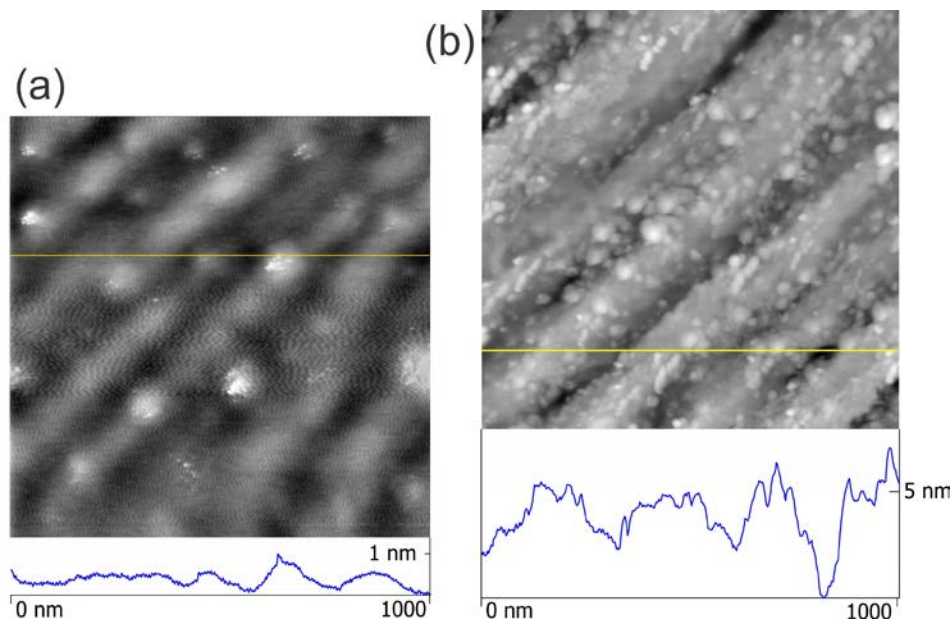


Figure 3
AFM images of (a) the bare muscovite (mica) substrate, and (b) a 6 nm thick ice film on mica.

As previously reported, e.g. by Ostendorf et al. [7], we also found that the structure of the mica surface depends on the exact preparation conditions after cleaving the sheets in air. Ref.[7] had shown, for example, that the mica's K^+ ions react with CO_2 from the air to form small carbonate crystallites. A systematic study of ice growth on mica comparing various substrate preparation schemes would be a worthwhile follow-up project. In a next step, co-depositing CO_2 with water would provide an even more direct link to current geophysics questions, related, for example, to underground CO_2 sequestration.

2.2. DFT calculations

2.2.1. DFT analysis of the 2D wetting layer of water on muscovite (mica)

This DFT study's goal was to find the lowest-energy configuration of the two-dimensional (one-molecule thick) wetting layer of water on muscovite. The widely accepted previous model, proposed by Odelius et al. [8], consisted of a bulk-ice like honeycomb water layer warped over the K atoms (Figure 4 (a,b)). The study in our project (Ref.[5]) revealed that better-bound structures can be found when also considering lower water coverages that allow the K atoms to be embedded and hydrated. Additional criteria to construct atomic models were, first, to optimize H-bonds also between water and substrate O atoms, and, second, to generate strong H-bonds by placing O-O pairs $2.67\text{-}2.97 \text{ \AA}$ apart. The example shown in Figure 4(c,d) has a binding energy improved by $\sim 40 \text{ meV}$ per water molecule compared to the non-hydrating structure of Ref. [8] (Figure 4(a,b)). This structure also reproduces better the work function changes measured by Bluhm *et al.* [9]. These results are extensively documented in Ref.[5].

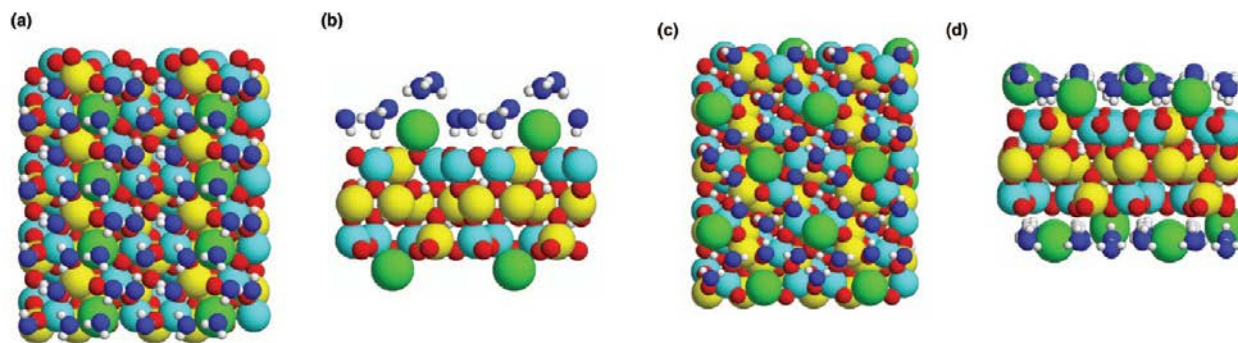


Figure 4 (a)Top and (b) side view of the non-hydrating water layer of Ref. [8], (c) top and (d) side views of a hydrating water layer. The O atoms of the adsorbed water molecules are colored blue. Otherwise, spheres representing K, Si, Al, O, and H atoms are green, cyan, yellow, red, and white. (Adopted from Fig. 3 and 4 of Ref.[5])

2.2.2. Simulating water flow in a narrow channel bounded by Mica walls

Ab initio molecular dynamics was used to simulate water flow in a narrow channel bounded by mica walls (see Figure 5). One result of interest is that contrary to a paper we stumbled on, the K atoms are easy to “rinse” off the surface (as Salmeron’s group has found), particularly the ones that lie higher up at T=0 K. Detaching K atoms from the mica does not require a very low pH. The charged surface sites are compensated by oriented water molecule dipoles. OH bonds are allowed to stretch or even dissociate in these simulations. But dissociation has not occurred in our preliminary study, which covered the passage of just a few ps.

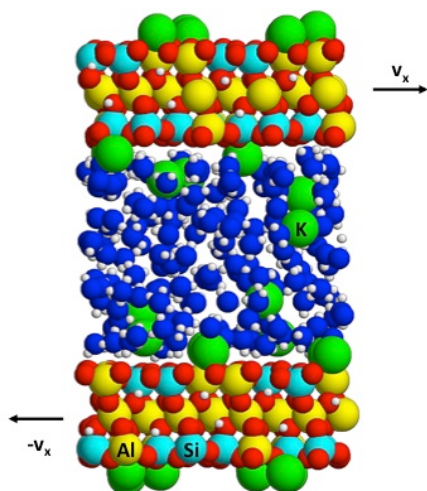


Figure 5: Snapshot of a molecular dynamics calculation simulating water flow in a narrow channel bounded by mica walls

3. Conclusions

Both the AFM and the DFT effort of this program yielded significant scientific insight as documented in the previous section and the peer-reviewed publications. Building up the AFM capability to examine delicate insulators was challenging. In the course of this project it became clear that the qPlus AFM implemented in our Variable Temperature Scanning Probe Microscope will not be able to achieve atomic resolution on delicate adsorbates. For this a low temperature setup (@~\$700k) is needed. But the ability to routinely resolve molecular ice steps opened the door to finally resolve a decades-old problem regarding the enigmatic relationship between the

two low-pressure phases of ice (Ref.[6]). Due to the limited AFM resolution and the inadequacy of the commercial sample holders for mica, AFM could not be used to support the DFT effort to find the atomic structure of the 2D wetting layer of water on mica. Nevertheless the DFT effort significantly improved our understanding of 2D water/mica (Ref.[5]). After designing a new sample holder we succeeded in growing and imaging water on mica films (Figure 3), “proof of concept” that we can examine adsorbates on minerals, i.e., systems relevant to the Geosciences.

4. Publications supported by this project

- K. Thürmer and S. Nie, *Formation of hexagonal and cubic ice during low-temperature growth*, Proceedings of the National Academy of Sciences **110**, 11757 (2013).
Covered by B. Verberck in News & Views: Cond. Mat.: *On thin ice*, Nat. Phys. **9**, 457 (2013).
- P. J. Feibelman, *K⁺-hydration in a low-energy two-dimensional wetting layer on the basal surface of muscovite*, J. Chem. Phys. **139** (2013).

5. References

-
1. S. Nie, Peter J. Feibelman, N.C. Bartelt, and K. Thürmer, *Pentagons and Heptagons in the First Water Layer on Pt(111)*, Phys. Rev. Lett. **105**, 026102 (2010).
 2. F.J. Giessibl, *AFM's path to atomic resolution*, Materialstoday **8**, 32 (2005).
 3. L. Gross, F. Mohn, N. Moll, P. Liljeroth and G. Meyer, *The Chemical Structure of a Molecule Resolved by Atomic Force Microscopy*, Science **325**, 1110 (2009).
 4. J. M. K. Donev, Q. Yu, B. R. Long, R. K. Bollinger and S. C. Fain, *Noncontact atomic force microscopy studies of ultrathin films of amorphous solid water deposited on Au(111)*, J. Chem. Phys. **123**, 044706 (2005).
 5. P. J. Feibelman, *K⁺-hydration in a low-energy two-dimensional wetting layer on the basal surface of muscovite*, J. Chem. Phys. **139** (2013).
 6. K. Thürmer and S. Nie, *Formation of hexagonal and cubic ice during low-temperature growth*, Proceedings of the National Academy of Sciences **110**, 11757 (2013).
 7. F. Ostendorf, C. Schmitz, S. Hirth, A. Kühnle, J. J. Kolodziej, and M. Reichling, *Evidence for Potassium Carbonate Crystallites on Air-Cleaved Mica Surfaces*, Langmuir **25**, 10764 (2009).
 8. M. Odelius, M. Bernasconi, and M. Parrinello, *Two Dimensional Ice Adsorbed on Mica Surface*, Phys. Rev. Lett. **78**, 2855 (1997).
 9. H. Bluhm, T. Inoue, and M. Salmeron, *Formation of dipole-oriented water films on mica substrates at ambient conditions*, Surf. Sci. **462**, L599 (2000).

DISTRIBUTION

1	MS0359	D. Chavez, LDRD Office	1911 (electronic copy)
1	MS0899	Technical Library	9536 (electronic copy)

