

[총회초청 I]

The Atomistic Surface Structures of Ice and Iron Oxide

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Ice and iron oxide are common every-day materials and their surfaces have great practical importance. Ice surfaces are slippery and thus dangerous, and they play a role in the ozone hole creation. Iron oxide is a leading form of unwanted rust, and is an active material in catalysis. Nevertheless, very few studies have investigated the atomistic surface properties of these materials.

These surfaces have been investigated in Berkeley in recent years by several research groups using diverse techniques: low-energy electron diffraction (LEED), scanning tunneling microscopy (STM), and photoelectron diffraction (PED). Both ice and iron oxide surfaces were prepared as ultrathin films grown on a Pt(111) single-crystal substrate. This avoids surface charging and allows the easiest use of these established techniques.

Ice was condensed from water vapor at about 140 K and cooled to 90 K for LEED intensity measurements[1-2]. The ice thickness was sufficient to make the Pt substrate undetectable. The LEED pattern, while not very sharp, indicates a surface lattice consistent with the naturally occurring hexagonal phase, exposing an unreconstructed (0001) face. A fully dynamical (multiple-scattering) analysis of the LEED intensities was used, together with total-energy calculations and molecular-dynamics simulations, to determine the detailed surface geometry [3]. It is concluded that the outermost plane of water molecules, while occupying essentially bulk-like positions, vibrates very strongly even at 90K (rms amplitudes of about 0.28 Å vs 0.10 Å in bulk ice), making it practically undetectable in LEED. These vibrations are the first sign of an amorphous surface layer that is believed to occur on ice at 190-220 K, the temperature range applicable in the ozone hole creation: this amorphous layer may catalyze Cl-containing molecules into Cl₂ molecules which subsequently are photo-dissociated and then attack ozone. These vibrations also signal the development of a liquid surface layer known to occur at temperatures above about 230 K (-30 °C), with thickness in the 10-1000 Å range. This liquid layer may be responsible for the slipperiness of ice, rather than the popular theory of pressure-induced melting.

Iron oxide was grown layer-by-layer on Pt(111) by depositing one monolayer (or a fraction of a monolayer) of pure iron, then oxidizing it and annealing the resulting oxide layer, repeating the process as often as desired [4-7]. The first oxide "bilayer" (consisting of a monolayer of Fe and a monolayer of O) produced very perfect STM images and LEED patterns: these imply an incommensurate, approximately (9×9), overlayer of composition FeO [8]. By PED and its forward focusing principles, it was possible to deduce that the O atoms

lie outside the Fe layer [7]. By STM calculations, further details of the local structures within the (9×9) supercell could be deduced [9]. The second oxide bilayer forms a ($\sqrt{3}\times\sqrt{3}$) R30° periodicity with respect to the first bilayer, which can be interpreted as having a Fe₂O₃ composition by analogy with the bulk structure. Thicker layers produce a moderately ordered (2×2) pattern, which similarly can be interpreted as having a Fe₃O₄ composition. This composition was verified in a detailed LEED intensity analysis, which also indicated strong relaxations from the bulk structure in the direction perpendicular to the surface [10]. The outermost atoms are found to be a "quarter monolayer" of Fe atoms, which may be the active sites for catalysis. This structure was also confirmed by a PED structural analysis, where slight differences in the results may however be due to a different preparation[7].

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