Supporting Information

Vibrational spectroscopic observation of ice dewetting on MgO(001)

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Experimental details

The experiments were performed in two separate UHV set-ups, one for IRAS, and one for SFG. Both setups consist of a UHV preparation/analysis section equipped with tools for single crystal cleaning, metal evaporation, sample characterization [i.e., Low Energy Electron Diffraction (LEED), and X-ray Photoelectron Spectroscopy (XPS)], and spectroscopy cells equipped with CaF$_2$ windows for SFG and IRAS experiments. The Ag(001) single crystal used as a substrate for MgO film growth was cleaned by repeated sputter(Ar$^+$)/anneal(700 K) cycles until a sharp LEED pattern was obtained. 20 ML thick MgO(001) films were deposited on Ag(001) by evaporating Mg in 1x10$^{-6}$ mbar oxygen while maintaining a constant sample temperature of 570 K.$^1$ The resultant films are well ordered with sharp (1×1) LEED spots. The MgO(001)/Ag(001) sample was flashed to 700 K prior to each adsorption experiment to desorb impurities accumulated from the chamber background, and the doses were performed at a sample temperature of 90 K (achieved by N$_2$ cooling of the sample manipulator). The SFG experiments were conducted with triple distilled H$_2$O while D$_2$O (Aldrich) was used for the IRAS work. In both cases, the water was further purified by several freeze-pump-thaw cycles prior to each experiment.

SFG vibrational spectroscopy was performed using a Nd:YAG laser (1064 nm, 30 mJ/pulse, 25 ps, 50 Hz, EKSPLA PL501) with part of the output converted to 532 nm and 355 nm in a harmonic generator. The 1064 nm and 355 nm beams were mixed in an optical parametric generator/difference frequency generator (EKSPLA PG401) to produce tunable infrared pulses in the range of 2.5–6 μm, with pulse energies of 60-200 μJ and a bandwidth of about 5 cm$^{-1}$. The 532 nm light, used as the VIS beam for SFG, had an energy of 200 μJ/pulse. To collect SFG spectra, the p-polarized IR and VIS pulses were overlapped on the sample surface, and the resulting sum frequency beam was detected with a photomultiplier tube after passing through a monochromator. To correct for frequency-dependent fluctuations in the intensity of the IR beam, we have normalized all SFG intensities using that of the incident IR pulses. The detected SF intensity is

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proportional to the intensity of the incident IR and VIS fields and the second-order nonlinear susceptibility, $\chi^{(2)}$, which contains contributions from a non-resonant substrate term, $\chi_{NR}^{(2)}$, and a resonant vibrational term, $\chi_{R}^{(2)}$.\(^2\) The Ag(001) substrate used in the present study generates a noticeable non-resonant signal, which, because of the phase difference between $\chi_{NR}^{(2)}$ and $\chi_{R}^{(2)}$, affects the line shape of the SFG spectrum.

The normalized SFG spectra were fitted with the standard Lorentzian model:

$$I_{SFG} = |A_{NR}e^{i\varphi} + \sum_{n} \frac{A_{n}}{\omega - \omega_{n} - i\Gamma_{n}}|^2$$

where $A_{NR}$ is the amplitude of the non-resonant background and $\varphi$ is the phase, and $A_{n}$, $\omega_{n}$ and $\Gamma_{n}$ represent the amplitude, resonance frequency and line width of the $n$-th resonant vibrational mode.

IRAS spectra were acquired using a Bruker IFS 66v FTIR spectrometer with an external MCT detector. Typically, 200 scans were accumulated for one spectrum and the resolution was set to 4 cm\(^{-1}\). The background spectrum was obtained from the surface of a freshly prepared, clean MgO(001)/Ag(001) sample.

References: