Surface-Induced Ferroelectric Ice on Pt(111)

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Optical sum-frequency vibrational spectroscopy and thermal desorption are used to study ice films grown on Pt(111). The strong enhancement of OH stretch resonances with film thickness provides clear evidence for the presence of polar ordering of water molecules in the films. The ordering is induced by the polar anchoring of the first ice monolayer on platinum. It exhibits a characteristic behavior of surface-induced ordering phenomena with a decay length of 30 monolayers. [S0031-9007(97)05196-X]

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Can ice be ferroelectric? This question has long attracted much attention. Ice has a variety of phases [1], but, in all cases, water molecules are held together by tetrahedral hydrogen bonding. The molecular orientations at the lattice points should obey the Bernal-Fowler-Pauling (BFP) rules which require that each molecule donates two protons to two of the attached water molecules and accepts two protons from the other two [2]. This, however, still leaves many possible ways to orient the water molecules in an ice lattice, giving rise to the residual entropy problem first tackled by Pauling [3,4]. Onsager and Slater [5,6] showed that, for all orientational configurations, the electrostatic energy (including dipole-dipole interaction) is the same. One would then expect from free energy consideration that random orientation of water molecules should prevail so that there exists no net polarization in ice. Polar ordering of water molecules would occur at 0 K or very low temperature. Indeed, ferroelectricity has never been found in pure ice. In a KOH-doped ice crystal poled by a dc electric field, Jackson and Whitworth [7] observed the appearance of a current pulse when the crystal was warmed through ~72 K. They attributed the current pulses to depolarization current resulting from a ferroelectric-paraelectric transition, although an alternative explanation based on a piezoelectric charging or discharging effect induced by a structural phase transition had been suggested.

In this paper, we present experimental results showing convincingly that ice films grown on Pt(111) at temperatures between 120 and 137 K are ferroelectric. (Here, "ferroelectricity" is used loosely to describe the existence of a net polar ordering of water molecules in the ice films.) The lower temperature was limited by our apparatus and the upper one by the onset of rapid ice sublimation. It is known that hexagonal ice can grow on Pt(111) [8]. Water molecules adsorbed directly on platinum have their oxygen bound to Pt and are polar ordered. From the BFP ice rules, one then expects that subsequently grown ice layers should all be polar ordered although, at finite temperatures, thermally generated defects could break the ice rules and reduce the polar ordering. The surface dipole layer, on the other hand, creates a dc field that would help the polar ordering. Thus, the growth of a thin film of ferroelectric ice on Pt(111) seems natural. We used infrared-visible sum-frequency generation (SFG) spectroscopy as a probe in our experiment [9]. SFG is a second-order nonlinear optical process that is forbidden in a medium with inversion symmetry. In its application to an ice film, the spectrum is expected to be dominated by the film surfaces if the water molecules in the film are randomly oriented in their allowed positions. With polar ordering of the molecules, however, the spectral intensity should increase with an increase of film thickness, as the square of the film thickness if the film structure is uniform. This is what we observed, although the increase was weaker than the square of the film thickness showing decay of the polar ordering in successive layers. We can, therefore, conclude that our thin-film ice samples were polar ordered or ferroelectric. We describe some of the experimental details in the following.

Consider the sample preparation. It was carried out in an ultrahigh vacuum chamber with a base pressure less than 1×10^{-10} Torr. The preparation of the Pt(111) crystal followed that for scanning tunneling microscopic studies of the Pt(111) surface [10]. The sample surface was first cleaned by cycles of argon ion bombardment and subsequently annealed at 1300 K for 3 min. The surface cleanliness and structure were checked routinely by Auger electron spectroscopy and low energy electron diffraction (LEED). After the surface cleanliness has been assured and a sharp (1×1) LEED pattern observed, the ice film was then grown on Pt(111) by vapor deposition either at 137 or at 120 K and subsequently brought to 137 K for annealing. Ultrapure, triply distilled, and deionized water was used as the vapor source after cycles of freeze-pump-thaw treatments. The growth rate of ice was about 0.03 monolayer (ML) per sec at a water pressure of 5×10^{-8} Torr.

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Temperature-programed desorption (TPD) was employed to characterize the grown films. Figure 1 shows the TPD results from ice films of various thicknesses. Two well-resolved peaks are generally observed in each spectrum. At 0.85 ML water coverage [11], only the high-temperature peak at 171 K is present, which is characteristic of desorption of water molecules directly influenced by binding to Pt(111). (Here, we use saturation of the 171 K peak as an indication that the coverage has reached 1 ML.) At 1 ML or more, the lower temperature peak also shows up. It first appears weakly at 154 K, but then grows and shifts to a higher temperature with increasing film thickness until ~5 ML, while the higher temperature peak remains unchanged in both amplitude and position. This low-temperature peak is associated with molecular desorption (or sublimation) from the multilayer ice except the first adsorbed monolayer. The spectra of Fig. 1 indicate that the film structure of ice on Pt(111) should have stabilized well before 5 ML. These results are in qualitative agreement with those reported by others [8,12,13].

The experimental arrangement of SFG spectroscopy has been described elsewhere [9]. Briefly, two input laser beams are directed to overlap at a sample, one tunable in the infrared and the other at a fixed visible frequency. The sum-frequency output in the reflected direction is detected, producing a spectrum when the tunable infrared input is scanned over resonances.

The spectrum measures $|\chi_S^{(2)}|^2$, where $\chi_S^{(2)}$ is the integrated nonlinear optical susceptibility defined as $\chi_S^{(2)} = \int_{0^-}^{d} \chi^{(2)}(z)\, dz$ with $\chi^{(2)}(z)$ being the local nonlinear susceptibility, z along the surface normal, and d the film thickness. We assume here that the bulk contribution from the substrate is negligible and d is much smaller than the coherent length for the SFG process. We can generally express $\chi_S^{(2)}$ as

$$\chi_S^{(2)} = \chi_{\mathrm{NR}}^{(2)} + \sum_q [A_q/(\omega_{\mathrm{IR}} - \omega_q + i\Gamma_q)]. \quad (1)$$

Here, $\chi_{\mathrm{NR}}^{(2)}$ is the nonresonant contribution to $\chi_S^{(2)}$, ω_{IR} is the input infrared frequency, and A_q, ω_q, and Γ_q are the strength, resonant frequency, and damping constant of the qth resonant mode of the sample, respectively. If the bulk of the film lacks inversion symmetry and d is sufficiently large, then the spectrum should be dominated by the film. Otherwise, the spectrum is dominated by the interfacial layers. The SFG technique allows *in situ* probing of surfaces and films and, therefore, is ideally suited for studying an ice film during growth.

Figure 2 depicts the vibrational spectra of ice in the OH stretch region obtained with this technique for a set of ice films of various thicknesses grown on Pt(111). The samples were measured at 120 K and all beams were p polarized in the experiment. It is seen that the spectrum of approximately a single monolayer of

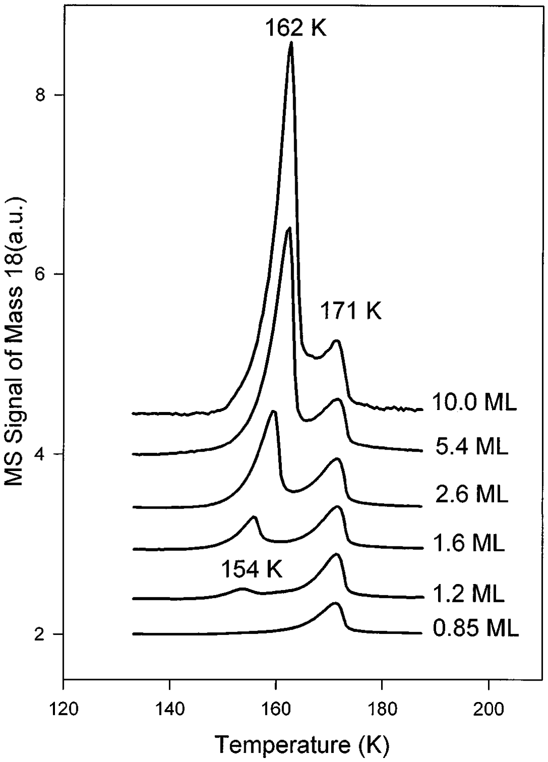

FIG. 1. TPD spectra for a set of ice films of different thickness on Pt(111). A heating rate of 3 K/sec was used. The base lines of the spectra are arbitrarily shifted.

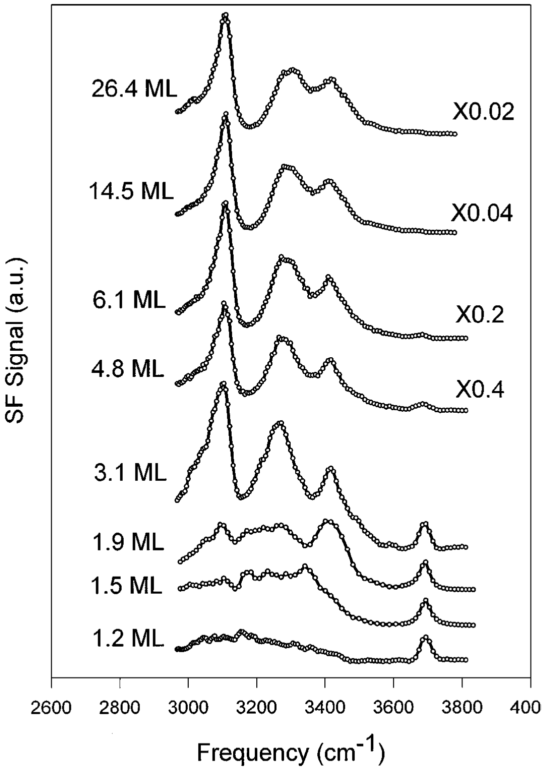

FIG. 2. SFG spectra in the OH stretch region for a set of ice films of different thickness on Pt(111).

ice (1.2 ML in Fig. 2) on Pt(111) is clearly different from those of multilayer ice as expected. For 2 ML and above, well resolved spectral peaks appear in the spectra. Except at 3690 cm^{-1}, all others grow strongly with film thickness. Their positions remain unchanged, but the relative intensities of the three prominent peaks vary from 2 to 5 ML and become nearly constant after 5 ML. This is in accord with the TPD result.

Compared to the existing infrared, Raman, and electron energy loss spectra of ice, our SFG spectra exhibit narrower peaks. The different selection rules may be partly responsible for the difference [14]. To identify the spectral features, we borrow results from earlier theoretical analyses of infrared and Raman spectra of bulk ice [15,16]. The narrow peak at 3690 cm^{-1} can be unequivocally assigned to the dangling OH bonds at the vacuum/ice interface. The same exists at the air/water interface [17]. Since it is associated only with the surface, as long as the polar ordering of the surface monolayer remains unchanged, its strength does not vary with the ice film thickness. With increasing film thickness, this peak gets swarmed rapidly by the growing peaks in the spectrum. The three prominent peaks appearing between 3000 and 3600 cm^{-1} are related to the lattice-coupled hydrogen bonded OH stretch modes. Two of them at 3100 and 3280 cm^{-1} can be assigned to the coupled in-phase symmetric (ν_1) and antisymmetric (ν_3) stretches, respectively. The one at 3410 cm^{-1} can be identified as a combination mode of the antisymmetric OH stretch (ν_3) with a lattice translation mode (ν_T). For film thickness larger than 5 ML, the spectra also exhibit a small peak at ~3000 cm^{-1}. This can be assigned to the difference combination of $\nu_1 - \nu_T$. Above 1 ML, each spectrum in Fig. 2 can be fit by $|\chi_S^{(2)}|^2$ using the expression of $\chi_S^{(2)}$ in Eq. (1), and the corresponding parameters A_q, ω_q, and Γ_q for different modes can be deduced. Because SFG is allowed only in a medium without inversion symmetry, the strength A_q should be a constant (like the 3690 cm^{-1} mode) if ice films are paraelectric, but should be directly proportional to the film thickness (or intensity $|A_q|^2$ proportional to the square of the film thickness) if the films are homogeneous and ferroelectric. In Fig. 3(a) we plot A_q and its derivative $\partial A_q/\partial z$ ($\hat{z}$ along the surface normal) versus film thickness (thicker than 6 ML) for the 3100 cm^{-1} peak. It is seen that A_q increases sublinearly and gradually saturates as $\partial A_q/\partial z$ decays away. Similar behavior for the 3280 and 3410 cm^{-1} peaks was found and depicted in Fig. 3(b).

The above experimental results suggest the following picture of ice film growth on Pt(111). The first H_2O monolayer absorbed on Pt(111) is clearly under the influence of the metal substrate. It is believed that water molecules adsorbed on Pt(111) tend to form an icelike structure [8], even at submonolayer coverage (in the form of ice patches). However, the lattice mismatch could cause severe strain or disorder in the adsorbed monolayer, as is evidenced by the very different SFG spectrum for the 1.2 ML of ice in comparison with the rest of Fig. 2. Subsequent film growth gradually eases the film into the ice bulk structure. It takes several monolayers to do so; our TPD and SFG spectra indicate that the contribution from the bulklike structure already dominates over the contribution from the strained surface layers at ~5 ML. The SFG spectra actually suggest that, starting at ~3 ML, the film structure is already close to that of the bulk because all of the prominent spectral peaks have appeared at the right positions with approximately the same shapes. The polar orientation of the boundary monolayer of ice on Pt(111) can induce polar ordering in the subsequent layers of the ice film. This is seen in the overall intensity variation of the SFG spectrum with film thickness. The sublinear increase of A_q with film thickness means that the film grows with a gradually decaying polar ordering. Figure 3 shows that this polar ordering has a decay length of about 30 ML. As a typical surface-induced effect, the polar ordering in successive layers is expected to vanish asymptotically as the film thickness increases.

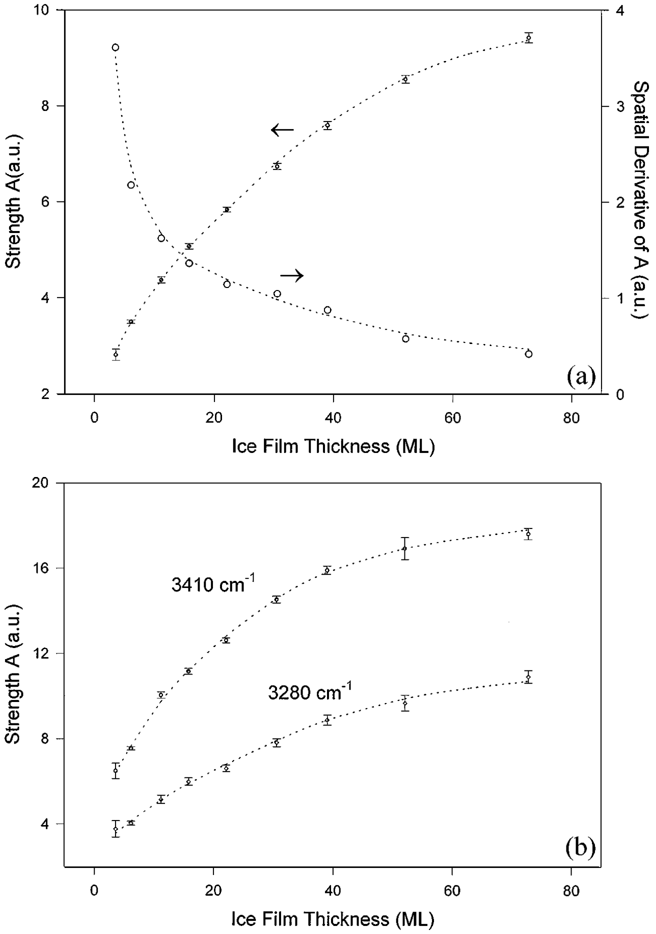

FIG. 3. (a) Strength A_q and its spatial derivative $\partial A_q/\partial z$ of the 3100 cm^{-1} resonant modes versus film thickness. (b) Strengths A_q of the 3280 and 3410 cm^{-1} modes versus film thickness.

The observed phenomenon of surface-induced polar ordering or ferroelectricity in ice on Pt(111) is very similar to that of surface-induced ferromagnetism in a paramagnetic system [18] or that of surface-induced orientational ordering of liquid crystals in the isotropic phase [19]. In our case, the local polarization $P(z) \propto \partial A_q/\partial z$ is the order parameter which exhibits a characteristic decay of surface-induced ordering in the surface-bulk transition region, as seen in Fig. 3(a). The general theories that have been developed for surface-induced magnetization or liquid crystal alignment can be adopted here with some modifications to account for the differences in the microscopic details of the systems.

Our experimental results presented in this paper show convincingly that ice films grown on Pt(111) can be ferroelectric for a limited film thickness. The same could be expected on other substrates such as Rh(111) and Ni(111). The polar ordering of water molecules in the films is induced by the ice-metal boundary layer. It exhibits a characteristic surface-induced ordering behavior with a decay length of ~30 ML.

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