Amorphous Water-Ice Relaxations Measured with Soft-Landed Ions

A. A. Tsekouras,* M. J. Iedema, and J. P. Cowin
Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory,
Box 999, M/S K8-88, Richland, Washington 99352
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D_3O^+ and Cs^+ ions ($\leq$1 eV) were soft landed on vacuum-deposited amorphous water ice at 30 K. The samples charged capacitively with an initial dielectric constant of 2. Then the voltage was measured via a Kelvin probe while the sample temperature was ramped. A sharp drop in voltage occurred near 50 K, due to dielectric responses occurring at much less than the expected 135 K. This was due to relaxations of the highly strained amorphous ice. Preannealing the ice could move the electrical relaxation up to as high as 120 K. Ion migration through the ice was not observed below 190 K. [S0031-9007(98)06347-9]

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Amorphous ice, created by depositing water from the vapor below 120 K, exhibits some of the structure of liquid water, and possibly its kinetic properties above its suspected glass transition temperature (T_{glass}) of 135 K [1,2]. Thus it is used in simulating water interfaces for atmospheric chemistry studies [3], neutral diffusion [4], and electrochemical systems [5]. To recreate ionic interfaces, we dosed ice films with a low energy ion beam. Our expectations were guided by several "well-established" principles, later contradicted by our data: (1) Below 100 K, the water's dielectric response to the ion's field would be limited by high barriers to reorientation of the water dipoles (approximately 0.6 eV in crystalline ice [1,2]), giving $\varepsilon = 3$. (2) Many believe [6] that hydronium should have a temperature-independent mobility, preventing this ion from lingering on top of the ice films.

We prepared samples by soft landing D_3O^+ and Cs^+ ions on amorphous ice, and then monitored the voltage across the ice versus temperature and time. The experimental UHV chamber had a low energy ion source, molecular beam source, Auger electron spectrometer, mass spectrometer, and a McAllister work function (Kelvin) probe. The ion source [7] generates mass-selected polyatomic ions with a narrow energy spread ($<$1 eV) that can be decelerated for deposition. The target was a Pt(111) crystal, atomically cleaned, then coated with amorphous ice at 27–30 K via a molecular beam of deuterated water vapor at 0.2 monolayers per second. Water coverages (crystalline or amorphous) are given in "monolayers" (ML) relative to a saturated crystalline first layer (or "bilayer") of the adsorbate. This is 1.05×10^{15} water molecules/cm^2 [8]. Ion coverages are relative to the exposed first layer Pt(111) atoms, $1.5 \times 10^{15}/\mathrm{cm}^2$.

The ions on the ice film create a potential difference across the ice which was measured with the Kelvin probe. The Kelvin probe gives the contact potential difference (CPD) between the sample and the gold-coated Kelvin probe, i.e., $\mathrm{CPD} = \Phi_{\mathrm{probe}} - \Phi_{\mathrm{sample}}$, where Φ_{probe} and Φ_{sample} are the work functions for the probe and the sample. A multilayer film of water near the desorption temperature lowers Φ_{sample} by 0.5 V. To focus on the ion-induced changes, all CPD curves were shifted by the CPD value measured around 150 K for Pt plus ice (no ions), to give the net ion-induced "film voltages."

The ion energy was controlled by the target bias. Charging during dosing was monitored by the shift of the ion "stopping curve" (current versus target bias). The target bias was adjusted during dosing to maintain 1 eV impact energy. After ion dosing, the film voltage was measured while the sample temperature was ramped slowly (0.2–0.5 K/s). D_2O desorption was monitored simultaneously with the mass spectrometer. The desorption has an unusual double peak structure, as about half of the crystal is obstructed by the Kelvin probe, which forces molecules desorbing behind it to return to the sample many times.

The charging of the ice film during ion deposition allows an estimate of the dielectric constant. For typical data, 60 ML of D_2O deposited on Pt at 30 K followed by 0.0025 ML (0.6 μC) of D_3O^+ ions yielded a plot (not shown here) of the shift of the ion stopping curves versus the integrated charge deposited (Q) that was a fairly straight line. Its slope gave a capacitance $C = 54$ nF ($C = Q/V$).

The parallel plate capacitor expression is $C = \varepsilon\varepsilon_0 A/L$, where ε is the permittivity (dielectric constant) of water, ε_0 is the vacuum permittivity, A is the area of the ion-dosed sample, and L is the film thickness. We estimated A as 0.9 cm^2. The water coverage yields the film thickness via the density. Recently it was found that amorphous ice's density [9,10] strongly depends on deposition temperature, being 0.93 g/cm^3 for H_2O at 160 K and only 0.63 g/cm^3 at 30 K. If we assume that the amorphous ice is isotropic, then the thickness is $L = (60\ \mathrm{ML})[1.05 \times 10^{15}\ (\mathrm{cm}^2\,\mathrm{ML})^{-1}]/[(0.63\ \mathrm{g/cm}^3)(6.02 \times 10^{23}\ \mathrm{mole}^{-1})/(18\ \mathrm{g/mole})] = 30$ nm. Calculating the dielectric constant from the measured capacitance, one gets 2.0. This agrees well with expectations, as discussed later.

Trace a in Fig. 1 shows the film voltage while the temperature was ramped at 0.17 K/s. A sharp drop in voltage occurs between 40–80 K. A second drop occurs when

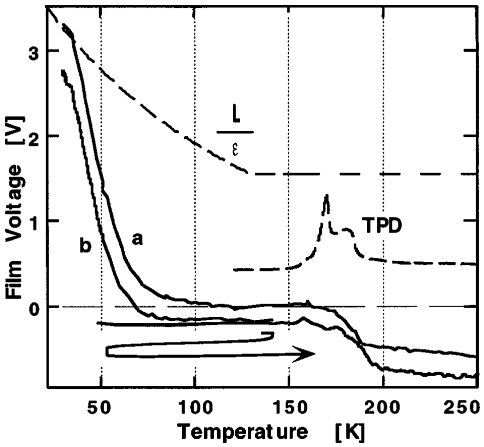

FIG. 1. Amorphous ice film voltage versus temperature. 60 monolayers (ML) of D_2O grown at 30 K were dosed at 30 K with 0.0025 monolayers of D_3O^+ (trace *a*) and Cs^+ ions (trace *b*, displaced by 0.2 V). *T*-ramp rates were 0.17 K/s, except (*b*) −0.3 K/s for 140 to 45 K (note hysteresis), and 0.5 K/s for 140 to 300 K. Split D_2O temperature programmed desorption (TPD) peak due to partial obstruction by the Kelvin probe. For the L/ε curve, see the text.

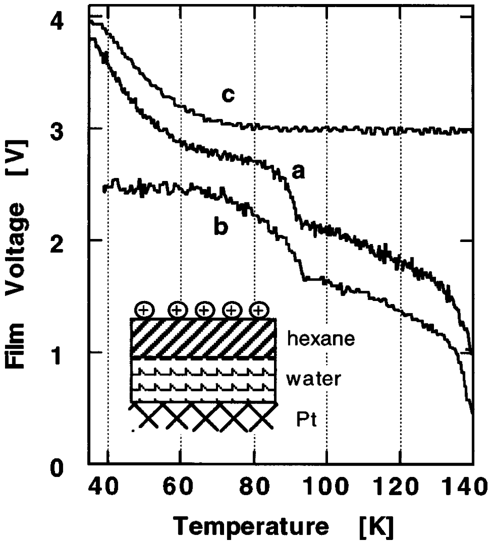

FIG. 2. Sandwich properties. Cs^+ ions deposited on a hexane-water sandwich should not be able to diffuse until 80 K [11]. Result (*a*) is a linear combination of that for pure hexane (*b*) and water (*c*) films, indicating a pure dielectric effect in the water. Ramp rates were (*a*) 0.17 K/s, (*b*) 0.33 K/s, and (*c*) 0.5 K/s.

the water desorbs, due to the change of the Pt work function from the first monolayer of water. The first drop could be due to ion migration enhanced by proton tunneling, electron transfer, and/or changes in dielectric constant. Electron transfer should occur with a clear voltage threshold, and not be sensitive to *T* since $kT \ll 5$ eV. We typically operated several volts below film voltages where electron leakage was suspected. Proton tunneling can be discounted, as Cs^+ ions act the same (Fig. 1). As the temperature was below T_{glass}, ion migration of Cs^+ was unlikely.

That the low temperature voltage drop is due to a dielectric effect is shown by the experiment in Fig. 2. Other experiments [11] showed that Cs^+ ions migrate through amorphous hexane ice in the 80–95 K range, but not at lower temperatures. By depositing a layer of amorphous hexane on the water before depositing the ions, the ions cannot reach the water layer until at least 80 K. 60 ML of D_2O was deposited on Pt(111) followed by 37 ML of *n*-hexane at 30 K. Next, Cs^+ ions were placed on top to charge it to 4 V. During the *T* ramp, the film voltage (Fig. 2, trace *a*) dropped by 1.2 V before reaching 70 K, similar to that for pure water (trace *c*). Between 80 and 140 K, the sandwich results are similar to that for pure hexane (trace *b* in Fig. 2, scaled to match the magnitude of trace *a*).

Thus the drop in the film voltage around 50 K for amorphous water ice is due to a dielectric response, not ion or electron transfer. The effect is irreversible, as seen by reversing the *T* ramp (Fig. 1). The film voltage remains constant as the temperature is lowered to 45 K and raised again to 140 K.

The effect of the thermal history of the ice on the dielectric response was explored. Water films of comparable thickness (60–100 ML) were deposited, then annealed for 100 s. Next, similar amounts of Cs^+ ions were deposited at 30 K. The samples were then *T* ramped while the film voltage was monitored. Figure 3 shows steep voltage drops at temperatures that correlate strongly with the annealing temperatures up to about 100 K. Annealing at temperatures between 120 and 140 K did not cause the temperature of the voltage drop to move above 120 K. Regardless of the preannealing temperature, the initial 30 K capacitance was similarly low. On occasion, following the experiments such as those in Fig. 3, we cooled the

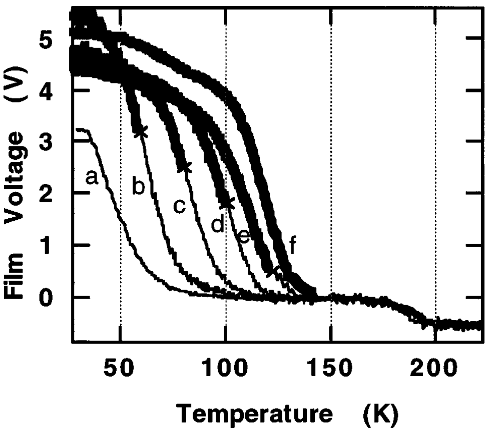

FIG. 3. Film voltage profiles versus annealing temperature. Prior to Cs^+ ion deposition at 30 K, samples were annealed to 30, 60, 80, 100, 120, and 140 K for 100 s (traces *a*–*f*). Ice coverage was (*a*) 80 ML, (*b*)–(*e*) 60 ML, and (*f*) 100 ML. Ramp rates were (*a*) 0.5 K/s and (*b*)–(*f*) 0.17 K/s. Heavy line indicates preannealing *T* range.

samples back to 30 K and dosed more ions. There was no discernible interference from the previous ion doses.

We can explain how water can reorient its dipoles as low as 50 K, by the densification that should occur as one warms the initially very "fluffy," highly stressed ice films. As the density increases upwards from 0.6 to eventually 0.9 for annealing near 120 K, nearly every molecule will have to move: In the presence of the field of the ions, they are then able to orient their dipoles to that field. With a continuum of activation barriers, preannealed ice is unresponsive to any new fields up to the annealing temperature (up to a maximum of 120 K). Above 120 K, the hydrogen bond defects are inherently mobile [1,6]. Other evidence and aspects of sintering of amorphous ice is well discussed in papers by Devlin, Buch, and co-workers [12].

Another explanation is considered: The increasing density during heating should cause a voltage drop, as it both increases the dielectric constant via the density ρ, and decreases the film thickness L. We do not know the ice density during the T ramps. Assuming it is the same for ice *grown* at the same temperature is an overestimate. As a rough estimate of how the dielectric constant should vary versus density, we employed the Clausius-Mossotti equation [13,14]: $(\varepsilon - 1)/(\varepsilon + 2) = K\rho$, where K depends on the molecule and temperature. K is determined using $\varepsilon_{\mathrm{ref}} = 3$ [15] at $\rho_{\mathrm{ref}} = 0.93\ \mathrm{g/cm^3}$ and assuming no dipole contribution (making K T independent). For $\rho = 0.63\ \mathrm{g/cm^3}$, ε is calculated to be 2.1 (close to the 2.0 we observe). If the ice contracts only vertically versus temperature, L would decrease as $1/\rho$. The calculated ratio L/ε should be proportional to the observed voltage for a fixed charge. The predicted L/ε scaled to the initial film voltage is shown in Fig. 1. The experimental voltage change takes place over a narrower and lower temperature range, and the observed change in dielectric constant is *much* larger than can be due to the change in L/ε. As the real density versus ramp temperature probably increases less quickly than we assumed, the actual L/ε effect should be more gradual than our estimate in Fig. 1, making it even less like the data. Thus *most* of the voltage drops seen in Fig. 1 are due to the transient turning on of the dielectric constant by thermally annealing of the highly stressed, fluffy ice, leading to irreversible polarization.

When we dosed 60 ML amorphous water films, then dosed with ions to about 6 V, and finally added an additional water or hexane dose, we typically found that the voltage drops up to a volt below that measured by the stopping curves, before we could start Kelvin probe measurements. We suspect the added overlayer applies stresses to the system below it, permitting it to structurally relax a little even at 30 K.

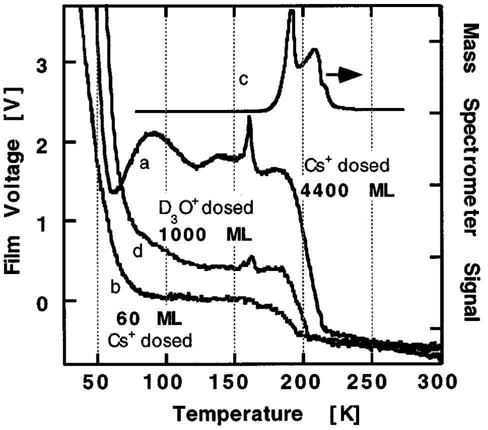

FIG. 4. Thick ice layer ion diffusion? Trace *a* shows the film voltage across a D_2O layer approximately 4400 monolayers thick after deposition of Cs^+ ions up to 38 V. The trace drops to 1.36 V at 60 K which is much higher than in the case of a 60 ML film (trace *b*) with a similar ion dose. This implies that ions remain on top of the ice up to the desorption temperature of D_2O. The thick film TPD peak (trace *c*) is also shown. Trace *d* is for D_3O^+ on top of 1000 ML of D_2O, charged initially at 30 K to 33 V. Ramp rate was (*a*)–(*d*) 0.17 K/s, except 0.5 K/s in the 130–300 K range for (*b*).

The "effective" dielectric constant when the amorphous water anneals is measured by how much voltage remains after the material polarizes. To see this more clearly, we prepared much thicker ice layers with similar ion doses, giving higher initial (and residual) film voltages. Figure 4 (trace *a*) shows the evolution with temperature of a 38 V initial film voltage due to Cs^+ on an unannealed, 4400 monolayer amorphous ice layer. The voltage drop near 60 K (not shown) is similar in form to that seen for thinner films in Fig. 1. The film voltage after this drop is clearly not zero. The ions have *not* all migrated through the ice film. The comparable D_3O^+ experiment gave similar results, as seen in trace *d* of Fig. 4. For the Cs^+ case, assuming that ε is 2.0 at 30 K, the density is 0.6 $\mathrm{g/cm^3}$ at 30 K, and 0.9 at 150 K, implies that ε is $2.0(\frac{38}{1.8})(\frac{0.6}{0.9}) = 28$ at 160 K, where the residual voltage is 1.8 V. Near 60 K, ε cannot be determined as easily since the film density is not known. But it should lie between $2(\frac{38}{1.36})$ and $2(\frac{38}{1.36})(\frac{0.6}{0.9})$, or 56 and 37. The same calculation for the D_3O^+ dosed film gives $\varepsilon = 110$ at 150 K. Fully activated, the dielectric constant of ice at 150 K ought to be close to 200.

The undulating voltages seen in Fig. 4(b) during the ramped heating of the Cs^+-dosed film is reproducible. A small voltage rise followed by a sharp, net drop near 160 K occurs when the amorphous ice crystallizes [16].

Few papers deal with *amorphous* ice permittivity. Crystalline ice depolarization studies have been done where high-temperature polarization is frozen into the samples [17]: Zero-biased relaxation upon reheating gives depolarization currents. No activity was reported below 100 K. Johari and co-workers [18] observed annealing effects on the dielectric properties of *amorphous* ice grown at 77 K. They understood some of the implications of annealing for awakening the dielectric behavior, though their limited temperature range, the proximity of T_{glass}, and mobilization of H-bonding defects made the effects less obvious than in our case. Amorphous ice has been shown [19] by

Orlando, Sanche, and co-workers to show shifts in resonant energies for electron stimulated reactions, and in its total work function, as it is warmed from 23 K. Some of the effects occur precisely in the 30 to 60 K region, where we observe the irreversible polarization.

The study's motivation was to lay foundations for recreating electrochemical double layers under UHV conditions. The unexpected awakening of the dielectric constant due to the amorphous water's relaxation provides a flexibility: If one preanneals the water to 140 K, the amorphous water acts mostly as anticipated, having a low dielectric constant until 120 K is reached. Via less preannealing, one can select the temperature at which the dielectric constant will turn on, from 55 to 120 K.

Neither Cs^+ nor D_3O^+ shows ion motion in amorphous water up to 190 K (where the water desorbs). This is a surprise, as above 135 K many would believe amorphous water is a true liquid (for example, neutral diffusion of D and O^{18} labeled water is observed below 160 K [4]). In work not shown here, we also see no motion of these ions in crystalline D_2O. Proton hopping has been claimed to occur with a zero-activation barrier in crystalline ice [6,20]. Others, however, have argued strongly that this is not the case [21]. It may be that there is a kinetic barrier to penetrating or moving within the water, or ions induce crystallization around themselves, or that amorphous water is not truly liquidlike above its glass temperature (see Fisher and Devlin [12]).

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*Currently at Laboratory of Physical Chemistry, University of Athens, Athens, GR-15771, Greece.

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