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Citation: The Journal of Chemical Physics 112, 11011 (2000); doi: 10.1063/1.481741
View online: http://dx.doi.org/10.1063/1.481741
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A helium atom scattering study of the structure and phonon dynamics of the ice surface

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(Received 26 January 2000; accepted 30 March 2000)

The structure and phonons of an ordered ice surface, prepared in situ under ultra high vacuum conditions, have been studied by high resolution helium atom scattering. The angular distributions are dominated by sharp hexagonal (1×1) diffraction peaks characteristic of a full bilayer terminated ice Ih crystal. Additional, very broad and weak, p(2.1×2.1) peaks may indicate the presence of small domains of antiphase oriented molecules. An eikonal analysis of the 1×1 peaks is compatible with either a proton disordered or a proton ordered surface with corrugations of 0.76 Å and 0.63 Å, respectively. Inelastic time-of-flight spectra reveal not only a dispersionless phonon branch reported previously at 5.9 meV, but also the first evidence for the surface Rayleigh phonons, which are reproduced well by a Born–von Kármán simulation of a full bilayer terminated ice surface using the unmodified force constants derived from neutron scattering bulk phonon measurements. Since the lattice dynamics simulations do not reproduce the dispersionless branch, it is attributed to the vibrations of single water molecules on the ice surface. © 2000 American Institute of Physics. [S0021-9606(00)70424-7]

I. INTRODUCTION

The properties of the surface of ice were first discussed by Faraday following his observation that two ice blocks stick together when brought in contact. 1 It has also been shown that the melted surface plays a major role in the environment, as reviewed by Dash et al. 2 More recently there has been renewed interest in the ice surface resulting from the realization that ice particles in the atmosphere play a major role in the reduction of ozone due to their ability to catalyze the production of ozone depleting chemicals. 3

Since it is primarily the interaction of molecules with the ice surface which determines whether they can be trapped in ice crystals, a detailed knowledge of the physical properties of the ice surface is highly desirable. Information such as surface structure and the vibrational dynamics are a prerequisite for a precise modeling of the surface in its melted state and for understanding how molecules can efficiently lose energy (energy accommodation) to the surface and become trapped. A study of the dynamics is, under normal conditions, extremely difficult because the ice surface is in a constant state of flux due to the dynamic equilibrium between the gas and solid phases, as recently studied in detail by Brown et al. 4 Thus, measurements are typically carried out either using techniques which are impervious to the high background vapor pressures necessary to stabilize the surface at temperatures up to 273 K, or they are restricted to ice crystals at temperatures below about 130 K where the surface is stable and the background vapor pressure is in the ultra-high vacuum (UHV) range.

In the high pressure regime probes such as neutron scattering, 5 X-ray scattering, 6 and infrared absorption spectroscopy (IRAS) 7,8 have been successfully employed due to their low scattering cross sections with gas phase molecules. Neutron scattering is sensitive only to the bulk properties of ice crystals, 5 whereas IRAS has provided useful information on the higher frequency internal modes of water both in the bulk and at the surface. 7,8 These methods, however, provide limited information on the thermal motions of the water molecules at the surface because precisely the low scattering cross section, which makes them suitable for high pressure measurements, makes them less sensitive to the surface layer. Thus, surface sensitive measurements using standard surface science techniques are only possible in the low pressure regime on ice crystals grown in UHV. These include electron diffraction, 9,10 electron energy loss spectroscopy, 11 helium scattering, 12 and, on very thin ice layers grown on metal substrates, scanning tunneling microscopy. 13

Recently it has been shown that well ordered ice surfaces can be grown on a Pt(111) surface under UHV conditions. 9,10,12 Low energy electron diffraction (LEED) measurements suggest that the ice crystals grow with the Ih structure which is characterized by the ice bilayer stacking ABBABAAB and not the Ic structure, which has a ABBCCA stacking similar to the diamond structure. 9,10 However, the LEED IV measurements could not provide any
evidence for the uppermost water molecules expected for a full bilayer terminated ice surface. This was interpreted as being due to a very large vibrational amplitude which was supported by molecular dynamics simulations,\(^9,10\) and was confirmed by helium atom scattering (HAS).\(^12\) These initial HAS results also showed that the ice surface is very soft providing easy energy accommodation for impacting atoms or molecules, leading to high sticking coefficients. However, these HAS measurements, which were carried out at an incident beam energy of 22 meV, did not provide any evidence for the dispersive surface phonon modes which are necessary to estimate the precise bond characteristics of the water molecules at the ice surface.

The aim of the present work is twofold: First, to provide a more detailed description of the ice surface structure using the elastic diffraction of helium atoms. The elastic helium diffraction patterns show that the prepared ice surface has a dominant hexagonal (1 \(\times\) 1) surface symmetry with a surface lattice constant of \(a = 4.52\) Å, confirming the earlier study.\(^12\) This structure exists in domains with an average dimension of nearly 30 Å and has a peak-to-peak corrugation amplitude of 0.63 Å or 0.76 Å, determined from eikonal calculations, depending on whether a proton ordered or disordered model is assumed, respectively. The calculations indicate, contrary to our previous conclusions,\(^12\) that the sharp (1 \(\times\) 1) diffraction peaks do not necessarily indicate a proton ordered ice surface. The experiments also show that there is a minority surface structure with an apparent \(D_u\) \(\approx\) 110 Å, thick ice layer had been deposited. Exposure was made at a surface temperature of \(T_s = 125\) K, which was reduced after exposure to \(T_s = 150\) K, to avoid sublimation of the ice.\(^4\) Although no clear intensity oscillations indicating layer-by-layer growth were resolved, this procedure lead to sharp (1 \(\times\) 1) diffraction peaks indicating a highly ordered ice surface.

\[ \Delta K_s = -2k_i \sin(\Delta \theta) \cos(\theta_{SD}/2), \]
\[ \Delta K_l = k_i \sin(\phi)[\cos(\theta_{SD}/2 - \Delta \theta) + \cos(\theta_{SD}/2 + \Delta \theta)]. \]

where \(k_i\) is the incident momentum of the helium atoms. Thus, the complete 2D parallel momentum transfer space can be mapped out systematically by changing \(\Delta \theta\) and \(\phi\) with the sample manipulator.

For time-of-flight (TOF) experiments, the helium beam is chopped into short duration pulses (10–20 \(\mu\)s) using a mechanical chopper placed in the beam line between the nozzle and the crystal. The flight time of helium atoms to the detector is then measured and transformed into energy transfer using the appropriate Jacobian transformation.\(^15\) The energy-momentum transfer dependence of the TOF peaks can then be determined using

\[ \Delta K = k_f \sin(\theta_{SD} - \theta_i) - k_i \sin \theta_i, \]

where \(\theta_i = \theta_{SD}/2 + \Delta \theta\) for in-plane scattering (\(\phi = 0\)).

The commercial platinum single crystal was first aligned along the (111) direction to within a stated accuracy of better than 0.2° and then cut and mechanically polished. In vacuum the surface was cleaned with repeated cycles of sputtering and annealing until no contamination could be detected with Auger spectroscopy (\(\Theta < 0.01\)) and elastic and inelastic helium scattering showed a smooth surface with a high degree of order. The sample temperature was controlled to well within \(\pm 1\) K with an absolute accuracy of \(\pm 5\) K using a Ni–CrNi (K-type) thermocouple attached to the side of the crystal. Sample cooling was provided via a liquid helium cold finger which is capable of cooling the sample to less than 30 K.

Thick ice films were grown by dosing ultrapure H\(_2\)O (Ref. 16) at room temperature from the vapor using a highly collimated, differentially pumped effusive source with a 40 mm long 4 mm diameter nozzle located approximately 60 cm from the surface close to the normal. Using this method, the water vapor pressure in the sample chamber could be kept to a minimum and, consequently, the unwanted growth of amorphous ice from the ambient vapor pressure\(^17\) at the low measurement temperatures could be reduced. The ice surface was prepared by first growing one complete bilayer slowly (30 min) and then increasing the dose rate to approximately one bilayer per minute until a 250 bilayer, or about 1000 Å, thick ice layer had been deposited. Exposure was made at a surface temperature of \(T_s = 150\) K, which was reduced after exposure to \(T_s = 125\) K to avoid sublimation of the ice.\(^4\) Although no clear intensity oscillations indicating layer-by-layer growth were resolved, this procedure lead to sharp (1 \(\times\) 1) diffraction peaks indicating a highly ordered ice surface.
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III. RESULTS AND DISCUSSION

The previous helium atom scattering measurements were carried out at incident energies of 22 and 40 meV. The present results indicate that at these incident energies the diffraction peak intensities are low and the multiphonon background is relatively high. As a result of this large multiphonon background, only one dispersionless phonon branch could be observed and no evidence for the dispersive surface Rayleigh phonon was found. This is confirmed by the new TOF spectra (Fig. 1) also measured at an incident energy of 39.7 meV and different surface temperatures between 25 K and the maximum of 125 K, determined by the onset of desorption. In order to facilitate their interpretation, the spectra have been converted from flight time to energy transfer. At the lowest temperature of 25 K the dispersionless phonon branch (×) is clearly visible with a peak intensity at ∆E = 5.85 meV. A very weak overtone can also be distinguished centered at about ∆E = 12 meV. However, even at this low temperature, the multiphonon intensity, which corresponds to the broad background hump centered on the energy loss side of the spectrum, is substantial. In addition, there is no evidence for the Rayleigh mode even this close to the specular position. As the temperature is raised, both the elastic and dispersionless mode peak intensities fall rapidly and for a surface temperature of 75 K the TOF spectrum shows only a very weak elastic peak. To avoid the extensive multiphonon background, the present measurements concentrated on much lower incident energies in the range 5–15 meV and low temperatures of T_s = 40–50 K.

A. Angular distributions

Some typical angular distributions are shown in Fig. 2 for the ice Γ−M and Γ−K azimuths. The distributions show, in addition to the first order peaks, weak second order peaks from the hexagonal ice surface along the Γ−M azimuth ([2 0] and [2 0]), and along the Γ−K azimuth ([1 1] and [1 1]). This direction also corresponds to the Pt(111) Γ−M azimuth, as reported previously. The width of the first order diffraction peaks ([1 0] and [1 0]) is about 0.39° compared with an instrument resolution of 0.30°, indicating a domain length of ≈60 unit cells, or about 280 Å.

Figure 3(a) shows a two-dimensional helium intensity contour diagram of the ice surface obtained from 61 angular distributions similar to Fig. 2 in which both the tilt and polar angles of the sample [see Eq. (1)] were varied systematically, as reported previously for the ice bilayer surface. As justified in the introduction to this section, a low beam energy of 10.4 meV and a surface temperature of T_s = 40 K were used. The polar angle axis is oriented along the ice surface Γ−K azimuth, as shown in Fig. 3(b).

Four sharp diffraction peaks are observed in addition to the specular peak at ∆θ = 0° and tilt φ = 0°. The position of these four peaks at ∆θ = ±13.3°, tilt φ = ±9.3° indicates a hexagonal surface structure, as shown schematically in Fig. 3(b), with a lattice constant of a_{ice} = 4.52 Å (G = 1.605 Å⁻¹). This is smaller by 6% than the v^3 a_p (a_p = 2.77 Å) length on Pt(111) of 4.80 Å, as was suggested previously.

These diffraction peaks correspond to an ideal surface termination of either the bulk ice Ih or Ic structures. The arrangement of the molecules in the topmost ice bilayer, characteristic of both the ice Ih and Ic surfaces, is shown in Fig. 4. A proton disordered surface is shown although, as discussed later, the present data alone cannot decide between
proton ordered and disordered surfaces. In addition, the present helium diffraction experiments cannot distinguish between Ih or Ic since in both structures the top bilayer molecules have the same positions. However, based upon extensive LEED experiments, Materer et al. have shown that the most likely structure is Ih rather than Ic.\(^9,10\) This determination was possible because, although the electrons cannot see the uppermost water molecules, they do penetrate several layers into the surface and are, therefore, sensitive to the bilayer stacking difference between ice Ih and Ic.

In addition to these sharp, intense peaks, broad peaks at \(\Delta \theta = \pm 7.3^\circ\) and \(\Delta \theta = \pm 13.4^\circ\) along the \(\Gamma - \bar{K}\) azimuth, and \(\Delta \theta = \pm 12.8^\circ\) along the \(\Gamma - K\) azimuth were observed for every ice surface grown. These peaks correspond to momentum transfer of \(\Delta K = 1.4\ \text{Å}^{-1}\), \(\Delta K = 0.75\ \text{Å}^{-1}\), and \(\Delta K = 1.3\ \text{Å}^{-1}\), respectively, possibly indicating a further unit cell structure with a lattice constant of \(a = 9.7\ \text{Å}\), or about 2.1 times the simple hexagonal unit cell. The significantly lower intensity and larger width of these peaks indicates that they are probably not from the same part of the surface producing the sharp, intense \((1 \times 1)\), \(a = 4.52\ \text{Å}\) diffraction peaks. Further, the much lower intensity suggests that this larger lattice constant structure covers a much smaller fraction of the surface than the ideal, bulk terminated structure. From the peak intensities, an estimate of 15:1 can be made for the relative domain probabilities assuming an otherwise identical diffraction probability. In addition, the larger peak widths of about 2.5° indicate much smaller domains of length \(l = 3a\) or about 30 Å.

The origin of the larger unit cell corresponding to the weak diffraction peaks is unclear. One possibility is that the peaks are due to an intermediate ice structure bridging two \((1 \times 1)\) domains with a different phase or rotation. Alternatively, the peaks could belong to a different facet of the ice crystal or result from regions of local order within the proton disordered surface.

Helium scattering angular distributions along the \(\Gamma - \bar{M}\) azimuth are shown in Fig. 5 for beam energies between 5.16 and 29.68 meV and a surface temperature of \(T_s = 50\ \text{K}\). The difference in the background signal due to multiphonon excitation is most noticeable between the lowest and highest beam energies in Fig. 5. In addition, due to the greater Debye–Waller attenuation for higher incident energies (see Sec. III C), for the lowest beam energy the diffraction peaks are one order of magnitude more intense. For reference, the observed integer order diffraction intensities are listed in Table I for all beam energies.

### B. Diffraction intensity calculations: The surface corrugation

In order to estimate the corrugation of the He–ice surface interaction potential for the \((1 \times 1)\) ideally terminated ice surface and determine the effect of proton disorder, eikonal calculations of the diffraction intensities were performed. This method, which is suitable for low corrugations\(^{20}\) and for beam energies much greater than the attractive well energy, relies on approximating the interaction by a hard wall potential.\(^{21}\) To account approximately for the phase shift of
the He wavefront due to the attractive potential at low beam energies, a small energy increment, known as the Beeby correction, is added to the incident energy.\(^\text{22}\)

Calculations were performed for incident energies of 20.1 and 25.0 meV. At these energies, up to third order diffraction peaks can be observed with reasonable accuracy, while the energy is sufficiently high to make the Beeby correction a reasonable approximation. Two possible surfaces were considered which follow the Bernal–Fowler–Pauling rules\(^\text{23}\) with the oxygen atoms in a fixed lattice with a nearest neighbor distance of 2.76 Å. They are, (a) a surface with all of the protons pointing upwards with a simple (1×1) unit cell, and (b) a proton disordered surface, shown in Fig. 4, consisting of 30 (1×1) oxygen atom unit cells with 15 lone-pairs and 15 H-atoms pointing upwards (from Ref. 24). Both surfaces were modeled using Gaussian functions of variable height \(h\) and width \(w\) to describe the uppermost part of the molecule, either the H-atom \((h_\text{h} \text{ and } w)\) or the lone-pair electrons on the O-atom \((h_\text{lp} \text{ and } w)\). Thus, including the Beeby correction energy, a total of 3 parameters were used to fit the 14 observed diffraction peaks. For the proton disordered surface the height difference \(\Delta h = h_\text{h} - h_\text{lp}\) between the Gaussian functions describing the H-atoms and the lone pairs was fixed at 0.2 Å in accord with the He–water scattering potential determined by Green et al.\(^\text{25}\) The width \(w\) used was the same in both cases.

In Fig. 6 the best-fit intensities from the calculations for the two corrugations are compared with the experimental diffraction intensities. In both cases, a Beeby correction of +2 meV was found to provide a good fit for both incident energies and is also consistent with the He–water potential.\(^\text{25}\) For the proton ordered surface, the optimum Gaussian parameters were \(h_\text{h} = 0.65\) Å and \(w = 1.95\) Å, whereas for the proton disordered surface they were \(h_\text{h} = 0.78\) Å \((h_\text{lp} = 0.58\) Å) and \(w = 2.10\) Å. This leads to a larger hard-wall corrugation peak-to-peak amplitude of 0.76 Å for the proton disordered surface compared with 0.63 Å for the proton ordered surface. These quantities are smaller than the \(h_\text{h}\) values used due to overlap of the Gaussian functions. The corrugation for the proton ordered surface is shown in Fig. 7 and for the disordered ice surface in Fig. 8.

It is interesting to observe that the calculations for the proton disordered surface predict negligible intensity contributions due to disorder\(^\text{26}\) between the diffraction peaks, as shown in Fig. 6. Thus, the calculations suggest that the proton order of the surface cannot be determined from the helium scattering data alone. Further they show that the height

![FIG. 5. Angular distributions measured along the ice surface \(\Gamma - \bar{M}\) azimuth for incident energies between 5.16 and 29.68 meV and a surface temperature \(T_s = 50\) K. Sharp, diffraction peaks from the hexagonal ice surface are observed for both energies with up to the third order visible at 29.68 meV due to the larger momentum transfers possible at the higher incident energy. Note that the first order diffraction peaks are about an order of magnitude more intense for the lower incident energy which, coupled with the lower background signal, indicates substantially smaller Debye–Waller attenuation.](Image 90x511 to 258x740)

**FIG. 6.** Comparison of the experimental diffraction peak intensities (shaded bars) with the results of eikonal calculations for a proton disordered surface (solid bars) and a proton ordered ice surface (striped bars) for incident He energies of (a) 20.11 meV and (b) 25.01 meV and a Beeby correction of +2 meV. The scattering azimuth was \(\Gamma - \bar{M}\) and the surface temperature was \(T_s = 50\) K in both cases. Note that the fractional order diffraction intensities for the proton disordered peaks are all negligibly small.

![FIG. 6.](Image 348x525 to 528x740)

**FIG. 6.** Comparison of the experimental diffraction peak intensities (shaded bars) with the results of eikonal calculations for a proton disordered surface (solid bars) and a proton ordered ice surface (striped bars) for incident He energies of (a) 20.11 meV and (b) 25.01 meV and a Beeby correction of +2 meV. The scattering azimuth was \(\Gamma - \bar{M}\) and the surface temperature was \(T_s = 50\) K in both cases. Note that the fractional order diffraction intensities for the proton disordered peaks are all negligibly small.

<table>
<thead>
<tr>
<th>Beam energy (E_i) [meV]</th>
<th>Azimuth</th>
<th>Normalized diffraction peak intensities (n = \pm 1)</th>
<th>(n = \pm 2)</th>
<th>(n = \pm 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.16</td>
<td>(\Gamma - \bar{M})</td>
<td>0.1331</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>10.50</td>
<td>(\Gamma - \bar{M})</td>
<td>0.4564</td>
<td>0.0171</td>
<td>...</td>
</tr>
<tr>
<td>10.50</td>
<td>(\Gamma - \bar{K})</td>
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<td>...</td>
<td>...</td>
</tr>
<tr>
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<td>0.0903</td>
<td>...</td>
</tr>
<tr>
<td>15.25</td>
<td>(\Gamma - \bar{M})</td>
<td>0.0115</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>20.11</td>
<td>(\Gamma - \bar{M})</td>
<td>0.2103</td>
<td>0.0508</td>
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</tr>
<tr>
<td>25.01</td>
<td>(\Gamma - \bar{M})</td>
<td>0.1772</td>
<td>0.0721</td>
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<td>(\Gamma - \bar{M})</td>
<td>0.2930</td>
<td>0.0813</td>
<td>0.0362</td>
</tr>
</tbody>
</table>

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difference between the H-atom and lone-pair protrusions must be fixed in the eikonal calculations because the fit is insensitive to differences $h_h - h_{lp}$, at least when they are small.

Evidence for the proton ordering of the surface of ice grown on Pt(111) has been provided by sum-frequency-generation experiments. This was attributed to the first layer bond in which the lone-pairs are directed towards the metal surface, dictating the order of the protons in the subsequent layers. In addition, earlier experiments have shown that bulk ice can be ferroelectric (net proton ordering) under certain conditions, suggesting that the same could be true of the surface. The ferroelectric phase of ice with the $Ih$ structure at zero pressure is also known as ice XI.

More recent measurements of the work-function change, which measures directly the average dipole moment as a function of ice coverage, indicate, however, that the degree of proton ordering is only about 0.2% per bilayer. The nonzero value is attributed to the long range effect of the metal substrate. The transition from the ordered lone-pair bonding of the water molecules in the first layer to a proton disordered top layer surface has been calculated to occur within the first few bilayers due to bond mismatches. In this way, the stresses built up due to the dipole alignment are rapidly dispersed.

As mentioned previously, the present simple analysis of the helium diffraction intensities from the ice surface do not directly provide further evidence to determine the degree of proton order at the surface, contrary to our previous appraisal. However, the calculations do show that there is a significant peak-to-peak corrugation difference of 0.13 Å, or 20%, between the proton ordered and disordered surfaces. Thus, in connection with detailed calculations of the corrugation, possibly via the electron density at the surface, it might be possible to relate the helium diffraction intensities to one of the two possible surfaces.

**C. Temperature dependence**

The diffraction patterns presented in the previous section indicated at high incident energies an enhanced background signal and reduced diffraction peak intensities (Figs. 1 and 5). In this section the temperature dependence of the elastic intensities, both from the incoherent and coherent diffraction, will be investigated in order to determine the Debye–Waller factor.

In Fig. 9 a series of TOF spectra are shown for different surface temperatures at a beam energy of 10.7 meV and an incident angle of $\theta_i = 41.9^\circ$ along the $\Gamma - M$ azimuth. The spectra are shown on an energy transfer scale following a transformation from flight time using the instrument parameters. At this particular incident angle the observed elastic peak at $\Delta E = 0$ is due to incoherent scattering from defects, e.g., water molecules, on the ice surface. As shown, for example, by Manson, the temperature dependence of the elastic intensity $I$ can be used to obtain the Debye–Waller attenuation and an estimate of an effective surface Debye temperature $T_D$ using the formulas.

**FIG. 7.** A two-dimensional plot of the hard-wall potential surface of a proton ordered ice surface obtained by fitting the observed helium diffraction intensities with the eikonal approximation and Gaussian functions to model the corrugation. The peak to peak amplitude is 0.63 Å. The peaks represent the uppermost H-atoms of the water molecules in the top layer.

**FIG. 8.** A two-dimensional plot of the hard-wall potential surface of a proton disordered ice surface obtained by fitting the observed helium diffraction intensities with the eikonal approximation and Gaussian functions to model the corrugation including a 0.2 Å height difference between the oxygen lone pairs and the protruding H-atoms. The peak to peak amplitude is 0.76 Å. The more prominent half of the peaks of the corrugation correspond to H-atoms while the other half correspond to the lone-pairs.

**FIG. 9.** A series of time-of-flight (TOF) spectra measured for a range of surface temperatures for an incident energy of 10.7 meV and an incident angle of $\theta_i = 41.9^\circ$ oriented along the $\Gamma - M$ azimuth. The spectra have been converted from flight time to energy transfer. The peaks which are centered at zero energy transfer, corresponding to incoherent elastic scattering, become significantly less intense with increasing surface temperature $T_s$. **This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions.**
Equation ~ produces the linear relationship shown in Fig. 10 from which a
the peaks shown in Fig. 9 versus surface temperature, pro-
plotting the logarithm of the integrated elastic intensity from
in Fig. 9 versus surface temperature. The intensity displays an almost perfect
exponential decrease with temperature which appears as linear on the loga-
metric scale. The slope of the linear best fit through the data points is
was used to fit both curves.

\[ I = I_0 e^{-2W}, \]

\[ 2W = \frac{24\mu T_s (\Sigma + E_i \cos^2 \theta_i)}{k_B T_D^2}, \]

where \( \mu \) is the ratio of the projectile mass to the mass of
individual surface atoms or molecules, \( \Sigma \) is an effective well
depth (Beeby correction), \( k_B \) is the Boltzmann constant, and
\( 2W \) is the Debye–Waller factor. Thus, for a particular esti-
mate of the effective well depth, the resulting effective De-
bye temperature can be used to predict the elastic and inel-
astic scattering probabilities for different projectile energies.

Equation (3) can be rewritten in terms of the scattered
 intensity and surface temperature in the form

\[ I = I_0 e^{-CT_s}, \]

where \( C = 2W/T_s \) is dependent on the incident energy. Thus,
plotting the logarithm of the integrated elastic intensity from
the peaks shown in Fig. 9 versus surface temperature, pro-
duces the linear relationship shown in Fig. 10 from which a
value of \( C = 0.0243 \pm 0.001 \) can be determined. The same
result was obtained by fitting the temperature dependence of
the specular peak intensity shown in the inset of Fig. 10 after
subtracting off the background due to multiphonon pro-
cesses.

Assuming the value of \( \Sigma = 2 \) meV for the effective well
depth obtained from the diffraction analysis, an effective sur-
face Debye temperature of \( T_D = 132 \) K is estimated using
Eq. (3). This is less than the value of \( T_D = 125 \) K (\( \Sigma = 0 \))
reported in our previous analysis\textsuperscript{12} which may have been
affected by the build-up of defects on the surface at low
 temperatures due to the higher background water pressure in

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reported in our previous analysis\textsuperscript{12} which may have been
affected by the build-up of defects on the surface at low
 temperatures due to the higher background water pressure in
the previous experiments.\textsuperscript{17} The bulk Debye temperature of
ice is 220 K.\textsuperscript{35} Due to the reduced coordination of atoms or
molecules at a surface it is usually estimated that the effec-
tive surface Debye temperature is 2/3 of this value, or about
146 K. This is close to the present estimate of \( T_D = 132 \) K
using \( \Sigma = 2 \) meV.

D. Time-of-flight measurements—The phonon dispersion curves

Figure 11 shows a series of TOF spectra along the \( \Gamma - \bar{M} \)
azimuth for several different incident angles at a beam
energy of 10.5 meV and a surface temperature of \( T_s = 45 \) K. In order to facilitate their interpretation, the spectra
have been converted from flight time to energy transfer. Sev-
eral inelastic peaks can be seen both for energy loss and gain
in addition to the dominant diffuse elastic peak. The energy
transfer of several of these features is observed to change
with incident angle as expected for a dispersive mode. These
peaks are marked by arrows in the spectra. Another broad
shoulder located at \( \Delta E \approx + 5.4 \) meV, which was reported in
the earlier study,\textsuperscript{12} can also be seen. Its position does not
change with incident angle (dispersionless), as shown by the
vertical dashed line.

A similar set of TOF spectra was measured under identi-
cal conditions along the \( \Gamma - \bar{R} \) azimuth. Several spectra are
shown in Fig. 12 for roughly the same incident angles as in
Fig. 11. Comparison of the spectra reveals that they are
nearly identical, both displaying the same dispersive peaks (1
and 1). The energy and momentum transfers corresponding to the observed TOF peaks measured at the three beam energies of 5.4, 10.5, and 15.3 meV are summarized for both azimuths in Fig. 13. This figure shows more clearly the dispersionless branch at $\Delta E = 5.4$ meV for both azimuths in addition to a well-defined Rayleigh mode branch at $\Delta K \approx 1 \text{ Å}^{-1}$. For the $\Gamma - \bar{M}$ azimuth there is also evidence for the Rayleigh mode peaks in the second Brillouin zone close to the ice diffraction peak positions. These peaks can be related to Umklapp processes whereby the acoustic phonon becomes visible in the second Brillouin zone through diffraction. The presence of Umklapp phonons in the present study is further evidence for the high degree of long range order of the ice surface prepared in the present experiments.

In Fig. 14 all of the data are summarized in a reduced zone plot. This shows more clearly that the dispersionless mode is centered at about $\hbar \omega = 5.4$ meV and, further, that it is independent of azimuth. The frequency of the dispersionless mode is 0.5 meV lower than at higher beam energies (see Fig. 1). This small difference, which is not very significant considering the width of the observed peak, may have several explanations. The previous HAS study$^{12}$ showed no strong shift of the dispersionless mode between 30 and 120 K ruling out an effect due to the different surface temperature of 50 K used in the present study. However, an interesting possibility is that the observed broad shoulder is, in fact, a band of modes, the higher frequency components of which are suppressed at lower beam energies due to their reduced excitation probabilities.

The remaining dispersive modes along the $\Gamma - \bar{M}$ and $\Gamma - \bar{K}$ azimuths, measured here for the first time, display an almost linear frequency increase with wave vector. The slope is the same along both azimuths, to within experimental error, and corresponds to a speed of sound of 1850 m s$^{-1}$, only slightly less than the speed of sound of the long wavelength mode in bulk ice Ih of 2000 m s$^{-1}$.\textsuperscript{36}

IV. PHONON DISPERSION CALCULATIONS

A. Model

In order to accurately describe the phonons of the ice surface shown in the last section, the forces between the water molecules in the ice crystal must first be considered. In the present calculations the valence force field (VFF) model, in which the water molecules are simply described by point masses ($M = 18$ amu), was used. In this model, the forces between the adjacent molecules are reduced to an O$\cdots$O stretching force constant $K$ and a three body O$\cdots$O$\cdots$O bond bending force constant $G$.\textsuperscript{5} Due to the proton disorder in ice these force constants represent an average over all hydrogen bonds within the ice network.

For proton disordered ice, which is most probably the case for the present ice layers grown on Pt(111),\textsuperscript{31} the collective sum of the individual dipole moments of the water molecules is zero. However, small displacements of groups of water molecules can lead to a local net dipole moment resulting in additional forces not in the VFF model. Fortunately, these displacements of groups of water molecules are

FIG. 12. A series of TOF spectra at different incident angles for helium scattering from the ice surface along the $\Gamma - \bar{K}$ azimuth. The surface temperature was $T_s = 45$ K and the incident beam energy 10.5 meV. The spectra have been transformed from flight time to energy transfer $\Delta E$. The spectra exhibit several inelastic features in addition to the intense diffuse elastic peak at zero energy transfer. The energy transfer of some of these peaks, marked by arrows, changes with incident angle, whereas the broad peak located at $\Delta E = +5.4$ meV does not.

FIG. 13. Plots of the energy and momentum transfers of the inelastic peaks observed from helium scattering measurements in a temperature range from $T_s = 40$ to 50 K and incident energies of 5.4, 10.5, and 15.3 meV for both the (1×1) ice (a) $\Gamma - \bar{M}$ and (b) $\Gamma - \bar{K}$ azimuths. Both show a distinct dispersionless mode at energy transfers of $\Delta E = \pm 5.4$ meV and a strongly dispersive mode focused on zero momentum and energy transfer. Along the $\Gamma - \bar{M}$ azimuth additional dispersive mode peaks can be observed close to the surface diffraction positions at $\Delta K = \pm 1.605$ Å$^{-1}$ which can be related to surface phonon Umklapp processes.
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FIG. 14. A reduced scheme presentation of the $(1 \times 1)$ ice surface phonon dispersion curves determined from the helium scattering TOF spectra measured in the present study. The dispersive modes measured for the $\Gamma-\bar{M}$ and $\Gamma-\bar{K}$ azimuths both have the same slope $d\omega/dQ$, which corresponds to a speed of sound of 1850 m s$^{-1}$. Also shown are the calculated Rayleigh wave dispersion curves using Renker’s VFF force constants (Ref. 5) (solid line), and those obtained by Li and Ross (Ref. 39) (dot–dashed line). The dispersionless mode at $h\omega \sim 5.4$ meV (dashed line) is not reproduced by either set of force constants.

expected to contribute mainly to the surface optical phonons which have frequencies above $20$ meV,\textsuperscript{5} well above the frequency range of the present measurements. Consequently, this effect of the water molecule dipole moment can safely be neglected.

A simple two parameter ($K$ and $G$) VFF model has been shown to fit the acoustic bulk phonon modes in the frequency range $h\omega < 10$ meV,\textsuperscript{5} corresponding to the HAS phonon measurements. The good fit is surprising since the model does not account for the different hydrogen bonds corresponding to different local arrangements of the water molecules imposed by the Bernal–Fowler–Pauling rules.\textsuperscript{37} Apparently the different hydrogen bond strengths affect mainly the O–O stretching force constant $K$, which, however, has little effect on the low frequency acoustical modes which are more sensitive to the bending force constant $G$.

In order to calculate the phonon dispersion curves, the Keating potential scheme has been employed to relate the force constants $G$ and $K$ of the VFF model to the motions of the molecules in the crystal.\textsuperscript{37} Within this scheme the potential is written as

$$V = \sum_{\kappa_1, \kappa_2} \alpha_{\kappa_1, \kappa_2} \left[ \frac{\Delta (r_{\kappa_1, \kappa_2} \cdot r_{\kappa_1, \kappa_2})^2}{8 (r_{\kappa_1, \kappa_2}^0)^3} \right] + \sum_{\kappa_1, \kappa_2} \sum_{\kappa_3} \beta_{\kappa_1, \kappa_2, \kappa_3} \left[ \frac{\Delta (r_{\kappa_1, \kappa_2} \cdot r_{\kappa_1, \kappa_3})^2}{2 r_{\kappa_1, \kappa_2}^0 \cdot r_{\kappa_1, \kappa_3}^0 \sin^2 \theta_{\kappa_1, \kappa_2, \kappa_3}} \right],$$

(5)

where $r_{\kappa_i}$ is the position vector of the point water molecule $\kappa_i$ and $\theta_{\kappa_1, \kappa_2, \kappa_3}$ is the angle between the hydrogen bonds connecting $\kappa_i \kappa_j$ and $\kappa_i \kappa_k$. In Eq. (5) $\Delta$ represents the variation of the vector positions due to small displacements from equilibrium. Therefore, both elongation and bond bending of the hydrogen bonds contribute to the potential energy in Eq. (5). The sums in Eq. (5) extend over the first nearest-neighbor hydrogen bonds. The parameters $\alpha$ and $\beta$ are related to $K$ and $G$ by $K = \alpha + 3 \beta/4$ and $G = \beta$, respectively, for an ideal tetrahedral network.\textsuperscript{38}

Two different sets of VFF force constants for bulk ice Ih have been derived from neutron scattering data. Renker obtained force constants from a fit to the bulk dispersion curves\textsuperscript{5} whereas Li and Ross fitted the overall measured bulk density of states for energies less than $40$ meV.\textsuperscript{39} Both sets of force constants are compared in Table II. There it can be seen that the two values obtained for $\alpha$ are very similar, whereas the values for $\beta$ differ by more than a factor of 2. Since the force constants derived by Renker\textsuperscript{5} have been fitted explicitly to the bulk acoustic phonons, these values are expected to represent the surface elastic properties better than those of Li and Ross. The larger value of $\beta$ obtained by Li and Ross\textsuperscript{39} compared to the Renker value\textsuperscript{5} probably arises from their attempt to fit both the general features of the optical and bulk phonons with a simple model. This point is particularly important since, in the previous HAS study of the ice surface phonons,\textsuperscript{12} the Li and Ross force constants, with the higher value of $\beta$, were used to interpret the observed dispersionless mode. Calculations for both sets of force constants are presented in the next section.

B. Calculated phonon dispersion curves

The ice film was represented by an extended slab of 33 H$_2$O bilayers with surfaces perpendicular to the (0001) axis and with a hexagonal structure consistent with the HAS diffraction patterns observed in Sec. III A. The dispersion curves and vibration polarizations were calculated using the Born–von Kármán model.\textsuperscript{40} The Rayleigh wave phonon dispersion curves for the complete unrelaxed bilayer ice surface calculated using the force constants determined by Renker are shown by the solid line curves in Fig. 14 for the $\Gamma-\bar{M}$ and $\Gamma-\bar{K}$ azimuths. For comparison the Rayleigh phonon branches obtained using the Li and Ross force constants (dot–dashed lines) are also shown.

The Rayleigh wave phonon branch calculated for a full bilayer ice surface using the Renker force constants provides the best agreement with the experimental data points for the observed dispersive mode. The calculated slope of the Rayleigh mode is close to the experimental value in support of the unmodified Renker force constants. There are small differences between the theory and the experiment along the $\Gamma-\bar{K}$ direction at $Q \sim 0.4$ Å$^{-1}$, where the experimental points lie $h\omega \sim 0.5$ meV below the calculated curve. However, the experimental error for these points is also of this

<table>
<thead>
<tr>
<th>Sets</th>
<th>Ref.</th>
<th>$\alpha$ [eVÅ$^2$]</th>
<th>$\beta$ [eVÅ$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Renker</td>
<td>5</td>
<td>1.5254</td>
<td>0.03658</td>
</tr>
<tr>
<td>Li and Ross</td>
<td>39</td>
<td>1.54487</td>
<td>0.07351</td>
</tr>
</tbody>
</table>

TABLE II. The parameters $\alpha$ and $\beta$ for the Keating potential [Eq. (5)] obtained from two different sets of bulk ice force constants.
order due to the close proximity of the Rayleigh phonon peak to the more intense and broader dispersionless mode peak (see Figs. 12 and 11).

As expected, the results of the slab calculations using the Li and Ross force constants overestimate the observed Rayleigh wave branch frequencies by almost 40%. As listed in Table II this is probably due to the nearly factor of 2 higher value of $\beta$ obtained by Li and Ross compared with Renker’s values. This also highlights that $G = \beta$, the bond-bending force constant, is more important than $K$ for a proper description of the low frequency acoustic phonons. In particular, the new calculations using Renker’s force constants do not reproduce the observed dispersionless mode at $h\omega = 5.4$ meV which was formerly assigned to a shear motion of the top bilayer against the deeper layers. Thus, the conclusions reached in our earlier paper based on calculations using the Li and Ross force constants must be reassessed.

The agreement between the theoretical and experimental Rayleigh phonon dispersion curves using Renker’s force constants indicates that the intermolecular forces at the ice surface do not differ significantly from the bulk ones. It should be noted that this is not in contradiction with the observation of Materer et al. that the surface water molecules have larger vibrational amplitudes along the (0001) axis than in the bulk. Materer et al. calculated the dynamics of single water molecules within a two bilayer $p(1 \times 1)$ ferroelectric film using $ab$ initio methods. They fitted their potentials to obtain effective force constants to describe the binding of a surface water molecule within the mean-field created by the other water molecules in the slab. In order to compare the present calculations with their results effective force constants were obtained in the present model by considering displacements of a single water molecule at the ice surface holding the remaining molecules fixed (mean-field approximation). The effective force constant for perpendicular motions of a molecule at the surface $K_{s_{\perp}}$ and in the second bilayer $K_{s_{\perp}}$ from the two theories are compared in Table III. The effective force constants are in excellent agreement, further supporting our use of the Renker force constants to model the surface phonons. In addition, the effective force constant for the uppermost water molecules $K_{s_{\perp}}$ is about a factor of 3 lower than for water molecules in the second layer, leading to a significantly larger vibrational amplitude at the surface. Since the intermolecular force constants linking the uppermost water molecules to the lower layers are the same as in the bulk, the lower effective force constants are due entirely to the reduction of the number of nearest neighbor water molecules at the surface.

The effective perpendicular force constant of the surface water molecules listed in Table III corresponds to vibrations with a calculated frequency of $h\omega = 11.4$ meV for a single water molecule assuming an effective mass of the water molecule of 18 amu. For thick ice layers, the molecules move collectively, and so a dispersionless mode is not expected. Several dispersionless phonon modes were measured for an $H_2O$ ice bilayer on Pt(111) in separate experiments with frequencies of 5.9, 9.85, and 13.9 meV. As mentioned previously, the bilayer mode at 5.9 meV lies close to the dispersionless mode at 5.4 meV reported here for thick ice layers. The intensity of the ice bilayer vibration at 9.85 meV is sharply peaked at zero momentum transfer indicating perpendicular polarization. The similarity of the frequency of this bilayer mode to the one estimated from the effective force constant given in Table III of 11.4 meV suggests that they probably have the same polarization, further supporting the present force constant model.

Further, it is interesting to note that the dispersion curve is completely described within the $p(1 \times 1)$ Brillouin zone without the back-folding necessary to describe the acoustical mode in the bulk. This would seem to suggest that the dispersive Rayleigh mode is apparently not sensitive to the proton disorder of the ice sample.

<table>
<thead>
<tr>
<th>Structure</th>
<th>$K_{s_{\perp}}$ [eV/Å$^2$]</th>
<th>$K_{s_{\perp}}$ [eV/Å$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref. 10</td>
<td>$(1 \times 1)$ ice Ih</td>
<td>0.51</td>
</tr>
<tr>
<td>Present work</td>
<td>$(1 \times 1)$ ice Ih</td>
<td>0.56</td>
</tr>
</tbody>
</table>

TABLE III. Effective surface force constants determined from $ab$ initio calculations and the present lattice dynamics calculations using the force constants determined by Renker from bulk neutron measurements (Ref. 5).

V. DISCUSSION

The dispersionless mode seen in the present measurements at 5.4 meV was previously assigned to a longitudinal shear motion of the uppermost water molecules with respect to the second layer. This assignment was based on calculations using the Li and Ross force constants. However, since the present calculations show that the Li and Ross force constants do not reproduce the observed Rayleigh phonon branch of the ice surface their validity for describing the low frequency modes must now be questioned. Further, the calculations based upon the force constants derived by Renker, which fit very well to the observed surface Rayleigh phonon, do not support the former interpretation because no longitudinal mode is predicted in the correct frequency range. Rather it now appears that this mode is not due to collective vibrations at the surface. One possibility is that it is due to surface disorder, e.g., isolated water molecules. Evidence supporting this interpretation is the similarity of the dispersionless mode from the present measurements to the $h\omega = 5.9$ meV mode observed for carefully prepared two-dimensional ice bilayers grown on the Pt(111) surface which are expected to be proton ordered.

In this connection it is worthwhile pointing out that a vibrational frequency of 5.0 meV was observed for small ice clusters ($\bar{n} = 110$) using inelastic helium scattering. By comparing with quantum and classical calculations of the ice cluster dynamics this mode was shown to be due to the vibrations of water molecules in threefold sites on the amorphous ice cluster surface. The similarity between the frequency of 5 meV measured for the ice clusters and the dispersionless 5.4 meV mode observed here also suggests that the dispersionless branch may be due to the vibrations of isolated water molecules adsorbed in threefold sites on the otherwise smooth $(1 \times 1)$ ice surface. In order to test this hypothesis further HAS experiments were undertaken on an
amorphous ice surface grown at a lower temperature of 30 K and comparisons were made with recent calculations of water on the ice surface.

Figure 15 shows an angular distribution measured for approximately ten bilayers of heavy water (D₂O) ice adsorbed on a cold Pt(111) surface at T_s = 30 K. At this low temperature the water molecules are not sufficiently mobile to form a crystalline structure and the structure is expected to be amorphous, i.e., random, as confirmed by the lack of diffraction peaks including the specular. The inset displays a TOF spectrum measured for the same conditions at an incident angle of θ_s = 57.9°. In addition to the intense diffuse elastic peak at τ ≈ 1900 μs and a multiphonon energy loss peak at τ ≈ 2150 μs, a low intensity peak is observed at τ ≈ 1600 μs which corresponds to an energy gain of 5.2 meV. The TOF spectrum has not been transformed to energy transfer because then this peak becomes very difficult to discriminate from the background.

VI. CONCLUSIONS

The surface of a 1000 Å thick ice crystal grown in situ on a Pt(111) single crystal surface was studied with high resolution helium atom scattering. The position and width of the diffraction peaks indicate a perfect hexagonal termination of the bulk Ih crystal with domains of about 300 Å across. Eikonal calculations of the helium diffraction intensities indicate that it is not possible to distinguish between proton ordered and disordered ice surfaces, contrary to our previous considerations.\(^\text{12}\) However, the small difference in the corrugation amplitude between these two surfaces suggests that a distinction may be possible in connection with electron density calculations for the two alternatives. At present, the most recent experimental\(^\text{31}\) and theoretical\(^\text{32}\) results favor a proton disordered surface.

Weak diffraction from very small domains of an additional structure was also observed. The enlarged lattice constant of 9.7 Å of these domains is 2.1 times larger than the lattice constant of 4.52 Å of the ideally terminated surface. This possibly indicates that the domains arise from the regions bordering ice crystal surfaces of different phase or orientation.

The time-of-flight experiments exhibit peaks corresponding to a dispersionless phonon branch at a frequency of \(\hbar \omega = 5.4\) meV which is close to the frequency of a mode observed in an earlier study.\(^\text{12}\) This dispersionless mode is not reproduced by the present simulations of the phonon dispersion characteristics of the ice bulk terminated films based upon the more suitable force constants determined from the bulk acoustic phonon dispersion curves by Renker.\(^\text{5}\) Comparisons with measurements for amorphous ice surfaces and recent calculations and experiments on small ice clusters\(^\text{44}\) and ice slabs\(^\text{45}\) indicate that this mode is probably due to parallel frustrated translational (T-mode) vibrations of isolated water molecules in threefold sites on the (1×1) ice surface.
In addition, the extensive time-of-flight measurements show, for the first time, the dispersive Rayleigh phonon branch along both high symmetry directions. The good agreement between the Rayleigh phonon dispersion curve and lattice dynamics calculations for a full bilayer terminated surface not only support the interpretation of the diffraction results, but also show that the intermolecular forces at the ice surface are not significantly different from the forces in the bulk. Thus, the large accommodation coefficients and surface vibrational amplitudes do not derive from anomalous surface properties, but largely reflect the low mass of the water molecules.

ACKNOWLEDGMENTS

The authors would like to thank Dr. J. Cowin, Professor U. Buck, and Professor V. Buch for fruitful discussions during the course of this work, Professor H. Jónsson for making his results available to us prior to publication, F. Traeger for critical reading of the manuscript, and H. Wuttke for technical support. P. Senet thanks the National Fund of Research (Belgium) F.N.R.S. for support during the course of this work and the Fund for Scientific Research—Flanders (Belgium) F.W.O. for a postdoctoral research position.

16 The H2O used was distilled in a Millipore ZFMQ230U4 purification unit. D2O was supplied by Aldrich Chemical Co. Inc., Milwaukee, USA, Min. 99.996% purity.
17 The background vapor pressure in the target chamber was about \( p \approx 10^{-11} \) mbar 24 h after exposure using the effusive source as compared to a background water pressure of several \( 10^{-13} \) mbar for the previous experiments in Ref. 12.

33 The insensitivity of the diffraction pattern to the proton order can be understood by considering the proton terminated and the lone-pair terminated lattices as two inter-woven lattice gases with identical symmetries. The observed diffraction pattern is a superposition of the two.
45 Due to the emphasis of the present measurements on the ordered ice surfaces, relatively few measurements of the amorphous ice surface were made. The bulk of these measurements were made using D2O rather than H2O, which was used both to look for isotope effects and discriminate the background water pressure due to adsorption of thick ice films from the intrinsic water partial pressure in the chamber prior to the experiments.
49 H. Jónsson (private communication).