Vertical diffusion of water molecules near the surface of ice

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We studied diffusion of water molecules in the direction perpendicular to the surface of an ice film. Amorphous ice films of H$_2$O were deposited on Ru(0001) at temperature of 100–140 K for thickness of 1–5 bilayer (BL) in vacuum, and a fractional coverage of D$_2$O was added onto the surface. Vertical migration of surface D$_2$O molecules to the underlying H$_2$O multilayer and the reverse migration of H$_2$O resulted in change of their surface concentrations. Temporal variation of the H$_2$O and D$_2$O surface concentrations was monitored by the technique of Cs$^+$ reactive ion scattering to reveal kinetics of the vertical diffusion in depth resolution of 1 BL. The first-order rate coefficient for the migration of surface water molecules ranged from $k_{i}=5.7(\pm 0.6)\times 10^{-4}$ s$^{-1}$ at $T=100$ K to $k_{i}=6.7(\pm 2.0)\times 10^{-2}$ s$^{-1}$ at 140 K, with an activation energy of 13.7±1.7 kJ mol$^{-1}$. The equivalent surface diffusion coefficients were $D_s=7\times 10^{-19}$ cm$^2$ s$^{-1}$ at 100 K and $D_s=8\times 10^{-17}$ cm$^2$ s$^{-1}$ at 140 K. The measured activation energy was close to interstitial migration energy (15 kJ mol$^{-1}$) and was much lower than diffusion activation energy in bulk ice (52–70 kJ mol$^{-1}$). The result suggested that water molecules diffused via the interstitial mechanism near the surface where defect concentrations were very high. © 2004 American Institute of Physics.

I. INTRODUCTION

Ice surfaces have received growing attention of researchers in chemistry and physics during recent years. Reactions taking place on ice surfaces may have relevance in environmental chemical processes such as ozone depletion reactions in Antarctic polar stratosphere and chemistry of aerosols in cold marine boundary regions, as well as molecular evolution on interstellar dust particles in dense molecular clouds. A fundamental property of ice that is related to a variety of dynamical phenomena is diffusion of water molecules, often referred to as self-diffusion. Self-diffusion is thought to be responsible for sintering of ice and solvation of adsorbates stuck on the surface of ice. Self-diffusion and adsorbate solvation may take place instantaneously in polar stratospheric conditions where the surface of ice particles is covered with a quasiliquid layer at temperatures 180–210 K. On the other hand, similar processes may be extremely retarded to take almost forever at the low temperature (~20 K) surface of interstellar ice grains. Recent laboratory studies suggest that self-diffusion and solvation not only control the speed of a reaction on ice surface, but they can also alter the reaction path.

Self-diffusion in bulk ice has been investigated by several research groups. In an early tracer experiment, Kuhn and Thürkauf showed that the diffusion coefficients of H and O are the same, and this indicates that self-diffusion occurs by the migration of whole molecules. A compilation of values from the later tracer experiments gives the diffusion activation energy of 51.9–56.7 kJ mol$^{-1}$ in the temperature range 238–273 K. Goto et al. examined diffusion of H$_2^{18}$O in H$_2$O-ice films at temperatures 155–165 K by using the laser-induced thermal desorption (LITD) technique. The measured diffusion activation energy and preexponential factor are $E_a=69.9\pm 6.7$ kJ mol$^{-1}$ and $D_0=9.7(\pm 0.5)\times 10^7$ cm$^2$ s$^{-1}$, respectively, and the diffusion coefficient at 160 K is $D(160 K)=1.5\times 10^{-15}$ cm$^2$ s$^{-1}$.

In contrast to the numerous studies of self-diffusion in bulk ice, only a small number of studies have been reported for diffusion at ice surfaces. Experimentally, study of the diffusion at an ice surface provokes a severe challenge. Properties of ice surface often critically depend on surface contamination, and it is difficult to completely avoid surface contamination unless the sample is handled in ultrahigh vacuum (UHV) where the sample temperature must be kept low (<160 K). Another difficulty is the lack of adequate spectroscopic tools that are surface sensitive and measure exclusively the surface molecules. Mizuno and Hanafusa employed nuclear magnetic resonance (NMR) to study the
motion of protons in finely powdered ice at temperatures 173–263 K, and concluded that the protons (or whole molecules) in at least the surface monolayer diffuse at a rate that is orders of magnitude faster than in bulk ice. They deduced $E_a = 23 \text{kJ mol}^{-1}$ from the diffusion coefficients measured at temperatures 253–273 K. George and co-workers in their LITD study.1,18 were not able to observe surface diffusion of water molecules (HDO) in the direction parallel to the (0001) surface of ice, from which they deduced an upper limit for the surface diffusion coefficient, $D^s(140 \text{K}) \leq 1 \times 10^{-9}$ cm$^2$ s$^{-1}$. They interpret that their experimental result may represent an average value over the depth distribution of HDO molecules reached by spontaneous diffusion into bulk.

In this paper, we examined diffusion of surface water molecules in the direction perpendicular to the surface of an ice film. In an UHV environment we deposited ultra thin films of H$_2$O-ice on Ru(0001) and then added a fractional coverage of D$_2$O onto them. Temporal change of the surface concentrations of H$_2$O and D$_2$O reflected their diffusion kinetics in the vertical direction. The surface concentrations of H$_2$O and D$_2$O were analyzed using the technique of Cs$^+$ reactive ion scattering (Cs$^+$ RIS) (Refs. 19–21) in depth resolution of 1 bilayer (BL), which meant that the experiment measured diffusion in the outermost surface region. The extreme surface sensitivity distinguishes the present work from the previous studies that use NMR (Ref. 17) or laser desorption techniques18 to measure self-diffusion in a quasiliquid layer or in a near-surface region. In addition to self-diffusion, proton exchange can also take place between water molecules on ice under conditions of the present experiment. The proton exchange occurs through proton hopping between water molecules, and thus it is mechanistically different from self-diffusion involving transport of whole molecules. Self-diffusion is distinguishable from the proton exchange in the RIS experiment, because proton exchange between H$_2$O and D$_2$O produces HDO isotopomer. This paper focuses on molecular self-diffusion and is the first member in a series of two papers investigating kinetics of water molecules on ice films. The other paper [immediately follows this one and addresses the proton exchange reaction.

II. EXPERIMENTAL METHODS

We used a Ru single crystal with a (0001) face as a substrate for growing ice films. The Ru crystal was attached to an UHV sample manipulator that controls the substrate temperature in the range 90–500 K and was cleaned by repeated cycles of Ar$^+$ sputtering and annealing at 1500 K in UHV. Ice films were deposited while the crystal was maintained at a selected temperature between 100 and 140 K, by backfilling the chamber with water vapor at a pressure of $1–5 \times 10^{-8}$ Torr. The films were prepared to the thickness of 1–5 BL, and the thickness was estimated from the temperature-programmed desorption mass spectrometry (TPDMS) measurements and from attenuation of the reflected Cs$^+$ beam intensity at the surface.23 An ice film grown at 100–140 K by the backfilling method is normally amorphous and free of micropores.24 Deposition at temperature above 140 K produces a crystalline film, either in a cubic or hexagonal phase with a (0001) face.25 The Ru(0001) substrate might be able to induce crystallization of the deposited film even at slightly lower temperature, especially for an ultra thin film. We did not examine this possibility further and assumed nonporous, amorphous films in the present experiments. The water samples (H$_2$O and D$_2$O) were purified by degassing through several freeze-vacuum-thaw cycles before introduction into the chamber. Separate leak valves were used for H$_2$O and D$_2$O in order to prevent prescrambling of two isotopomers.

The principle and experimental procedure for Cs$^+$ RIS experiments on ice films have been described in detail elsewhere.8,19–21 Inside a vacuum chamber maintained at base vacuum of $1 \times 10^{-10}$ Torr, a Cs$^+$ beam generated from a surface ionization source was scattered at a sample surface to be analyzed. The Cs$^+$ beam energy was chosen to be typically between 10 and 20 eV, and the beam current density at the sample was 1–3 nA cm$^{-2}$. The scattered positive ions were measured with a quadrupole mass spectrometer (QMS) with its ionizer switched off. The beam incidence and the detector angles both were 45° with respect to the surface normal. Surface contamination by incident Cs$^+$ beams was avoided by reducing the beam exposure and by preparing fresh ice films whenever necessary for the measurement. In particular, for making kinetic measurements as a function of reaction time, a fresh film was prepared for measurement at each reaction time. The chamber was equipped with an Auger spectrometer to monitor surface cleanness and elemental composition. Residual gas analysis and TPDMS experiments were done with a QMS detector that was also used for RIS.

III. RESULTS

Figure 1 shows a typical RIS spectrum obtained from an ice film that has both H$_2$O and D$_2$O molecules on the surface. The ice film was prepared first by depositing a H$_2$O layer to 2–3 BL thickness on Ru(0001) at 100 K by backfilling the chamber with H$_2$O vapor at a pressure of $1 \times 10^{-8}$ Torr, and then by depositing D$_2$O onto it for a frac-
The probing depth of the analysis technique. The probing intensity dropped almost to zero as the D$_2$O coverage increased continuously for about 40 min along with a concomitant decrease of D$_2$O surface concentration. These changes reflected inward migration of surface D$_2$O and the accompanying reverse migration of subsurface H$_2$O, measured with a vertical resolution of 1 BL at the surface.

Slight increase of HDO population was seen in Fig. 3, which might be interpreted to indicate occurrence of H/D exchange reaction between H$_2$O and D$_2$O. However, control experiments revealed about an equal level of HDO population on pure H$_2$O films, indicating that the HDO population came from adsorption of HDO from background gas. Residual gas analysis showed the presence of HDO in the background gas produced by isotope scrambling of H$_2$O and D$_2$O on the chamber wall. Subtraction of the estimated amount of adsorbed HDO impurity from Fig. 3 leaves only negligible contribution of H/D exchange on the ice film between H$_2$O and D$_2$O. Other factors that might have affected the kinetic plot included adsorption of water (H$_2$O and D$_2$O) from the background gas and spontaneous desorption of water from the ice surface. The adsorption effects were negligible during the time scale of the measurement, according to a control experiment on a pure H$_2$O film. Water molecules do not desorb below 140 K, and this was also checked by a thick-ness measurement of the film. A recent study suggests that D$_2$O molecules in the first adsorption layer may be partially dissociated. To check if the dissociated species on Ru(0001) affected the molecular diffusion and H/D exchange reactions on ice films, we varied the film thickness between 1 and 3 BL. The rates of molecular diffusion and the build up of HDO concentration were independent of film thickness, suggesting the negligible effect of the metal substrate.

Exchange of D$_2$O molecules between the first and the underlying layers is expressed by
where \([D_2O]_s\) and \([D_2O]_b\) represent the surface and bulk concentrations, respectively. In the present experiment all \(D_2O\) molecules were at the surface at \(t=0\), and thus \([D_2O]_s+\[D_2O]_b=\[D_2O]_{s,0}\), where \([D_2O]_{s,0}\) is the initial surface concentration. The rate expression accounting for both inward and outward migration of \(D_2O\) is given by

\[
-\frac{d[D_2O]_s}{dt} = k_1[D_2O]_s - k_2[D_2O]_b
\]

\[
= (k_1 + k_2)[D_2O]_s - k_1[D_2O]_{s,0}.
\]

Converting this differential equation to an integrated rate expression, we obtain

\[
\ln \frac{[D_2O]_s - [D_2O]_{eq}}{[D_2O]_{s,0} - [D_2O]_{eq}} = -(k_1 + k_2)t,
\]

where \([D_2O]_{eq}\) indicates the \(D_2O\) surface concentration at \(t=\infty\). Analogous expressions to Eq. (3) can be derived for the case of \(H_2O\) migration. For self-diffusion \(k_1\) is numerically equal to \(k_2\), if the diffusion geometry is symmetric and there is no isotopic preference in the surface segregation. Fitting the kinetic data of \(D_2O\) and \(H_2O\) in Fig. 3 into the integrated rate expression of Eq. (3) gave a straight line whose slope was equal to \(k_1+k_2\). The value of \(k_1\) obtained by this analysis was \(k_1(D_2O) = 5.8(\pm 0.6) \times 10^{-4} s^{-1}\) and \(k_1(H_2O) = 5.6(\pm 0.6) \times 10^{-4} s^{-1}\) at \(T = 100 K\). The two values were equal within the experimental uncertainty, as they should be. We considered their average value to be the rate coefficient for surface water diffusion, \(k_1 = 5.7(\pm 0.6) \times 10^{-4} s^{-1}\) at \(100 K\).

One might expect that the rate coefficients for other temperatures can be obtained by a simple extension of the kinetic measurements like those in Fig. 3, but it was not always so. Upon increase of the sample temperature, the speed of molecular water diffusion was accelerated as expected. At the same time, however, H/D exchange reaction between \(H_2O\) and \(D_2O\) started to occur appreciably. For example, on the ice film prepared at 120 K, the H/D exchange reaction produced \(HDO\) to have relative population of 18% after 40 min, which far exceeded the level of \(HDO\) impurity adsorption. In addition, at 140 K self-diffusion occurred too fast to be measured by the procedure used in Fig. 3. \(D_2O\) at the surface and \(H_2O\) in the sublayer became rapidly mixed within <1 min at this temperature. Obviously, such a fast reaction speed was problematic for a kinetic study, because the diffusion significantly advanced even during the time of sample preparation before the RIS measurement.

In order to slow down the unwanted molecular mixing during the sample preparation, we deposited an ice film at 100 K, raised the sample temperature to 140 K, and then immediately did RIS measurements. Figure 4 shows the result of such kinetic measurements. The ice films were prepared to have a \(H_2O\) multilayer of 3–4 BL thickness on which \(D_2O\) was added to a coverage of about 0.5 BL. The temperature was raised from 100 to 140 K at a ramping rate of 0.22 K s\(^{-1}\) in 3 min, as displayed in the upper panel of the figure for the time duration indicated as -3 to 0 min on the abscissa. Even during the initial 3 min of temperature increase, the relative surface abundance of \(D_2O\) and \(H_2O\) underwent drastic changes from 54% and 43%, respectively, to 10% and 82%. This final ratio was equivalent to the \(D_2O: H_2O\) content ratio in the whole film, indicating that self-diffusion occurred to a completion. Apparently, the RIS measurement needs to be done much faster in order to follow the diffusion kinetics. By contrast, the H/D exchange reaction generating \(HDO\) proceeded more slowly than the molecular diffusion. The relative population of \(HDO\) increased by only a few percent during the initial 3 min period, much less than the change of \(D_2O\) and \(H_2O\) populations due to molecular diffusion. The \(HDO\) population approached the value of complete isotope scrambling only after 30 min or so.

When the molecular diffusion occurs simultaneously with the H/D exchange reaction described by Eq. (4), the complete rate expression for the change of \(D_2O\) concentration at the surface, \([D_2O]_s\), is given by Eq. (5):

\[
[H_2O]_s + [D_2O]_s = 2[HDO]_s,
\]

\[
-\frac{d[D_2O]_s}{dt} = k_1[D_2O]_s - k_2[HDO]_s
\]

\[
+ k_2[D_2O]_s[H_2O]_s - k_1[D_2O]_b.
\]

Equation (5) cannot be directly used for analysis of the measured kinetic curves unless further simplified. The molecular diffusion and H/D exchange channels in Eq. (5) can be decoupled, if the kinetic measurements are done in two widely separated time scales. At 140 K, for instance, the change of \(D_2O\) and \(H_2O\) populations during the first 1–2 min period will reflect mostly the molecular diffusion kinetics, because H/D exchange reaction proceeds only to a small or negligible
extent according to Fig. 4. On the other hand, the population change after several minutes will represent the H/D exchange kinetics.

We examined the diffusion kinetics by doing rapid RIS measurements after a short, initial period of reaction time. The result is shown in Fig. 5. In this experiment, all ice films were prepared in the same isotopomeric composition but at different temperatures between 100 and 140 K. H$_2$O and D$_2$O populations at the initial surface were 43% and 55%, respectively. The changed surface concentrations after an initial reaction time of 23 s was monitored, and the result was plotted in the vertical axis of the figure. Estimation of the "initial reaction time" was inherently somewhat uncertain, because only a short time delay (3 s) was given for a prompt RIS analysis of the surface, whereas a longer time was spent for film deposition (25 s) and RIS data acquisition (15 s). The reaction time was estimated by adding the actual time delay and half of the durations of film deposition and RIS analysis, and this estimate had uncertainty of probably several seconds. This reaction time was kept consistently to be the same in all measurements, which was important for the kinetic study. Figure 5 shows that the rate of molecular diffusion has increased at higher temperature. The H/D exchange rate also increased to have the HDO population of <10% at 140 K. The H/D exchange channel, however, was neglected in the kinetic analysis to be presented below. By having done so we may have lost an accuracy of <10% for the rates of molecular diffusion at 100–140 K, but this approximation provided clarity as well as simplicity in the kinetic analysis.

We analyzed the results in Fig. 5 by using the first-order rate expression for vertical migration of surface D$_2$O molecules, given by

$$\ln \left[ \frac{[D_2O]^T_{i=0}}{[D_2O]^T_{i}} \right] = k_1(T) t.$$  

Equation (6) is a reduced form of Eq. (3) and neglects the upward migration of D$_2$O from the sublayer to the surface because it is applied to the initial rates. In Fig. 5 all the surfaces had the same isotopomeric composition at $t = 0$, i.e., 

$$[D_2O]^T_{i=0} = [D_2O]^T_{i=2}$$

for any $T_1$ and $T_2$. Under this condition, Eq. (6) is rearranged to Eq. (7), which relates the rate constants at two different temperatures,

$$\ln \left[ \frac{[D_2O]^{100K}}{[D_2O]^{110K}} \right] = k_1(T) - k_1(100 \text{ K}) t.$$  

Equation (7) allowed us to calculate $k_1(T)$ for $T =$ 100–140 K from the results of Fig. 5. Kinetic parameters at 100 K, obtained from Fig. 3, were used as the reference values. The results of H$_2$O migration in Fig. 5 were also analyzed by using the equations analogous to Eqs. (6) and (7).

The rate coefficients calculated according to the above-described procedure are presented in the Arrhenius plots in Fig. 6. The plots of $\ln[k_1(T)]$ vs $1/T$ for H$_2$O and D$_2$O fitted nicely to straight lines over the temperature range 100–140 K. From the slope ($-E_a/R$) of the straight lines, the diffusion activation energy was calculated to be $E_a(D_2O) = 13.9(\pm 1.5) \text{ kJ mol}^{-1}$ and $E_a(H_2O) = 13.5(\pm 0.9) \text{ kJ mol}^{-1}$. The two agreeing values supported validity of the kinetic model in the analysis, and two values were averaged to give the activation energy of water diffusion, $E_a = 13.7(\pm 1.7) \text{ kJ mol}^{-1}$. The associated preexponential factor was $A = 1 \times 10^4 \text{ s}^{-1}$. As mentioned before, the estimated “reaction time” of 23 s could have a systematic uncertainty of several seconds. When we varied the reaction time between 13 and 33 s, a range much wider than the possible uncertainty, the $E_a$ value changed between 12.7(±1.3) and 15.3(±2.2) kJ mol$^{-1}$.

The rate coefficient derived here, $k_1 = A \exp(-E_a/RT)$, represents the rate of molecular migration between the first and the underlying layers. The vertical diffusion coefficient near the surface, $D^z = D_0^z \exp(-E_a/RT)$, is often used in the literature to represent the rate of diffusion. $k_1$ can be converted to $D^z$ by assuming that the probing depth of molecular migration in the present study, $x$, is equal to the interlayer spacing between two (0001) planes of ice (3.66 Å) (Ref. 5) and $(x^2) = 2Dt$ in the one-dimensional Einstein-
Smoluchowski equation, where $\tau$ is the time for diffusion. From these relationships, the equivalent surface diffusion coefficient is calculated to be $D'(100 \text{ K}) = 7 \times 10^{-19} \text{ cm}^2 \text{ s}^{-1}$ and $D'(140 \text{ K}) = 8 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ with the preexponential factor, $D_0 = 1 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$. In the present study, the films grown at temperatures below 140 K are considered to be amorphous films without a well-defined (0001) surface. However, even in such cases the interlayer spacing may be a reasonable approximation for the molecular migration depth.

### IV. DISCUSSION

Only a small number of studies\textsuperscript{2,17,18} have been reported on self-diffusion of water molecules on ice surfaces. To our knowledge, there has been only one experimental study that measures the diffusion coefficient of water molecules exclusively in the surface region.\textsuperscript{17} The other reports\textsuperscript{2-18} are measurements into the convoluted processes of surface and bulk diffusion. In NMR study of finely powdered ice samples, Mizuno and Hanafusa\textsuperscript{17} report diffusion coefficients ranging from $D = 1.35 \times 10^{-9}$ to $3.08 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ and the diffusion activation energy of $E_a = 23 \text{ kJ mol}^{-1}$ for $T = 253-273 \text{ K}$. The measurement corresponds to diffusion in the “quasiliquid” surface layer with unknown thickness. The activation energy obtained in the NMR study is larger than the present activation energy ($13.7 \pm 1.7 \text{ kJ mol}^{-1}$). The different magnitudes of $E_a$, however, may not be very surprising, because two experiments were done under quite different conditions including the temperature range (100–140 versus 253–273 K), nature of the surface (the outermost 1–2 bilayers vs a quasiliquid layer), and type of the sample (thin film vs powder). Yet, a point to emphasize here is that both activation energies are still very low compared to the activation energy in bulk, the latter being in the range of $E_a^{\text{bulk}} = 52–70 \text{ kJ mol}^{-1}$ according to various experimental investigations.\textsuperscript{10-15}

Few theoretical calculations\textsuperscript{29-32} have been performed for diffusion of water molecules on single-crystal ice surfaces. An effective pair-potential model\textsuperscript{20} predicts an activation energy of 10 and 13 kJ mol$^{-1}$ for diffusion parallel to the basal and prism faces, respectively, of hexagonal ice. More recently, molecular dynamics simulations have studied surface disordering of the basal face of hexagonal ice.\textsuperscript{30-32} Computer simulations of diffusion trajectories as slow as the experiments are beyond the present computational capacity, and the simulations have been done only for a short time period (<1 ns) and at higher temperatures (>190 K).

The rate of diffusion near the surface is faster than that in the bulk for the temperature range examined here. For example, at 140 K the surface diffusion coefficient is $D' = 8 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$, whereas the bulk diffusion coefficient is $D^{\text{bulk}} = 1 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$ at the same temperature, the latter being estimated from extrapolation of the $D^{\text{bulk}}$ values for $T = 153-170 \text{ K}$ for diffusion perpendicular to the (0001) basal plane of hexagonal ice.\textsuperscript{14,15} With these diffusion coefficients, the time that it takes for surface water molecules to migrate from the first to the second basal plane is calculated to be 8 s at 140 K, whereas inside the bulk the same interplanar migration will take 11 min. In this respect, the translational motions of water molecules in the bulk are considered effectively frozen at temperature <140 K, and only the molecules near the surface are relatively mobile. The thickness of such a translationally activated surface region is only 1–3 bilayers from the surface at 140 K, according to the study of isotopic exchange between surface water molecules.\textsuperscript{22} $D^{\text{bulk}}$ increases with temperature more rapidly than $D'$ due to its higher activation energy, and extrapolation of the Arrhenius plot in Fig. 6 predicts that the rates for surface and bulk diffusion will cross at $T = 153 \text{ K}$, where $D' = D^{\text{bulk}} = 2 \times 10^{-16} \text{ cm}^2 \text{ s}^{-1}$. Incidentally, this temperature is close to the onset of the liquidlike translational diffusion (155 K) which occurs in concert with crystallization of an amorphous ice film.\textsuperscript{16}

An interesting issue to address is the magnitude of $E_a'$ which is several times smaller than $E_{a^{\text{bulk}}}$. Intuitively, one can imagine that disorder and unstability of surface molecules will reduce the diffusion energy barrier. A quantitative approach should consider the molecular mechanism of self-diffusion in relation to the Arrhenius form of diffusion coefficient, $D = D_0 \exp(-E_a/(RT))$. It is widely accepted\textsuperscript{8,12,13} that molecular self-diffusion in bulk ice occurs through motions of defects, most probably interstitials which dominate over vacancies in ice crystals. In this case, the diffusion coefficient of water molecules is equivalent to that of interstitials in ice. The activation energy of the interstitial diffusion can be given as the sum of two components, $E_{a^{\text{bulk}}} = E_{a} + E_{\text{im}}$, where $E_{\text{im}}$ is the interstitial formation energy which accounts for the probability of finding an interstitial site in the adjacent site, and $E_{\text{im}}$ is the interstitial migration energy corresponding to the height of the potential energy barrier. X-ray topographic measurements of dislocation loops in ice\textsuperscript{12,13} show that $E_{a^{\text{bulk}}} = 54 \text{ kJ mol}^{-1}$ and that this value can be divided into $E_{a} = 39 \text{ kJ mol}^{-1}$ and $E_{\text{im}} = 15 \text{ kJ mol}^{-1}$. Now imagine water molecules migrate between the first and the second layers of an ice film surface. Surface water molecules are rotationally and vibrationally activated in the temperature range of the present study, and these activated motions produce a greater molecular disorder and higher defect concentrations at the surface. Studies investigating surface charge on crystalline ice suggest that the surface concentration of ionic and orientational defects can be extremely high and can approach the bulk molecular concentrations.\textsuperscript{33} Interstitial concentrations may also be greatly increased near the surface as a result of the activated molecular motions. Here the “interstitials” may have a broader meaning, indicating not only the interstitials in a crystalline network but also some weakly bound molecules in disordered environment of the surface region. If a water molecule can find an interstitial site in the neighborhood to jump with probability close to unity, then the contribution of $E_{a}$ to the diffusion activation energy will be reduced effectively to zero. Therefore, $E_{a}^{\text{surf}} = E_{a^{\text{im}}}$ under these circumstances. Indeed, $E_{a} = 13.7 \pm 1.7 \text{ kJ mol}^{-1}$ obtained in the present work is close to $E_{a^{\text{im}}} = 15 \text{ kJ mol}^{-1}$ deduced from x-ray topographic measurements.\textsuperscript{12,13} The agreement supports the interstitial mechanism of molecular self-diffusion and suggests that $E_{a}^{\text{surf}}$ is low because the surface of an ice film is molecularly disordered and has extremely high defect concentrations.
V. CONCLUSION

This work measured the rate of vertical migration of water molecules at the outermost surface of an ice film. The migration between the first and the underlying layers occurred in the time scales ranging from about 10 s at 140 K to 1000 s at 100 K. Kinetic measurements yielded the first-order rate coefficient for migration, and it increased from \( k_1(100 \text{ K}) = 5.7(\pm 0.6) \times 10^{-4} \text{ s}^{-1} \) to \( k_1(140 \text{ K}) = 6.7(\pm 2.0) \times 10^{-2} \text{ s}^{-1} \) with the activation energy of \( E_a = 13.7 \pm 1.7 \text{ kJ mol}^{-1} \). The equivalent surface diffusion coefficients were \( D^s(100 \text{ K}) = 7 \times 10^{-19} \text{ cm}^2 \text{ s}^{-1} \) and \( D^s(140 \text{ K}) = 8 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1} \). The activation energy of surface diffusion was much smaller than that in bulk and was close to the interstitial migration energy, \( E_{im} = 15 \text{ kJ mol}^{-1} \). The observation supports that self-diffusion occurs through migration of interstitials and that the outermost region of the surface is greatly disordered and has extremely high defect concentrations.

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