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Hydration of polar and nonpolar molecules at the surface of amorphous solid water

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On the basis of time-of-flight secondary ion mass spectrometry, properties of amorphous solid water above the glass transition temperature (136 K) and the hydration of polar ($HCOOH, C_3H_7OH$) and nonpolar (C_6H_{14}, C_6F_{14}) molecules on the D_2O-ice surface have been investigated. No evidence was obtained for the irreversible transition of the amorphous solid water into the crystalline phase: the self-diffusion of water molecules occurs above 140 K irrespective of the preparation temperatures of the water-ice film ranging from 15 K to 165 K, whereas the morphology of the film changes drastically at 165 K due to the evolution of liquidlike water. It is also demonstrated that the change in conformation of the hydrated HCOOH molecule, as well as the occurrence of hydrophilic/hydrophobic hydration of the C_3H_7OH molecule, can be analyzed successfully from the temperature evolutions of the secondary-ion intensities. These polar molecules basically stay on the surface and tend to quench the morphological change of the water film due to the reduction of surface tension. The nonpolar C_6H_{14} and C_6F_{14} molecules readily dissolve in the D_2O layer below 100 K and dehydration of the incorporated molecules occurs at 165 K concomitantly with the evolution of the liquidlike water. It is thus concluded that the hydrophobic hydration of nonpolar molecules is intimately related to the properties of water films.

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I. INTRODUCTION

Amorphous solid water (ASW) is of special interest since it is a model system for liquid water and glassy materials. There is still debate about the properties of ASW above the glass transition temperature (136 K). Devlin *et al.*[1] assumed that ASW freezes directly to crystalline ice near 150 K without passing through the intermediate liquid state, whereas Jenniskens *et al.*[2] suggested that viscous liquid water coexists with cubic crystalline ice in the temperature range 140–210 K. Kay and co-workers[3,4] concluded that a liquid phase appears just before the irreversible transition into crystalline ice at 155–160 K. It is an open question whether such a liquid phase, if any, is a thermodynamic extension of normal liquid water or a distinct phase. In any case, the water-ice surface, whether crystalline or amorphous, would be a complex disordered system, as inferred from the fact that the surface structure of the vapor-deposited “crystalline-ice” film is hardly analyzed by low-energy electron diffraction[5] and helium atom scattering[6] at temperatures above 100 K.

Many phenomena of scientific and technological importance occur at a solute-water interface, so that a molecular level understanding of structural and thermodynamic aspects of the interfacial processes is of crucial importance. However, our current understanding of the adsorption structures of molecules on the surface of liquid or solid water and the transport of solute molecules into the bulk water is still insufficient. To date, the hydrate formation in the bulk water ice has been studied extensively by means of transmission FT-IR.[7,8] This method has a disadvantage of relatively poor surface sensitivity. Electron spectroscopic techniques have been applied to the hydration phenomena on the water-ice surface,[9,10] but they sometimes encounter difficulties in characterizing highly insulating ASW surfaces. Secondary ion mass spectrometry (SIMS) is established as one of the most surface sensitive techniques, and the static SIMS has been utilized for the analysis of molecular solids in terms of the cluster ion formation[11,12] and the surface chemistry.[13] Very recently, it is demonstrated that hydration of simple molecules adsorbed on the ASW surface can be analyzed at the molecular level on the basis of temperature-programmed time-of-flight SIMS (TP-TOF-SIMS) experiments:[14–17] the hydration and H/D exchange of NH_3, CH_3OH, and CH_3NH_2 molecules adsorbed on the D_2O-ice surface have been discussed as a function of temperature. However, there is still lacking of wide-ranging adsorption data for the ASW surface especially in terms of the hydrophobic hydration. In this respect, the interaction between the lipophilic moieties of organic molecules and water is one of the most important forces in nature: it plays a major role in the conformations of proteins and is central to the formation of micelles and biological membranes. The hydrophobic hydration is such that the nonpolar solute species enhances the ordering of the solvent water structure, creating icelike or clathratelike structures near the lipophilic entity.[18] However, the exact nature of this structural ordering has remained unclear.

The purpose of this paper is to clarify the properties of ASW above the glass transition temperature and the interactions of water with some polar ($HCOOH, C_3H_7OH$) and nonpolar (C_6H_{14}, C_6F_{14}) molecules adsorbed on the ASW surface, on the basis of the TP-TOF-SIMS experiments. These molecules were chosen carefully in order to shed light on the role of such functional groups as -CH, -CO, -OH, and -CF in interactions with the D_2O molecules. It is found that the polar molecules stay on the surface of ASW, while the nonpolar ones are preferentially incorporated in the bulk. These behaviors can be understood as a consequence of the interplay between the hydrophilic and hydrophobic hydrations. It is demonstrated that the hydration/dehydration of nonpolar molecules are intimately related to the property of water itself.

II. EXPERIMENT

Experiments were conducted in a stainless steel ultrahigh-vacuum chamber of base pressure below 1×10^{-8} Pa. The vacuum system was equipped with an electron-impact-type ion source, a linear-TOF tube, and a differentially pumped quadrupole mass spectrometer (QMS) for temperature programmed desorption (TPD). The He^+ ions were chopped by an electrostatic deflector into pulses with width of 60 ns and frequency of 40 kHz. The TOF-SIMS measurements were made in such a manner that the sample, floated with a bias voltage of +500 eV, was irradiated with a primary He^+ beam of 2 keV through a grounded stainless-steel mesh placed 4 mm above the sample surface (the ion impact energy was 1.5 keV), and the positive ions extracted into the field-free region of the TOF tube were detected with a channel electron multiplier. To minimize charging and damage of a surface, a pulsed He^+ beam with a low incident flux $(0.1\ \mathrm{nA/cm^2})$ was used. No appreciable damage of the surface was detected even after the prolonged TOF-SIMS measurements up to 30 min. The substrate was a Ni(111) surface mounted on a sample holder cooled to 15 K by means of a closed-cycle He refrigerator. The surface was cleaned by annealing around 1200 K by electron bombardment from behind. The molecules were dosed from separate gas inlet systems to the substrate by backfilling the vacuum system. The coverage of the adsorbed molecules was estimated from the evolution curves of the sputtered ion intensities as a function of exposure. In the present experiment, one-monolayer (1 ML) of molecules was attained by exposure of around 2–5 L $(1\ \mathrm{L} = 1.3 \times 10^{-4}\ \mathrm{Pa\ s})$. The film thickness was estimated on the basis of this value. The substrates were heated at a ramp rate of 0.1 K/s from 15 K to a temperature above which the water multilayer had completely desorbed. The TOF-SIMS spectra were accumulated continuously every 30 s.

III. EXPERIMENTAL RESULTS

A. $H_2{}^{18}O$ adsorption on the $H_2{}^{16}O$ layer

The nonporous ASW film was prepared by the deposition of water molecules at 100 K. It would be converted irreversibly into the thermodynamically more stable crystalline ice by heating above 140 K though this phase transition temperature is not well defined. In order to evaluate the diffusivity of the water molecules at the surface, the extent of intermixing between the isotopically labeled water molecules is studied by TP-TOF-SIMS. Figure 1 displays the temperature evolutions of typical secondary-ion intensities sputtered from the $H_2{}^{18}O/H_2{}^{16}O$ surface. The $H_2{}^{16}O$ ice substrate was prepared in such a way that a thin film (50 ML) of ASW deposited at 100 K was heated to 145 K and kept at this temperature for a few minutes. By this procedure, a crystalline-ice film is thought to be created. The $H_2{}^{18}O$ molecules (1 ML) were deposited on it after cooling down to 15 K. The H^+ and $H^+(H_2O)$ ions are the dominant species from water and the Ni^+ ion is emitted, together with the $Ni^+(H_2O)_n$ ions, during or after evaporation of the multilayer water. The surface is covered almost completely with the $H_2{}^{18}O$ molecules below 130 K and the intermixing becomes remarkable above 140 K, resulting in the dominance of the $H_2{}^{16}O$ molecules above 160 K. This result clearly shows that self-diffusion of water molecules occurs even on the "crystalline ice" film above the glass transition temperature.

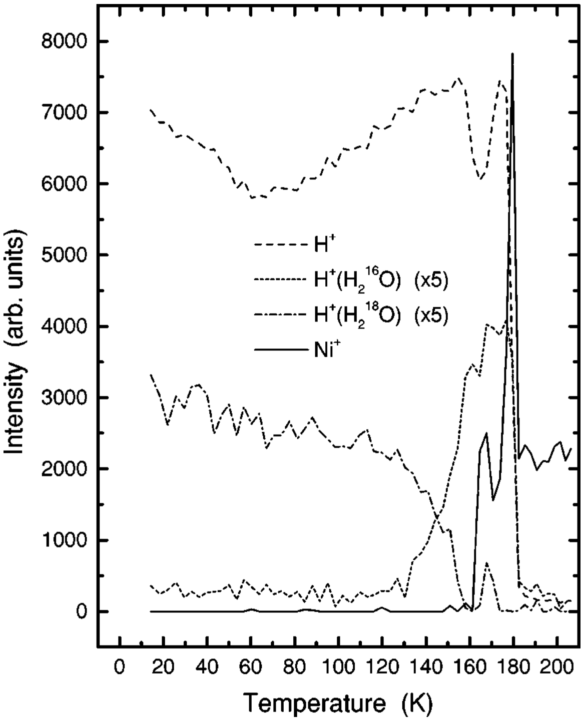

FIG. 1. Evolutions of TOF-SIMS cation intensities from the 1 ML $H_2{}^{18}O$ adsorbed $H_2{}^{16}O$ (50 ML) surface as a function of temperature. The $H_2{}^{16}O$ layer was deposited on the Ni(111) surface at 100 K and then heated up to 145 K, thereby forming the "crystalline ice" film. The $H_2{}^{18}O$ molecules were deposited on it after cooling down to 15 K. The surface was heated at a ramp rate of 0.1 K/s.

An interesting feature is observed in the Ni^+ intensity: it appears above 160 K, forming a hump, and then exhibits a sharp peak at 180 K where the multilayer water desorbs. The adsorbed water molecules play a crucial role in the Ni^+ emission, as evidenced by the fact that Ni^+ is hardly sputtered from the clean Ni(111) surface. Figure 2 shows the secondary ion intensities from the Ni(111) surface as a function of coverage of the H_2O molecule. The measurements were made at 100 K. The Ni^+ intensity exhibits a maximum at around 1 ML and then decreases gradually with increasing coverage. This result can be interpreted as follows: The Ni^+ ion undergoes efficient resonance neutralization at the clean Ni(111) surface, thereby resulting in the almost complete neutralization. The submonolayer of water would have a higher work function than the clean surface so that it quenches the ion neutralization considerably. The sputtering of Ni^+ itself is suppressed by the thicker water layer, but it should be noted that Ni^+ can be emitted through up to four monolayers of H_2O. Thus, the Ni^+ peak appearing at 180 K in Fig. 1 occurs in the course of desorption of the multilayer water.

The hump in the Ni^+ intensity at 165 K cannot be ascribed to the desorption of the H_2O molecules since less than

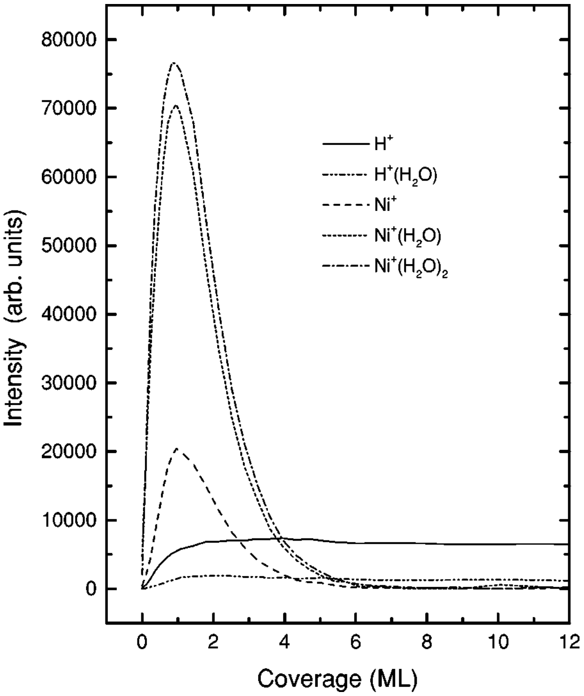

FIG. 2. Secondary-ion intensities from the Ni(111) surface as a function of coverage of the H_2O molecules. The measurements were made at 100 K.

5% of the H_2O molecules evaporate up to this temperature (see also the TPD spectra of D_2O shown later). This fact clearly shows that desorption of the water molecule does not proceed via the simple layer-by-layer fashion but is preceded by the drastic morphological change leading to the roughening of the layer or the microscopic "water droplet" formation at the surface. In this respect, Smith and Kay[4] observed a bump in the water TPD spectra around this temperature and ascribed it to the occurrence of the irreversible phase transformation of ASW into crystalline ice. At this temperature, they also observed the explosive desorption of the CCl_4 molecules buried underneath the thick ASW layer and concluded that it is caused by the formation of connected desorption pathways by the crystallization.[3] In reality, however, no direct evidence for the crystallization of ASW has been presented and the morphological change of the water-ice layer has been ignored completely. The origin of this phenomenon is detailed in the following sections. In order to confirm the possibility of crystallization of ASW at higher temperatures, the $H_2{}^{16}O$ layer was prepared by annealing at 160–165 K (in this case, the evaporation of the water molecules was so severe that the sample was heated in the $H_2{}^{16}O$ ambient of 1×10^{-4} Pa). The $H_2{}^{18}O$ molecule was adsorbed on it after cooling down to 15 K and the temperature was ramped. The intermixing was observed for this surface at the same temperature as in Fig. 1. Moreover, no differences were observed in the uptake behaviors of the $H_2{}^{18}O$ molecule adsorbed on the surfaces of porous ASW (deposited at 15 K), nonporous ASW (100 K), and "crystalline ices" (heated to 145 K and 165 K). If the crystalline water-ice layer were created irreversibly, the intermixing of the water molecules should be frozen out. Thus, the present study shows no experimental evidence for the occurrence of irreversible crystallization of the ASW layer.

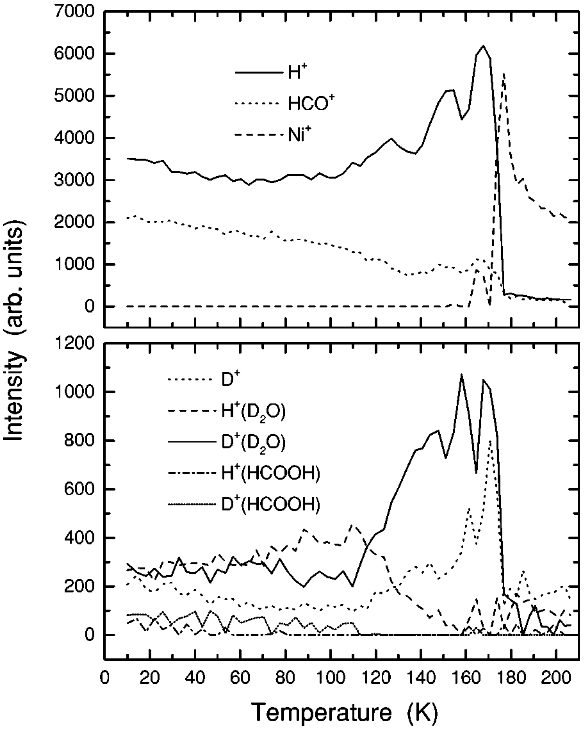

FIG. 3. Temperature evolutions of TOF-SIMS intensities from the HCOOH (1 ML) adsorbed D_2O surface (50 ML, nonporous ASW). The HCOOH molecule was deposited on the D_2O layer at 15 K.

In Fig. 1, a dip is observed in the H^+ intensity at 165 K, concomitantly with the hump of Ni^+, but the $H^+(H_2O)$ intensity shows no structures at this temperature, suggesting that the origins of bare and hydrated protons are different to each other: the former is emitted from the dangling -OH bond of the water molecules at the topmost surface layer whereas the latter is caused by the proton transfer reactions during energetic molecular collisions, $2H_2O \rightarrow H_3O^+ + OH^-$, associated with the formation of hydrogen bonds. Indeed, the protons created in the hydrogen-bond network of water molecules are readily hydrated, forming hydronium ions, due to the strong ion-dipole interactions. The invariance of the $H^+(H_2O)$ intensity around 165 K indicates that the Ni(111) surface is covered with the multilayer water, whereas the water molecules at the topmost surface undergo the hydrogen-bond reorganization during the morphological change.

B. HCOOH on the D_2O surface

Figure 3 shows the temperature evolutions of typical secondary-ion intensities sputtered from the HCOOH (1 ML) molecules adsorbed on the D_2O-ice surface (50 ML, nonporous ASW). The HCOOH molecule was deposited at 15 K and then the temperature was ramped. The fragment ions such as H^+ and HCO^+ are sputtered intensively from HCOOH but the H^+ or D^+ attached molecular ions are rather small in intensity compared to the $H^+(D_2O)$ and $D^+(D_2O)$

ions from the substrate. This is because protons are transferred preferentially from HCOOH to D_2O during breakage of the hydrogen bonds: $HCOOH + D_2O \rightarrow HCOOH^- + H^+(D_2O)$. The $H^+(HCOOH)_n$ ions are known to be sputtered from the islanded HCOOH molecules formed at higher coverage.[14] The absence of such molecular ions and the emission of the $H^+(D_2O)$ ion show that most of the HCOOH molecules form the hydrogen bonds with the D_2O molecules in the present experiment. The decay of the $H^+(D_2O)$ intensity above 120 K is caused by the H/D exchange in the D_2O layer.[14] With increasing temperatures, the HCO^+(H^+) intensity gradually decreases (increases), and both HCOOH and D_2O molecules evaporate at 175 K where the Ni^+ intensity increases steeply. The HCOOH molecule basically stays on the surface without incorporation into the thin-layer bulk of water despite that the mobility of the D_2O molecules should be increased above 140 K.

Some interesting features are observed in the evolution curves above 125 K: (i) the increase (decrease) of the H^+ (HCO^+) intensity is correlated to the evolution of the $D^+(D_2O)$ intensity, and (ii) the oscillatory behavior is observed not only in the H^+ and HCO^+ intensities but also in the $D^+(D_2O)$ intensity with the opposite phase. These results suggest that the strong interactions exist between the HCOOH and D_2O molecules at the surface. In addition to the hydroxyl group, the carbonyl group of the HCOOH molecule also provides an active site for the hydrogen-bond formation. Therefore, it is reasonable that the intensity of the HCO^+ ion decreases as the hydration of the HCOOH molecule proceeds. On the other hand, the H^+ ion should be emitted from the hydrophobic CH group, and the increase in the H^+ intensity is caused by the reorientation of the molecules: i.e., the CH group faces toward the vacuum side as a consequence of the hydrogen-bond formation at the -OH and -CO sites of HCOOH. The oscillatory behaviors would be caused by the change in conformation of such a $HCOOH/D_2O$ complex.

It should be noticed that the D^+ ion is considerably small in intensity relative to the $D^+(D_2O)$ ion. For the pure D_2O layer, the intensity of the D^+ ion is about 2–3 times as high as that of the $D^+(D_2O)$ ion. Therefore, the $D^+(D_2O)$ ion in Fig. 3 is not simply caused by the emergence of the pure D_2O layer. As mentioned earlier, the D^+ ion is sputtered from the dangling OD bonds. This result should be ascribed to the hydration structure of the formic acid: the number of the dangling bonds decreases since the D_2O molecules hydrate HCOOH in such a way that the -OD group is oriented towards oxygen of the -CO and -OH groups. A similar phenomenon is observed for the hydration of the HCl molecule,[19] in which the electrostatic interaction between the Cl^- ion and the polar D_2O molecules would play a role. Although the acidity of HCOOH is much smaller than HCl, the electrostatic interaction between the polar HCOOH and D_2O molecules might also be responsible for the decrease in the D^+ intensity.

C. C_3H_7OH on the D_2O surface

In Fig. 4 are displayed temperature evolutions of the secondary ions from the C_3H_7OH (1 ML) molecules adsorbed on the D_2O layer (50 ML, nonporous ASW). Fragment ions are the dominant secondary-ion species from the C_3H_7OH molecule. It is known that the protonated molecular ions are sputtered intensively from smaller alcohols such as CH_3OH,[15] but the intensity of the protonated C_3H_7OH molecule is considerably small since the fragmentation of the alkyl group occurs more preferentially than the proton transfer reaction. Similar to the HCOOH molecule, the C_3H_7OH molecule basically exists on the topmost layer without incorporation into the D_2O layer up to 180 K.

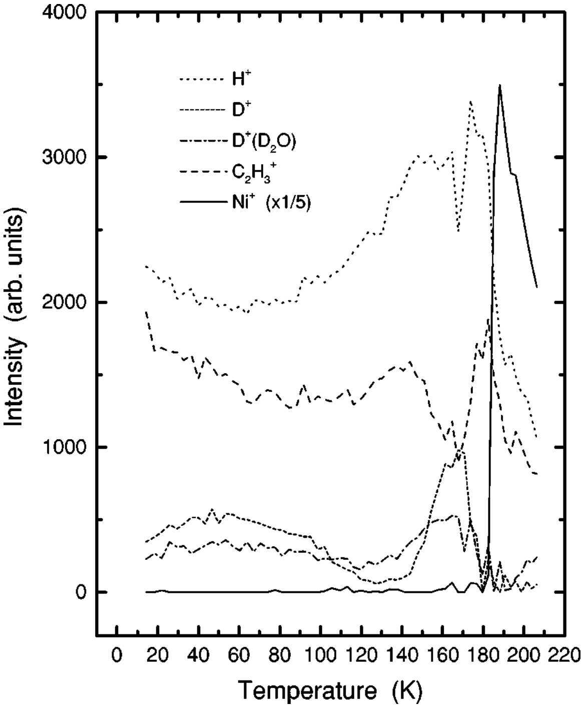

FIG. 4. Temperature evolutions of TOF-SIMS intensities from the C_3H_7OH (1 ML) adsorbed D_2O surface (50 ML, nonporous ASW). The C_3H_7OH molecule was deposited on the D_2O layer at 15 K.

The intensity of the D^+ ion changes relative to that of the $D^+(D_2O)$ ion with increasing temperature. As mentioned earlier, this phenomenon should be ascribed to the hydrogen-bond reorganization: a marked decrease in the D^+ intensity for $100\ K < T < 145\ K$ results from the formation of hydrogen bonds between the D_2O and C_3H_7OH molecules. In this respect, it is known that the hydrogen-bond reorganization of methanol starts to occur on the D_2O-ice layer above 60 K and is almost completed up to 100 K.[15] A higher temperature is required for the reorganization of the C_3H_7OH molecules probably due to the larger alkyl group.

In the temperature range between 145 and 175 K, the D^+ and $D^+(D_2O)$ ions (H^+ and $C_2H_3^+$ ions) exhibit a peak (a dip) in intensity. The increase in intensity of D^+ relative to $D^+(D_2O)$ indicates that "free" water molecules evolve on the surface due to the enhanced mobility of the D_2O molecules. This result can be interpreted in terms of the hydrophobic hydration or the onset of the formation of the first hydration shell around the alkyl group, as manifested by the concomitant decay of the $C_2H_3^+$ ion. It should be noticed that such hydrophobic hydration ($T > 145$ K) costs no dangling bonds

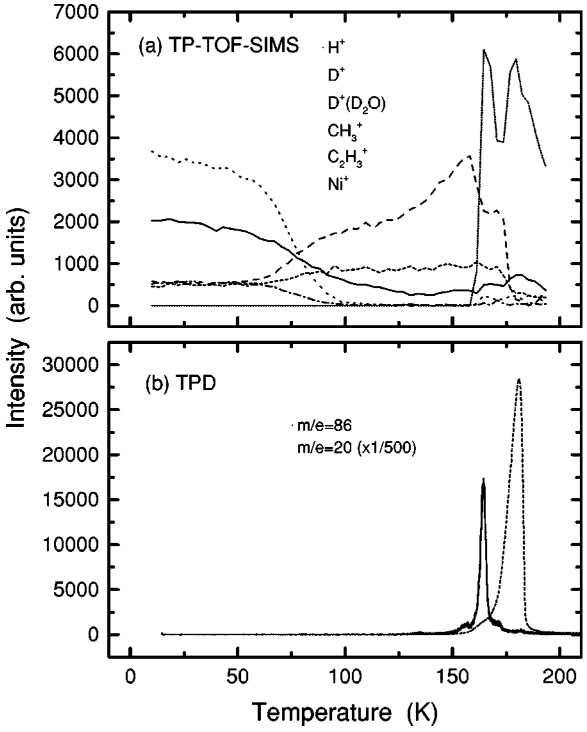

FIG. 5. (a) The TP-TOF-SIMS intensities of typical secondary ions from the C_6H_{14} (1 ML) adsorbed D_2O-ice surface (50 ML, nonporous ASW). (b) The TPD spectra of the C_6H_{14} ($m/e=86$) and D_2O (20) molecules obtained under the same temperature ramp as in (a).

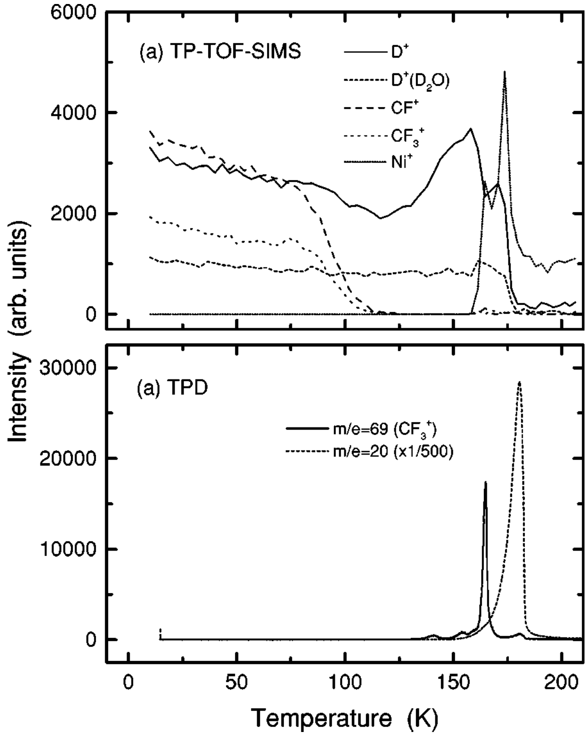

FIG. 6. (a) The TP-TOF-SIMS intensities of typical secondary ions from the C_6F_{14} (1 ML) adsorbed D_2O-ice surface (50 ML, nonporous ASW). (b) The TPD spectra of the C_6F_{14} (the fragment CF_3^+ ion; $m/e=69$) and D_2O molecules obtained under the same temperature ramp as in (a).

of the D_2O molecules, providing a sharp contrast to the hydrophilic hydration ($100\ \mathrm{K} < T < 145\ \mathrm{K}$). The hump of the Ni^+ intensity, which occurs for the pure water films at 165 K, is missing. Similarly, the Ni^+ intensity from the HCOOH-adsorbed D_2O layer exhibits a considerably small hump as shown in Fig. 3. These results indicate that the monolayer of the polar molecules tends to suppress the morphological change of the "bulk" water films.

D. Nonpolar molecules on the ASW surface

Figure 5(a) shows the typical TOF-SIMS intensities from the C_6H_{14} (1 ML) molecule adsorbed on the D_2O layer (50 ML, nonporous ASW). Only the fragment ions are emitted from the C_6H_{14} molecule. Their intensities decrease steeply above 70 K, and the surface is finally covered with the pure D_2O layer above 100 K. This result might be elucidated by the simple desorption of the C_6H_{14} molecule from the surface. In order to deny such a possibility, the TPD spectrum of the C_6H_{14} molecule ($m/e=86$) was measured: the result is shown in Fig. 5(b). The main desorption peak of the C_6H_{14} molecules occurs at 164 K, indicating that they are once incorporated completely in the thin-layer bulk of D_2O and then desorb. The bump occurs in the TPD spectrum of D_2O simultaneously with the peak of C_6H_{14}. These features in the TPD spectra are quite similar to those reported by Kay and co-workers,[3] but the film preparation in the present study is completely different from the previous ones in which nonpolar molecules are first deposited and then it is covered with the thick water layer. No experimental evidence for the dissolution of the nonpolar molecules at the surface of the nonporous ASW has been presented in the previous studies. It should be noticed that the desorption of the C_6H_{14} molecules occur concomitantly with the morphological change of the D_2O layer. The incorporated C_6H_{14} molecules have very little effect on the property of the ASW layer, providing a sharp contrast to the adsorption of amphiphiles.

In Fig. 6 are shown (a) the TP-TOF-SIMS intensities and (b) the TPD spectra for the C_6F_{14} (1 ML) molecule adsorbed on the D_2O (50 ML: nonporous ASW) layer. The fragment ions are the main species from the C_6F_{14} molecule in both SIMS and TPD. The adsorbed molecules disappear completely from the surface above 110 K. This result should be ascribed to the incorporation of the molecules into the D_2O layer, since the main TPD peak of the C_6F_{14} molecule occurs at 165 K. The features in the TPD spectra are quite similar to those in Fig. 5(b). Note that the intensity of the sputtered $D^+(D_2O)$ ion is almost independent of the presence/absence of the C_6F_{14} molecules on the surface. Probably, the C_6F_{14} molecules are so hydrophobic that they tend to form scattered islands on the D_2O layer. Therefore, the incorporation of the molecule should occur at the limited interfaces. This might be the reason for a delay in the complete uptake of the C_6F_{14} molecule compared to the C_6H_{14} molecule which has a better wettability on the D_2O layer. Thus, basically the same results are obtained for the hydration/dehydration of the nonpolar molecules.

IV. DISCUSSION

The hydrophobic hydration in liquid water has so far been discussed extensively in terms of solute size, shape, and temperature effects by means of analytical theories, computer simulation, and experiment.[18,20–31] However, there remains considerable debate about its molecular origins.[25] In particular, the changes in the hydrogen bonding structure of water in the vicinity of a nonpolar solute molecule are still not well understood. In the framework of the so-called "iceberg" model suggested by Frank and Evance,[18] it has been believed that hydrophobic solutes increase the hydrogen bonding structure of water in the first hydration shell and that the cavity formation is the important first step in solvating any nonpolar solutes in water. This model assumes the spontaneous formation of a highly ordered cage of water molecules around the nonpolar solute. However, the idea of almost crystalline hydration structures is not supported by recent experiments of neutron diffraction and extended x-ray absorption fine structure spectroscopy:[29–31] the hydration cage, existing in the liquid, is more loosely defined than in the solid system. According to the small-size model,[20,21] on the other hand, a poor solubility of nonpolar molecules in water is attributed to the excluded volume effect, which is amplified by the small size of water molecules themselves. Thus, the exact nature of the structural ordering and cavity formation has remained unclear, but the nonpolar solvation process results in a net loss of entropy.

The ASW prepared at 15 K contains nanometer-sized cavities and small molecules such as N_2, CO, and CO_2 are known to be incorporated preferentially in the inner pores rather than adsorbed on the surface.[32,33] This phenomenon might be instructive to understand the hydrophobic hydration in terms of the role of cavities. The experimental result is interpreted by the diffusion of adsorbed molecules on the inner-pore surfaces and their stabilization at the higher coordination sites formed in cavities. However, the heavier C_6H_{14} and C_6F_{14} molecules are not incorporated in cavities of the porous ASW due to the poor mobility at 15 K. The polar molecules are hardly incorporated in the cavities as well because of the preferential formation of hydrogen bonds at the surface.[14,15] In any case, the cavities collapse up to 70 K, so that this phenomenon is not straightforwardly related to the hydrophobic hydration observed in the present experiment. On the nonporous ASW film, therefore, the hydrophobic hydration should occur via the opening of cavities followed by the formation of cage structures but is independent of the bulk diffusion of the water molecules.

There exist some experimental evidences for the presence of mobile molecular species on the surface even below 100 K. The polar molecules, such as CH_3OH, HCOOH, and CH_3NH_2, undergo the hydrogen-bond reorganization on the D_2O layer in the temperature range 60–100 K.[14,16] It is also likely that the surface diffusion of the D_2O molecules is promoted by the interplay with the adsorbates, as inferred from the fact that the D_2O molecules adsorbed on the surfaces of the condensed CH_3OH and CH_3NH_2 molecules are readily incorporated in the bulk in this particular temperature range.[14,16] Thus, the interaction between the mobile D_2O and nonpolar molecules on the surface may result in some form of hydrates even below 100 K. However, the mechanism of the cavity formation or the incorporation of the molecules into the bulk ASW below 100 K is not clear. The opening a cavity requires breaking the hydrogen bonds, but no drastic change is observed in the intensity of D^+ relative to $D^+(D_2O)$ during the uptake of the C_6H_{14} and C_6F_{14} molecules [see Figs. 5(a) and 6(a)]. In any case, the hydrogen-bond reorganization occurs at the "interface" of the solute molecules, where none of the hydrogen bonds of water is pointed directly towards the solute, thereby maximizing the number of water-water hydrogen bonds. There exist many hydrogen-bond defects in the bulk ASW, so that the reorganization of the D_2O molecules can be realized by rotation without diffusion. The cavities might be formed spontaneously around the nonpolar molecules in the course of the ordering of the D_2O molecules.

The solubility of nonpolar molecules in ASW, though not determined exactly from the present experiment, should be much higher than that in liquid water [e.g., the molar fraction of hexane dissolved in water at room temperature is in the order of 10^{-6} (Ref. 34)], suggesting that ASW is not a simple supercooled extension of liquid water. This phenomenon may be better explained on the basis of the polyamorphism of glassy and supercooled water at low temperatures.[35–38] Unlike other substances, water can form at least two distinct forms of glass, known as low-density and high-density amorphous ice (LDA and HDA, respectively), and the nature of the supercooled and stable water can be understood by the transition between LDA and HDA. Although the properties of the vapor-deposited ASW film depend sensitively on the growth condition and substrate, etc., the annealed ASW is basically identical to LDA in structure.[37,38] As far as the short-range structures are concerned, there exist significant similarities between LDA and ice-Ih, and between HDA and liquid water.[39] Therefore, the formation of crystalline ice or clathratelike hydration shell would be facilitated in the bulk LDA with a relatively open structure, in which the nonpolar solute may play a role as a nucleus for the ice crystallization. The distinct phases of LDA and HDA terminate above the critical point, so that the properties of stable liquid water should be different largely from those of LDA. It is thus concluded that the formation of water cage presumed in the conventional "iceberg" model of hydrophobic hydration is rather realized in LDA or ASW but, in liquid water and probably HDA, the imperfect hydration shell causes a much poorer solubility of nonpolar molecules. In this context, the abrupt dehydration of the C_6H_{14} and C_6F_{14} molecules above 165 K invokes the emergence of the other phases of water. They are most likely liquid water, as inferred from the poor solubility of nonpolar molecules and the occurrence of the morphological change of the film induced by the surface tension. In this respect, Angell and coworkers[41] have recently suggested that the glass transition temperature should be reassigned to 165 ± 5 K instead of the commonly accepted value of 136 K though it is hardly observable experimentally due to the preceding crystallization above 150 K. In reality, the crystallization is not complete up to 165 K so that such a phase transition is observed clearly in the present experiment.

V. CONCLUSION

It is demonstrated that TP-TOF-SIMS is a quite powerful technique for the analysis of weak intermolecular interactions at the water-ice surface. The isotopically labeled water molecules adsorbed on the water-ice surface are incorporated into the bulk above 140 K irrespective of the preparation temperatures of the surface between 15 K and 165 K. Thus, no indication of the irreversible crystallization of ASW is obtained as far as the intermixing of water molecules is concerned. It is well known that the "crystalline" ice films (ice-Ih) are created epitaxially on the Pt(111) surface,[5,6] but they should be a metastable state formed due to the substrate effect and the local structural similarities between ASW and ice-Ih. So far, most of the studies regarding the important properties of water ice, such as crystallization[4] and proton transfer,[40] have been performed without considering the morphological change of the water-ice layer. As discussed in the present paper, however, the droplets of liquidlike water evolve above 165 K. Therefore, reinterpretation of these studies should be necessary by taking the self-diffusion and roughening phenomena into account properly.

The polar molecules such as HCOOH and C_3H_7OH exist basically on the D_2O-ice surface without incorporation in the bulk. They act as surfactants to reduce the surface tension of the liquidlike D_2O layer, as evidenced by the fact that the morphological change of the D_2O layer above 165 K is suppressed or quenched by the existence of the monolayer of these molecules. The HCOOH molecule undergoes hydration at the hydrophilic -OH and -CO groups, resulting in the reorientation of the molecule by facing the hydrophobic -CH group towards the vacuum side. The evolution of the hydrogen bonds between the HCOOH and D_2O molecules may induce the conformation change of the hydration complex, leading to the oscillatory behavior of the sputtered ion intensities as a function of temperature. The C_3H_7OH molecules undergo not only the hydrophilic hydration ($100\ \mathrm{K} < T < 145\ \mathrm{K}$) but also the hydrophobic hydration ($T > 145\ \mathrm{K}$) due to the emergence of the mobile D_2O molecules at the surface.

The nonpolar solutes such as C_6H_{14} and C_6F_{14} are incorporated in the D_2O layer completely even below 100 K due to the hydrophobic hydration. This phenomenon is characteristic in ASW, as a consequence of the local structure similarities between ASW and crystalline ice, and arises from the hydrogen-bond reorganization of D_2O leading to the ice-cage formation around the nonpolar solutes. The solubility of nonpolar molecules in liquid water is much smaller than in ASW due to the imperfect cage formation. In any case, the strongest interactions in aqueous solutions are hydrogen bonds and, hence, the nonpolar molecules are considered as "hard spheres" which are simply accommodated in the cavities. The hydrophobic hydration is intimately related to the properties of water itself and the ASW is not a simple extension of the liquid water. No dangling bonds of water molecules are thought to exist in the cavities. Therefore, the TOF-SIMS intensities of bare protons emitted from the dangling OH (or OD) bonds are not reduced if the hydrophobic hydration takes place. In the case of the hydrophilic hydration, on the other hand, the emission of bare protons is suppressed considerably relative to the hydrated protons, depending on the hydration structures.

The incorporation of the polar molecules in ASW seems to be more difficult than that of the nonpolar molecules. Probably, this is because the formation of the hydrogen bonds at the -OH and -CO sites disturbs restructuring of water molecules to form hydration cage around the hydrophobic moieties. As a consequence, the polar molecule stays on the surface by excluding the hydrophobic end group from the hydrogen-bond network of the water layer. The polar molecules undergo hydrophobic hydration in part only if the liquidlike water evolves.

It is thus concluded that the surface of water ice is highly dynamic in nature and there exist some characteristic temperatures by which the water properties and the hydration phenomena can be elucidated: the hydrogen-bond reorganization associated with the surface diffusion of molecules takes place in the temperature range 60–100 K, whereas the mobile water molecules evolve in the bulk above 140 K, leading to the morphological change of the film at 165 K.

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