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# Hydrogen bonding between water and methanol studied by temperature-programmed time-of-flight secondary ion mass spectrometry

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The interactions between condensed molecules at cryogenic temperatures (15–200 K) have been investigated on the basis of secondary ion mass spectrometry. It is demonstrated that the protonated molecular ions, emitted via the proton transfer reactions, provide us unique information about the reorganization of hydrogen-bonded molecules. From the CH<sub>3</sub>OH molecules adsorbed on the D<sub>2</sub>O–ice surface, the D<sup>+</sup>(CH<sub>3</sub>OH) ions are sputtered predominantly in the temperature range between 100 and 150 K since most of the CH<sub>3</sub>OH molecules are bound to the D<sub>2</sub>O layer via hydrogen bonds. A rapid and almost complete H/D exchange, yielding the D<sup>+</sup>(CH<sub>3</sub>OD) species, occurs above 150 K due to the enhanced mobility of the surface D<sub>2</sub>O molecules. Up to the desorption temperature of 180 K, a considerable amount of methanol exists on the surface without mixing with the heavy-water layer due to hydrophobicity of the methyl group. On the methanol–ice surface, the adsorbed D<sub>2</sub>O molecules form hydrogen bonds preferentially with the CH<sub>3</sub>OH molecules and tend to be incorporated in the thin-layer bulk of methanol above 120 K. © 2003 American Institute of Physics. [DOI: 10.1063/1.1602055]

## I. INTRODUCTION

Alcohol–water solutions are an important solvent used in a wide range of chemical processes. The degree of hydrogen bonding in the coordinating water network would have a profound effect on the rate of chemical reactions in solvents. The hydroxyl group allows alcohols to form hydrogen bonds and is responsible for their good solubility in water. In contrast, the hydrophobic alkyl group does not participate in the hydrogen bonding network in water. Because of such amphiphilic nature of alcohols, the microscopic structures of hydrated methanol in liquid water have attracted considerable attention.<sup>1–6</sup> At water-rich compositions, it has been revealed that the hydrophobic hydration occurs with clathrate structure around the nonpolar methyl group. In a methanol-rich solution, the methanol–methanol molecular interactions may be perturbed by the presence of water.

As the first step of solvation or chemical reactions in solvents, the adsorption of molecules on the surface of liquid and solid water and the transport of adsorbed molecules into the bulk across the gas–water interface are of importance. The vibrational data are useful for characterization of molecular adsorbates on a crystalline water–ice surface, and extensive studies have been performed on the basis of infrared absorption spectroscopy.<sup>7,8</sup> Recently, the surfaces of condensed water and methanol have been investigated by employing electron spectroscopic techniques<sup>9,10</sup> such as metastable impact electron spectroscopy (MIES) and ultra-

violet photoelectron spectroscopy (UPS). On the other hand, secondary ion mass spectrometry (SIMS) may have a potentiality for characterization of molecules on the surface due to its extremely high surface sensitivity. The protonated water cluster ions, H<sup>+</sup>(H<sub>2</sub>O)<sub>n</sub>, are known to be sputtered preferentially from the water–ice surface by impact of keV-He<sup>+</sup> ions<sup>11</sup> and very low-energy Cs<sup>+</sup> ions<sup>12</sup> as a consequence of the hydration of excess protons. Since protons come from the neighboring water molecules and are created in the course of the breakage of hydrogen bonding, the intermolecular interactions in terms of hydrogen bonds would be studied by the detection of the protonated molecular ions. In order to ensure such a possibility as well as the high surface sensitivity of SIMS, the ion-emission mechanism from the molecular-solid surfaces should be clarified in more detail.

In the present paper, we report on the temperature-programmed time-of-flight SIMS (TP-TOF-SIMS) investigation of the interactions between D<sub>2</sub>O and CH<sub>3</sub>OH molecules on the heavy-water and methanol surfaces in the temperature range from 15 to 200 K. The possibility for the hydration (methanolation) of the CH<sub>3</sub>OH molecules (the D<sub>2</sub>O molecules) is explored on the basis of the evolutions of protonated molecular ions, as well as thermally activated H/D exchange.

## II. EXPERIMENT

Experiments were conducted in a stainless steel ultrahigh-vacuum chamber of base pressure below  $1 \times 10^{-8}$  Pa. The vacuum system was equipped with an

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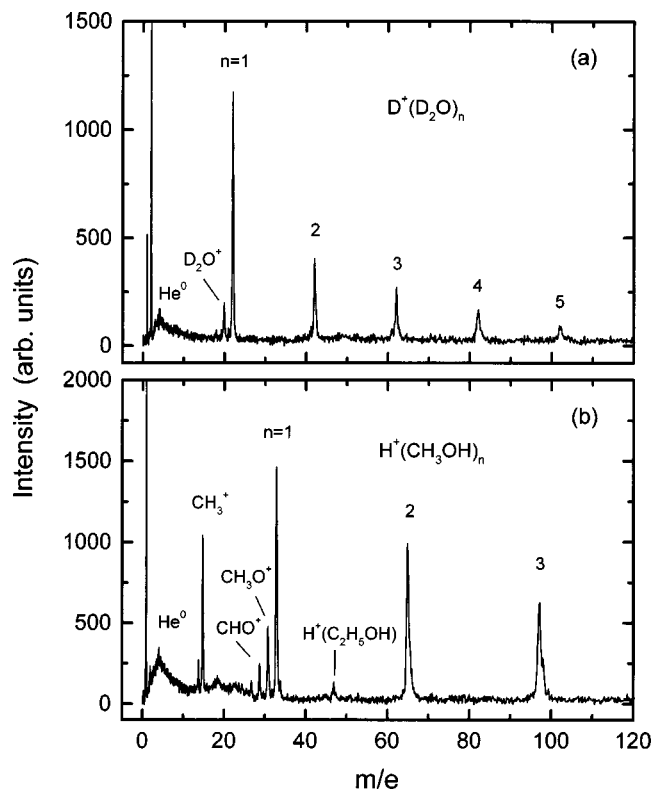


FIG. 1. TOF-SIMS spectra of positive ions from thin layers (50 ML) of  $\text{D}_2\text{O}$  and  $\text{CH}_3\text{OH}$  deposited at 15 K by bombardment of 1.5 keV  $\text{He}^+$  ions.

electron-impact-type ion source, a linear-TOF tube, a quadrupole mass spectrometer for gas analysis, a hemispherical electrostatic analyzer, an x-ray source, an UV source, and a low-energy electron gun. The  $\text{He}^+$  ions were chopped by an electrostatic deflector into pulses with width of 200 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  $\text{He}^+$  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  $\text{He}^+$  beam with a low incident flux ( $0.2 \text{ nA/cm}^2$ ) was used. The substrate was a polycrystalline Ni sheet 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. The  $\text{D}_2\text{O}$  and  $\text{CH}_3\text{OH}$  molecules were dosed from separate gas inlet systems to the substrate by backfilling the vacuum system. One-monolayer (1 ML) coverage of the adsorbed molecules was determined from the decay curve of the sputtered ion yields from the substrate as a function of exposure, and the film thickness was estimated on the basis of this value. The TOF-SIMS spectra were collected at time intervals of 30 s with the temperature increasing rate of about  $0.1 \text{ K s}^{-1}$  ( $T > 100 \text{ K}$ ).

### III. EXPERIMENTAL RESULTS

Figure 1 shows TOF-SIMS spectra of positive ions sputtered from (a)  $\text{D}_2\text{O}$  and (b)  $\text{CH}_3\text{OH}$  layers by bombardment

of 1.5 keV  $\text{He}^+$  ions. The films were deposited with a thickness of 50 ML at substrate temperature of 15 K. The most dominant secondary ion species from the  $\text{D}_2\text{O}$  and  $\text{CH}_3\text{OH}$  layers, respectively, were  $\text{D}^+$  and  $\text{H}^+$  ions. The cluster ions, such as  $\text{D}^+(\text{D}_2\text{O})_n$  and  $\text{H}^+(\text{CH}_3\text{OH})_n$ , are emitted, together with some fragment ions such as  $\text{CH}_3^+$  and  $\text{CH}_3\text{O}^+$ . A broad structure starting from  $m/e=0$  is not due to the secondary ions but is caused by the energetic  $\text{He}^0$  atoms backscattered from the surface. Regarding the water cluster-ion formation, Rabalais and co-workers<sup>11</sup> reported the cluster-size distribution, the onset energies for sputtering, and the energy distributions of the sputtered  $\text{H}^+(\text{H}_2\text{O})_n$  ions by keV- $\text{He}^+$  ion bombardment. The present results are basically in agreement with their results except that the intensities of higher mass cluster ions are relatively small. Probably this is due to the difference in the ion detection techniques between these two studies (TOF versus  $Q$ -mass analysis). The cluster ions of the type  $(\text{D}_2\text{O})_n^+$  are not emitted except  $\text{D}_2\text{O}^+$ , suggesting that the  $\text{D}^+$  ion plays a key role in the cluster ions formation. The underlying mechanism for the creation of hydrated  $\text{D}^+$  ions is the ion-dipole interaction and the hydrogen bonding, so that the smaller sized  $\text{D}^+$  ion may collect the polar  $\text{D}_2\text{O}$  molecules efficiently. The same is true for the formation of the  $\text{H}^+(\text{CH}_3\text{OH})_n$  ions as well. In Fig. 1(b), a small peak at  $m/e=47$  can be assignable either to the protonated ethanol,  $\text{H}^+(\text{C}_2\text{H}_5\text{OH})$ , or to a complex of  $\text{CH}_3^+$  and  $\text{CH}_3\text{OH}$ . The former may be more likely in terms of the ion size.

Figure 2 shows evolutions of typical secondary-ion yields from the  $\text{D}_2\text{O}$ -ice film (50 ML) as a function of temperature. The yields of the  $\text{D}^+(\text{D}_2\text{O})_n$  ( $n \geq 2$ ) ions decay considerably in the temperature range of 50–120 K whereas the decrease in the  $\text{D}_3\text{O}^+$  yield is not so remarkable. The  $\text{D}_2\text{O}$  molecules desorb from the surface at temperatures of 180–185 K as revealed from sudden drops of the  $\text{D}^+$  and  $\text{D}_3\text{O}^+$  yields as well as the steep evolution of the  $\text{Ni}^+$  and  $\text{Ni}^+(\text{D}_2\text{O})_n$  yields. The peak position of the latter agrees well with the decay onset of the former, but an additional hump appears in the  $\text{Ni}^+$  and  $\text{Ni}^+(\text{D}_2\text{O})$  yields around 170 K. Probably, this is because the morphological change or roughening occurs before desorption of the  $\text{D}_2\text{O}$  layer. The  $\text{D}_2\text{O}$  molecules still remain on the surface above 180 K as evidenced by the emission of the  $\text{Ni}^+(\text{D}_2\text{O})$  ion. The sputtering yields of  $\text{Ni}^+$  from the clean substrate are negligibly small. It is known that the metal complex ions evolve, together with the bare metal ions, provided that the surface is covered with thin layers of molecules.<sup>13</sup>

In Fig. 3 are shown evolutions of the typical secondary-ion yields sputtered from the  $\text{CH}_3\text{OH}$  layer (50 ML) as a function of temperature. The yields of the protonated cluster ions decay markedly at temperatures above 50 K, whereas the yield of the fragment  $\text{CH}_3^+$  ion is relatively little changed. The evolution of the other fragment-ion species, such as  $\text{CHO}^+$  and  $\text{CH}_3\text{O}^+$ , is similar to that of the  $\text{CH}_3^+$  ion (not shown explicitly). The  $\text{CH}_3\text{OH}$  layer desorbs at temperatures above 160 K where sharp peaks emerge in the yields of the  $\text{CH}_3^+$ ,  $\text{H}^+(\text{CH}_3\text{OH})$ , and  $\text{Ni}^+$  ions. This is in contrast to the desorption behavior of the  $\text{D}_2\text{O}$  ice. Above 160 K, the chemisorbed  $\text{CH}_3\text{OH}$  molecules remain on the surface as

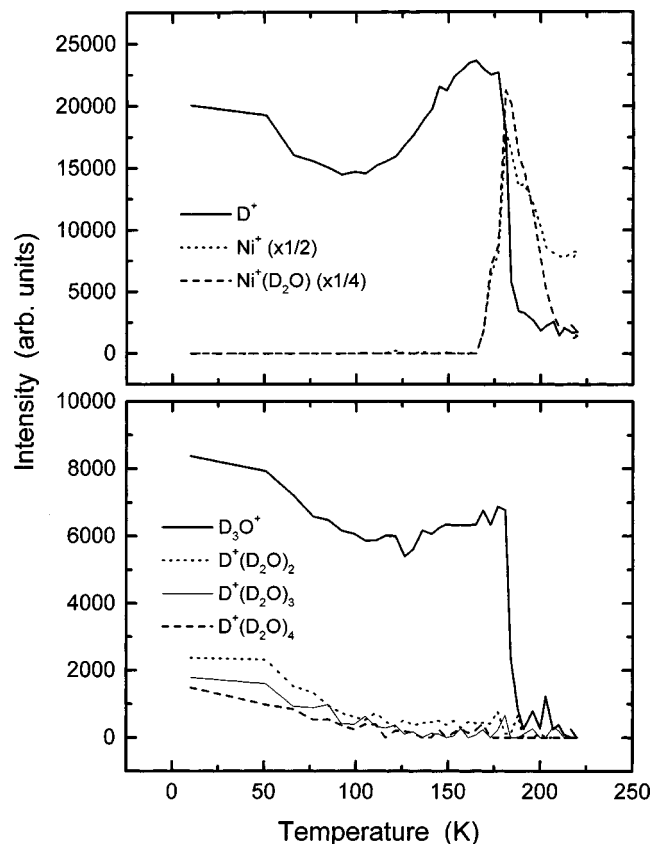


FIG. 2. Evolutions of typical secondary-ion yields from the pure  $D_2O$  layer (50 ML) as a function of temperature. The  $D_2O$  molecules were deposited at temperature of 15 K and the surfaces were irradiated with a pulsed  $He^+$  beam of 1.5 keV.

evidenced by the emission not only of the  $CH_3^+$  ion but also of the  $Ni^+(CH_3OH)$  ion.

The difference in the evolution curves between  $CH_3^+$  and  $H^+(CH_3OH)_n$  may be ascribed to the hydrogen bonds: The yields of the  $H^+(CH_3OH)_n$  ions are thought to be affected by the presence/absence of the hydrogen bond whereas the hydrophobic methyl group has a relatively weak interaction with the neighboring molecules. Therefore, the decay of the  $H^+(CH_3OH)_n$  yields by annealing would be related to the reorganization of the  $CH_3OH$  molecules to form the hydrogen bonds. The same holds true for the  $D_2O$  layer, where the hydrogen bond is formed more readily than methanol due to the absence of hydrophobic groups, resulting in the completion of reorganization at lower temperatures. Thus, it is suggested that the yields of the solvated protons or deuterons depend on the formation of hydrogen bonds whereas the yield of the  $CH_3^+$  ion is basically related to the number of the  $CH_3OH$  molecules or their orientations on the surface.

Of interest is how the mixing occurs between the  $D_2O$  and  $CH_3OH$  molecules on the surface. Figure 4 shows the evolutions of typical secondary ions sputtered from the  $CH_3OH$ -adsorbed  $D_2O$ -ice surface as a function of temperature; the  $D_2O$  (50 ML) and  $CH_3OH$  (1 ML) molecules were deposited successively at 15 K. The deuterated methanol,  $D^+(CH_3OH)$ , is sputtered considerably relative to  $H^+(CH_3OH)$ . The former should be created at the water-methanol interface via the breakage of the hydrogen bonds

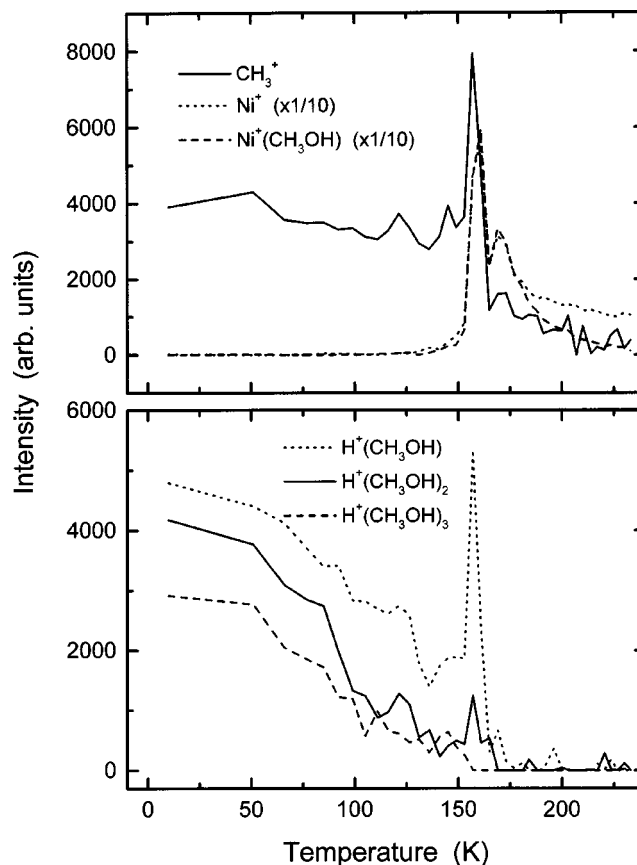


FIG. 3. Evolutions of secondary-ion yields from the pure  $CH_3OH$  layer as a function of temperature. The  $CH_3OH$  molecules were deposited at temperature of 15 K and the surfaces were irradiated with a pulsed  $He^+$  beam of 1.5 keV.

while the latter comes from the condensed  $CH_3OH$  molecules (or islands). With increasing temperature, the  $H^+(CH_3OH)$  yield decays due to reorganization of the  $CH_3OH$  molecules in the island, resulting in the formation of hydrogen bonds with the  $D_2O$  layer. In the temperature range of 100–140 K, the  $D^+(CH_3OH)$  ion becomes a dominant species, where most of the  $CH_3OH$  molecules are bound to the  $D_2O$  surface or hydrated partly in the thin-layer bulk. Above 150 K, the isotope exchange occurs drastically between the hydroxyl groups of the  $D_2O$  and  $CH_3OH$  molecules, resulting in the dominance of the  $D^+(CH_3OD)$  ions. The desorption of the  $D_2O$  layer occurs above 185 K together with the  $CH_3OH$  molecules. The  $CH_3^+$  and  $D_3O^+$  yields are enhanced for  $100\text{ K} < T < 170\text{ K}$ . This might be caused by the reorientation of the  $CH_3OH$  molecule as a result of the hydration: the  $CH_3OH$  molecule stands with the hydrophobic  $CH_3$  end toward the vacuum. Such a phenomenon is well known to occur for water-methanol mixtures in the liquid phase at room temperature:<sup>14,15</sup> methanol keeps the hydrophobic methyl group on the surface to minimize their potential energy in the water solvent. No marked decay of the  $CH_3^+$  yield occurs up to the desorption temperature, indicating that a considerable amount of methanol exists on the surface without mixing with the  $D_2O$  layer. The proton-attached or isotope-exchanged heavy water ions, such as  $H^+(D_2O)$  and  $H^+(HDO)$ , are trivial at any temperature.



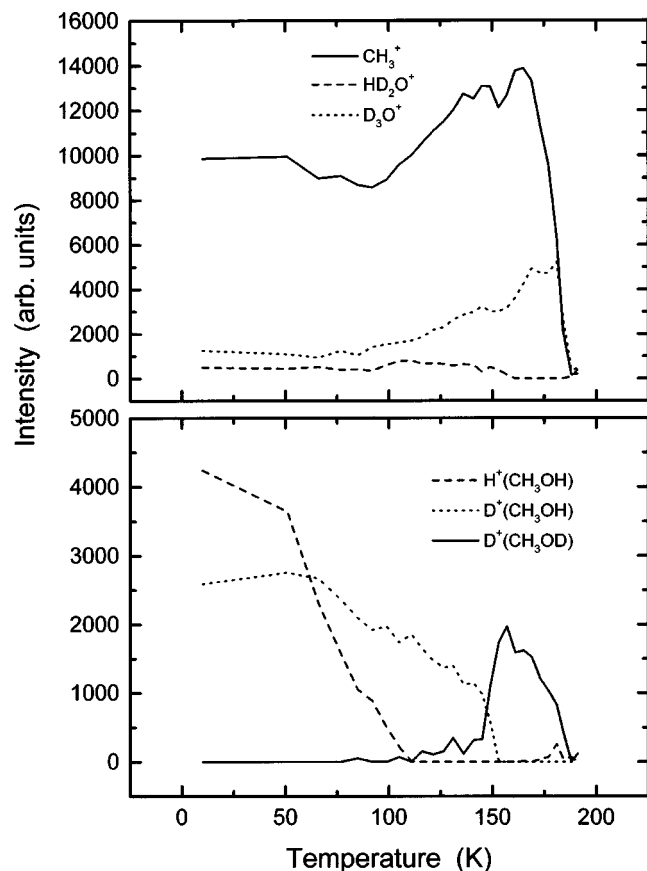


FIG. 4. Temperature evolutions of some secondary ion yields from the  $\text{CH}_3\text{OH}$ -adsorbed  $\text{D}_2\text{O}$  layer. The  $\text{CH}_3\text{OH}$  molecule (1.0 ML) was deposited on the  $\text{D}_2\text{O}$  layer (50 ML) at temperature of 15 K.

The experimental results for the opposite combination, i.e., the adsorption of the  $\text{D}_2\text{O}$  molecule (1 ML) on the  $\text{CH}_3\text{OH}$  layer (50 ML), are shown in Fig. 5. The yield of the  $\text{D}_3\text{O}^+$  ion sputtered from the adsorbed  $\text{D}_2\text{O}$  molecules decays monotonically by annealing and disappears almost completely above 120 K. The same tendency is observed for the sputtered  $\text{D}^+$  ion. Regarding the proton transfer, the protonated heavy water,  $\text{H}^+(\text{D}_2\text{O})$ , is a minor species whereas the deuterated methanol,  $\text{D}^+(\text{CH}_3\text{OH})$ , is dominant for  $T < 100$  K, indicating that the excess protons (or deuterons) created in the hydrogen bonds are preferentially attached to the  $\text{CH}_3\text{OH}$  molecule. After the  $\text{D}_3\text{O}^+$  ion disappears completely at 120 K, the  $\text{H}^+(\text{CH}_3\text{OH})$  ions evolve. Since the  $\text{H}^+(\text{CH}_3\text{OH})$  ion is created due to breakage of the hydrogen-bonded methanol molecules, its evolution indicates that the surface tends to be covered with a pure methanol layer above this temperature. In contrast to the results shown in Fig. 4, very few  $\text{D}^+(\text{CH}_3\text{OD})$  ions are sputtered at any temperature. The  $\text{D}_2\text{O}/\text{CH}_3\text{OH}$  layer desorbs at 160 K; the same temperature as for pure methanol. The  $\text{CH}_3^+$  yield is considerably high at low temperatures despite the fact that the surface might be covered with the  $\text{D}_2\text{O}$  molecules. The yield is rather higher than that for the pure methanol layer (110 K  $< T < 150$  K, see also Fig. 3). These results also have some implications for hydrophobic interactions of the methyl group with  $\text{D}_2\text{O}$ , which are governed by the perturbation of the near-neighbor solvation structure.

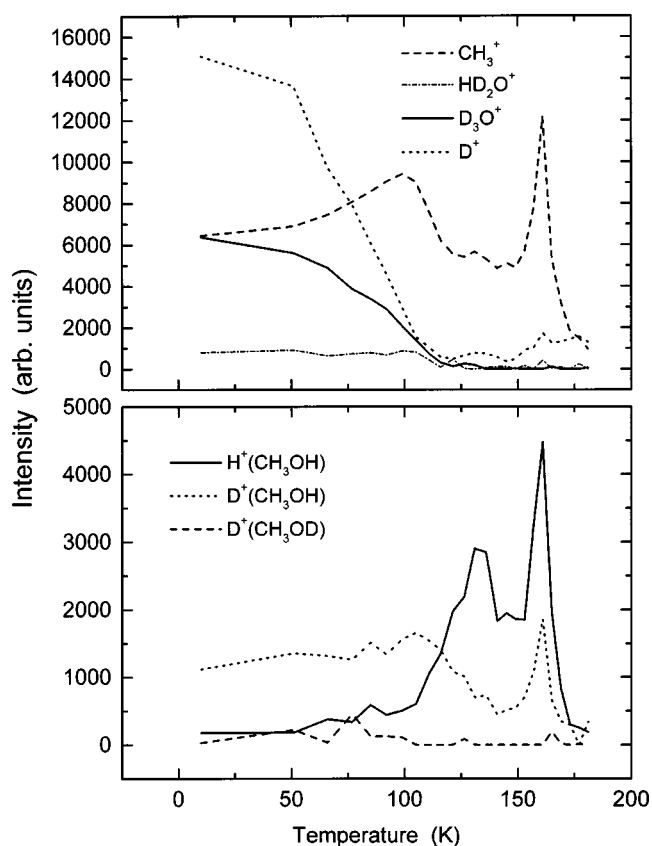


FIG. 5. Temperature evolutions of some secondary-ion yields from the  $\text{D}_2\text{O}$ -adsorbed  $\text{CH}_3\text{OH}$  layer. The  $\text{D}_2\text{O}$  molecule (1.0 ML) was deposited on the  $\text{CH}_3\text{OH}$  layer (50 ML) at temperature of 15 K.

## IV. DISCUSSION

### A. Mechanisms of ion emission during molecular collisions

In addition to the thermally induced reorganization of molecules, some interesting results invoking the cations emission mechanism from the hydrogen-bonded molecules are obtained. It is well known that emission of singly charged atomic ions from metal and semiconductor surfaces is enhanced largely due to the adsorption of oxygen atoms.<sup>16</sup> This phenomenon has been elucidated in terms of the bond breaking mechanism: the ionization of the sputtered atom is believed to be the result of the breakage of partly ionic chemical bonds with oxygen.<sup>17–19</sup> The sputtered ion yields depend on the difference in the ionization potentials and the affinity levels. In the present case, similar charge exchange processes would occur during the intermolecular collision as a consequence of the breakage of the hydrogen bonds, where the exchange of protons, rather than electrons, is responsible for the formation of cations. Therefore, such an ionization channel, based on the proton-transfer reaction, can be elucidated in terms of the *hydrogen-bond breaking mechanism*, in which the difference in the proton affinity between hydrogen-bonded molecules should be the most important ingredients for determining the sputtered ion species and their yields. Since the proton affinity of methanol (184.9 kcal/mol) is higher than that of water (173.0 kcal/mol),<sup>20</sup> the deuterated methanol (protonated heavy water) is sputtered

intensively (negligibly) from the hydrogen-bonded  $\text{CH}_3\text{OH}$  and  $\text{D}_2\text{O}$  molecules;  $\text{CH}_3\text{OH} + \text{D}_2\text{O} \rightarrow \text{D}^+(\text{CH}_3\text{OH}) + \text{OD}^-$ .

For the emission of cluster ions, the microscopic surface structures or morphology of the water and methanol layers would be important. Amorphous solid water (ASW) is formed at temperatures between 80 and 140 K, while cubic crystalline ice is created irreversibly above 140 K. The ASW grown at temperatures below 70 K is characterized by a microporous structure (referred to as porous amorphous solid water: PASW). Therefore, the heavy-water films prepared in the present study (deposited at 15 K) should include pores in the thin-layer bulk. Some molecules, such as  $\text{N}_2$  and  $\text{CO}$ , are incorporated in the pores of PASW.<sup>21</sup> There is extensive information about this topic from combined spectroscopic and simulation studies.<sup>22</sup> This phenomenon can also be studied by the TOF-SIMS experiments: the saturation exposure of  $\text{N}_2$  molecules on the PASW was increased by about 20–50 times as high as that on the nonporous ASW film, depending on its thickness. In the present case, however, the amount of methanol to saturate the porous  $\text{D}_2\text{O}$  film at 15 K is comparable to that for the saturation of the nonporous film prepared at 100 K, indicating that methanol adsorbs only on the top-most surface irrespective of the presence/absence of the inner pores. Probably, this is because the surface migration of these molecules is quenched due to the formation of hydrogen bonds.

The sputtering yields of the cluster ions,  $\text{D}^+(\text{D}_2\text{O})_n$  ( $n > 2$ ), decay by annealing the  $\text{D}_2\text{O}$ –ice film as seen in Fig. 2, but no strong correlation is seen between the porosity of the  $\text{D}_2\text{O}$  ice ( $T < 70$  K) and the sputtered  $\text{D}^+(\text{D}_2\text{O})_n$  yields. In crystalline ice, each  $\text{D}_2\text{O}$  molecule can form four hydrogen bonds with four other  $\text{D}_2\text{O}$  molecules in a tetrahedral arrangement. On the ASW surface, there exist three sets of water molecules;<sup>22</sup> two- or three-coordinated molecules with a dangling hydrogen, two- or three-coordinated molecules with a dangling oxygen coordination, and four-coordinated molecules with distorted tetrahedra. A larger number of hydrogen-bond disorders should exist on the ASW and PASW surfaces compared to the crystalline-ice surface. The yields of the cluster ions should be related to the imperfection of such hydrogen bonds at the surface since they are created via the breakage of hydrogen bonds. As regards the methanol layer shown in Fig. 3, it requires a higher temperature or longer time for annealing such hydrogen-bond defects, as inferred from gradual decay curves of the  $\text{H}^+(\text{CH}_3\text{OH})_n$  yields. Presumably, this is because the hydrophobic methyl group blocks reorientation of the deposited molecules and therefore the formation of hydrogen bonds.

In order to further investigate the effects of such hydrogen-bond defects, experiments similar to that in Figs. 4 and 5 were performed for ASW and methanol layers (50 ML) prepared at 100 K on which  $\text{CH}_3\text{OH}$  and  $\text{D}_2\text{O}$  molecules, respectively, were deposited at 15 K (not shown explicitly). The temperature evolutions of the sputtered ions from these surfaces are essentially the same as the present ones. Only one difference is that the  $\text{D}^+(\text{CH}_3\text{OH})$  yield in Fig. 4 is higher than that from the ASW in the temperature range below 100 K, indicating that a larger number (or size) of the  $\text{CH}_3\text{OH}$  islands tend to grow on the ASW surface at low

temperatures. On the PASW surface, the formation of methanol–methanol bonds is quenched considerably due to the presence of a larger number of dangling OD bonds or the shorter diffusion length of methanol on the rougher surface.

Another ingredient determining the sputtered ion yield is the neutralization effect. Recently, it was revealed from the experiments of low-energy proton scattering (LEPS)<sup>23</sup> and electron stimulated desorption (ESD)<sup>24</sup> that valence hole(s) can hop between the hydrogen-bonded water molecules within the time scale of ion desorption (10–100 fs). Some covalency in hydrogen bonds may be responsible for the delocalized nature of valence holes. Although the kinetic sputtering process is not so simple compared to the LEPS and ESD, the protonated molecular ions may undergo such an ion neutralization process during sputtering. The higher the number of the hydrogen-bond defects is, the less efficiently the sputtered ions are neutralized. Probably, this provides another reason for the decay in the  $\text{D}^+(\text{D}_2\text{O})_n$  and  $\text{H}^+(\text{CH}_3\text{OH})_n$  yields by annealing.

## B. Thermally induced H/D exchange and reorganization of hydrogen bonding

It is thus concluded that the protonated (deuterated) molecular ions should provide us unique information about the hydrogen bonding or solvation between water and methanol molecules. In Fig. 4, the  $\text{D}^+(\text{CH}_3\text{OH})$  ions are dominant in the temperature range of 100–150 K, indicating that most of the adsorbed  $\text{CH}_3\text{OH}$  molecules form hydrogen bonds with  $\text{D}_2\text{O}$ . Such surface-bound methanol molecules undergo a rapid and complete H/D exchange above 150 K without hydration in the bulk. It should be noted that the H/D exchange is a thermally activated process and, hence, it is a totally different phenomenon from the proton transfer reactions during sputtering. So far, the isotope exchange in bulk water has been studied extensively on the basis of Fourier transform infrared (FTIR) spectroscopy,<sup>25–27</sup> where the critical temperature around 140 K is also observed for  $\text{H}_2\text{O}/\text{D}_2\text{O}$  and  $\text{NH}_3/\text{D}_2\text{O}$  systems. Such a common feature of the H/D exchange should be ascribed to some propensity inherent in water. The ASW undergoes a phase transition to cubic ice (Ic) around this temperature, but this may not be responsible for the rapid H/D exchange: most of the FTIR experiments were done for bulk crystalline ice but basically the same results were obtained for ASW as well. In order for the H/D exchange to occur, proton transfer and rotation of water molecules are required.<sup>26</sup> On the other hand, it is recently claimed that protons are not mobile in the bulk water ice at temperatures up to 190 K on the basis of the soft landing experiment of the  $\text{H}_3\text{O}^+$  ion on the crystalline water–ice surface.<sup>28</sup> Thus, a controversy seems to exist in the detailed mechanism of the thermally activated H/D exchange in the bulk water ice.

The present result clearly shows that the hydration in the bulk is not prerequisite for the occurrence of complete H/D exchange. This is characteristic of methanol having the hydrophobic  $\text{CH}_3$  group. The dominance of the  $\text{D}^+(\text{CH}_3\text{OD})$  ion above 150 K would be related to the presence of the mobile  $\text{D}_2\text{O}$  molecules on the surface. In fact, the surface of ice, whether crystalline or amorphous, is a complex disorder-

dered system with a greater molecular mobility than that of bulk ice. It is well known that the water–ice surface is so soft that the surface structure analysis by low-energy electron diffraction<sup>29</sup> and helium atom scattering<sup>30</sup> is difficult at temperatures above 90–125 K. Although the proton jump might be quenched in the bulk water ice, the protons can migrate through the hydrogen-bond network of the mobile water layer via the structural diffusion mechanism.<sup>31</sup> In this framework, the formation of the  $D^+(CH_3OD)$  ion is facilitated since the HDO molecule, which is formed by passage of a proton through the  $CH_3OH \cdots OD_2$  hydrogen bond, can be replaced rapidly with the unreacted  $D_2O$  molecule. In this respect, the transition of water into viscous liquid, coexisting with the cubic ice, has been suggested at a critical temperature of 140 K,<sup>32</sup> but this result might be confused by heating of the ice by the incident electron beam. So far, no conclusive evidence of the liquid-like water–ice surface has been presented below 200 K, but the present result strongly suggests that the enhanced mobility of the surface  $D_2O$  molecule is responsible for the rapid H/D exchange above 150 K.

For adsorption of the  $D_2O$  molecule on the  $CH_3OH$  layer (Fig. 5), the H/D exchange would be induced for the methanolated  $D_2O$  molecules as well, but the H/D exchange was not observed explicitly. The  $D_2O$  molecules bonded to methanol are hardly detectable as ions, so that the emission of the  $D_3O^+$  ion for  $T < 100$  K shows that the islanded  $D_2O$  molecules exist on the surface. The  $D^+$  ion is sputtered from the dangling O–D bond of the outermost-layer  $D_2O$  molecules and, hence, the  $D^+$  yield varies concomitantly with the  $D_3O^+$  yield. With increasing temperature above 120 K, the surface is covered with the unreacted methanol. The decay of the  $D^+$  and  $D_3O^+$  yields by annealing implies either that the  $D_2O$  molecules dissolve in the thin-layer bulk of methanol, forming hydrogen bonds, or that the  $D_2O$  island is covered by the  $CH_3OH$  molecules without mixing. The latter would be denied since the  $H^+(CH_3OH)$  yield evolves steeply only after the complete disappearance of the  $D_3O^+$  and  $D^+$  yields. The absence of the isotope-exchanged  $D^+(CH_3OD)$  ion is simply due to the small amount of the  $D_2O$  molecules relative to the  $CH_3OH$  molecules in the mixed layer. The present result is consistent with the MIES/UPS observation<sup>10</sup> that the water layer hardly grows on the methanol multiplayer at temperature of 100 K.

As regards the behaviors of molecular desorption, there exists a noticeable difference between heavy water and methanol. At the desorption temperature, a characteristic peak appears in the yields of secondary ions from  $CH_3OH$  (see Figs. 3 and 5) whereas no such peaks occur for  $D_2O$  (Figs. 2 and 4). The sputtering yield is enhanced on substrates of heavy elements due to the formation of collision cascades towards the surface. Therefore, the ion sputtering yields would be enhanced when molecular layers are formed on the Ni substrate with a certain thickness. It is also possible that the ionization of adsorbed molecules is catalyzed by the Ni substrate or sputtered Ni atoms.<sup>13</sup> The peaks due to such an enhanced sputtering yield would be observed if the molecules desorb in the “layer-by-layer” fashion, but the peaks should be quenched or broadened if the morphological

change of the adsorbed layer occurs prior to desorption. Probably, the former (the latter) holds for the  $CH_3OH$  ( $D_2O$ ) layer.

## V. CONCLUSION

The ion-stimulated proton-transfer reactions and the thermally activated H/D exchange have been investigated between  $D_2O$  and  $CH_3OH$  molecules on the thin layers of heavy water and methanol. The protonated molecular ions are created during collisions of hydrogen-bonded neutral molecules as a consequence of the proton transfer reactions (hydrogen-bond breaking mechanism). It is demonstrated that the reorganization of hydrogen bonding between  $D_2O$  and  $CH_3OH$  molecules can be investigated successfully on the basis of the evolutions of the solvated protons (deuterons) as a function of temperature. The surface bound state is formed for the  $CH_3OH$  molecules on the  $D_2O$  layer in the temperature range above 100 K. The adsorbed methanol undergoes the almost complete H/D exchange above 150 K, suggesting that the  $D_2O$  molecules are exchanged rapidly on the surface. On the methanol layer, the adsorbed  $D_2O$  molecules form hydrogen bonds with the  $CH_3OH$  molecules preferentially and most of them are incorporated in the bulk above 120 K.

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