Hydration of ammonia, methylamine, and methanol in amorphous solid water

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A B S T R A C T

Interactions of polar protic molecules with amorphous solid water (ASW) have been investigated using temperature-programmed desorption and time-of-flight secondary ion mass spectrometry. The ammonia and methylamine are incorporated into the interior of porous ASW films. They are caged by water molecules and are released during water crystallization. In contrast, the methanol–water interaction is not influenced by pores of ASW. The methanol additives tend to survive water crystallization and are released during ASW film evaporation. The hydration of n-hexane in ASW is influenced significantly by methanol additives because n-hexane is accommodated in a methanol-induced hydration shell.

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1. Introduction

Interactions of small functionalized organic molecules with water are useful to elucidate biomolecular systems in their aqueous environments. Two important molecules in this respect are alcohols and amines. Because they have hydrophilic and hydrophobic moieties, their interaction with water is complicated. The increase in the entropy of water–alcohol mixture is much less than that expected from the ideal solution. This phenomenon has been explained by the formation of highly ordered clathrate-like water structures around the aliphatic group (the so-called 'iceberg' model) [1]. In fact, the neutron diffraction study suggested that a distorted cage is formed around the methanol molecule for a dilute methanol solution in water [2]. Furthermore, more recent neutron diffraction [3] and X-ray emission [4] data suggest that mixing of a concentrated methanol–water solution is incomplete at the molecular level. The hydration and protonation behaviors of methylamine in water have been discussed mainly based on Monte Carlo and molecular dynamics simulations [5–8]. The first hydration shell of an amino group contains three or fewer water molecules participating in hydrogen bonding. A strong hydrophobic association of methyl groups is suggested, but the hydration structure in aqueous methylamine solution can differ from that in the methanol–water mixture.

To date, intermolecular interactions or hydration of adspecies have been investigated extensively using thin films of amorphous solid water (ASW) at cryogenic temperatures [9–24]. The water molecules become mobile at the glass-transition temperature ($T_g = 136$ K) [25], as demonstrated by experiments of time-of-flight secondary ion mass spectrometry (TOF-SIMS) [26]. The crystallization kinetics of water is discussed based on temperature-programmed desorption (TPD) of simple molecular additives in ASW [27–31]. Nonpolar molecules such as CCl_4 embedded underneath thin ASW films are released explosively at the crystallization temperature of water via the 'molecular volcano' mechanism [28]. The volcano peak is also observed when N_2, O_2, CO, H_2S, OCS, CO_2, C_2H_2, SO_2, CS_2, and CH_3CN molecules are adsorbed onto porous ASW films, although the peak is absent for HCOOH, CH_3OH, and NH_3 adspecies [31]. The result of NH_3 is obscure because the TPD spectrum of ammonia is not separable from that of water, but it is categorized intuitively as a group of polar protic molecules. The specificity of methanol might be ascribed to formation of a type II clathrate hydrate [32]. Small amounts of methanol additives can modify the properties of ASW [21,26]. However, no report in the literature describes a systematic study that has elucidated the interactions of polar protic molecules with ASW. The roles of hydrogen bond formation at the polar group and water cage formation around the hydrophobic moiety are the most intriguing questions related to hydration of amphiphiles.

As described herein, the ammonia and methylamine additives interacting with porous and nonporous ASW films are studied in comparison to water–methanol interactions using TOF-SIMS and TPD. The uptake and diffusion of additives in the ASW film are investigated using TOF-SIMS. In addition, the hydration–dehydration processes of additives in the thin film interior are discussed based on TPD spectra. The roles not only of the hydrogen bond formation with water molecules but also of pores of ASW films for hydrophobic caging are specifically examined. The H/D exchange

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rate between adspecies and water is examined based on TPD as a measure of the hydrogen bond formation in the hydration state. The nonpolar *n*-hexane additive is coadsorbed with methanol and methylamine additives. Their TPD spectra are measured to shed light on hydrophobic hydration and the association of these additives in the ASW film interior.

2. Experiment

Experiments were performed in an ultrahigh vacuum (UHV) chamber with base pressure of $<1 \times 10^{-10}$ Torr. Actually, TOF-SIMS measurements were made using a primary beam of 2-keV He$^+$ ions generated in an electron-impact-type ion gun (IQE 12/38; Specs GmbH). The ion beam was incident to the sample surface at an angle of 70° after chopping into pulses using electrostatic deflectors. To extract low-energy secondary ions efficiently, a bias voltage ($\pm$500 V) was applied to the sample and a grounded mesh was placed approximately 4 mm in front of the surface. Secondary ions ejected perpendicularly to the surface were detected using a microchannel plate after passage through a field-free TOF tube. The fluence of He$^+$ in TOF-SIMS measurements was restricted below 1×10^{12} ions cm^{-2} to minimize thin film decomposition. The TPD spectra were recorded using a quadrupole mass spectrometer (QMS; IDP 300S; Hiden Analytical Ltd.) placed in a differentially pumped housing. A retractable orifice was placed approximately 3 mm distant from the sample to detect molecules desorbed from the surface.

A Ni(1 1 1) surface was used as a substrate. It was heated several times in UHV to approx. 1300 K by electron bombardment from behind. The substrate was mounted on a Cu cold finger extended from a closed-cycle helium refrigerator. Then it was cooled to 20 K. The cold finger temperature was monitored close to the sample position using Au(Fe)-chromel thermocouples. It was controlled using a digital temperature controller and a cartridge heater attached to the finger. The temperature was ramped at a rate of 5 K min^{-1} for both TPD and TOF-SIMS measurements. Thin films were deposited onto the clean Ni(1 1 1) surface by backfilling the UHV chamber with gaseous samples admitted through high precision leak valves. Liquid samples of water (H$_2$^{16}O, H$_2$^{18}O, and D$_2$O), methanol, and *n*-hexane were degassed using several freeze-pump-thaw cycles. Gaseous ammonia was admitted from a glass bottle without further purification. Methylamine vapor was created from its aqueous solution (40%) after several pumping repetitions. The vapor includes ca. 20% of H$_2$O, as estimated from comparison of the water TPD peak area of a multilayer film formed by the deposition of methylamine with that of pure water at the same exposure. Surface cleanliness of Ni(1 1 1), as well as purity of other films, was confirmed in situ by the absence of impurity peaks in TOF-SIMS spectra.

3. Results and discussion

The coverage of ASW was determined based on evolution curves of secondary ion intensities as a function of exposure [20–22]. It requires ca. 2.5 L (Langmuir: 1 L = 1×10^{-6} Torr s) to form a monolayer (ML) of water on Ni(1 1 1) at temperatures below 100 K. All additives studied here (NH$_3$, CH$_3$NH$_2$, CH$_3$OH, and C$_6$H$_{14}$) were deposited at 20 K on or underneath the ASW film at exposure of 1 L. Figure 1 shows temperature-programmed TOF-SIMS intensities from an ammonia-adsorbed ASW film. The H$_2$^{18}O molecule (20 L or 8 ML) was deposited onto Ni(1 1 1) at 20 K, forming a porous ASW film. Then the NH$_3$ molecule was adsorbed onto the film surface. The NH$_3$ adspecies disappears from the surface at T > 130–150 K, as revealed from steep decay of the NH$_4$$^+$ intensity. The increase of the Ni$^+$ ion at 160 K indicates that the ASW film dewets the Ni(1 1 1)
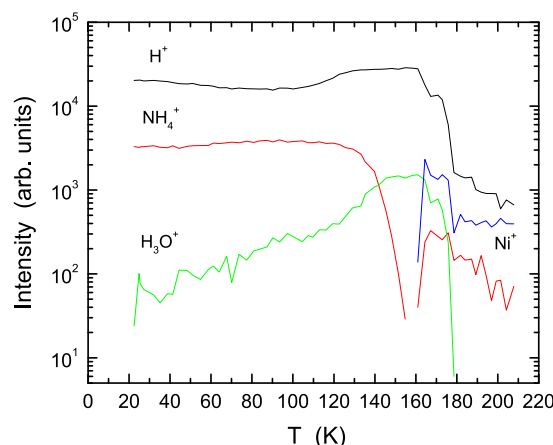

Figure 1. TOF-SIMS intensities of the ammonia adsorbed porous ASW film as a function of the substrate temperature. The H$_2$^{18}O molecule (20 L) was deposited on Ni(1 1 1) at 20 K. Then the NH$_3$ molecule (1 L) was adsorbed onto it at 20 K. The temperature ramp rate was 5 K min^{-1}.
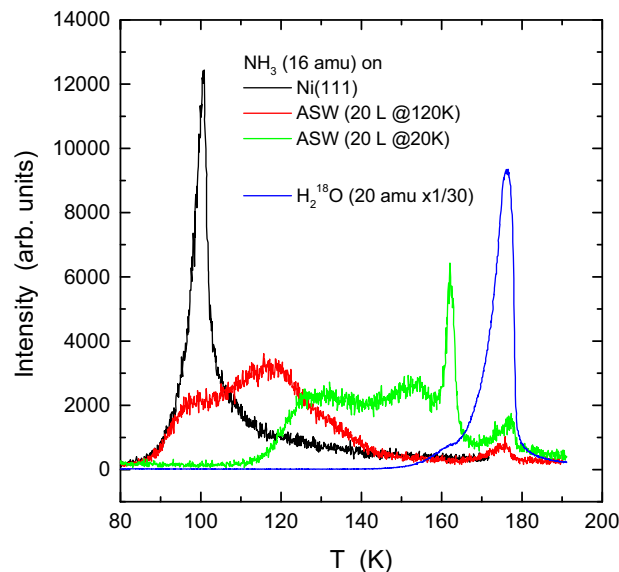

Figure 2. TPD spectra of NH$_3$ (1 L) and H$_2$^{18}O (20 L) molecules from the porous ASW film deposited at 20 K. Also shown are TPD spectra of NH$_3$ (1 L) from the nonporous ASW film (prepared by deposition of 20 L H$_2$^{18}O at 120 K) and Ni(1 1 1) substrate. The temperature ramp rate was 5 K min^{-1}.

substrate at this temperature. Dewetting of a pure ASW film is associated with water crystallization because nucleation occurs in a liquid-like phase [26]. Consequently, the NH$_3$ adspecies have no effects on the crystallization kinetics of water.

Figure 2 displays TPD spectra of the H$_2$^{18}O and NH$_3$ molecules desorbed from the porous ASW film prepared in the same manner that shown in Figure 1. For comparison, TPD spectra of 1 L NH$_3$ adsorbed onto Ni(1 1 1) and a nonporous ASW film (formed by deposition of 20 L H$_2$^{18}O at 120 K) are also shown. The NH$_3$ molecule desorbed in the gas phase is monitored using a 16 amu signal to reduce the contribution from the background H$_2$O molecule. The NH$_3$ molecule desorbs from the porous ASW film over a wide temperature range with a characteristic peak at ca. 160 K. At this temperature, the H$_2$^{18}O TPD spectrum exhibits a shoulder as a result of water crystallization. Based on the TPD result, the decay of the TOF-SIMS NH$_4$$^+$ intensity at T > 130 K (Figure 1) is not ascribable to desorption of NH$_3$ from the ASW film surface. The NH$_3$ molecules forming a peak at 160 K come from the ASW film interior during water crystallization. Desorption occurs after the