



TOF-SIMS investigation of hydration of acetic acid adsorbed on amorphous water-ice surface

M. Kondo ^{a,b}, T. Shibata ^{a,b}, H. Kawanowa ^{a,b}, Y. Gotoh ^b, R. Souda ^{a,b,*}

^a *Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

^b *Department of Materials Science and Technology, Science University of Tokyo, Noda, Chiba 278-8510, Japan*

Available online 28 April 2005

Abstract

In order to gain insight into the acid–base reaction in the hydrogen bond systems, we have been investigating the hydration and ionization of the CH₃COOH molecules adsorbed on the non-porous D₂O-ice surface by time-of-flight secondary ion mass spectrometry. At temperatures above 60 K, the H⁺(CH₃COOH) intensity (the H⁺(D₂O) intensity) increases (decreases) due to the hydrogen-bond formation between the CH₃COOH and D₂O molecules. The D⁺(CH₃COOD) ion evolves above 130 K as a result of the thermally induced proton transfer reactions between the CH₃COOH and D₂O molecules. The translational diffusion of the water molecules is responsible for the H/D exchange. © 2005 Elsevier B.V. All rights reserved.

Keywords: Acetic acid; Water; Hydration; Proton transfer reaction; Time-of-flight secondary ion mass spectrometry

1. Introduction

Hydration and proton transfer reaction are important processes for the electrochemistry, biochemistry and atmospheric science. Most of the biopolymers, such as proteins and nucleic acids, have the carbonyl or carboxyl groups and their

conformation in aqueous solution is determined by the hydrogen-bond formation. The acetic acid has been utilized extensively in this respect since it is the prototype molecule containing both hydrophilic (carboxyl) and hydrophobic (methyl) groups. So far, the interactions between acetic acid and water molecules have been investigated in the gas phase [1,2] and the aqueous solution [2–11]. It is well known that the acetic acid molecules form the cyclic dimer in the gas phase. In the liquid phase, however, the experimental evidences are still poor whether the dimerization of the acetic acid molecules occurs or not. Regarding the properties of amorphous solid water, it is claimed that

* Corresponding author. Address: Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan. Tel.: +81 29 860 4429; fax: +81 29 851 6280.

E-mail address: souda.ryutaro@nims.go.jp (R. Souda).

the liquid phase coexists with cubic ice above 140 K [12], or the supercooled liquid water evolves around 150 K [13]. In our previous studies [14,15], the enhancement in mobility of the water molecules above 140 K has been confirmed, suggesting that the hydration process of molecules in liquid-like water can be investigated at cryogenic temperatures. Despite its importance, there exist only a few reports on the interaction between the acetic acid and water molecules at cryogenic temperatures [16,17].

In the present paper, we study the interactions of the CH_3COOH molecules adsorbed on the water-ice surface by utilizing time-of-flight secondary ion mass spectrometry (TOF-SIMS) in the temperature range 15–230 K. The sputtered protonated molecular ions, such as $\text{H}^+(\text{D}_2\text{O})$ and $\text{D}^+(\text{CH}_3\text{COOH})$, provide fruitful information about the hydrogen bonds between the CH_3COOH and D_2O molecules. Here, the reorganization of hydrogen bonds and the resulting isotope exchange are investigated as functions of the temperature and coverage of acetic acid, and the mechanism of the proton transfer and the hydration in aqueous solution is discussed.

2. Experiment

The experiments were carried out 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, a differentially pumped quadrupole mass spectrometer for residual gas analysis, a hemispherical electrostatic analyzer, an X-ray source, a UV source, and a low-energy electron gun. The He^+ ion beam was 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 V, was irradiated with a primary He^+ ion 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.

A pulsed He^+ beam with a low incident flux (0.2 nA/cm^2) was used. We already proved that this level of incident flux hardly induces the surface damage [18]. The substrate was a Ni(111) surface mounted on a sample holder cooled down to 15 K by means of a closed-cycle He refrigerator. The CH_3COOH and D_2O molecules were dosed from independent variable-leak valves 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 intensities from the substrate as a function of exposure, and the film thickness was estimated on the basis of this value. The temperature was monitored by using Au–Fe7% chromel thermocouples with an accuracy of ± 1 K. The temperature increasing rate of all measurements was about 0.1 K s^{-1} .

3. Experimental results

The evolutions of typical cation intensities from the CH_3COOH -adsorbed D_2O -ice surface are shown in Fig. 1 as a function of temperature. Non-porous D_2O -ice film with a thickness of 50 ML was prepared [19] to exclude the possibility that the CH_3COOH molecules are incorporated into the bulk cavities. The protonated molecular ions are sputtered from the surface provided that hydrogen-bonded molecules overcome the potential barrier as a consequence of the energetic cascade collision (collision-induced proton transfer reaction) [14,15]. Above 60 K, the $\text{H}^+(\text{CH}_3\text{COOH})$ ion intensity decreases steeply, whereas $\text{H}^+(\text{D}_2\text{O})$ ion intensity increases. This is due to the hydrogen-bond formation between the CH_3COOH and D_2O molecules. The $\text{D}^+(\text{D}_2\text{O})$ ion evolves remarkably above 125 K instead of the $\text{H}^+(\text{D}_2\text{O})$ ion. In addition, the $\text{D}^+(\text{CH}_3\text{COOD})$ ion emerges simultaneously with the enhancement of the $\text{D}^+(\text{D}_2\text{O})$ intensity. So far, the mechanism of the isotope scrambling in the bulk crystalline ice has been discussed extensively: it may occur even for the crystalline ice without diffusion of the water molecules, as a result of the sequential proton transfer and rotation of the hydronium ions [20]. In reality,

Download English Version:

<https://daneshyari.com/en/article/9818101>

Download Persian Version:

<https://daneshyari.com/article/9818101>

[Daneshyari.com](https://daneshyari.com)