Metastable hydronium ions in UV-irradiated ice

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We show that the irradiation of UV light (10−11 eV) onto an ice film produces metastable hydronium (H$_3$O$^+$) ions in the ice at low temperatures (53−140 K). Evidence of the presence of metastable hydronium ions was obtained by experiments involving adsorption of methylamine onto UV-irradiated ice films and hydrogen-deuterium (H/D) isotopic exchange reaction. The methylamine adsorption experiments showed that photogenerated H$_2$O$^+$ species transferred a proton to the methylamine arriving at the ice surface, thus producing the methyl ammonium ion, which was detected by low energy sputtering method. The H$_2$O$^+$ species induced the H/D exchange of water, which was monitored through the detection of water isotopomers on the surface by using the Cs$^+$ reactive ion scattering method. Thermal and temporal stabilities of H$_2$O$^+$ and its proton migration activity were examined. The lifetime of the hydronium ions in the amorphized ice was greater than 1 h at ~53 K and decreased to ~5 min at 140 K. Interestingly, a small portion of hydronium ions survived for an extraordinarily long time in the ice, even at 140 K. The average migration distance of protons released from H$_2$O$^+$ in the ice was estimated to be about two water molecules at ~54 K and about six molecules at 100 K. These results indicate that UV-generated hydronium ions can be efficiently stabilized in low-temperature ice. Such metastable hydronium ions may play a significant role in the acid-base chemistry of ice particles in interstellar clouds. © 2012 American Institute of Physics.

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I. INTRODUCTION

Water-ice is one of the most abundant solid materials in planetary atmospheres, comet tails, and interstellar media. In these environments, ice is usually under bombardment of energetic photons, ions, and electrons. For this reason, the interaction of high-energy radiation with ice surfaces is a subject of astrophysical relevance and also of fundamental interest in the physics and chemistry of ice. Many studies have been conducted in the past decades to investigate the effects of energetic photons incident on ice surfaces.1-22 These studies have discovered that UV radiation can change the morphology of an ice sample4,12 and induce photochemical reactions in the ice,6,10,20,21 producing species such as H atoms,1,16,19 OH radicals,1,10 and H$_2$ and H$_2$O$_2$ molecules.1,9 Photodesorption studies have observed the emission of H atoms,16,19 H$^+$ ions,2,11 and H$_2$O$^+$ ions11 from water-ice samples subjected to UV irradiation at different photon energies, and the photodesorption of constituent molecules from mixture ice samples.7,18,21

Of particular interest in the present work is the formation of ionic products in ice by UV irradiation, which is relatively not well understood compared to photofragmentation and radical recombination processes in ice. Specifically, we examine the formation of H$_2$O$^+$ in ice irradiated with UV light at an energy of 10−11 eV, which is less than the vertical ionization energy of free water molecules (12.6 eV). We also examine the stability of the photogenerated H$_3$O$^+$ species and its proton transfer dynamics in ice. In Secs. II–V, the H$_2$O$^+$ species are referred to as “hydroniums” or “positive ion defects.” These terms are used interchangeably because H$_2$O$^+$ in the UV-exposed, and hence amorphized, ice may take on forms that are not identical to the positive ion defects in crystalline ice or hydroniums in liquid water. Relatively fewer experimental works have investigated ion formation in ice during the photolysis with UV and lower energy photons. Devlin23 reported that the dissociative ionization of ice can be induced by visible (2.5 eV) photons, based on the observation that the hydrogen–deuterium (H/D) exchange of ice is induced by incident light. Petrenko and co-workers5,6,8 measured the photoconductivity of ice during its UV irradiation at an energy above 6.5 eV and concluded that UV light creates positive photo-charge carriers in ice, which are responsible for the observed long-term photoconductivity of the ice. Apart from these works investigating the effects of photon radiation on ice, the properties of H$_2$O$^+$ in ice have been extensively studied using ice samples doped with strong acids or acid precursors.24-38 These investigations have greatly improved our understanding about the mobility of H$_3$O$^+$ in ice, the transport mechanisms,24-35 and the reactivity toward base molecules.36-38 In an earlier communication,22 we reported the occurrence of the protonation of methylamine (MA; CH$_3$NH$_2$) adsorbrates on an ice film exposed to UV radiation, which indicated the formation of H$_3$O$^+$ in the ice. In the present work, we seek further evidence of the UV-induced formation of H$_3$O$^+$ in ice and examine the thermal and temporal stabilities and migration activity of the photogenerated H$_3$O$^+$ species.

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II. EXPERIMENT

The experiments were performed in an ultrahigh vacuum (UHV) chamber equipped with surface analysis tools.39 The ice sample was grown on a single-crystal Ru(0001) surface by exposing it to water vapor either through a tube doser or using a backfilling method. Two types of ice samples were used for the study: an amorphous solid water (ASW) film, which was grown by water deposition at a temperature below 125 K, and a crystalline ice (CI) film, which was grown at 140 K and subjected to brief annealing at 155 K to ensure crystallization.40 The thickness of the ASW films was 9–20 bilayers (BLs; 1 BL = 1.1 × 1015 water molecules cm−2),41,42 and the thickness of the CI films was >100 BL. The use of a thicker film was necessary for the CI because a bulk-like crystalline structure with a flat surface can be formed only above this thickness, after the initial Stranski–Krastanov growth stage on the Ru(0001) surface.43 These film growth conditions ensured the formation of a uniform ice film without regions of bare metal substrate or the first wetting monolayer of water. The film thickness was determined by performing temperature-programmed desorption experiments. Methylamine gas was introduced onto the sample surface through a tube doser, and during this procedure the chamber background pressure increased only by a small amount (∼5 × 10−11 Torr). The UV light source was a radio frequency (rf)-powered Kr lamp (Resonance Ltd.), which produced photons with two sharp intensity maxima at energies of 10.03 and 10.64 eV. The photon flux reaching the sample was estimated to be ∼2.1 × 1013 photons cm−2 s−1. Photoelectrons emitted from the Ru substrate did not affect the reactions under investigation to any noticeable degree, according to control experiments conducted with ice films of various thicknesses above the attenuation length (∼3 BLs) of photoelectrons through ice.44

The chemical composition of the ice sample surface was analyzed by reactive ion scattering (RIS) and low energy sputtering (LES) methods.25 The principles of RIS and LES techniques and their applications to ice surface studies have been described in detail previously.25,39 These methods use a low energy (<50 eV) Cs+ beam as a primary beam that collides with the target surface. In the RIS process, a Cs+ projectile scattering from a target picks up a neutral molecule (X) from the surface, leading to the formation of a Cs+–molecule adduct (CsX+) as a RIS product. In the LES process, pre-existing ionic species (Y+ or Z−) at the surface are ejected due to the Cs+ impact. The resultant Cs+–molecule clusters and low-energy sputtered ions were detected by a quadrupole mass spectrometer with its ionizer filament switched off. Therefore, RIS detects neutral molecules at the surface, while LES detects ionic species. The Cs+ beam energy was controlled in a range that avoided secondary ion emission and beam-induced surface reactions. As optimal conditions, we used a 30 eV beam energy for ASW samples and a 38 eV beam energy for thick CI samples (∼150 BL thickness), unless otherwise mentioned. The Cs+ beam flux was kept below 1.0 nA cm−2 to minimize the accumulation of Cs+ ions at the surface.

III. RESULTS AND ANALYSIS

A. Evidence of hydronium ion formation induced by UV radiation

We show evidence of the production of H3O+ in ice caused by UV irradiation by conducting two different experiments: the MA adsorption experiment and the H/D isotopic exchange experiment. The results of the MA adsorption experiment are shown in Fig. 1, which compares the LES and RIS spectra of the ice films adsorbed with MA, before and after UV irradiation. Figure 1(a) shows RIS signals measured from a pristine H2O-ASW film (20 BL thickness). In addition to the reflected Cs+ signal at m/z = 133 amu/charge, the RIS signals include Cs(H2O)3+n+ (n = 1–3) appearing at m/z = 151, 169, and 187 amu/charge, respectively, produced by surface water molecule pickup. Figure 1(b) shows the result obtained after adsorbing MA molecules on the film surface for coverage of 0.2 monolayer (ML; 1 ML = 1.1 × 1015 molecules cm−2). A CsMA+ signal newly appeared at m/z = 164, indicating the presence of MA molecules on the surface. Figure 1(c) shows the result of a UV-irradiation experiment. In this experiment, a pristine ASW film was irradiated with UV light for 15 min at a temperature of 53 K, corresponding to a total photon exposure of ∼2 × 1016 photons cm−2. After the UV lamp was switched off, MA was adsorbed onto the film surface for a coverage of 0.15 ML. The RIS signals observed from this surface include Cs(H2O)n+ and CsMA+ (Fig. 1(c)), similar to those shown in Fig. 1(b). Interestingly, however, the LES spectrum shows a methylammonium (MAH+) ion peak at m/2l = 32. This signal is absent from Fig. 1(b), and therefore, it must be due to the UV irradiation.

It is known5,6,8,10,13–16,20,24 that UV photolysis of ice can generate various types of lattice point defects and water dissociation products such as H, OH, and H2O2. Among the various possible products of ice photolysis, only H3O+ is sufficiently acidic to donate a proton to a weak base molecule.
such as MA.\textsuperscript{36–38} This proton transfer reaction is expressed as
\[ MA + H_2O^+ \rightarrow MAH^+ + H_2O. \] (R1)

Therefore, the MAH\textsuperscript{+} signal indicates the presence of H\textsubscript{3}O\textsuperscript{+} in the ice. For Reaction (R1) to occur, a proton must travel from the location of H\textsubscript{2}O\textsuperscript{+} in the ice film to the MA at the surface. Proton transfer efficiency is not always as high as unity even across a short distance in ASW at low temperature.\textsuperscript{46} For this reason, the amount of MAH\textsuperscript{+} produced at the surface represents the lower limit of the mobile H\textsubscript{3}O\textsuperscript{+} content in the ASW film. In the present case, the adsorption of MA molecules may perturb the ice film structure\textsuperscript{47} and this may increase the proton transfer efficiency to the surface. The intrinsic H\textsubscript{3}O\textsuperscript{+} population in pristine ice is negligible, which is confirmed by the absence of the MAH\textsuperscript{+} signal on the ice surface, as shown in Fig. 1(b).

Results of the H/D isotopic exchange experiments are shown in Fig. 2. Figure 2(a) shows a RIS spectrum obtained from an ice film of H\textsubscript{2}O-D\textsubscript{2}O mixture before UV irradiation. The ice film (9 BL thickness) was prepared by codeposition of H\textsubscript{2}O and D\textsubscript{2}O vapor on Ru(0001) through separate dosing facilities. The bottom 6 BL of the film was grown in a crystalline phase at a temperature of 140 K, and the top 3 BL was grown in an ASW phase below 80 K. The low temperature employed for the growth of the upper film suppressed the thermal H/D exchange reaction of water.\textsuperscript{48} The RIS spectrum was obtained below 80 K. The spectrum showed dominant RIS signals of H\textsubscript{2}O and D\textsubscript{2}O at \( m/z = 151 \) and 153 amu/charge, respectively, confirming the negligible occurrence of H/D exchange reactions at the surface. A weak HDO signal also appeared at \( m/z = 152 \), which corresponded to \~5\% of total surface water. This HDO signal was produced by the adsorption of residual HDO vapor remaining in the chamber after the H\textsubscript{2}O and D\textsubscript{2}O adsorption experiments.

The RIS spectrum in Fig. 2(b) was taken after UV irradiation of the H\textsubscript{2}O-D\textsubscript{2}O film at a temperature of 90 K. The HDO signal magnitude markedly increased by UV irradiation, i.e., from \~5\% of the surface water population in Fig. 2(a) to \~37\% in Fig. 2(b). This indicates the occurrence of H/D exchange in surface water. The experiments with acid-doped ice samples show that externally provided hydroniums induce the H/D exchange reaction efficiently even at low temperatures.\textsuperscript{26,27,33} The UV radiation produced a similar effect to that of externally provided hydroniums. This provides additional evidence of the UV-induced formation of hydroniums in an ice film.

We considered the possibility that species other than H\textsubscript{3}O\textsuperscript{+} contribute to the observed H/D exchange reaction. Photofragment radicals including H and OH cannot induce efficient H/D exchange reactions in the ice because they do not mediate a proton transfer relay, unlike H\textsubscript{3}O\textsuperscript{+}. Stoichiometric reaction of these radicals with water such as H or OH replacement reaction would cause the H/D exchange of ice to occur to a far lesser degree. If OH\textsuperscript{−} is produced in the ice as a counter anion of H\textsubscript{3}O\textsuperscript{+}, OH\textsuperscript{−} may also induce H/D exchange reactions. However, recent study results indicate that the proton transfer activity of OH\textsuperscript{−} is much lower than that of H\textsubscript{3}O\textsuperscript{+} in cold ice.\textsuperscript{39,50} For this reason, if both H\textsubscript{3}O\textsuperscript{+} and OH\textsuperscript{−} were formed in the ice sample, H\textsubscript{2}O\textsuperscript{+} would mainly contribute to HDO production.

\textbf{B. Thermal and temporal stabilities of hydronium ions}

To examine the stability of UV-generated hydroniums in the ice sample, we modified the procedure of the MA adsorption experiment such that MA gas was adsorbed onto the ice film after a certain time delay (\( T_{\text{delay}} \)) following UV exposure. The sample was maintained at a specific temperature (\( T_{\text{delay}} \)) during the time delay. This procedure allowed us to estimate the survival time of hydroniums in the ice at \( T_{\text{delay}} \). The experimental routine involved preparing a pristine H\textsubscript{2}O-ice film on Ru(0001) and then irradiating it with UV light for \~2 \times 10^{16} \) photons cm\textsuperscript{−2} at a low temperature (<60 K). After switching off the UV lamp, the UV-exposed ice was maintained at \( T_{\text{delay}} \) for a period of \( t_{\text{delay}} \). The sample was quickly quenched at a sufficiently low temperature (<60 K), which was followed by MA gas adsorption. Next, the MAH\textsuperscript{+} population was measured with LES at <60 K. To measure the MAH\textsuperscript{+} population as a function of \( t_{\text{delay}} \) and \( T_{\text{delay}} \), this procedure was repeated at different \( t_{\text{delay}} \) values (0–30 min) and \( T_{\text{delay}} \) values (53–140 K).

Since ASW samples transform into crystalline ice at 140 K, a CI sample was used in the experiment for \( T_{\text{delay}} = 140 \) K to avoid the phase transition effect and accompanying change in LES intensity. All other ice samples were ASW.

Figure 3 shows MAH\textsuperscript{+} intensity variation as a function of \( t_{\text{delay}} \) at different \( T_{\text{delay}} \) values. MAH\textsuperscript{+} intensity is displayed using a normalized scale, where the reference is the signal intensity measured at \( t_{\text{delay}} = 0 \) and \( T_{\text{delay}} = 53 \) K. The MAH\textsuperscript{+} intensity decreased as \( t_{\text{delay}} \) increased, and there was a clear trend that the MAH\textsuperscript{+} intensity decreased faster at a higher \( T_{\text{delay}} \). For example, considering only the initial 5 min period, the MAH\textsuperscript{+} intensity dropped by \~20\% at \( T_{\text{delay}} = 80 \) K, \~50\% at 125 K, and \~57\% at 140 K. At \~53 \) K, the MAH\textsuperscript{+} intensity remained almost unchanged during the entire duration of the kinetic measurement. Because the MAH\textsuperscript{+}
FIG. 3. MAH$^+$ signal intensity (displayed using a normalized scale) measured as a function of delay time ($t_{\text{delay}}$) from the termination of UV irradiation. The MAH$^+$ intensity indicates the quantity of hydroniums present in the ice film, as detected by MA titration experiments. The experimental conditions for MA adsorption (0.2 ML) and UV photolysis (∼2 × 10$^{16}$ photons cm$^{-2}$) were identical to those in the procedure used for Fig. 1. The ice film thickness was ∼15 BL for ASW samples at ∼53, 80, and 125 K and ∼150 BL for the CI sample at 140 K (see text).

intensity reflects the amount of H$_2$O$^+$ in the sample at a given $t_{\text{delay}}$ and $T_{\text{delay}}$, these kinetic measurements indicate the lifetime of H$_2$O$^+$ in the sample, and show that the lifetime increases at a lower temperature. It is noted that the decay time of MAH$^+$ intensity is comparable to the migration time of protons in ASW. For example, the average time for proton migration across a distance of 4 BL in an amorphous ice film is reported to be ∼5 min at 130 K,29 which is in general agreement with the observed MAH$^+$ decay time at 125–140 K. This supports the idea that photogenerated H$_2$O$^+$ releases a proton into the ice lattice and that the migration of the proton eventually removes H$_2$O$^+$ via a recombination reaction with OH$^-$.

Interestingly, the MAH$^+$ intensity did not drop to zero even after a long delay time. For example, at $T_{\text{delay}}$ = 140 K and $t_{\text{delay}}$ = 30 min, the MAH$^+$ intensity decreased to ∼24% of its initial value (Fig. 3), and this intensity persisted even after 60 min (not shown). Such a long tail is in peculiar contrast to the sharp decay of intensity during the early $t_{\text{delay}}$ period. It indicates that a certain portion of H$_2$O$^+$ species did not completely disappear from the ice even at 140 K. This phenomenon is discussed in Sec. IV.

C. Quantum yield of H/D exchange reaction

The H/D exchange kinetics of surface water was examined under continuous UV light illumination, and the results are shown in Fig. 4. The ice samples were prepared in the same manner as used for Fig. 2. The sample was maintained at a fixed temperature between 54 and 100 K during the UV irradiation, and the change in the surface population of HDO was measured with RIS as a function of the irradiation time. Figure 4 shows an increasing HDO population with UV exposure and a faster rate of HDO formation at higher temperatures. Without UV radiation, HDO formation was negligible on the ice sample even at 100 K, as previously mentioned. These results indicate that thermal energy increases the yield of the UV-induced H/D exchange reaction, although the H/D exchange reaction cannot occur by thermal energy alone.

We analyze the kinetic data shown in Fig. 4 using a kinetic model of the H/D exchange reaction under a constant UV flux condition. The reaction is expressed by

$$\text{H}_2\text{O} + \text{D}_2\text{O} \xrightarrow{\sigma/\Phi_{\text{H/D}} F} 2\text{HDO}. \quad (R2)$$

Here, $\sigma$ is the UV absorption cross section of water molecule, $\Phi_{\text{H/D}}$ is the quantum yield for a proton (deuteron) exchange process between water molecules, and $F$ is the photon flux. $\sigma$ has a value of 8 × 10$^{-18}$ cm$^2$ in the photon energy range of 8–11 eV$^{51}$ and $F$ ∼ 2.1 × 10$^{13}$ photons cm$^{-2}$ s$^{-1}$ in the present experiment. The rate expression of reaction (R2) is given by Eq. (1):

$$\frac{1}{2} \frac{d\theta_{\text{HDO}}(t)}{dt} = \frac{\sigma \Phi_{\text{H/D}} F \theta_{\text{HDO}}(t) \theta_{\text{D2O}}(t) - \frac{1}{4} \sigma \Phi_{\text{H/D}} F \theta_{\text{HDO}}(t)^2}{\theta_{\text{H}}(t) + \theta_{\text{D}}(t) + \theta_{\text{D2O}}(t) + \theta_{\text{H2O}}(t) + 1} = \theta_{\text{H2O}}(t) - \frac{1}{2} \theta_{\text{D2O}}(t). \quad (1)$$

$\theta_X(t)$ denotes the surface coverage of $X$ ($X = \text{H}_2\text{O}$, HDO, or D$_2$O) at time $t$ and $\theta_{\text{H2O}}(t) + \theta_{\text{D2O}}(t) + 1 = 1$. Equation (1) can be rewritten in terms of $f_x$ ($x = \text{H}$ or D), which indicates the relative portion of H or D in the water, defined by $f_x = \theta_{2x} / (1 + \theta_{\text{H2O}} + \theta_{\text{D2O}})$ as follows:

$$\frac{1}{2} \frac{d\theta_{\text{HDO}}(t)}{dt} = \frac{\sigma \Phi_{\text{H/D}} F \left( f_{\text{H}} f_{\text{D}} - \frac{1}{2} \theta_{\text{HDO}}(t) \right) }{f_{\text{H}} + f_{\text{D}}}. \quad (2)$$

Note that although the H/D exchange reaction changes the isotopomeric distribution of water, it does not consume or produce H or D in the water, and thus, $f_x$ is constant during the reaction. This differential equation has the analytical solution

$$\theta_{\text{HDO}}(t) = 2 f_{\text{H}} f_{\text{D}} - [2 f_{\text{H}} f_{\text{D}} - \theta_{\text{HDO}}(0)] \exp(-\sigma \Phi_{\text{H/D}} F t) = c_2 - c_1 \exp(-\sigma \Phi_{\text{H/D}} F t), \quad (3)$$
where \( c_1 \) and \( c_2 \) are constants. Equation (3) is used to fit the experimental kinetic curves in the form of \( \ln([C_2 − \theta_H Do(t)]/c_1) = −\sigma \Phi_H D F_t \). Figure 5 shows the fitted lines. From the slope of the linear fit, the value of \( \sigma \Phi_H D F \), and thus \( \Phi_H D \), can be obtained, and these values are summarized in Table I. This quantum yield represents the H/D exchange reaction of surface water, and it is denoted as the apparent quantum yield (\( \Phi_{H/D}^{app} \)) in Table I. Table I shows that \( \Phi_{H/D}^{app} \) increases with temperature. This trend indicates that the ability of hydroniums to release a proton and induce the H/D exchange of ice increases at higher temperatures. In Sec. IV, we discuss the correction of \( \Phi_{H/D}^{app} \) by considering the effect of proton migration in the vertical direction in the sample.

### IV. DISCUSSION

First, we discuss the UV photoionization mechanism of ice that leads to \( H_3O^+ \) formation. The UV photon energy used in the present experiment (10–11 eV) is lower than the vertical ionization energy of water molecules in gas phase (12.6 eV), but greater than the photoionization threshold of amorphous ice (\( \sim 9 \) eV) observed in photoelectron emission spectroscopic studies. Therefore, we consider it possible that a similar direct photoionization process occurs in the present ice samples. In this case, the \( H_3O^+ \) forming process can be the photoionization of water molecules to \( H_2O^+ \) in the ice (Reaction (R4)) followed by proton transfer from \( H_2O \) to \( H_2O^+ \) (Reaction (R4)):

\[
H_2O(s) + hv \rightarrow H_2O^+(s) + e^-(s),
\]

\[
H_2O^+(s) + H_2O(s) \rightarrow H_3O^+(s) + OH(s).
\]

The photoelectrons generated in the first step may initially be trapped in the ice film and might then participate in subsequent reactions in the ice, or they may be ejected from the sample into vacuum or a Ru substrate.

In addition, indirect photoionization of ice with a lower energy threshold may occur during UV irradiation. There are several reports on the occurrence of the indirect photoionization of ice at lower photon energies. Petrenko et al.\(^\text{5,6,8} \) observed enhanced electrical conductivity of ice during UV irradiation at an energy as low as 6.5 eV. They proposed that the UV irradiation generates \( H_2O^+ \) in the ice as positive charge carriers responsible for the observed photoconductivity, along with photoelectrons, OH radicals, and various defects (Reaction (R5)):

\[
2H_2O(s) + hv \rightarrow H_3O^+(s) + OH(s) + e^-(s) + \text{defect(s)}.
\]

Devlin\(^\text{23} \) reported that the dissociative ionization of cubic ice occurs with 2.5 eV photons, based on the observation of a H/D isotopic exchange reaction in D\(_2\)O-doped \( H_2O\)-ice. Earlier, Goodall and Greenhow\(^\text{53} \) reported the dissociative ionization of liquid water by 1.2 eV photons from photoconductivity experiments, which supports the concept of ionization of water via single photon vibrational excitation. At these low photon energies, the dissociative ionization reaction (Reaction (R6)) may be the only possible channel for water ionization:

\[
2H_2O(s) + hv \rightarrow H_3O^+(s) + OH^-(s).
\]

It should be mentioned that \( OH^- \) has not yet been detected in the UV photolysis experiments of ice. Nonetheless, it is acceptable that \( OH^- \) can be formed in the UV photolysis of ice, regardless of whether the process occurs via a dissociative ionization process (Reaction (R6)) or via a series of complex reactions involving OH radicals.\(^\text{54} \) In the discussions that follow, as supported by the above-mentioned studies, we assume that \( H_3O^+ \) is produced by both direct and indirect photoionization channels in the present experiment.

Next, we discuss the metastability of UV-generated \( H_3O^+ \) species in ice. Our study shows that the \( H_3O^+ \) species are stable in ice at low temperatures (\( \sim 53 \) K) during the entire period of the kinetic measurement (30 min), although the stability decreases at higher temperatures. Such metastability of \( H_3O^+ \) may be explained in terms of proton dynamics in the ice lattice, that is, trapping of photogenerated protons as \( H_3O^+ \), proton release, and proton migration along the hydrogen-bond chain of water. It is known\(^\text{52} \) that some defect sites in the ice lattice, e.g., orientational L-defects, act as a proton trap and generate \( H_2O^+ \) as a positive ion defect. To release a proton from \( H_3O^+ \), a sufficient amount of energy needs to be supplied, which requires a high temperature condition. Once a proton is released from the trap, it moves along the hydrogen-bond chain of the ice lattice via a proton hopping relay (Grotthuss) mechanism.\(^\text{41,42} \) Proton migration
stops when a mobile proton encounters another trap and forms H$_3$O$^+$. Alternatively, when a mobile proton recombines with OH$^-$ (or with OH + e$^-$), H$_3$O$^+$ disappears permanently via the neutralization reaction (R7):

$$\text{H}_3\text{O}^+(s) + \text{OH}^-(s) \rightarrow 2\text{H}_2\text{O}(s). \quad (R7)$$

Proton migration along a hydrogen-bond chain induces the H/D exchange reaction in H$_2$O-D$_2$O mixed ice.\textsuperscript{28,29,34} Therefore, the quantum yield of the H/D exchange reaction increases as the proton migration activity increases at higher temperature. We may estimate the migration distance of protons in the ice from the quantum yield data in Table I. The proton migration length can be expressed as the number of proton hops ($N_{\text{hop}}$) along a hydrogen-bond chain. If a proton hops $N_{\text{hop}}$ times on average in the ice lattice of a random H$_2$O–D$_2$O mixture, then there is a relationship (Eq. (4)) between the quantum yield of the H/D exchange reaction ($\Phi_{\text{H/D}}$) and the quantum yield of hydronium formation ($\Phi_{\text{hyd}}$) in the ice:

$$\Phi_{\text{H/D}} = N_{\text{hop}} \Phi_{\text{hyd}}. \quad (4)$$

This intuitively deduced relationship can be shown to be accurate by explicitly writing the kinetic equations for the individual steps of HDO formation and removal due to proton transfers. The present experiment, however, measures the quantum yield for the H/D exchange reaction of surface water ($\Phi_{\text{H/D}}^{\text{app}}$). The H/D exchange reaction of surface water is contributed from H$_3$O$^+$ present in the surface as well as below the surface within a depth of $N_{\text{hop}}$. The upward migration of interior H$_2$O$^+$ species can occur due to proton mobility in the ice as well as thermodynamic affinity of H$_2$O$^+$ for the ice surface.\textsuperscript{29} The contributions of both surface and interior H$_2$O$^+$ species being included, the relationship between $\Phi_{\text{H/D}}^{\text{app}}$ and $\Phi_{\text{hyd}}$ can be expressed as

$$\Phi_{\text{H/D}}^{\text{app}} \approx N_{\text{hop}} \Phi_{\text{hyd}} \times (\text{proton migration depth}) \approx N_{\text{hop}}^2 \Phi_{\text{hyd}}. \quad (5)$$

$\Phi_{\text{hyd}} \times (\text{proton migration depth})$ indicates the amount of hydronium in the sample that are available for the H/D exchange reaction of surface water. The value of $\Phi_{\text{hyd}}$ can be estimated from separate experiments that measure the quantum yield of MAH$^+$ formation ($\Phi_{\text{MAH}^+}$). For a sufficiently thin ice film, most of photogenerated protons will be captured by MA adsorbates at the surface and, in this case, Eq. (6) will be a good approximation:

$$\Phi_{\text{MAH}^+} = \Phi_{\text{hyd}} \times (\text{proton migration depth}) \approx \Phi_{\text{hyd}} \times (\text{ice film thickness}). \quad (6)$$

Adsorbate-induced restructuring of the ice film may also increase the proton migration efficiency to the surface.\textsuperscript{47} Based on the $\Phi_{\text{MAH}^+}$ value reported from previous studies performed with a thin (~5 BL) ice film,\textsuperscript{22} we estimate $\Phi_{\text{hyd}} \sim 0.16$ photon$^{-1}$ by using the UV absorption cross section of water molecule ($8 \times 10^{-18}$ cm$^2$)\textsuperscript{23} as a conversion factor. From these $\Phi_{\text{H/D}}^{\text{app}}$ and $\Phi_{\text{hyd}}$ values, the proton migration length ($N_{\text{hop}}$) is estimated through Eq. (5). This, in turn, gives the quantum yield of H/D exchange reaction in the sample volume ($\Phi_{\text{H/D}}$) through Eq. (4). Note that there is a relationship, $\Phi_{\text{H/D}}^{\text{app}} = \Phi_{\text{H/D}} N_{\text{hop}}$. The $N_{\text{hop}}$ and $\Phi_{\text{H/D}}$ values are listed in Table I. The uncertainty in these values mainly arises from the uncertainty in the $\Phi_{\text{hyd}}$ value.

A few aspects of the proton migration length listed in Table I may be mentioned. First, one can notice that the temperature dependency of $N_{\text{hop}}$ correlates with that of the hydronium lifetime shown in Fig. 3. At a low temperature (~54 K), protons can migrate only across a short distance ($N_{\text{hop}} \sim 2.4$), and thus, photogenerated hydroniums are efficiently trapped and can survive for an extremely long time. At higher temperatures, $N_{\text{hop}}$ increases and the hydronium lifetime decreases. These correlations again support the interpretation that the metastability of hydroniums is related to proton trapping, release, and migration processes. Second, for the estimation of $N_{\text{hop}}$, we assume that the H/D exchange reaction is catalyzed by H$_3$O$^+$ but not OH$^-$. This will be a reasonable approximation for low-temperature ice because the proton transfer activity of OH$^-$ is significantly lower than that of H$_3$O$^+$, according to recent reports.\textsuperscript{46,49} Third, the proton migration length may change with the structure and defect density of an ice sample. Therefore, the $N_{\text{hop}}$ value reported here may not be quantitatively applicable for other types of ice samples, although the observed temperature dependency may be qualitatively useful. For example, studies of the H/D exchange reaction of acid-doped ASW samples\textsuperscript{28} report that excess protons are deeply trapped and immobile in ASW below ~100 K. However, the present work resolves the temperature dependency of proton mobility in ASW even below 100 K. This difference may be related to experimental sensitivity and the use of different samples. UV photolysis of the ice sample may generate various types of defects with a wide distribution of proton trapping energy, such that some weakly bound protons are mobile even below 100 K.

An interesting feature shown in Fig. 3 is that the MAH$^+$ intensity does not drop to zero even at a high temperature (140 K) and after a long time (>60 min). The persisting MAH$^+$ intensity indicates that a substantial portion of hydroniums remain in the sample. At 140 K, self-diffusion and proton migration are very active in an ice film,\textsuperscript{29} and therefore, it is expected that H$_2$O$^+$ would be efficiently removed by the neutralization reaction (Reaction (R7)) within a few minutes. On the contrary, H$_3$O$^+$ survives for a seemingly indefinite time. One possible explanation for this is a stoichiometric imbalance between H$_3$O$^+$ and OH$^-$ in the sample. If the photoelectrons generated from ice by Reaction (R3) escape the sample and enter into a vacuum or a metal substrate, it will result in a charge imbalance in the sample and eventually a relative deficiency of OH$^-$ compared to H$_2$O$^+$. The photoelectrons have a short inelastic mean-free-path in ice,\textsuperscript{44} but the electrons will eventually escape the ice film after thermalization if there is no effective mechanism of electron trapping in the ice. As a result, the neutralization reaction of H$_2$O$^+$ with OH$^-$ will be incomplete and the excess portion of H$_2$O$^+$ may survive for an extraordinarily long time in the ice. Note that the population of intrinsic hydroniums is very small in pristine ice at 53–140 K and they cannot be a source of the persisting MAH$^+$ intensity. In support of this interpretation, a MAH$^+$ signal did not appear upon MA adsorption onto the surface of a pristine crystalline ice film at 140 K.
Finally, we discuss the astrophysical implications of metastable hydroniums in ice. H$_3$O$^+$ could be formed in the ice particles of interstellar clouds by penetrating UV light or cosmic rays. If the temperature dependence of the hydronium lifetime observed here is extendible to lower temperatures following an Arrhenius behavior, then the lifetime of H$_3$O$^+$ at the typical temperature of an interstellar molecular cloud (∼10 K) is expected to be ∼2 × 10$^7$ yr or longer. Although this is a very crude estimation, it is clear that H$_3$O$^+$ can survive for a very long time in ice under conditions similar to those of interstellar clouds. The charge imbalance in the ice mentioned above could also increase the lifetime of H$_3$O$^+$. The metastable H$_3$O$^+$ species in interstellar ice particles may induce acid-base reactions, such as protonation of the constituent molecules of the ice. Recently, a laboratory model study with interstellar ice analogues demonstrated that UV-generated H$_3$O$^+$ species react with NH$_3$ to produce NH$_4^+$, which may be a source of the 6.85 μm band observed from interstellar molecular clouds. Relevant situations for metastable H$_3$O$^+$ species may also be found in the outer solar system or cirrus clouds in the earth atmosphere, where cold ice surfaces are exposed to high-energy radiations.

V. SUMMARY

UV photolysis of an ice film at photon energies of 10–11 eV produces metastable hydroniums in the ice. Evidence for the presence of hydroniums includes the formation of MAH$^+$ by the acid-base reaction with MA adsorbates and the occurrence of the H/D exchange reaction in the ice. The photogenerated hydroniums survive for a long time at low temperatures due to the efficient trapping of protons at defect sites as H$_3$O$^+$. The metastable properties of hydroniums are explained in terms of proton dynamics in ice. The hydronium population decays as a result of the release of a proton from H$_3$O$^+$ and the proton migration along the hydrogen-bond chain of the lattice. The proton migration distance is about two water molecules in ice at ∼54 K and increases to about six molecules at 100 K. A sizable portion of hydroniums survive for an extraordinarily long time even at 140 K, probably due to the deficiency of OH$^-$ in comparison to H$_3$O$^+$ in the ice sample. We consider the UV-induced formation of hydroniums to be consistent with observations from previous photoionization studies, including the enhanced electrical conductivity of UV-irradiated ice and the occurrence of the H/D exchange reaction in ice. Further, we suggest the possibility that metastable hydroniums play an important role in the acid-base chemistry of ice in UV-irradiated environments. For example, metastable hydroniums formed in the ice mantle of interstellar dust particles may protonate base molecules in the ice, even when the ice does not originally contain acids. In this respect, H$_3$O$^+$ may act as an invisible acid in interstellar ice chemistry, playing a role analogous to that of H$_3^+$ in interstellar gas-phase chemistry.

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