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Formation of H_2^+ by Ultra-Low-Energy Collisions of Protons with Water Ice Surfaces

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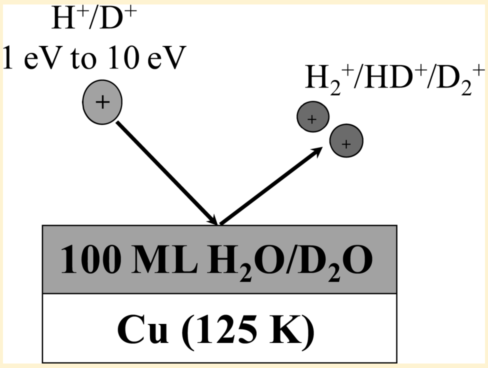
S *Supporting Information*

ABSTRACT: The molecular ion of dihydrogen (H_2^+) is produced by 1 eV collisions of protons (H^+) on amorphous water ice surfaces. The reaction is also observed on crystalline ice surfaces, but with lower efficiency. Collisions of D^+ on amorphous H_2O and D_2O ices yield D_2^+ on the former, subsequent to isotope exchange on the H_2O surface. Ultra-low-energy collision-induced dihydrogen ion production is also observed from alkanol surfaces, with decreasing efficiency as the alkyl chain length increases. There is no corresponding reaction on solid hexane. This endothermic reaction, with implications for interstellar chemistry and plasma etching processes, is proposed to occur as a result of stabilization of the other reaction product, a hydroxyl radical ($OH^•$), on water surfaces through hydrogen-bonding interactions with the surface. These results point to an interesting chemistry involving ultra-low-energy ions on molecular solids.



INTRODUCTION

The proton (H^+) is the simplest of chemical reagents. Even so, the proton has a profound effect in chemistry. The classic text by Bell expands elegantly and authoritatively on the chemical impact of the proton.[1] In particular, Bell discusses the pivotal role played by hydrated protons in numerous processes in the solid, liquid, and gas phases. Our understanding of the formation of, and characterization of, hydrated protons in their numerous forms $[H^+(H_2O)_x]$ is well advanced in the gas[2−4] and liquid phases.[5−12] Characterization of the hydrated proton in the solid phase is equally advanced, but some aspects of its formation, in contrast to that in the liquid and gas phases, are poorly understood. Although direct interaction between H^+ and H_2O molecules in the gas and liquid phases are clearly known to result in the formation of hydrated protons, proton interactions at solid H_2O surfaces have been poorly investigated. Intuition is reinforced, in part, by simulations, such as those of Sanfelix et al.,[13] which confirm the expectation that the result of the interaction of H^+ with solid H_2O surfaces will be hydrated protons. However, in this paper, we wish to report the counter-intuitive observation that one of the products of the interaction of low-energy (<10 eV) H^+ with solid H_2O surfaces at cryogenic temperatures is the gaseous hydrogen molecular ion, H_2^+!

Our probe of low-energy H^+ interactions at solid H_2O surfaces is low-energy ion scattering (LEIS). Surface scattering processes involving ions of energy less than 100 eV are highly sensitive to the first few atomic layers of molecular surfaces;[14] consequently, low-energy ion-surface scattering has revealed a wealth of new surface chemistry and physics, including novel ion-surface reactions, such as surface hydrogen abstraction[15,16] at ultrathin molecular films.[17] Ongoing instrumental development has now made it possible to investigate mass-selected ion-surface collisions on molecular solids with energies below 10 eV at energy resolutions significantly less than 500 meV.[18]

Solid H_2O (also D_2O) has itself been a target for a variety of studies that have explored a range of phenomena using photons, electrons, and ions.[19−25] Measurements by Orlando and others have shown that the major gas-phase species produced by electrons with energies in the range of 5−50 eV are H(D) and O atoms.[26] These are produced only when electrons with energies in excess of 6.5 eV are used, and the yield increases monotonically with electron energy. At energies above 10 eV, a minor reaction channel produces gas-phase O_2 via a mechanism that involves dissociative electron attachment to a stable reaction product originating from the primary electron-induced chemistry of $H_2O(D_2O)$.[27] The nature of this intermediate is as yet unknown, but it may well be H_2O_2. Only the atomic H(D) channel shows any evidence for resonance effects probably associated with dissociative $3a_1 \rightarrow 4a_1$ and $1b_2 \rightarrow 4a_1$ excitations within the solid.[26] Production of $H^-(D^-)$ is also observed in this energy regime and shows significantly more resonance structure with features observed in both the 6−12 eV and the 18−32 eV ranges that have been assigned to dissociative electron attachment resonances.[28] As the energy of the incident electrons is increased beyond 20 eV, electron-stimulated desorption of positive ions occurs with observations of $H^+(D^+)$, $H_2^+(D_2^+)$, O^+, $OH^+(OD^+)$,

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and protonated water cluster ions.[29−35] $H^+(D^+)$, $H_2^+(D_2^+)$, and protonated water clusters come to dominate the electron-stimulated desorption spectra of ice at all energies above 100 eV.[29−35] Production of these ions also shows significant dependence on the morphology of the ice film.[29−35] Measurements of Kimmel and Petrik have even gone as far as to demonstrate that the low-energy electron-induced chemistry in water ices occurs specifically at the interface of the ice with the underlying substrate and, most importantly, from the surface processing standpoint, at the ice−vacuum interface.[36] Energy deposited in the bulk of the ice in the form of excitons diffuses to the interfaces where chemistry subsequently occurs.

Likewise, there is substantial literature on high-energy ion-surface interactions. In particular, these have latterly focused on exploring structural relaxation of water, alcohols, and mixed phases of the two.[23,24] In such experiments, the scattered H^+ ion yield reflects the molecular arrangement of the film at its surface. The total scattering yield of H^+ is influenced by the relaxation of the bulk structure or the change in film morphology. The results from this work suggest that the aliphatic groups in alcohols play an important role in the structural relaxation of their solid films[23] and that, for both water and methanol, a liquid phase persists above their respective glass-transition temperatures.[24] High-energy collisions of Au^+, Au_3^+, and C_{60}^+ on water ice produce both $(H_2O)_nH^+$ and $(H_2O)_n^+$ clusters, in contrast to the gas phase where $(H_2O)_nH^+$ dominates the mass spectrum.[37]

It is now timely to consider applying the techniques of low-energy ion-surface scattering to probing the interaction of near thermal ions, as might be found in atmospheric pressure plasmas, at high altitude in planetary atmospheres, or in the interstellar medium, with solid H_2O surfaces relevant to atmospheric pressure plasma processing and plasma-assisted desorption mass spectrometries,[38] chemistry in the upper atmosphere,[39] and in the interstellar medium.[40]

■ EXPERIMENTAL SECTION

The instrumental setup and an outline of the experiment procedures are given elsewhere.[18,41−43] The low-energy collision experiments and the precautions used were described earlier.[18] Briefly, the experiments described here were conducted in a double-chamber ultrahigh vacuum (UHV) system with a base pressure of $<5.0 \times 10^{-10}$ mbar. Each region of the system is pumped by a 210 L/s Pfeiffer (TMU 261) turbomolecular drag pump. These two pumps are backed by a further 60 L/s Pfeiffer (TMU 071P) turbomolecular pump that, in turn, is backed by a 3.3 m^3/h Pfeiffer (MVP 055) dry pump. In the present experiment, ions (i.e., H^+ and D^+) are produced by a 70 eV electron impact (EI) of the precursor gases (i.e., H_2 and D_2) in a source block maintained at varying potentials. They are mass-selected using a quadrupole filter and collided with the ice surface at a specific collision energy. The mass resolution, $\Delta m/m$, of the quadrupole mass filter is 1800.

A high-precision UHV specimen translator with *xyz* axis movement and tilt was used to support the substrate for preparing amorphous and crystalline ice films;[18,41−45] polycrystalline copper as used in previous experiments was employed. The substrate potentially plays a crucial role in determining the quality of the grown film, but in the present case, this substrate effect is negligible due to the higher coverages employed. The solid H_2O surface is prepared by exposing the cold copper substrate to water vapor at a specific pressure as described below. Solid H_2O films grown in UHV at deposition temperatures below 120 K are known to be amorphous in nature and of low porosity (hence, compact amorphous solid water, cASW), whereas deposition above 140 K results in the growth of crystalline solid H_2O (CW).[45] It may be noted that the dewetting temperature is much higher (∼160 K) for 50 monolayer (ML) ice films.[46] We restricted our study to amorphous ice (125 K) and crystalline ice (142 K) to see changes in product ion intensity. The temperatures we kept just below and just after the crystallization regime. Lowering the temperature to around 110 K in a limited number of experiments did not make significant changes.

As in the previous experiments, the copper surface was grounded in all the experiments. By varying the potential of the ion source block and tuning the rest of the ion optics, it was possible to produce a beam current of 1−2 nA for the mass-selected ions. The mass-selected ions collide with the surface at an angle of 45° with reference to the surface normal, and the scattered ions were collected and mass-analyzed by a second quadrupole. The entire scattering region feels the same potential, and the einzel lenses on either side of the target surface are at nearly the same potential, which was always close to the collision energy investigated. Thus, the ions are subjected to field free conditions around the scattering center. The ion energy spread is larger at 1 eV, but reduces significantly at higher energies. The measured full width at half-maximum (fwhm) of the ion kinetic energy spread for 1 eV Ar^+ was around 0.62 eV. The energy spread at 3 and 5 eV was smaller at around 11.5%.[18] Typically, the energy spread is around this value until about 10 eV. The larger ion energy width at 1 eV seems to be due to the poor optimization of the ion optics at extremely low energies.[18] This larger energy spread near 1 eV is important while considering the results presented.

Deionized water was used after triple distillation for preparing solid water. D_2O and alcohols were purchased from Aldrich; *n*-hexane and carbon tetrachloride (CCl_4) were from Rankem. The substances used in our study (H_2O, D_2O, CCl_4, alkanols, and *n*-hexane) were purified before use by many freeze−pump−thaw cycles. Molecular solid surfaces were prepared by depositing the corresponding vapors on the cooled polycrystalline copper substrate and were delivered very close to the substrate through a tube. The distance between the gas delivery tube and polycrystalline copper substrate was adjusted to obtain uniform sample growth on the substrate. Delivery of molecules near the substrate ensured that the vapors were not deposited in unwanted areas. Although it was not possible to avoid deposition at unwanted areas completely, this was much better than background deposition. The film formed in such tube dosing was found to be uniform in previous experiments.[46] Exposure of the substrate to the vapor was controlled by a leak valve that was adjusted to give a vapor deposition flux of approximately 0.1 ML/s. The gas line connected to the leak valve was pumped thoroughly by a rotary pump to avoid contamination by impurities. The thickness of the overlayers was estimated assuming that 1.33×10^{-6} mbar·s = 1 ML. In all of our experiments with cASW, the deposition temperature was kept at 125 K. The partial pressure(s) of the gas(es) inside the scattering chamber during deposition time was 1×10^{-7} mbar. The films prepared on the copper substrate are identified as Cu@A, implying the growth of a layer of molecule A over Cu. The spectra presented here were averaged for 75 scans, and the data acquisition time was approximately 0.5 s per scan. The present instrumental setup does not allow temperature-programmed desorption (TPD) measurements.

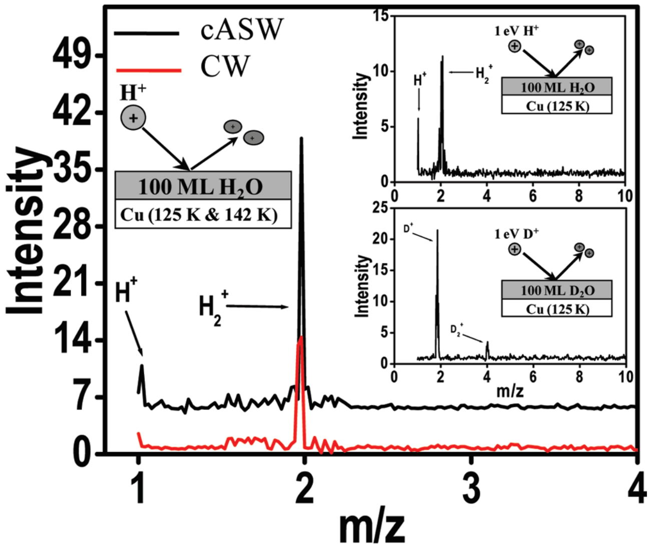

Figure 1. Mass spectrum generated after bombardment of 2 eV H^+ on cASW and CW. The spectrum from cASW is shifted vertically for clarity. The insets show the result of collision of 1 eV H^+ on cASW and D^+ on condensed D_2O, respectively, at 125 K. The experiment is shown in a simplified manner in another inset.

RESULTS

Figure 1 shows the product mass spectrum resulting from collisions of H^+ at a translational energy of 2 eV with cASW and CW surfaces held at 125 K. The spectra in the figure clearly show features at m/z = 1 and 2, which are assigned to H^+ and H_2^+, respectively. The intensity of scattered H^+ is small compared to that of H_2^+. We do not attribute this observation to reaction efficiency alone, as ion transmission varies significantly across this mass window and the quadrupole mass filter has a lower mass limit of m/z = 1. The inset in Figure 1 shows the corresponding spectrum for 1 eV H^+ collisions on cASW. At this energy, the product ion intensity depends on the time of ion exposure, increasing with increasing exposure to the H^+ primary ions, possibly as a consequence of changes in the cASW surface structure. On increasing the incident H^+ kinetic energy up to 10 eV, no additional signals were observed other than m/z = 1 and 2. Collisions of protons with the cASW surface, therefore, make the molecular ion of H_2! This has been confirmed by collisions of D^+ on D_2O at 1 eV, which make D_2^+ (inset of Figure 1).

Figure 1 also shows the effect of replacing the cASW target with CW grown on the copper substrate at 142 K. Independent experiments confirm that deposition of H_2O at this temperature results in the growth of crystalline water ice films. The mass spectra generated were similar to those observed for cASW. However, detailed comparison of the data from the CW surface with that from the cASW surface indicates that the signal intensity was lower under identical conditions of ion flux and signal averaging. This clearly indicates that the efficiency of hydrogen abstraction has reduced significantly in changing from cASW to CW target. Reflection—absorption infrared spectroscopy (RAIRS) has shown that dangling −OH groups are present on the cASW surface in significant concentration, but not on CW.[47] Consequently, this contrast in reactivity may reflect the lack of these groups on the CW surface, implying that projecting −OH groups may be largely responsible for the formation of the dihydrogen cation. The extent of neutralization at the water ice surface and difference in surface structure are factors important in deciding the reflected H^+ projectile ion intensity. Although a direct measurement of reaction efficiency is not made, we estimate that it is a factor of 2 larger for cASW than for CW.

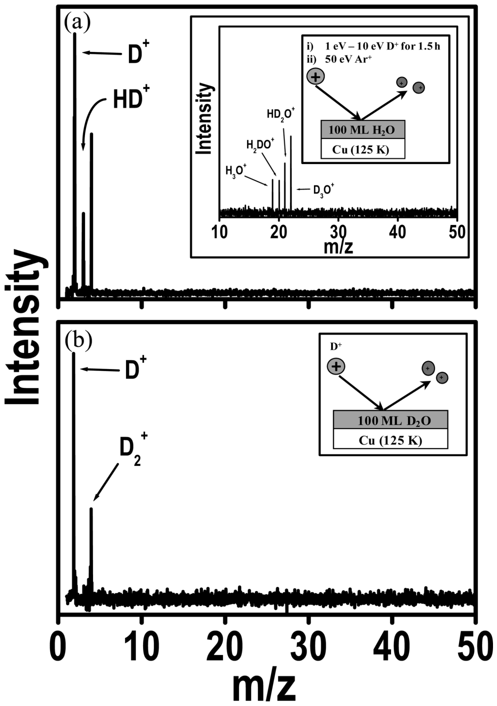

Figure 2. (a) Mass spectra observed after collision of 2 eV D^+ ions on ASW at 125 K. The inset shows the result of chemical sputtering performed using 50 eV Ar^+ on the reacted ASW surface. A simplified representation of the process is shown by a cartoon. (b) Mass spectra obtained after collision of 2 eV D^+ ions on solid D_2O at 125 K. A simplified representation of the process is shown in the inset.

To confirm the reaction, the H^+ projectile was replaced with one of its isotopes (D^+). Figure 2a shows the resulting spectra at a D^+ kinetic energy of 2 eV. As can be seen, m/z = 3 along with m/z = 2 (D^+) and m/z = 4 (D_2^+) are all detected upon the collision of D^+ with cASW at 125 K. The peak at m/z = 3 is assigned to HD^+ (see the Supporting Information, Figure S1, which summarizes spectra at different collision energies) formed upon interaction of D^+ projectiles with O—H bonds at the cASW surface. It is important to emphasize that HD^+ is observed even at a collision energy of 1 eV, although the intensity is weak (Supporting Information, Figure S1). As the mass spectrum shows no ions above m/z = 10, all spectra in the Supporting Information are shown only in the m/z = 1—10 window. The appearance of m/z = 4 (D_2^+) may be explained through a two-stage process involving D^+ interaction with isotopically exchanged cASW (HDO or D_2O) or the reaction products, H_2DO^+ and HD_2O^+. That is, an initial D^+ encounter with cASW generates a D-labeled species, and then, subsequent interactions with a second D^+ on the modified surface generate the gas-phase species D_2^+. Soft-landing of low-energy ions and associated surface modification have been established in a number of cases.[48,49] In agreement with this, the exchange product D_2^+ was not observed immediately, rather only after D^+ irradiation of the cASW surface for 6 min or more. By way of confirmation, a cASW surface was irradiated with D^+ at collision energies in the range of 1—10 eV for 1.5 h. Immediately after this irradiation, chemical sputtering, using

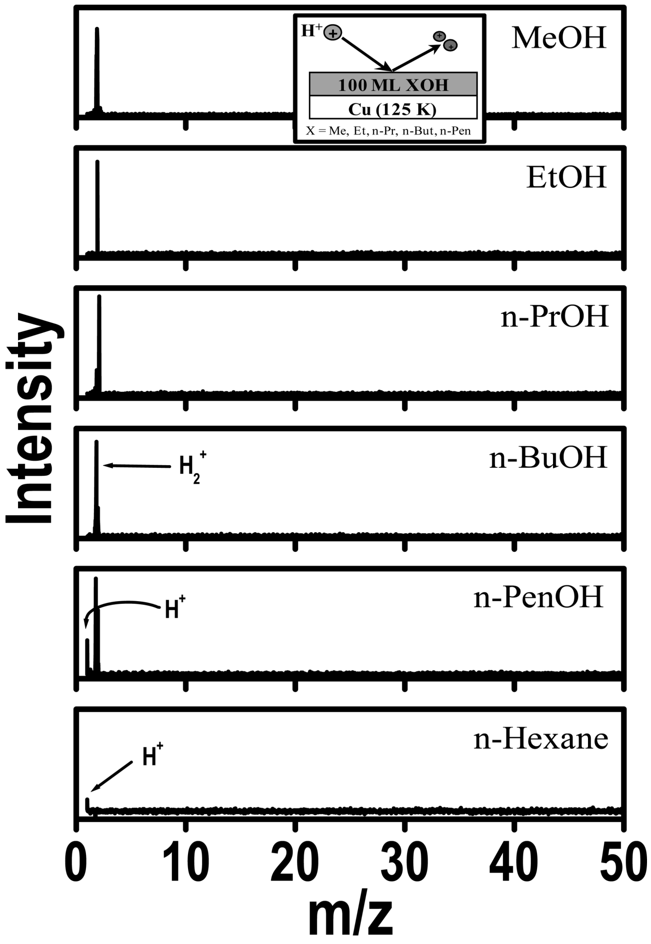

Figure 3. Mass spectra upon the collision of 2 eV H^+ ions on different substrates at 125 K. The inset shows the schematic of the experiment. Other than methanol and ethanol, the spectra were collected 10 min after ion exposure.

50 eV argon ions (Ar^+), was used to reveal the nature of the cASW surface. The inset in Figure 2a shows the result of this experiment. Peaks at m/z = 19, 20, 21, and 22 were observed, which are assigned as H_3O^+, H_2DO^+, HD_2O^+, and D_3O^+, respectively. These data confirm that D^+ irradiation of cASW results in isotopic exchange at the cASW surface. The suggested D^+ interaction with isotopically exchanged cASW (HDO or D_2O) or the reaction products, H_2DO^+ and HD_2O^+, may be taken in the context of the proposed mechanism presented below. We do not imply a direct collision of H^+/D^+ with H_2DO^+/HD_2O^+ as the collision partner is ice and the charge on the hydronium ion formed is rapidly delocalized (see below).

Figure 2b shows the results of collisions of D^+ on the D_2O analogue of cASW at 125 K. Peaks at $m/z = 2$ and 4 are assigned to D^+ and D_2^+, respectively. In this case, at a collision energy of 1 eV, only D^+ was observed; D_2^+ started appearing with high intensity at collision energies of 2 eV and above (see the Supporting Information, Figure S2). Although the gross features of the mass spectra are highly reproducible, the scattered ion intensities do show variations from spectrum to spectrum, especially at very low collision energies.

Further investigations were carried out in which water ice (H_2O or D_2O) was replaced with the homologous series of alkanols (methanol to *n*-pentanol) or a solid hydrocarbon, *n*-hexane. Figure 3 shows the comparative results from frozen alcohols and *n*-hexane when irradiated with H^+ at a kinetic energy of 2 eV. The alcohols clearly behave in a similar manner to water; although the longer-chain alcohols require more exposure time to yield a stable product ion signal. Initial exposure to H^+ produces a weak signal of H_2^+ (see the Supporting Information, Figure S3). This observation can be explained as follows. For short-chain alkanols at low temperature, a significant fraction of O—H bonds project toward the surface, but as the chain length increases, the number of O—H bonds projecting out into the vacuum is reduced. In other words, the surface becomes more hydrophobic with increasing chain length. Such surface hydrophobicity is consistent with sum frequency studies of liquid alcohols.[50] In the case of long-chain alkanols, therefore, the proton reaction pathways to H_2^+ are not immediately available. Longer exposure to the ion beam is required to alter the surface structure of the condensed long-chain alkanols to present hydroxyl groups at the surface. In contrast to the alcohols, *n*-hexane does not possess an O—H bond and the incident kinetic energy of H^+ was insufficient to produce H_2^+ abstraction from C—H bonds. The impinging H^+ is simply reflected from the *n*-hexane surface with reduced intensity due to charge neutralization at the molecular solid.

DISCUSSION

The present experimental apparatus permits only detection of gas-phase ions. The molecular solid surface has not directly been investigated; nevertheless, the ions detected carry information about the surface species. The results reported here do not point to large hydronium ion concentration at the surface, but they do not completely rule this out as ion ejection to the gas phase requires substantial momentum transfer from the projectile, which is not possible in these experiments. As a consequence, hydronium ions are not detected. The simplest possible reaction to account for the observations is the process

$$H^+ + H_2O \rightarrow H_2^+ + HO^\bullet \qquad (1)$$

Note that $HO^\bullet$ is not detected in this experiment, although all the other species are observed. It could be argued that the copper substrate on which the ice film was grown could supply electrons to promote neutralization and the proposed surface reaction. However, this is not the case, as was confirmed by performing experiments in which a 50 ML CCl_4 film was first deposited on the copper substrate before growing the cASW layer. As these CCl_4 films are insulating, electron transport from the copper to the ice and hence to the incoming proton is prevented (see the Supporting Information, Figure S4). In addition, CCl_4 will not interfere in the reaction because it cannot diffuse through a 100 ML thick ice film.[43] Experiments have also been conducted as a function of ice film thickness, and no change in ion intensity or in the nature of the products was detected at thicknesses of 10, 50, 100, and 200 ML (the 200 ML data are presented in the Supporting Information, Figure S5). This further confirms that the underlying substrate or thickness of the ice film has no effect on the observed chemistry.

In considering the likely reaction pathways and their energetics, it is worthy of note that the dissociation energy of H_2O^+ to H_2^+ and O is theoretically 10.4 ± 2 eV,[51] and therefore, this channel is impossible to access given that all the collision energies employed in this study are below 10 eV, even if H_2O^+ were to be formed by primary ion neutralization.

Thermochemically, reaction 1, in the case of 1 eV protons, is highly endothermic. Using standard thermochemical values, for H_2O in the gas phase, Δ_rH is endothermic by 2.63 eV, ignoring the translational energy of the incident proton. However, the presence of dangling O−H bonds on the surface of cASW (and, to a lesser extent, CW) and the different extent of the hydration of the product radical in comparison to the reactant might make the thermochemistry more favorable. For water, the solvation energy of $HO^{\bullet}$ is almost equal to that of H_2O and so the reaction enthalpy remains around 2.63 eV.[52] Of course, there could be some differences in the case of other systems, such as alcohols.

It is interesting to note the reports of production of H_2^+ from H_2O surfaces during electron irradiation from Orlando and coworkers.[31−35] H^+ and H_2^+ production by electron impact on ice exhibits a threshold around 20 eV and a electron flux dependence consistent with a single electron-impact event. Orlando and coworkers speculate that the production of H_2^+ is consistent with unimolecular decomposition of excited H_2O^+ and reactive stripping of H atoms from the ice surface by energetic protons. The H^+ kinetic energy observed in these experiments is adequate to overcome the 2.63 eV endothermicity of reaction 1 identified in the paragraph above. The feasibility of H_2^+ formation as seen in our experiment reaffirms the importance of the stripping reaction proposed in ESD experiments. However, the present observations of H_2^+ formation in an endothermic regime requires additional consideration.

A number of alternative multistep processes may well be possible. The first of which is reaction 2 (reactions 2a and 2b)

$$H^+ + H_2O \rightarrow H_3O^+ \tag{2a}$$

$$H^+ + H_3O^+ \rightarrow H_2^+ + H_2O^+ \tag{2b}$$

In the gas phase, reaction 2a releases of the order of 6.54 eV. Reaction 2b is estimated to have a Δ_rH of the order of 8.06 eV. Hence, overall, for reaction 2 ($2H^+ + H_2O \rightarrow H_2O^+ + H_2^+$), the Δ_rH is endothermic by some 1.52 eV. Of course, reaction 2a is likely to result in multiple steps such that H_3O^+ is suitably solvated. As a result, the charges of the reactants and products of reaction 2b reside at distant locations so that there is no Coulombic repulsion between them. Given a typical time scale for proton transfer in ice of 1×10^{-13} s,[53,54] if we consider the hopping length as 2.5 Å, that is, the hydrogen bond length between water and hydronium ion,[54] then within a few tens of picoseconds, there is time for the charge to move several nanometers away from the colliding partner. Stabilization of the reaction products of this multistep event in this manner may make the proposed reaction viable at ice surfaces. This type of reactivity would also be facilitated by increased acidity at the ice surfaces.

Reaction 3 (reactions 3a−3c) presents a further alternative, but still proceeding via the H_3O^+ intermediate

$$H^+ + H_2O \rightarrow H_3O^+ \tag{3a}$$

$$H_3O^+ \rightarrow H_2O^+ + H \tag{3b}$$

$$H + H^+ \rightarrow H_2^+ \tag{3c}$$

Whereas reaction 3a can release about 6.54 eV in the gas phase, as mentioned above, reaction 3b requires an input of 10.58 eV.[55] The hydrogen atom formed can combine with a second incident proton to give the molecular hydrogen ion as in reaction 3c. Taking reaction 3c to be 2.52 eV exothermic (based on ionization potentials and bond dissociation energy), the energy required for H_2^+ formation by the overall reaction sequence of reaction 3 is 8.06 eV. However, this process requires that the second colliding H^+ interact with the dissociation product, H (in reaction 3b), which is unlikely because the retention time of H atoms on the ice surface at the experimental temperature is very short.[56] Furthermore, with an incident H^+ ion current of less than 1 nA, it is also unlikely that the molecular collision partner at the surface (reaction 3a) will interact with a second H^+ to form the product. This is the case for all low-energy ion/surface collision experiments. At the same time, in view of the mobility of the proton on ice, H may well be formed well away from the site of initial H^+ impact. In such a situation, however, the endothermic step 3b is unlikely as the energy released by step 3a would have dissipated into the bulk ice. These points suggest that this proposed alternative process is unlikely.

Another alternative channel producing H_2^+ is shown in reaction 4 (reactions 4a and 4b)

$$H^+ + H_2O \rightarrow H_2O^+\,(\text{ground state}) + H \tag{4a}$$

$$H + H^+ \rightarrow H_2^+ \tag{4b}$$

The enthalpy of reaction 4a is 4.04 eV, and the overall enthalpy change for reaction 4 is endothermic by 1.52 eV. All the unfavorable aspects of reaction 3 are valid here too.

There are other channels worth considering. H_2O^+ formed upon ion neutralization reacts instantaneously with a neighboring H_2O by proton transfer, leading to $HO^{\bullet}$ and H_3O^+. The neutralized H reacts with the incoming H^+ leading to H_2^+. This may be presented as

$$H^+ + 2H_2O \rightarrow H + H_2O^+ + H_2O \rightarrow H + HO^{\bullet} + H_3O^+ \tag{5a}$$

$$H + H^+ \rightarrow H_2^+ \tag{5b}$$

The overall reaction, $2H^+ + 2H_2O \rightarrow H_3O^+ + H_2^+ + HO^{\bullet}$, is 3.91 eV exothermic. Although neutralization (the first step in 5a) is likely to be efficient, as seen in the scattered ion intensity, the dissociation step requires collisional activation. However, reaction 5b is unlikely in view of the points above. Despite this, we see that, because the overall thermochemistry is favorable, there is a distinct possibility for this channel to occur if H is present away from the site of initial proton impact.

In light of these arguments, we suggest that the possible reaction by the proton is the abstraction of H from dangling −OH bonds at the surface of the ice. The results from alcohols support this suggestion.

What are the implications of these observations? Thermal ion-surface processes are likely to be important in a variety of environments: in plasma-surface processing, plasma-induced surface analysis, planetary atmospheres, and in the interstellar medium.

The interaction of ambient atmospheric plasmas with surfaces for analytical and surface modification purposes is an increasingly active area of surface science. Atmospheric pressure plasmas in rare gases and air, though, in principle, chemically simple, are a complex mixture of ground- and excited-state neutral atoms, ions, and electrons.[56−58] In environments in which these plasmas interact with H_2O in the atmosphere or on surfaces, H^+, H_2^+, and protonated and hydroxylated water clusters come to dominate the mass spectra of the plasma. Which species promote desorption, ionization, and surface change and whether synergistic combinations of species can enhance these processes, are obvious questions. It is likely that metastable species (e.g., rare gas atoms in their $^3S_1$ state) are an important species in promoting chemical processes as plasmas interact with surfaces. Such species have long lifetimes and promote Penning ionization of gaseous species. Energy exchange at surfaces mediated via transient electron transfer to unoccupied surface states is sufficient to promote desorption and other chemistry. Metastable atoms and molecules, when close to a surface, can also promote electron detachment from the surface and electron attachment to adsorbates. Thus, metastable species will induce desorption and other chemical processes. This type of activity seen, in particular, with metastable He, has made metastable atom beams an important tool in surface analysis.[59] However, the role of metastable species in promoting more chemical processes at surfaces warrants further investigation, although there is some speculation as to the importance of metastable He-induced desorption in relation to plasma-assisted desorption/ionization mass spectrometry.[37] Such chemistry naturally parallels that induced by UV light and low-energy electrons, which, in contrast, have received much more attention recently.[60] The possible roles of surface proton transfer in promoting desorption, surface ionization, and chemical change are also open questions given the likely presence of adsorbed water on many surfaces in ambient environments.

As a further illustrative example, icy dust grain surfaces are known to play a significant role in the cold dense interstellar medium (ISM).[57] The interstellar medium is also rich in ions; indeed, the dominant gas-phase chemistry responsible for driving chemical change in the ISM is ion—molecule chemistry.[57] This thermal ion—molecule chemistry typically occurs at temperatures of a few Kelvin, that is, collision energies of a few tens of millielectron volts. This does not mean that ions with translational energies in the range of 1 eV are unlikely. Kinetic energy release from dissociation reactions can produce sufficiently energetic ions. Furthermore, the dust grains in the ISM are likely to be charged (indeed potentially multiply charged) as a consequence of ionization or attachment of electrons/ions to their surfaces. Interactions between such charged grains and ions will have a large electrostatic component, increasing the kinetic energy above the available thermal energy. Collisions between typical ISM ions and ices may produce new molecular species in the solid state and, through ion-stimulated desorption, in the gas phase of direct relevance to the chemical evolution of the ISM.[19,20,58]

H^+ and H_2^+ are key progenitors to chemistry in the gaseous ISM. Both are readily produced by interaction with cosmic rays, H^+ in the diffuse ISM and H_2^+ in the dense ISM, reflecting the dominant form of hydrogen in the two environments. Indeed, much of the gas-phase chemistry in the cold dense medium is initiated by H_2^+. H_2^+ is believed to be the intermediate in the formation of H_3^+ from gaseous hydrogen in the presence of cosmic rays in the dense ISM.[59] Understanding the origins of, and accounting for the observed density of H_2^+, therefore, is an important goal in astrochemistry. The present work presents an additional channel for H_2^+ formation in dense environments where the normal H_2 photoionization channels are limited and cosmic ray ionization of H_2 is the dominant gas-phase mechanism for H_2^+ production, which involves collisions of ultra-low-energy H^+ with icy grains. This work also allows us to reiterate the potential for H_2^+ formation via a stripping mechanism induced by low-energy (>20 eV) secondary electrons produced in interstellar ices by cosmic ray interaction that the work of Orlando and co-workers has revealed.[31−35]

Even the preliminary results reported herein point to a new chemistry that will undoubtedly enrich our understanding of ice surface chemistry relevant to a range of applications in diverse environments.

SUMMARY

In summary, the present work has revealed that protons react differently with H_2O (ice) compared to liquid water. Reaction with H_2O (gas or liquid) typically makes H_3O^+, but upon collision on ice, H_2^+, a gaseous molecular ion, is produced in reasonable yield. Solvation of the hydroxyl radical generated by the reaction of H^+ with H_2O (ice) may make this reaction thermodynamically feasible. H_2^+ is formed more efficiently on cASW than CW, reflecting differences in the surface concentration of dangling O—H moieties that may be implicated in this chemistry. D^+ reacts similarly with ice surfaces. D^+ additionally promotes isotopic exchange on the ice surface with surface O—H moieties transformed into O—D. Simple primary alkanols behave in a similar manner, with evidence for longer alkyl chains protecting the O—H group and requiring significant surface disruption before H_2^+ (HD^+, D_2^+) formation can take place. The absence of labile H atoms in *n*-hexane prevents reaction upon low-energy H^+ impact entirely. The results presented here are preliminary. Additional experiments are required, especially focusing on the kinetic energy release in the products. Such experiments in combination with detailed calculations will undoubtedly be necessary to develop a complete understanding of the mechanistic steps involved in this unusual reaction. This additional knowledge will also be helpful in developing our understanding of the potential implications of the observations reported herein on, for example, isotopic fractionation on grains in cold, dense astronomical environments. Although elementary steps in the reaction and the role of neutrals in the observed chemistry are inconclusive, the formation of H_2^+ in such collisions is established. We believe that this observation itself is the most important aspect of this paper.

ASSOCIATED CONTENT

Supporting Information. Mass spectra observed (1) upon collision of varying energy D^+ ions on cASW at 125 K, (2) upon collision of varying energy D^+ on D_2O at 125 K, (3) immediately upon collision using 2 eV H^+ on solid alcohols and *n*-hexane at 125 K, (4) upon collision of varying energy D^+ ions on 100 ML generated on 50 ML of CCl_4, and (5) immediately upon collision of various energy D^+ ions on 200 ML cASW. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ REFERENCES

(1) Bell, R. P. *The Proton in Chemistry*, 2nd ed; Chapman and Hall, 1973.

(2) Larson, J. W.; McMahon, T. B. *J. Am. Chem. Soc.* **1986**, *108*, 1719.

(3) Lau, Y. K.; Ikuta, S.; Kebarle, P. *J. Am. Chem. Soc.* **1982**, *104*, 1462.

(4) Yang, X.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 6845.

(5) Voth, G. A. *Acc. Chem. Res.* **2006**, *39*, 143.

(6) Berkelbach, T. C.; Lee, H.-S.; Tuckerman, M. E. *Phys. Rev. Lett.* **2009**, *103*, 238302.

(7) Kusaka, I.; Oxtoby, D. W. *J. Chem. Phys.* **2000**, *113*, 10100.

(8) Ushiyama, H.; Takatsuka, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 587.

(9) Botti, A.; Bruni, F.; Imberti, S.; Ricci, M. A.; Soper, A. K. *J. Mol. Liq.* **2005**, *117*, 77.

(10) Headrick, J. M.; Diken, E. G.; Walters, R. S.; Hammer, N. I.; Christie, R. A.; Cui, J.; Myshakin, E. M.; Duncan, M. A.; Johnson, M. A.; Jordan, K. D. *Science (Washington, DC, U.S.)* **2005**, *308*, 1765.

(11) Marx, D.; Tuckerman, M. E.; Hutter, J.; Parrinello, M. *Nature (London)* **1999**, *397*, 601.

(12) Petersen, P. B.; Saykally, R. J. *J. Phys. Chem. B* **2005**, *109*, 7976.

(13) Sanfelix, P. C.; Al-Halabi, A.; Darling, G. R.; Holloway, S.; Kroes, G.-J. *J. Am. Chem. Soc.* **2005**, *127*, 3944.

(14) Cooks, R. G.; Ast, T.; Pradeep, T.; Wysocki, V. *Acc. Chem. Res.* **1994**, *27*, 316.

(15) Williams, E. R.; Jones, G. C., Jr.; Fang, L.; Zare, R. N.; Garrison, B. J.; Brenner, D. W. *J. Am. Chem. Soc.* **1992**, *114*, 3207.

(16) Cooks, R. G.; Ast, T.; Mabud, M. A. *Int. J. Mass Spectrom. Ion Processes* **1990**, *100*, 209.

(17) Brenner, D. W.; Garrison, B. J. *Phys. Rev. B: Condens. Matter* **1986**, *34*, 5782.

(18) Cyriac, J.; Pradeep, T. *J. Phys. Chem. C* **2008**, *112*, 5129.

(19) Gerakines, P. A.; Moore, M. H.; Hudson, R. L. *Astron. Astrophys.* **2000**, *357*, 793.

(20) Sieger, M. T.; Simpson, W. C.; Orlando, T. M. *Nature (London)* **1998**, *394*, 554.

(21) Russo, M. F.; Wojciechowski, I. A.; Garrison, B. J. *Appl. Surf. Sci.* **2006**, *252*, 6423.

(22) Hudson, R. L.; Moore, M. H. *Radiat. Phys. Chem.* **1995**, *45*, 779.

(23) Souda, R. *Phys. Rev. Lett.* **2004**, *93*, 235502.

(24) Souda, R. *J. Phys. Chem. B* **2010**, *114*, 11127.

(25) Park, S.-C.; Moon, E.-S.; Kang, H. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12000 and references cited therein.

(26) Kimmel, G. A.; Orlando, T. M.; Cloutier, P.; Sanche, L. *J. Phys. Chem. B* **1997**, *101*, 6301 and references cited therein.

(27) Herring-Captain, J.; Grieves, G. A.; Alexandrov, A.; Sieger, M. T.; Chen, H.; Orlando, T. M. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *72*, 035431 and references cited therein.

(28) Orlando, T. M.; Kimmel, G. A.; Simpson, W. C. *Nucl. Instrum. Methods Phys. Res., Sect. B* **1999**, *157*, 183 and references cited therein.

(29) Orlando, T. M.; Kimmel, G. A. *Surf. Sci.* **1997**, *390*, 79 and references cited therein.

(30) Orlando, T. M.; Sieger, M. T. *Surf. Sci.* **2003**, *528*, 1 and references cited therein.

(31) Sieger, M. T.; Orlando, T. M. *Surf. Sci.* **2000**, *451*, 31 and references cited therein.

(32) Sieger, M. T.; Orlando, T. M. *Surf. Sci.* **2000**, *451*, 97 and references cited therein.

(33) Chen, H.; Aleksandrov, A.; Chen, Y.; Zha, S.; Liu, M.; Orlando, T. M. *J. Phys. Chem. B* **2005**, *109*, 11257 and references cited therein.

(34) Herring, J.; Aleksandrov, A.; Orlando, T. M. *Phys. Rev. Lett.* **2004**, *92*, 187602 and references cited therein.

(35) Orlando, T. M.; Aleksandrov, A. B.; Herring, J. *J. Phys. Chem. B* **2003**, *107*, 9370 and references cited therein.

(36) Lane, C. D.; Petrik, N. G.; Orlando, T. M.; Kimmel, G. A. *J. Phys. Chem. C* **2007**, *111*, 16319 and references cited therein.

(37) Conlan, X. A.; Fletcher, J. S.; Lockyer, N. P.; Vickerman, J. C. *J. Phys. Chem. C* **2010**, *114*, 5468 and references cited therein.

(38) Ratcliffe, L. V.; Rutten, F. J. M.; Barrett, D. A.; Whitmore, T.; Seymour, D.; Greenwood, C.; Aranda-Gonzalvo, Y.; Robinson, S.; McCoustra, M. *Anal. Chem. (Washington, DC, U.S.)* **2007**, *79*, 6094.

(39) Zhu, C.; Xiang, B.; Chu, L. T.; Zhu, L. *J. Phys. Chem. A* **2010**, *114*, 2561.

(40) Moon, E.-S.; Kang, H.; Oba, Y.; Watanabe, N.; Kouchi, A. *Astrophys. J.* **2010**, *713*, 906.

(41) Cyriac, J.; Pradeep, T. *J. Phys. Chem. C* **2008**, *112*, 1604.

(42) Kumar, G. N.; Cyriac, J.; Bag, S.; Pradeep, T. *J. Phys. Chem. C* **2009**, *113*, 14258.

(43) Cyriac, J.; Pradeep, T. *J. Phys. Chem. C* **2007**, *111*, 8557.

(44) Trakhtenberg, S.; Naaman, R.; Cohen, S. R.; Benjamin, I. *J. Phys. Chem. B* **1997**, *101*, 5172.

(45) Kimmel, G. A.; Petrik, N. G.; Dohnalek, Z.; Kay, B. D. *J. Chem. Phys.* **2007**, *126*, 114702.

(46) Stevenson, K. P.; Kimmel, G. A.; Dohnalek, Z.; Smith, R. S.; Kay, B. D. *Science (Washington, D.C.)* **1999**, *283*, 1505.

(47) Callen, B. W.; Griffiths, K.; Norton, P. R. *Surf. Sci.* **1992**, *261*, L44.

(48) Miller, S. A.; Luo, H.; Pachuta, S. J.; Cooks, R. G. *Science (Washington, D.C.)* **1997**, *275*, 1447.

(49) Gologan, B.; Green, J. R.; Alvarez, J.; Laskin, J.; Graham, C. R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1490.

(50) Stanners, C. D.; Du, Q.; Chin, R. P.; Cremer, P.; Somorjai, G. A.; Shen, Y. R. *Chem. Phys. Lett.* **1995**, *232*, 407.

(51) Leclerc, J. C.; Horsley, J. A.; Lorquet, J. C. *Chem. Phys.* **1974**, *4*, 337.

(52) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, 80th ed.; CRC Press: Boca Raton, FL, 1999.

(53) Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

(54) Agmon, N. *Chem. Phys. Lett.* **1995**, *244*, 456.

(55) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 80th ed.; Chemical Rubber Pub. Co.: Boca Raton, FL, 1999.

(56) Matar, E.; Congiu, E.; Dulieu, F.; Momeni, A.; Lemaire, J. L. *Astron. Astrophys.* **2008**, *492*, L17.

(57) Fraser, H. J.; McCoustra, M. R. S.; Williams, D. A. *Astron. Geophys.* **2002**, *43*, 10.

(58) Lee, C.-W.; Kim, J.-K.; Moon, E.-S.; Minh, Y. C.; Kang, H. *Astrophys. J.* **2009**, *697*, 428.

(59) Herbst, E. *Philos. Trans. R. Soc., A* **2000**, *358*, 2523.