Efficient Thermal Reactions of Sulfur Dioxide on Ice Surfaces at Low Temperature: A Combined Experimental and Theoretical Study

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Supporting Information

ABSTRACT: The interaction of sulfur dioxide (SO2) gas with a crystalline ice surface at low temperature was studied by analyzing the surface species with low energy sputtering (LES) and reactive ion scattering methods and the desorbing gases with temperature-programmed desorption mass spectrometry. The study gives direct evidence for the occurrence of efficient hydrolysis of SO2 with low energy barriers on the ice surface. Adsorbed SO2 molecules react with the ice surface at temperatures above ∼90 K to form anionic molecular species, which can be detected by OH, SO2, and HSO3− emission signals in the LEES experiments. Heating the sample above ∼120 K causes the desorption of SO2 gas from the surface-bound hydrolysis products. As a result, the hydrolysis of SO2 on an ice surface is most efficient at 100−120 K. The surface products formed at these temperatures correspond to metastable states, which are kinetically isolated on the cold surface. Quantum mechanical calculations of a model ice system suggest plausible mechanistic pathways for how physisorbed SO2 is transformed into chemisorbed HSO3− species. HSO3− is formed either by direct conversion of physisorbed SO2 or through the formation of a stable H2SO3 surface complex, both involving proton transfer on the ice surface with low energy barriers. These findings suggest the possibility that thermal reactions of SO2 occur efficiently on the ice surface of Jovian satellites even without bombardment by high-energy radiation.

KEYWORDS: Sulfur Dioxide, Ice, Jovian Satellites, Hydrolysis, Proton Transfer, Reaction Mechanism

1. INTRODUCTION

Fundamental studies of the interactions of sulfur dioxide (SO2) gas with ice surfaces are important for the understanding of the heterogeneous reactions of SO2 on ice surfaces in the Earth’s atmosphere or the outer planets of the solar system.1,2 The interaction of SO2 with ice in the temperature range of the Earth’s atmosphere (190−273 K) have been extensively studied.1 Ice surfaces are covered with quasi-liquid layers at these temperatures.1 The reactivity of an ice surface under these conditions is predominantly influenced by this quasi-liquid layer and may be understood as an extension of the reaction behavior of the surface of liquid water. The present study focuses on the interactions of SO2 with an ice surface at lower temperatures (90−160 K) in which the surface is devoid of a quasi-liquid layer and is stable under vacuum without sublimation. This environment is relevant to Jupiter’s icy satellites, including Europa (86−132 K), Ganymede (∼124 K), and Callisto (∼115 K),1,2 where remote sensing has detected surfaces with significant amounts of water ice and minor amounts of SO2, CO2, and H2O2.2,3,5−7

Several research groups have studied the interactions of SO2 gas with ice surfaces below the temperature of quasi-liquid layer formation.7−11 Devlin and co-workers14 examined the interactions of ice nanoparticles with SO2 gas in the 120−140 K temperature range using infrared (IR) spectroscopy. They observed IR absorption bands for SO2 molecular species as well as bands that are similar to those of SO2 in aqueous solution and assigned the latter to anionic products arising from SO2 ionization based on an ab initio normal-mode analysis of HSO3−. Using IR spectroscopy, Loeffler and Hudson10 reported that sulfur oxyanions such as HSO3− and SO42− are formed in H2O−SO2 mixed films at cryogenic temperatures; S2O52− is formed by the reaction between two HSO3− molecules at high SO2 concentrations. Photoelectron spectroscopic studies10 of SO2 adsorption on ice films at 100 K indicated the presence of molecular SO2 adsorbates as well as sulfuric acid-like species with distinguishable S(2p) electron binding energies. Kim et al.11 examined the reaction of SO2 with a frozen water film on a Ru(0001) substrate using low energy sputtering (LES) and reactive ion scattering (RIS) techniques; various ions related to SO2 hydrolysis on the ice surface were detected. However, thin frozen-water films undergo a roughening phase transition upon heating12,13 and

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this structural change may affect reactions on the sample surface. To avoid such complications in the present work, we prepared a thick crystalline ice film on a Pt(111) substrate, which remains stable during sample heating to ~160 K without undergoing any phase transition. The surface products resulting from the interaction of SO2 gas with the ice surface, as well as the desorbing gases, were examined as functions of temperature by conducting LES, RIS, and temperature-programmed desorption (TPD) experiments. Quantum mechanical calculations for a model ice system were performed to understand the reaction mechanism of SO2 on the ice surface.

2. METHODS

2.1. Experimental Section. Experiments were conducted in an ultrahigh vacuum (UHV) surface analysis chamber14,15 equipped with instrumentation for RIS, LES, and TPD experiments. An ice film was grown on the (111) face of a Pt single crystal by backfilling the chamber with H2O vapor at a partial pressure of 1.0 × 10−7 Torr. The substrate temperature was maintained at 150 K during the growth of the ice film, and the film was flash-annealed at 165 K. It is known16−19 that this procedure produces a nonporous crystalline ice film with predominant Ih(0001) surfaces. The thicknesses of the ice films were typically 90−110 ML (monolayer; 1 H2O ML = 1.1 × 1019 molecules m−2) as estimated from the water desorption signal in the TPD experiment. The growth of the ice films took ~15 min under these conditions.

SO2 (99.99+\% purity) gas was introduced into the chamber through a separate leak valve and guided close to the sample surface through a tube doser to minimize chamber wall contamination. SO2 was adsorbed onto the ice film at 95 K. The amount of adsorbed SO2 gas was estimated from TPD measurements. The intensity of the SO2 desorption signal was converted to SO2 coverage through calibration against water desorption signal in the TPD experiment. The growth of the ice films took ~15 min under these conditions.

The amount of adsorbed SO2 gas was estimated from TPD experiments. An ice film was grown on the (111) face of a Pt single crystal by backfilling the chamber with H2O vapor at a partial pressure of 1.0 × 10−7 Torr. The substrate temperature was maintained at 150 K during the growth of the ice film, and the film was flash-annealed at 165 K. It is known16−19 that this procedure produces a nonporous crystalline ice film with predominant Ih(0001) surfaces. The thicknesses of the ice films were typically 90−110 ML (monolayer; 1 H2O ML = 1.1 × 1019 molecules m−2) as estimated from the water desorption signal in the TPD experiment. The growth of the ice films took ~15 min under these conditions.

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Chemical species present on the ice film surface were analyzed using RIS and LES methods. The principles of these methods have been described previously.20 In these experiments, a Cs+ beam from a low-energy ion gun (Kimball Physics) collided with the sample surface at an incident energy of 35 eV. The positive and negative ions emitted from the surface were detected by a quadrupole mass spectrometer (ABB Extrel) located at the scattering angle of 55° with its ionizer−center by−center dipole moment of the crystal. The internal coordinates of the water molecules in the reference ice crystal were set such that the O−O distances, O−H distances, and O−O−O angles matched the experimentally determined values of 2.75 Å, 1.00 Å, and 109.3°, respectively. The specific combination of quantum mechanics (QM) and effective fragment potential (EFP) schemes in this paper involves a two-layer model (QM-relaxed region/EFP water), where the coordinates in the QM-relaxed region are fully relaxed during geometry optimization. A large ice crystal consisting of 27 QM waters and 457 EFP waters, referred to as “HDB2(27/457),” is depicted in Figure 2. The “HDB2” term in this nomenclature system refers to a hexagonal binding site with two HDBs, which are indicated by the arrows in Figure 2a. This model simultaneously includes both the effect of geometry relaxation due to adsorption and the long-range electrostatic interactions of ice crystals.

2.2. Theoretical Methods. 2.2.1. Ice Surface Model. The ice model was constructed to have a crystalline ice (Ih) structure with a (0001) surface plane. The model consisted of bilayers (BLs) of tetrahedrally bonded H2O molecules connected by hydrogen bonds; the oxygen planes were separated by 2.75 Å between bilayers and 0.92 Å within the bilayer. The Ih ice structure has bilayers in an ABCABC... stacking sequence. Each O atom was surrounded by four other hydrogen-bonded oxygens that are 2.75 Å away. The H atoms were not centered between two O atoms in the hydrogen bonds but remained off-center by ~0.38 Å in a random distribution that satisfies the Bernal−Fowler structure.4 The (0001) surface of the ice model had “full bilayer” terminations, which are energetically favored (by 30 kJ/mol per unit cell) over the “half-bilayer” terminated surface4 because of the larger number of intermolecular hydrogen bonds. In the “full-bilayer” terminated surface, each of the outermost O atoms in the upper layer is hydrogen-bonded to three neighbors of the lower layer. It has been reported13 that the “full bilayer” terminated surface is predominantly formed when an ice film is annealed at ~150 K, the condition employed in the present experiment.

At the basal surface of the “full bilayer” terminated ice Ih structure, each of the outermost water molecules has one dangling bond, either an oxygen dangling bond (ODB) or a hydrogen dangling bond (HDB), that points outward, as shown in Figure 1a and b, respectively. These dangling bond sites are considered to be the primary reactive places due to their outermost positions on the ice surface. Their statistical distributions on the ice surface reflect the microscopic heterogeneity of the surface, which in turn provide various reaction environments, including multiple interaction sites for adsorbates. We employed a systematic strategy to build the model ice surfaces. The coordinates of a reference ice crystal of 36 hexagons by 15 hexagons and 5 BLs deep were generated by randomizing the hydrogen-bonding distribution to ensure a (near to) zero dipole moment of the crystal. The internal coordinates of the water molecules in the reference ice crystal were set such that the O−O distances, O−H distances, and O−O−O angles matched the experimentally determined values of 2.75 Å, 1.00 Å, and 109.3°, respectively. The specific combination of quantum mechanics (QM) and effective fragment potential (EFP) schemes in this paper involves a two-layer model (QM-relaxed region/EFP water), where the coordinates in the QM-relaxed region are fully relaxed during geometry optimization. A large ice crystal consisting of 27 QM waters and 457 EFP waters, referred to as “HDB2(27/457),” is depicted in Figure 2. The “HDB2” term in this nomenclature system refers to a hexagonal binding site with two HDBs, which are indicated by the arrows in Figure 2a. This model simultaneously includes both the effect of geometry relaxation due to adsorption and the long-range electrostatic interactions of ice crystals.

2.2.2. Computational Details. All stationary points for the HDB2(27/0/457) ice model were calculated at the MP2/6-31+ +G(d)//HF/6-31G(d) and B3LYP/6-31+G(d)//HF/6-
31G(d) levels of theory. The energies obtained using MP2/6-31++G(d) are discussed in the sections below. All calculations were performed without any symmetry constraints unless otherwise specified. The GAMESS program was used for all calculations.

3. RESULTS

3.1. Experimental Results. TPD, RIS, and LES measurements were conducted to study the reactions of SO2 gas on a crystalline H2O film surface. Figure 3 displays the TPD SO2 desorption spectra of ice films adsorbed with different surface coverages (0.04–0.65 MLE; 1 monolayer equivalent of H2O = 1.1 × 10^19 molecules m^-2) of SO2. The desorption of SO2 was observed to occur over a broad temperature range (105–130 K), and the desorption profile changed with changes in SO2 coverage. At the lowest coverage (0.04 MLE), the desorption profile exhibits a single peak at temperatures of 120–140 K. At higher coverages, the profiles are broadened toward lower temperatures. These broadened profiles were deconvoluted into two desorption components: one at 120–140 K and the other at 105–130 K. The low-temperature peak grew in proportion to SO2 coverage above ~0.1 MLE, whereas the growth of the high-temperature peak, with SO2 coverage, was much less pronounced. These peak positions did not significantly change at moderately low SO2 coverage (0.10–0.28 MLE), indicating that they correspond to first-order desorptions. Accordingly, we assign the low-temperature peak to the desorption of chemisorbed SO2 species and the high-temperature peak to "chemisorbed" (strongly bound) SO2 species. The low-temperature peak shifted slightly to a higher temperature at high coverage (0.28–0.65 MLE). This indicates a certain degree of contribution of zeroth-order desorption, which may be attributed to the SO2 cluster or multilayer formation at high coverage. The high-temperature peak grown by ~3 times in intensity as SO2 coverage was increased from 0.04 to 0.65 MLE. Deconvolution of the TPD curve at 0.65 MLE into two peaks indicates that "chemisorbed" SO2 species had a coverage of ~0.16 MLE. This coverage, which was near the saturation point, seems reasonable as will be shown in section 3.2. SO2 adsorption sites must have at least one ODB and one HDB, and strong SO2 adsorption typically occupies two HDBs, where the surface density of HDB is 0.25 ML. Most of the SO2 species desorbed from the surface before the onset of water desorption at ~150 K with only insignificant overlap observed between the high-temperature SO2 desorption tail and the peak corresponding to water desorption. The well-separated desorption peaks observed for SO2 and water indicate that SO2 did not dissolve into the ice sample.

Figure 4a shows the RIS mass spectrum of an ice film covered by a small amount (0.04 MLE) of SO2 at 95 K. The large peak at m/z = 133 corresponds to the primary Cs+ ions. RIS signals include Cs(H2O)+ at m/z = 151 due to the pickup of H2O by the Cs+ projectiles and Cs(SO2)+ at m/z = 197 and...
199 (magnified in the inset) due to the pickup of $^{32}\text{SO}_2$ and $^{34}\text{SO}_2$. A very low intensity peak is evident at $m/z = 215$, which is assigned to $\text{Cs(H}_2\text{O)}(\text{SO}_2)$, produced by the double collection of $\text{H}_2\text{O}$ and $\text{SO}_2$. The low intensity of this signal is consistent with the double pickup process. Alternatively, this signal might also correspond to $\text{Cs(H}_2\text{SO}_3)$, which would indicate the formation of $\text{H}_2\text{SO}_3$ by the reaction of $\text{SO}_2$ with the ice surface. This interpretation, however, is not supported by the LES measurements (vide infra, Figure 5), which show no evidence of surface $\text{H}_2\text{SO}_3$ species at 95 K.

Figure 5. TPRIS and TPLES measurements for a 0.04 MLE adsorbed $\text{SO}_2$ ice film. The $\text{SO}_2$ RIS yield (black line; left ordinate scale) monitors the population of surface $\text{SO}_2$ species. The TPLES curves show the signal intensities of $\text{OH}^-$, $\text{SO}_2^-$, and $\text{HSO}_3^-$ (right ordinate), which indicate the populations of the surface anionic species. The TPD spectra of $\text{SO}_3$ and $\text{H}_2\text{O}$ are also shown in gray and red shading, respectively; these indicate the temperature regions of the corresponding gas desorptions. The temperature ramping rate was 0.5 K s$^{-1}$, and the Cs$^+$ beam energy was 35 eV.

Figure 4b depicts the LES mass spectrum of the negative ions measured from the sample described above. In this experiment, the sample temperature was gradually increased from 113 to 118 K during which time the spectrum was acquired through repeated scans. Consequently, the spectrum displays all anionic species appearing on the sample surface in this temperature range. This range was selected because most of the LES signals were very intense over these temperatures; these signals were almost negligible at 90 K. This spectrum shows LES signals corresponding to $\text{OH}^-$ at $m/z = 17$, $\text{SO}_2^-$ at $m/z = 64$, and $\text{HSO}_3^-$ at $m/z = 81$. These ion emissions indicate that $\text{SO}_2$ has reacted to produce negatively charged molecular species on the surface.

The LES measurements did not detect any cationic signals on the surface (data not shown). If we interpret this straightforwardly, cationic species are simply not formed on the surface. Alternatively, cationic species are formed, but they are difficult to detect by LES because, for instance, they are formed in a subsurface region or as part of a large molecular structure that is difficult to desorb by Cs$^+$ impact. The latter possibility will be further discussed in section 4 when the $\text{SO}_2$ reaction mechanism is presented with the aid of theoretical calculations.

We examined the reaction of $\text{SO}_2$ as a function of temperature by conducting temperature-programmed LES (TPLES) and RIS (TPRIS) experiments. Figure 5 shows the results of these experiments for the signals of interest over a 90–160 K temperature scan. The sample was prepared in an identical fashion to that used to generate the results shown in Figure 4. The RIS intensity for $\text{Cs(SO}_2)^+$ is plotted in terms of its RIS yield, which is defined as the intensity ratio of $\text{Cs(SO}_2)^+/\Sigma \text{CsX}^+_z$, where $\Sigma \text{CsX}^+_z$ is the sum of the intensities of all RIS signals. The RIS yield is a more reliable measure of surface population than the RIS intensity; various circumstantial factors that affect the RIS intensity, in particular the changes in surface morphology, are canceled out by dividing with $\Sigma \text{CsX}^+_z$. In support of this rationale, the RIS yield for the $\text{H}_2\text{O}$ signal from the sample surface remained almost constant with increasing temperature until the point of water desorption was reached at around 150 K (not shown). Beyond the water desorption temperature, the RIS and LES intensity variations were no longer proportional to the surface population changes because of severe surface modification. The TPRIS curve for $\text{SO}_2$ shown in Figure 5 indicates that the surface population of $\text{SO}_2$ decreases monotonically as the temperature is increased from 90 to 110 K.

TPLES signals for $\text{OH}^-$, $\text{SO}_2^-$, and $\text{HSO}_3^-$ appeared at 90–100 K and grew stronger with increasing temperature until they reached their maximum values at 110–120 K. The TPLES intensities shown were not calibrated against any internal standard (e.g., externally added halide ions). Therefore, the TPLES profiles only reflect changes in the surface ion populations, but also surface structural changes due to reactions with $\text{SO}_2$. At this point, we neglect the latter effect in interpreting the TPLES curves. Two main features are noticeable in Figure 5. First, increases in the intensities of the $\text{OH}^-$, $\text{SO}_2^-$, and $\text{HSO}_3^-$ signals over the 90–115 K range correlate with decreases in the $\text{SO}_2$ surface population. This indicates that $\text{SO}_2$ adsorbates are hydrolyzed in this temperature region. The emitted anions may correspond to hydrolysis products themselves or originate from the collisional fragmentation of hydrolysis products with larger structure; these two possibilities cannot be distinguished at this point. Nevertheless, the TPLES curves refute the possibility that the anionic signals arise from the secondary ionization of $\text{SO}_2$ molecules; this conclusion is based on the negative correlation between the intensities of the anionic signals and the $\text{SO}_2$ adsorbate population.

Second, the hydrolysis of $\text{SO}_2$ precedes the desorption of $\text{SO}_2$ gas by a substantial temperature gap, as can be seen from the different onset temperatures for $\text{SO}_2$ hydrolysis (90–100 K) and $\text{SO}_2$ desorption (~110 K). Rather, the increased rate of $\text{SO}_2$ desorption at 110–130 K correlates with decreases in the anionic signal intensities. These observations indicate that the $\text{SO}_2$ gas is evolved from hydrolysis products on the surface rather than from physiosorbed $\text{SO}_2$ species.

The TPRIS and TPLES data indicate that physiosorbed $\text{SO}_2$ molecules on the ice surface are efficiently hydrolyzed at 90–120 K. This hydrolysis efficiency must be of the order of unity because the majority of the physiosorbed $\text{SO}_2$ molecules “disappeared” without any $\text{SO}_2$ gas desorption over this temperature range. A direct estimate of the efficiency for the conversion of $\text{SO}_2$ into hydrolysis products, however, is difficult to make because the TPRIS intensities for the various ions may not quantitatively reflect their surface populations.

Only the results for low $\text{SO}_2$ coverage (0.04 MLE) have been discussed so far. When the $\text{SO}_2$ coverage was increased to 0.1–0.65 MLE, a few changes were observed in the corresponding spectra. First, as shown in Figure 3, the low-temperature $\text{SO}_2$ desorption peak at 105–130 K in the TPD spectra gradually
increased in intensity with increasing SO₂ coverage. In addition, in the TPRIS experiments, the decay of the SO₂ RIS yield curve shifted to higher temperatures with increasing SO₂ coverage (not shown) as compared to the original decay observed over the 90–110 K region at SO₂ coverage of 0.04 MLE (Figure 5). The shifted decay of TPRIS curve nicely correlated with the increased intensity of the low temperature peak in TPD spectra (Figure 3); the correlation is based on the relationship that the first derivative of TPRIS curve with temperature (dθ/dT) is proportional to TPD intensity (desorption flux). Therefore, under these conditions, a large portion of growing populations of physisorbed SO₂ species must be directly desorbed from the surface during the sample heating rather than undergoing reactions. As a result, the hydrolysis efficiency of SO₂ will decrease at higher SO₂ coverage. The change in SO₂ hydrolysis efficiency can be seen from the changing TPD profiles in Figure 3. The hydrolysis yield can be defined as the population ratio of “chemisorbed” SO₂ species to all adsorbed SO₂ species, which in turn is proportional to the areal ratio of the high temperature (120–140 K) peak to the whole desorption profile if we neglect the dissolved species in the sample that do not desorb. Because the rate for the increase of the high-temperature peak is much slower than that for the low-temperature peak, the hydrolysis efficiency is correspondingly lower at higher SO₂ coverage.

On the basis of the results shown in Figures 3–5, we propose the following reaction sequence for the hydrolysis of SO₂ on an ice surface. Upon adsorption of SO₂ gas at 90–120 K, SO₂ becomes transformed to anionic molecular species that produce LES signals for OH⁻, SO₂⁻, and HSO₃⁻. This process occurs efficiently without SO₂ desorption at this low temperature. The surface products do not penetrate to the interior of the ice during sample heating, as indicated by the well-separated TPD signals for SO₂ and water (Figure 3). Rather, the surface species are transformed back into SO₂ gas above ~120 K. Therefore, the surface species formed at 100–120 K are considered to be metastable products of SO₂ hydrolysis that are trapped on the surface rather than representing final reaction products that are obtained by reactions in aqueous solution. The desorption of SO₂ gas from the ice surface may be kinetically favored over the penetration of SO₂ into the ice interior, thereby effectively blocking reaction pathways that lead to solvation and the further hydrolysis of SO₂ to energetically more stable products.

3.2. QM Study of the Interaction of SO₂ with an Ice Surface. When SO₂ is adsorbed on an ice surface, the ODBs and HDBs of the surface preferentially interact with the sulfur and oxygen atoms of SO₂, respectively. Therefore, appropriate SO₂ adsorption sites on the surface must have at least one ODB and one HDB. With these considerations in mind, HDB₂-type adsorption sites, which are the hexagonal sites with two HDBs and one ODB, were adopted. Figure 6a shows the initial adsorption structure of a physisorbed SO₂ molecule on the HDB₂(27/0/457) model ice surface. In this adsorption structure, two hydrogen bonds (Ο(3)–Η(18) = 2.06 Å and Ο(2)–Η(11) = 2.17 Å) are formed between SO₂ and surface water molecules. The binding energy of the physisorbed structure is fairly large (97.9 kJ/mol at MP2/6-31+G(d)//HF/6-31G(d)) and is responsible for the efficient entrapment of impinging gaseous SO₂ molecules on the ice surface. This adsorption energy can be used for surface chemical transformations of SO₂ before quickly dissipating into the lattice. It can be noted that the binding energy of SO₂ is significantly larger than the experimental desorption energy of water (48.25 kJ/mol) from crystalline ice, which might appear contradictory to the observation that SO₂ desorbs prior to water. Two main features need to be considered before comparing our theoretical binding energy with the desorption energy. First, the theoretical binding energy comes from the most stable physisorbed structure among other possible ones. There are three interfacial binding interactions including two hydrogen bonds, which makes the structure of Figure 6a exceptionally stable. We have also found other physisorbed structures with weaker binding energies. Second, direct SO₂ desorption from Figure 6a is unlikely to occur due to its multiple interfacial bindings. Instead, desorption paths through intermediate adsorption stages with weaker binding energies are highly expected, which would significantly reduce the final desorption energy of SO₂.

Our theoretical investigation focused mainly on determining pathways for the hydrolysis of physisorbed SO₂ that produce...
anionic molecular species that are observed by LES experiments. We found two plausible pathways that lead to the formation of HSO₃⁻ species. This structure is negatively charged and could produce OH⁻, SO₂⁻, and HSO₃⁻ ions by either collisional fragmentation or desorption during low energy surface sputtering.

\[
\text{SO}_2 \rightarrow \text{H}_2\text{SO}_3 \rightarrow \text{HSO}_3^- : \text{indirect path} \quad (1a)
\]

\[
\text{SO}_3 \rightarrow \text{HSO}_3^- : \text{direct path} \quad (1b)
\]

In reaction 1a (indirect path), a neutral H₂SO₃ complex is formed first, and subsequent deprotonation leads to HSO₃⁻. The other channel directly converts physisorbed SO₂ to HSO₃⁻ (reaction 1b). These two mechanisms are discussed in order.

**Indirect Path.** In this pathway, the electrophilic attack of S(1) at surface O(4) initiates the transfer of surface proton H(6) → O(7). This also produces a transient hydronium in the transition state TSDirect (see Figure 6b) in which two hydrogen bonds are slightly shortened (O(3)···H(18) = 1.86 Å and O(2)···H(11) = 1.89 Å). The formation of a S–O bond is considered to be the signature of hydrolysis because a water molecule is added to the physisorbed SO₂. TSDirect links the physisorbed SO₂ (Figure 6a) to the surface H₂SO₃ (Figure 6d) by concerted H(9) → O(10) and H(11) → O(2) proton transfers. The barrier height for the formation of H₂SO₃ from the physisorbed SO₂ is calculated to be 51.0 kJ/mol at MP2/6-31G(d) optimization located HSO₃⁻. The TS of this reaction is a thermodynamically transient structure between the structures in Figure 6c and e is almost a bonding experiment (Figures 3 and 5). This process shifts the equilibrium further toward the hydrolyzed species. We stress that the present energy calculations, which do not consider entropy effects, are limited in their ability to quantitatively predict the thermodynamic and kinetic behavior of these reactions.

### 4. DISCUSSION

The present calculations predict that HSO₃⁻ (Figure 6e) can be formed on the ice surface via either direct or indirect pathways.

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**Table 1. Energy Barriers (kJ/mol) for the Hydrolysis of SO₂ at Different Adsorption Sites Calculated with Different Levels of Theory with the Initial Physisorbed SO₂ Serving as the Reference**

<table>
<thead>
<tr>
<th>model</th>
<th>method</th>
<th>energy barrier (kJ/mol)</th>
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<tr>
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<tr>
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<td>51.0</td>
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<td>H₂O–SO₂</td>
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<tr>
<td>Previous Studies</td>
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</table>

On the other hand, our improved HDB₅(27/457) model provides a barrier for the formation of H₂SO₃ of 51.0 kJ/mol (MP2 result) as measured from physisorbed SO₂, which is 40.6 kJ/mol lower than the lowest value previously reported. With a barrier height of similar magnitude (62.3 kJ/mol), hydrolyzed HSO₃⁻ can also be formed through the direct pathway. The differences between the present and earlier predictions indicate that a large surface model, such as HDB₅(27/457), is required to properly take into account surface relaxation and long-range effects in ice surface reactions. In summary, unlike the previous theoretical predictions, the hydrolysis of SO₂ is feasible on cold ice surfaces due to low reaction barriers that lead to the formation of H₂SO₃ and HSO₃⁻. These low barriers are associated with reaction mechanisms that involve proton transfers that can occur relatively easily on cold ice surfaces. The barrier heights for surface reactions are much lower than the energy required for the desorption of physisorbed SO₂ (97.9 kJ/mol). Therefore, the hydrolysis of SO₂ is energetically favored over the desorption of SO₂ at low temperatures, which is consistent with our experimental observation.

**Reversible Hydrolysis.** Although physisorbed SO₂ requires 51.0–62.3 kJ/mol to overcome the energy barrier for hydrolysis to H₂SO₃ or HSO₃⁻, the reverse reactions require merely 3.3 to 15.1 kJ/mol for the transformations shown in Figure 6e → c and d → b, respectively. Therefore, the relative concentration of physisorbed SO₂ would be higher than that of the hydrolyzed species. This result seems inconsistent with the efficient conversion of SO₂ into hydrolyzed species observed in the 100–120 K temperature range. However, irreversible desorption of SO₂ gas from the hydrolyzed species can occur, as observed at temperatures above ~110 K in the TPD experiment (Figures 3 and 5). This process shifts the equilibrium further toward the hydrolyzed species. We stress that the present energy calculations, which do not consider entropy effects, are limited in their ability to quantitatively predict the thermodynamic and kinetic behavior of these reactions.
involving proton transfers. The barriers for these pathways are sufficiently low such that they can occur even at a low temperature. Therefore, HSO$_3^−$ offers a reasonable explanation for the identity of the anionic molecular species observed in the LES experiment. Intact desorption of this species upon Cs$^+$ impact results in a signal corresponding to HSO$_3^−$. Collisional fragmentation of this structure following Cs$^+$ impact can generate LES signals for SO$_2^−$ and OH$.^−$. The generation of HSO$_3^−$ is consistent with the results of previous IR spectroscopic studies for H$_2$O–SO$_2$ mixtures prepared in the forms of nanoparticles' and thin films.\(^3\)

The relative stabilities of different adsorbates explain the occurrence of SO$_2$ hydrolysis at a lower temperature than that for SO$_2$ desorption. The physisorbed SO$_2$ (Figure 6a) is energetically the most stable state on the ice surface. The energy barriers for its conversion into neutral H$_2$SO$_3$ and anionic HSO$_3^−$ are $51.0$ and $62.3$ kJ/mol, respectively, which are substantially lower than the SO$_2$ desorption energy of $97.9$ kJ/mol. Consequently, hydrolysis to H$_2$SO$_3$ and HSO$_3^−$ will first occur upon sample heating. These surface products, however, are only metastable, possibly corresponding to intermediate reaction stages rather than the final products that would be obtained in aqueous solutions. Further SO$_2$ hydrolysis would require extensive structural rearrangement of the adsorbate and the ice surface, which is kinetically prohibitive for a solid ice surface at low temperature. On the other hand, the desorption of SO$_2$ gas from the metastable products is entropically favored and can occur relatively easily at elevated temperatures. Accordingly, above $\sim120$°K, H$_2$SO$_3$ and HSO$_3^−$ are transformed back into SO$_2$ gas to desorb from the surface.

Although the LES experiments revealed molecular anions on the ice surface, their countercations were not detected. The most likely countercation candidate is the hydronium (H$_3$O$^+$) ion, which is predicted to form by the theoretical calculations (Figure 6e). SO$_2$ gas dissolved in liquid water at room temperature produces moderate concentrations of HSO$_3^−$(aq) and H$_2$O$(aq)$ with the acid dissociation constant $pK_a = 1.8$. If approximately the same degree of acid ionization is assumed for the ice surface, then the surface population of H$_2$O$^+$ is expected to be $\sim0.05$ MLE at a SO$_2$ coverage of $0.4$ MLE; ions of this surface concentration would readily be detected by LES. However, the countercations were not detected despite their search under a wide range of experimental conditions, including a variety of SO$_2$ coverages ($0.04$–$0.4$ MLE) and Cs$^+$ beam energies (up to $50$ eV). One possible explanation for the absence of a H$_2$O$^+$ signal is that H$_2$O$^+$ is formed by the reaction but is not ejected from the surface by impact with Cs$^+$\(^2\). This is possible if H$_2$O$^+$ is very mobile in the ice lattice or exists below the surface.\(^2,26\) The structure shown in Figure 6(e) is informative in terms of this explanation. Because H$_2$O$^+$ is formed as part of an extended H-bonded water chain, and the excess proton is mobile along the water chain with a very small barrier via the Grothuss mechanism,\(^25\) the impact of Cs$^+$ at low energy may only facilitate the migration of H$_2$O$^+$ along the water chain, making its ejection into a vacuum very unlikely to occur. As such, H$_2$O$^+$ formed on the ice surface will be invisible in the LES experiments.

It is worth mentioning that the hydrolysis products observed in this work are somewhat different from those produced by SO$_2$ hydrolysis on a thin (4 ML) frozen water film reported previously.\(^11\) The reaction of SO$_2$ on a thin (4 ML) D$_2$O film prepared on Ru(0001) produced LES signals corresponding to OD$^+$, SO$_2^−$, DSO$_2^−$, and DSO$_3^−$. If we assume that isotopic difference between H$_2$O and D$_2$O films does not influence the reactions, the main change in the present observation is that DSO$_3^−$ is not formed. To understand this difference, we examined the hydrolysis of SO$_2$ on a D$_2$O monolayer prepared on a Ru(0001) substrate (Supporting Information). This surface produced signals corresponding to OD$^+$, SO$_2^−$, DSO$_2^−$, SO$_3^−$, and DSO$_3^−$. Therefore, the ion signals produced from the thin ice films\(^11\) are explainable as a superposition of the signals originating from the surfaces of crystalline ice and a water monolayer. It is quite likely that the thin ice films underwent a roughening transition during sample heating, which generated patches of water monolayers and small ice-crystal domains.\(^5,13\) As a result, the hydrolysis products from two different surfaces appeared simultaneously.

Finally, we wish to mention the implications of these discoveries for SO$_2$ chemistry on Jovian satellites. Discussions about the reactions of SO$_2$ on surface ices of Europa, Ganymede, and Callisto usually emphasize the effects of Jovian magnetospheric radiation, which induces radiolytic and photolytic reactions at the ice surface.\(^2,5,6\) This interpretation, in part, stems from the idea that thermal reactions are difficult on the surface or interior of ice at the low temperatures found on these satellites. There are, however, indications that thermal reactions of SO$_2$ can occur in ice environments at low temperature.\(^7,11\) For example, Loeffler and Hudson\(^2\) observed that thermal reactions of SO$_2$ occurred in a solid H$_2$O–SO$_2$ mixture to consume up to $30\%$ of the SO$_2$ molecules at $100$°K, and they claimed that similar processes may take place on the ices of Jovian satellites. Our study further supports the occurrence of thermal SO$_2$ reactions at low temperature by demonstrating that SO$_2$ is efficiently hydrolyzed by adsorption on the ice surface even without full solvation by water molecules as in a H$_2$O–SO$_2$ mixture. The surface reaction is most efficient in the $100$–$120$°K temperature range and is significantly retarded at lower temperatures, and SO$_2$ gas desorbs from the surface at higher temperatures. These favorable conditions for SO$_2$ hydrolysis are found on Europa ($86$–$132$°K), Ganymede ($\sim124$°K), and Callisto ($\sim115$°K).\(^2\) Furthermore, our theoretical study of the hydrolysis reaction mechanism reveals that a low barrier for the reaction is related to pathways involving proton transfer, which can occur on ice surfaces even at low temperatures.\(^2,21\) These observations support the possibility that efficient heterogeneous reactions of SO$_2$ occur on the ice surfaces of Jovian satellites even without the assistance of Jovian magnetospheric radiation. One can imagine that these ices contain substantial amounts of hydronium ions and sulfurous anions as well as other sulfur compounds resulting from unique, low-temperature reactions of SO$_2$ with the ice surface.

5. SUMMARY AND CONCLUSIONS

This work reports direct evidence of SO$_2$ hydrolysis on the ice surface through mass spectrometric detection of surface products and TPD measurements of desorbing SO$_2$ gas. In addition, plausible hydrolysis mechanisms are suggested based on quantum chemical calculations. SO$_2$ gas efficiently reacts with a crystalline ice surface at temperatures of $100$–$120$°K. The hydrolysis of SO$_2$ leads to the formation of molecular anions on the surface, which is evidenced by signals in LES experiments corresponding to OH$^+$, SO$_2^−$, and HSO$_3^−$. H$_2$O$^+$ may also form on the surface as the counterion, although it was invisible to LES. A theoretical investigation into the
reaction mechanism reveals that SO₂ hydrolysis is aided by proton transfer on the ice surface, leading to small energy barriers that make this process feasible even at low temperatures. There are at least two SO₂ hydrolysis channels that lead to HSO₃⁻ and H₂SO₄ surface complexes. The maximum hydrolysis yield observed at 100–120 K is the result of competition between the thermal activation of the reaction on the ice surface and desorption of SO₂ gas. The products observed in this work may correspond to metastable species that are kinetically trapped on the cold ice surface at intermediate stages of the reactions. The experimental observations and theoretically determined reaction mechanisms support the possibility that heterogeneous reactions of SO₂ occur efficiently on Jovian satellites via thermal reactions on ice surfaces even without bombardment by high-energy radiation.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsearthspacechem.7b00064.

TPRIS and TPLEs measurements for the reaction of SO₂ on a water monolayer prepared on a Ru(0001) substrate (PDF)

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Notes
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