

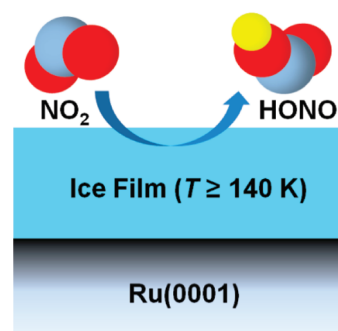
Efficient Conversion of Nitrogen Dioxide into Nitrous Acid on Ice Surfaces

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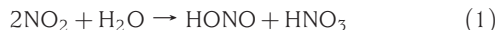
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ABSTRACT The hydrolysis of nitrogen dioxide (NO₂) on ice surfaces is studied by measuring the reaction products on the surface with the reactive ion scattering (RIS) technique, and the desorbing species is studied with temperature-programmed desorption (TPD) mass spectrometry. NO₂ adsorbs molecularly on an ice film surface at a temperature of 90 K. Upon heating the film to 140 K, NO₂ adsorbates are readily converted into nitrous acid (HONO), and nitrous acid products desorb intact from the surface at higher temperatures. The result indicates the efficient formation of nitrous acid gas on the ice surface with only a small activation energy. It is shown that the hydrolysis occurs from isolated NO₂ adsorbates rather than through NO₂–NO₂ interactions. The implications of these findings for the atmospheric heterogeneous reaction of NO₂ are mentioned.

SECTION Surfaces, Interfaces, Catalysis



It is well-known that nitrogen dioxide (NO₂) hydrolyzes in aqueous solution to form nitrous acid (HONO) and nitric acid (reaction 1).¹



Reaction 1 is important in a number of technologies and in atmospheric chemistry. For example, the heterogeneous hydrolysis of NO₂ on wet surfaces is potentially important as a source of atmospheric nitrous acid (HONO) gas,^{2,3} which is recognized as a precursor for hydroxyl radicals. The mechanism of this reaction has been the subject of many studies.^{4–9} These studies show that the reaction of NO₂ with water is more complex than its simple stoichiometry suggests. The rate of nitrous acid formation has been observed to be first-order with respect to the concentrations of both NO₂ and water vapor.^{4–9} This suggests that reaction 1 does not occur in a single step as a termolecular process. Several proposals have been made for the heterogeneous hydrolysis mechanism of NO₂, which include the formation of a NO₂–water complex at the air–water interface^{5–9} as well as reaction pathways involving N₂O₄ intermediates.^{10,11} In general, it is difficult to unambiguously identify the mechanism of atmospheric heterogeneous reactions owing to the complexity of the reactions involving surfaces and adsorbed species.⁴ In the case of NO₂ hydrolysis, even the solution-phase mechanism is not completely understood at the molecular level,¹ and this poses additional difficulties for studying the reaction mechanism at the gas–solution interface. Moreover, only limited information is available at present about the chemical properties of NO₂ residing at the surface of condensed water or ice.^{12–16}

Ice surfaces offer an interesting model for the investigation of NO₂–water interactions in a two-dimensional water environment. On a cold ice surface, the speed of a reaction is greatly reduced compared to that on a liquid water surface at

room temperature, and sometimes, the reaction intermediates can be isolated on the ice surface as a result of kinetic trapping, as demonstrated for several reactions in recent investigations.^{17–20} Spectroscopic identification of reaction intermediates trapped on the ice surface is important for the study of reaction mechanisms, and it may also provide valuable information about the corresponding reaction on liquid water surfaces. The interactions of NO₂ with ice surfaces have been studied in previous works with infrared reflection–absorption spectroscopy (IRAS), temperature-programmed desorption (TPD) mass spectrometry, and photoelectron spectroscopy,^{12–16} and these studies reveal the adsorption states of NO₂ on ice and its thermal desorption behavior. In the present work, we study the reaction of NO₂ on ice films by examining the surface species with reactive ion scattering (RIS) and the desorbing species with TPD. Efficient conversion of NO₂ into nitrous acid is observed on the ice surface at a temperature of 140 K, which is below the surface premelting regime. We also provide evidence that the reaction occurs through the interactions of isolated NO₂ adsorbates with water, which opposes a reaction mechanism involving NO₂–NO₂ intermediates.

The present experiments were conducted in an ultrahigh vacuum (UHV) surface analysis chamber equipped with instrumentation for RIS, TPD, and Auger electron spectroscopy.¹⁷ A D₂O–ice film was grown on a Ru(0001) substrate at a growth rate of 0.01 BL s^{–1} (bilayer; 1 BL = 1.1 × 10¹⁵ water molecules cm^{–2}) by backfilling the chamber with D₂O vapor. The ice film thickness was typically 4 BL, as deduced from the TPD experiments. For this thickness, the reaction of

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NO_2 on the ice film surface was not affected by the catalytic effect of the Ru substrate. The ice films were prepared in a polycrystalline phase by controlling the water deposition temperature at 135 K and by postannealing the ice film at 140 K for 5 min. The results presented in this paper were obtained with these polycrystalline ice films, but we should mention that qualitatively similar results were observed with amorphous ice films grown at 90 K. NO_2 gas (99.99+ % purity) was introduced into the chamber and guided close to the sample surface through a separate dosing line. NO_2 was adsorbed on the ice films at the temperature of 90 K and a NO_2 partial pressure of 1.0×10^{-9} Torr as read by an ionization gauge located ~ 20 cm away from the sample. The actual NO_2 pressure near the sample surface was about 10 times higher. At this pressure, the equilibrium population ratio of N_2O_4 in NO_2 gas was negligible ($\sim 10^{-10}$). The surface coverage of NO_2 on the ice films was measured from TPD experiments.

Chemical species present on the ice films were identified by RIS.¹⁷ In this technique, a low-energy (30 eV) Cs^+ ion beam was directed onto a sample surface, and the scattered ions were analyzed for their mass. The scattered ions were composed of reflected Cs^+ primaries and RIS products (CsX^+), which were formed by an ultrafast (<1 ps) association reaction between scattering Cs^+ projectiles and neutral species (X) on the surface.²¹ The RIS products were detected by a quadrupole mass spectrometer with its ionizer filament switched off, thereby obtaining the ion mass spectrum with almost zero background noise. It has been shown²² that RIS measurement at this low energy has a probing depth of 1 BL on ice films, and the measured signals have a negligible contribution from the secondary surface reactions induced by the Cs^+ beams.

Figure 1 shows the result of RIS measurements on a polycrystalline D_2O -ice film adsorbed with NO_2 for the coverage (θ) of 0.8 monolayer (ML). The RIS spectrum in Figure 1a was obtained at the sample temperature of 90 K, and it shows RIS peaks of $\text{Cs}(\text{D}_2\text{O})_n^+$ ($n = 1, 2$) at $m/z = 153$ and 173 amu/charge and CsNO_2^+ at $m/z = 179$ amu/charge. A reflected Cs^+ peak appeared at $m/z = 133$ amu/charge. The $\text{Cs}(\text{D}_2\text{O})_n^+$ signals were due to the pickup of surface water molecules by the scattering Cs^+ projectiles, and the CsNO_2^+ signal was due to NO_2 adsorbates. These signals indicate that NO_2 adsorbs onto the surface in molecular states without undergoing dissociation or hydrolysis reactions at 90 K.

Figure 1b shows the result obtained after the sample temperature was increased to 140 K. A new RIS peak appeared at $m/z = 181$ amu/charge, which corresponded to CsDNO_2^+ . Also, a smaller peak appeared at $m/z = 201$ amu/charge, which was assigned as $\text{Cs}(\text{DNO}_2)(\text{D}_2\text{O})^+$ produced by the pickup of independent D_2O and DNO_2 species on the surface. This interpretation is supported by the fact that the CsDNO_2^+ and $\text{Cs}(\text{DNO}_2)(\text{D}_2\text{O})^+$ signals have an intensity ratio of about 6:1, similar to the ratio of $\text{Cs}(\text{D}_2\text{O})^+$ and $\text{Cs}(\text{D}_2\text{O})_2^+$. The CsDNO_2^+ and $\text{Cs}(\text{DNO}_2)(\text{D}_2\text{O})^+$ signals indicate the formation of DNO_2 on the surface through the reaction of NO_2 and D_2O . We believe that the DNO_2 species is nitrous acid (DONO), which is a well-known product of NO_2 hydrolysis. Its structural isomer $\text{DNO}(\text{O})$, which is energetically less stable, has not been observed in NO_2

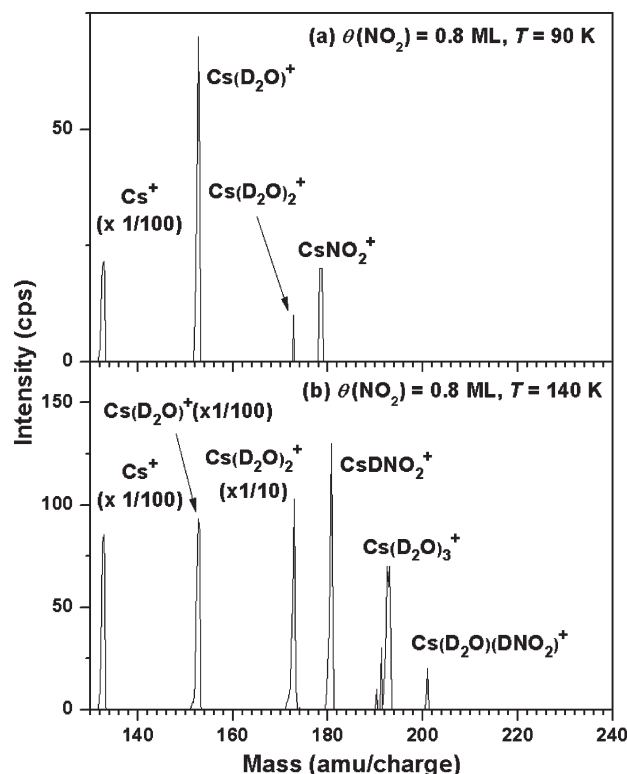


Figure 1. RIS mass spectra taken from D_2O -ice films (4 BL thickness) after NO_2 gas adsorption for the coverage of 0.8 ML at 90 K. The sample temperature was maintained at 90 K during the RIS measurements in spectrum (a), and the temperature was raised to 140 K in spectrum (b). The Cs^+ beam energy was 30 eV. The signal intensities shown are reduced by the factors indicated.

hydrolysis studies. In the remaining text, describing our experimental results, however, we will denote nitrous acid by its molecular formula (DNO_2) to be consistent with the mass spectrometric information. In spectrum (b), the CsNO_2^+ signal disappeared from the surface, and this was attributed to the desorption of NO_2 , which occurred at temperatures above 130 K.^{14,16} Also, N_2O_4 species were not detected on the surface.

Figure 2a shows a RIS spectrum obtained after NO_2 adsorption for a multilayer coverage (6 ML) on a D_2O -ice film at a temperature of 90 K. The RIS signals include CsNO^+ ($m/z = 163$), CsNO_2^+ ($m/z = 179$), CsN_2O_3^+ ($m/z = 209$), and CsN_2O_4^+ ($m/z = 225$). CsNO_2^+ is the strongest among these peaks. The $\text{Cs}(\text{D}_2\text{O})^+$ intensity is greatly reduced due to the presence of a NO_2 overlayer. The CsN_2O_3^+ and CsN_2O_4^+ peaks indicate that N_2O_3 and N_2O_4 molecules are present on the NO_2 multilayer surface. One might consider that these peaks are produced by the pickup of independent NO_2 and/or NO species on the surface, but their intensity being stronger than CsNO^+ refutes this possibility. A small CsNO^+ signal may indicate NO on the surface; however, this interpretation is only tentative because the CsNO^+ signal can also be produced by the fragmentation of N_2O_3 due to collision during the RIS process. The detection of N_2O_3 and N_2O_4 species confirms the observation of IRAS studies^{12–14,16} that a mixed adsorbate layer of N_2O_3 ($\text{ON}-\text{NO}_2$) and N_2O_4 ($\text{O}_2\text{N}-\text{NO}_2$) is formed upon the multilayer adsorption of NO_2 on ice films at temperatures below 100 K.

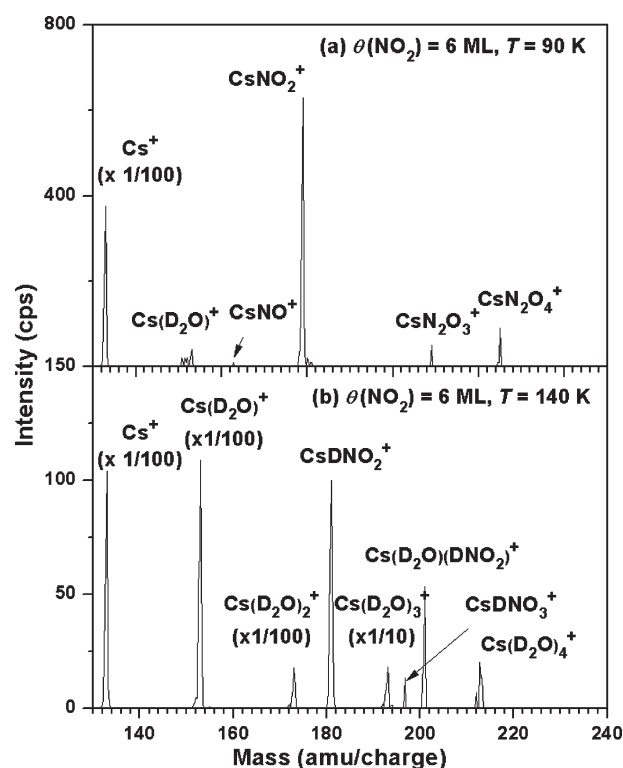


Figure 2. RIS mass spectra obtained after multilayer (6 ML) adsorption of NO_2 on a D_2O -ice film (4 BL thickness). NO_2 was adsorbed on the surface at 90 K, and the RIS measurements were made at 90 (a) and 140 K (b). Other details of the measurements were the same as those for Figure 1.

When this ice film was warmed to 140 K, shown in Figure 2b, CsNO^+ , CsNO_2^+ , CsN_2O_3^+ , and CsN_2O_4^+ signals disappeared from the surface. Instead, a CsDNO_2^+ peak appeared along with a $\text{Cs}(\text{DNO}_2)(\text{D}_2\text{O})^+$ peak, which indicated the formation of a DNO_2 species. A CsDNO_3^+ peak ($m/z = 197$) of small intensity also appeared, indicating that DNO_3 (nitric acid) was also formed. The CsDNO_3^+ peak was not seen in the spectrum of Figure 1b obtained at $\theta(\text{NO}_2) = 0.8$ ML, but this signal appeared at small levels of intensity for ice samples with submonolayer NO_2 coverages as well when the sample temperature was higher than 140 K. The observations indicate that NO_2 hydrolysis produces DNO_2 as a major product at 140 K. A small amount of DNO_3 is also formed at a high temperature and preferably at a high NO_2 coverage. This suggests the occurrence of NO_2 hydrolysis in a sequence in which DNO_2 is formed first and then transformed into DNO_3 at a higher temperature.

The effect of NO_2 surface coverage on the reaction was examined, and Figure 3 shows the signal intensities for the species of main interest (CsNO_2^+ , CsN_2O_4^+ , and CsDNO_2^+) as a function of $\theta(\text{NO}_2)$. $\theta(\text{NO}_2)$ was estimated from the TPD peak area of NO_2 desorption. The CsNO_2^+ and CsN_2O_4^+ signal intensities were measured at the temperature of 90 K, and the CsDNO_2^+ signal intensity was measured at 140 K. The figure shows that the CsNO_2^+ intensity increased continuously with the increase in $\theta(\text{NO}_2)$, as expected. In the submonolayer region, the CsNO_2^+ intensity was linear with

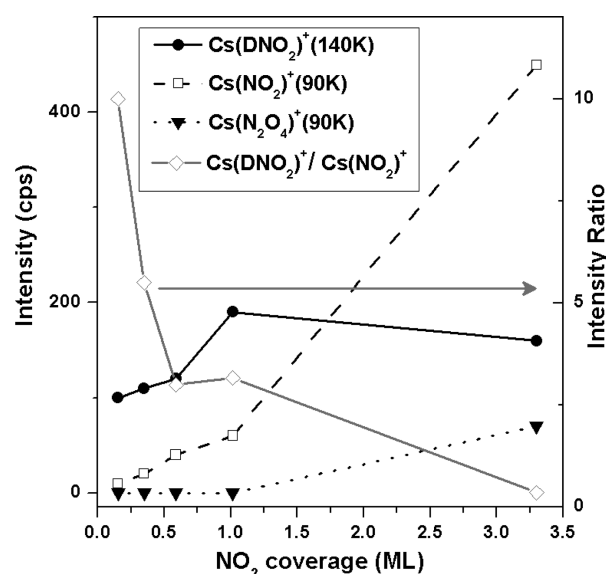


Figure 3. Variation in the RIS signal intensities of $\text{Cs}(\text{DNO}_2)^+$ (●), $\text{Cs}(\text{NO}_2)^+$ (□), and $\text{Cs}(\text{N}_2\text{O}_4)^+$ (▼) as a function of NO_2 coverage on a D_2O -ice film. The intensity ratio of $\text{Cs}(\text{DNO}_2)^+$ to $\text{Cs}(\text{NO}_2)^+$ is also plotted (◇). CsNO_2^+ and CsN_2O_4^+ signals were measured at the sample temperature 90 K, and the CsDNO_2^+ signal was measured at 140 K. The lines are for an eye guide only.

$\theta(\text{NO}_2)$, which illustrates the semiquantitative nature of NO_2 adsorbate detections by RIS and TPD methods. The CsDNO_2^+ intensity increased with $\theta(\text{NO}_2)$ up to 1.0 ML but then decreased at higher levels of $\theta(\text{NO}_2)$. Also shown in the figure is the ratio of the CsDNO_2^+ and CsNO_2^+ signal intensities. This ratio continuously decreased with increasing $\theta(\text{NO}_2)$ over the entire range of the investigation (the bend at $\theta = 1.0$ ML is due to the fluctuation in this particular data set, not a general trend). The DNO_2/NO_2 ratio indicates the conversion efficiency of NO_2 adsorbates into DNO_2 . Therefore, it reveals that NO_2 hydrolysis occurs more efficiently at a lower NO_2 coverage. The CsN_2O_4^+ signal is undetectably small for $\theta(\text{NO}_2) < 1.0$ ML, and its intensity increases with NO_2 coverage for $\theta(\text{NO}_2) > 1.0$ ML. The inverse correlation between the population changes of DNO_2 and N_2O_4 suggests that N_2O_4 is not a precursor to DNO_2 in the reaction, and vice versa.

We performed TPD measurements on NO_2 -adsorbed ice films. The TPD signals of NO (30 amu) and NO_2 (46 amu) appeared in the temperature region of 120–150 K, in agreement with the report of previous TPD studies.^{12–14,16} In addition, a small TPD signal appeared at the mass of 48 amu, which corresponded to the desorption of DNO_2 and/or $^{14}\text{N}^{16}\text{O}^{18}\text{O}$. The isotopomeric abundance of $^{14}\text{N}^{16}\text{O}^{18}\text{O}$ is very small (4×10^{-3}) relative to $^{14}\text{N}^{16}\text{O}_2$, yet it can make a substantial contribution to the small-intensity 48 amu signal. The TPD spectrum of DNO_2 was extracted from the 48 amu spectrum after quantitative subtraction of the $^{14}\text{N}^{16}\text{O}^{18}\text{O}$ desorption signal, which was proportional to the $^{14}\text{N}^{16}\text{O}_2$ desorption signal (46 amu), in accordance with its isotopomeric abundance. The inset of Figure 4 shows the TPD spectrum of DNO_2 thus obtained, along with a NO_2 spectrum recorded at 46 amu. They show that the desorption temperature of DNO_2 (130–160 K) is somewhat higher than the NO_2

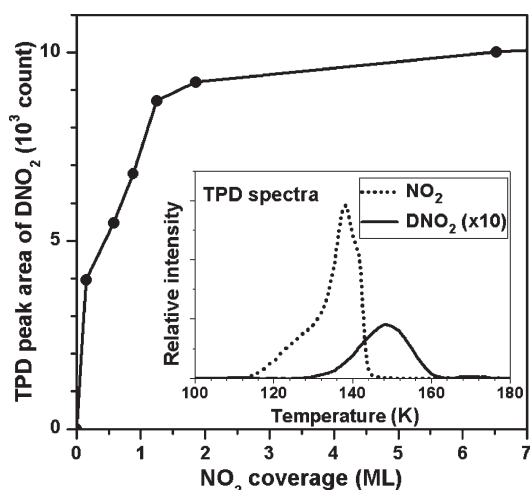


Figure 4. TPD peak areas of DNO₂ as a function of NO₂ coverage for 0.15–6.5 ML on a D₂O-ice film. The inset displays the TPD spectra of NO₂ (dashed line) and DNO₂ (solid line) measured on the ice film at $\theta(\text{NO}_2) = 0.8$ ML. The temperature ramping rate in TPD was 0.5 K s⁻¹.

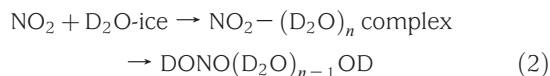
desorption temperature (120–145 K). Figure 4 also shows a plot of the TPD peak area of DNO₂ as a function of $\theta(\text{NO}_2)$. The amount of DNO₂ desorption rapidly increased with $\theta(\text{NO}_2)$ from 0 to 1.2 ML, but the increase slowed down at higher NO₂ coverages. This indicates more efficient DNO₂ formation and desorption at lower $\theta(\text{NO}_2)$, in agreement with the RIS results shown above. From the comparison of TPD peak areas, it is estimated that the desorption flux of DNO₂ constitutes about 4% of the initial NO₂ coverage when $\theta(\text{NO}_2) = 0.8$. From RIS signal intensities, the population of DNO₂ surface species at 140 K is estimated to be 4–6% of the initial NO₂ coverage for the same sample, according to the data shown in Figure 1. These estimates indicate that a large portion of surface DNO₂ species is desorbed as DNO₂ gas upon the heating of the sample, without undergoing further surface reactions.

We can summarize the key observations of the RIS and TPD experiments as follows. (i) The hydrolysis of NO₂ on an ice surface produces nitrous acid as a major product at 140 K. A nitrous acid product is formed regardless of whether NO₂ coverage is small or multilayer, yet the conversion efficiency of NO₂ into nitrous acid is higher at lower NO₂ coverage. (ii) A large portion of surface nitrous acids desorb intact at a high temperature. (iii) At high temperatures, nitric acid is produced in small amounts. (iv) N₂O₃ and N₂O₄ species are formed only when a NO₂ multilayer exists on the ice film at 90 K. Nitrous acid is not formed under these conditions, and the surface populations of nitrous acid and N₂O₄ exhibit inverse correlation as a function of NO₂ coverage. Combined together, these observations provide clear evidence that NO₂ hydrolysis occurs through the interaction between isolated NO₂ adsorbates and water molecules on the ice surface, rather than through the formation of N₂O₃ or N₂O₄ intermediates. The efficiency of nitrous acid formation is not enhanced but decreased by the presence of additional NO₂ molecules near the reaction sites.

An important feature of NO₂ hydrolysis on the ice surface is that it requires only a small activation energy, which is

evidenced by the efficient nitrous acid formation at a low temperature (140 K). Apparently, the ice surface provides an efficient reaction pathway for nitrous acid formation. On the other hand, NO₂ hydrolysis is difficult to occur in the gas phase and requires a substantially high activation energy (~120 kJ mol⁻¹).²³ Kinetic studies^{4–9} have shown that the rate of NO₂ hydrolysis is accelerated in the presence of liquid water films, but the detailed mechanism of the heterogeneous hydrolysis is not clearly understood. Theoretical studies have examined the effect of water solvation on the reaction^{23,24} and calculated the energetic stability of the water complexes of NO₂ and nitrous acid.²⁵ These studies indicate that the presence of multiple (up to three) water molecules does not significantly reduce the energy barrier of the hydrolysis compared to nonsolvation. In contrast with such theoretical expectation, the present study shows that once NO₂ molecules are accommodated onto the ice surface, they can be converted into nitrous acid almost spontaneously.

The observation is informative for understanding the NO₂ hydrolysis mechanism in its early stage, where the reaction occurs only to the formation of nitrous acid and nitric acid is not yet formed. A plausible reaction mechanism in this stage may be



NO₂ adsorption on the ice surface forms a NO₂–water complex first, and then it is converted into a “nitrous acid” structure at 140 K. In molecular details, however, the reaction mechanism is expected to be more complex than expressed by these simple chemical formula. For instance, nitrous acid and hydroxyl radical may not form as isolated molecular species as written in this equation, but actually, they may be a part of a larger molecular structure connected through hydrogen bonds on the ice surface. The reaction is driven in such an extended molecular system by hydrogen-bonding interactions and proton (or H atom) transfers between NO₂ and water molecules.

The present study may have the following implications for the atmospheric chemistry of NO₂. Considering that NO₂ hydrolysis is efficient on cold ice surfaces, it is expected that the corresponding reaction will readily occur under atmospheric conditions at the surfaces of water films, aerosols, and icy particles. There seems to be no critical factor that will, in principle, prevent the occurrence of the reaction on these surfaces at ambient temperatures, which offer higher molecular mobility, solvation efficiency, and thermal energy than the cold ice surface environment of the present experiment. Since the reaction has a very small activation energy, it can easily occur with thermal energy in the absence of any extra energy input, such as the absorption of sunlight. Therefore, nitrous acid gas is expected to be produced efficiently during the night time by the heterogeneous hydrolysis of NO₂ on the surfaces of condensed atmospheric moisture, in accordance with measurements taken during field observations.² The early stage hydrolysis mechanism of NO₂ suggested here, the reaction between an isolated NO₂ molecule and water, agrees with the kinetic observations of laboratory studies^{4–9}

that nitrous acid formation is first-order in both NO_2 and water vapor concentrations. If this mechanism is efficient in the atmosphere, it will not be necessary to consider alternative complex mechanisms such as those involving N_2O_4 intermediates.^{10,11} It is very difficult to build up a significant amount of N_2O_4 population at the gas–water interface or in its interior due to low concentrations of NO_2 in the atmospheric conditions. Finally, the facile, intact desorption of nitrous acid from ice surfaces strengthens the possibility that the heterogeneous hydrolysis of NO_2 is an important source of nitrous acid gas in the atmosphere.

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