IRAS Studies of NO₂, N₂O₃, and N₂O₄ Adsorbed on Au(111) Surfaces and Reactions with Coadsorbed H₂O

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Adsorption or bonding geometries of pure adlayers of several N₂O species, i.e., nitrogen dioxide (NO₂), dinitrogen trioxide (N₂O₃), and dinitrogen tetroxide (N₂O₄), on Au(111) were determined by utilizing infrared reflection—absorption spectroscopy (IRAS). Dosing NO₂ on Au(111) at 85 K produced, in our experiments, mixtures of NO₂ and N₂O₃ (from contaminant NO) at submonolayer coverages and NO₂, N₂O₃, and N₂O₄ at monolayer coverages. However, a pure adlayer of chemisorbed NO₂ could be prepared by forming the monolayer on Au(111) at 85 K and then heating to 185 K or by NO₂ exposures on Au(111) at 185 K. Chemisorbed NO₂ is bonded to the surface in an O₂O-chelating geometry with Cᵥ symmetry. A monolayer of adsorbed N₂O₃ was produced by exposing the pure, chelating NO₂ adlayer to NO(g). The adsorbed complex with N₂O₃ has Cᵥ symmetry, and we believe that N₂O₃ is bonded to the surface through one oxygen. Large NO₂ exposures can be used to produce crystalline N₂O₄ multilayers that have a preferential orientation of the N-N bond perpendicular to the Au(111) surface. To probe important aspects of the reactivity of these species with water and to investigate structure—reactivity relationships in this chemistry, we studied the reaction of each of these species with coadsorbed H₂O. Upon being heated, reactions proceed via two pathways. One route produces nitrous acid (HONO) and nitric acid (HNO₃) and occurs for all of the nitrogen oxide species listed above. These reactions do not depend on the degree of crystallinity of the condensed water clusters. A separate path occurs only for co-condensed amorphous ice clusters and multilayer N₂O₃ films, as signaled by the formation of oxygen adatoms on the Au(111) surface. These results reveal new information about fundamental interactions of nitrogen oxides and water in condensed phases.

1. Introduction

Nitrogen oxides exhibit a wide variety of structures and have a rich chemistry. Also, many different metastable N₂O intermediates can be formed during reactions, and taken together, this has limited the understanding of the chemistry of nitrogen oxides and the development of structure—reactivity relationships. In particular, for interactions with metal atoms, a variety of bonding geometries are usually available. For example, NO₂ is well-known as a versatile linkage isomer in a variety of bonding geometries are usually available. For example, NO₂ is well-known as a versatile linkage isomer in coordination compounds and on metal surfaces. However, we believe that it is possible to exploit this versatility to cleanly prepare and probe the condensed-phase chemistry of NO₂ and other nitrogen oxides by utilizing suitable substrates in surface-science-type experiments.

Au(111) surfaces are very unreactive and thus can be used in many cases to serve as an inert support for condensed phases. Recently, we have studied reactions after NO₂ exposures on ice films on Au(111). We proposed that two separate reaction channels occur. One pathway forms nitrous acid (HONO) and nitric acid (HNO₃) and occurs for reactions of either amorphous or crystalline ice with NO₂, N₂O₃, and N₂O₄ at temperatures below 145 K. Another pathway ultimately forms oxygen adatoms on the Au(111) surface. In these reactions, we believe that Au(111) does not play a significant role in the nascent chemistry of H₂O + NO₂ but rather serves as an integrating detector for certain reaction products by decomposing those products at higher temperatures to produce surface oxygen. In this latter reaction channel, we observed two intermediates, the nitrito isomer of N₂O₄ (ONO²–) and nitrosium nitrate (NO⁺•NO₃⁻), and we proposed that N₂O₃ was responsible for the formation of oxygen adatoms as shown in the following mechanism.

\[
\begin{align*}
\text{N} &= \text{N} \quad T=130 \text{ K} \\
\text{O} &= \text{O} \quad T=183 \text{ K} \\
\text{D} &\quad T=275 \text{ K} \\
\text{O} &\quad T=500 \text{ K}
\end{align*}
\]

In these reactions, however, the specific reactivity of NO₂ or N₂O₃ with ice and their role in oxygen formation remains unclear. Use of a Au(111) substrate also allows us to address these issues. Previously, we have studied NO₂ adsorption on Au(111) and Au(poly) by HREELS and TPD and proposed methods to produce pure NO₂ and N₂O₃ monolayers on Au surfaces. Because we can separately form pure NO₂ and N₂O₃ monolayers on Au(111), we can better understand the individual reactivities of NO₂ and N₂O₃ with H₂O, as either amorphous or crystalline ice, by preadsorbing pure NO₂ and N₂O₃ monolayers on Au(111) and studying the subsequent surface reactions with postdeposited water to form ice films.

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This paper presents results of temperature-programmed desorption (TPD) and infrared reflection-absorption spectroscopy (IRAS) investigations of the composition and adsorption geometry of NO$_2$, N$_2$O$_3$, and N$_2$O$_4$ adlayers on Au(111). We also obtain new information on the reacting species in condensed films of NO$_2$ + H$_2$O that lead to oxygen formation on the Au(111) surface. Pure N$_2$O$_3$ and chemisorbed, chelating NO$_2$ monolayers do not react with amorphous ice to form oxygen on Au(111). Only N$_2$O$_4$ multilayers produce oxygen adatoms in these reactions, and the results are identical to those obtained by reacting N$_2$O$_4$ films on ice films pre-formed on the Au(111) surface. This further supports our proposal that formation of the nascent intermediates that lead to oxygen deposition on the Au(111) surface is not caused by the presence of the Au surface atoms but is caused by "free OH" groups on the amorphous ice surface.

2. Experimental Methods

The stainless steel ultra-high vacuum (UHV) chamber used in these experiments was pumped by a 240 L/s ion pump, a 240 L/s turbomolecular pump, and a titanium sublimation pump. The base pressure was typically $2 \times 10^{-10}$ Torr. The UHV chamber was equipped with a double-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), reverse-view four-grid optics for low-energy electron diffraction (LEED), a UTI 100 C quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD), and gas-dosing facilities.

Infrared reflection-absorption spectroscopy (IRAS) studies were carried out in a reaction antechamber attached to the top of the surface analysis chamber by using a Mattson Galaxy 6020 FTIR spectrometer. Ar$^+$ ion sputtering was also performed in this antechamber. The IR beam from the interferometer was focused on the crystal at a grazing incidence angle of $\sim 86^\circ$. The reflected light along the specular direction was recollimated and focused onto a narrow-band, liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. IR spectra were collected with the sample at 86 K using 8 cm$^{-1}$ resolution and 1000 scans in a 4 min. period. Clean surface (background) spectra were acquired after annealing the crystal to 550 K to desorb adsorbrates and quickly cooling to 86 K, and these were then subtracted from the adsorbate-covered surface spectra.

TPD experiments were carried out using a random flux shield over the end of the QMS, with the sample approximately 0.5 cm away from the entrance aperture and in the line-of-sight of the QMS ionizer. Two high-transparency screens, one biased at $-55$ V on the end of the ionizer cage and one at ground potential on the flux shield, were used to suppress the low-energy electron flux from the QMS.$^{10}$ The heating rate in TPD was 3.5 K/s.

The Au(111) crystal was mounted as reported before.$^{6,7}$ The sample could be cooled to 85 K using liquid nitrogen or resistively heated to 1100 K. The temperature was measured by a chromel-alumel thermocouple pressed firmly into a hole drilled into the side of the crystal. The Au(111) surface was cleaned by repeated sputtering-annealing cycles using 500 eV Ar$^+$ bombardment at 300 K followed by annealing to 973 K for 10 min. The cleanliness and structure of the surface were checked by AES and LEED.

NO, NO$_2$, and H$_2$O exposures were made by means of a directed molecular beam doser utilizing a microcapillary array. NO (Matheson, 99.9%) and NO$_2$ (Matheson, 99.9%) were used as received. Deionized water (H$_2$O) was used after degassing via several freeze-pump-thaw cycles. To minimize reactions of NO$_2$ in the doser gas lines, stainless steel and gold-plated gaskets were utilized and the entire dosing manifold gas line was initially passivated at $\sim 150$ °C under NO$_2$ pressure for 30 min.

Adsorbate coverages herein are referenced to $\Theta = 1$ ML for the saturation monolayer coverage of a given adsorbate on the Au(111) surface. NO$_2$ monolayer coverages were determined by TPD, referenced to saturation of the chemisorbed NO$_2$ peak at 220 K, which was defined as $\Theta_{\text{NO}_2} = 1$ ML (or $4.2 \times 10^{14}$ molecules/cm$^2$).$^9$ The H$_2$O monolayer coverage was much less certain and was difficult to establish. Briefly, we used a background gas dose sufficient to adsorb one-half of the molecules required for the water bilayer ($1.0 \times 10^{15}$ molecules/cm$^2$) found on Pt(111)$^{11}$ assuming unit sticking probability.

3. Results and Discussion

3.1. Formation of Pure NO$_2$, N$_2$O$_3$, and N$_2$O$_4$ Adlayers on Au(111). Figure 1 shows TPD spectra for NO$_2$ desorption following NO$_2$ exposures on Au(111) at 86 K. NO$_2$ desorption initially occurs in a peak that shifts from 230 to 217 K with increasing coverage and then in a low-temperature peak at 141 K at higher exposures. This is consistent with earlier studies of NO$_2$/Au(111) that found completely reversible adsorption and assigned a peak at 223 K to desorption from the chemisorbed monolayer and a peak at 141 K to desorption from physisorbed N$_2$O$_4$ multilayers.$^8,9,12$ In Figure 1, we do not see any desorption at 325 K, which is an important feature in NO$_2$ TPD from Au(111) surfaces,$^9$ indicating that our crystal had a negligible number of defects. The desorption activation energy for chemisorbed NO$_2$ was previously estimated to be 58 kJ/mol, and that for N$_2$O$_4$ multilayers was estimated to be 35 kJ/mol.$^8$

Chemisorbed NO$_2$ on Au(111) has been assigned as an O$_2$-nitrito surface chelate with $C_2$$_{2}$ symmetry based on HREELS.$^8$ Often, however, when working with HREELS resolutions of 80 cm$^{-1}$ or so, there is a chance that overlapping peaks are not resolved and there is a small possibility that the loss peak at 1180 cm$^{-1}$ in the work cited above could be due to two peaks of nearly the same energy arising from the asymmetric $\nu_3$(NO$_2$) and symmetric $\nu_4$(NO$_2$) NO$_2$ stretching modes. Interaction with the Au(111) surface could markedly decrease the energies of
both of the \( \nu_a(\text{NO}_2) \) and \( \nu_s(\text{NO}_2) \) modes, which are 1618 and 1318 cm\(^{-1}\), respectively in the \( \text{NO}_2 \) gas-phase IR spectrum.\(^{13}\)

For example, the \( \text{NO}_2 \) group in \( \text{Ni}([\alpha\text{-picoline}]_2(\text{NO}_2))^{14} \) has \( \Delta(\nu_a(\text{NO}_2) - \nu_s(\text{NO}_2)) = 73 \text{ cm}^{-1} \).

To better elucidate the adlayer composition and bonding geometry with increasing coverage and film thickness, we have obtained IRAS spectra of the adsorbed layers following \( \text{NO}_2 \) exposures on \( \text{Au}(111) \) at 86 K, as shown in Figure 2. Our assignments of these spectra are given in Table 1, and these exposures on \( \text{Au}(111) \) at 86 K, as shown in Figure 2. Our assignments of these spectra are given in Table 1, and these agree with our previous HREELS data\(^8\) very well. At 0.5 ML \( \text{NO}_2 \) coverage, a mixture of chemisorbed \( \text{NO}_2 \) and \( \text{N}_2\text{O}_3 \) exists on \( \text{Au}(111) \). \( \text{N}_2\text{O}_3 \) is formed by reaction of chemisorbed \( \text{NO}_2 \) with residual \( \text{NO} \) that arises from decomposition of \( \text{NO}_2 \) in the UHV chamber. Chemisorbed \( \text{NO}_2 \) has two peaks at 1178 and 806 cm\(^{-1}\) assigned previously to the symmetric stretching, \( \nu_s(\text{NO}_2) \), and symmetric bending, \( \delta(\text{NO}_2) \), modes, respectively, for a species bonded in an \( \text{O}_2\text{O}^-\) chelating geometry with \( \text{C}_2\text{v} \) symmetry.\(^8\) Two peaks due to \( \text{N}_2\text{O}_3 \) are seen at 1900 and 1265 cm\(^{-1}\) which overlap with the same modes of chelating \( \text{NO}_2 \). At 1 ML \( \text{NO}_2 \) coverage, the adsorbed species are chelating \( \text{NO}_2 \), \( \text{N}_2\text{O}_3 \), and \( \text{N}_2\text{O}_4 \). The peaks at 1178 and 810 cm\(^{-1}\) are due to the \( \nu_a(\text{NO}_2) \), \( \nu_s(\text{NO}_2) \), and \( \delta(\text{NO}_2) \) modes, respectively, of \( \text{N}_2\text{O}_3 \). When the \( \text{NO}_2 \) coverage is 7.5 ML, only bands due to \( \text{N}_2\text{O}_4 \) were observed. Annealing this multilayer to 120 K does not change the IRAS spectra. This multilayer film can be described as pure crystalline \( \text{N}_2\text{O}_4 \) with a preferential orientation of the \( \text{N}^--\text{N} \) bond almost perpendicular to the \( \text{Au}(111) \) surface, since it shows strong peaks due to \( \nu_s(\text{NO}_2) \) modes along with fairly weak peaks due to \( \nu_a(\text{NO}_2) \) modes.\(^{15,16}\)

While the top two spectra in Figure 2 nicely characterize a condensed film with a pure \( \text{N}_2\text{O}_4 \) surface layer, we also wanted to obtain pure \( \text{NO}_2 \) and \( \text{N}_2\text{O}_3 \) layers. These were made by the procedure outlined in Bartram et al.\(^8\) and our IRAS spectra for chemisorbed \( \text{NO}_2 \) are shown in Figure 3. The pure, chemisorbed monolayer of \( \text{NO}_2 \) can be made by dosing \( \text{NO}_2 \) on \( \text{Au}(111) \) at 185 K or by dosing a \( \text{NO}_2 \) monolayer at 86 K and then heating to 185 K. Peaks at 1179 and 804 cm\(^{-1}\) are characteristic for chelating \( \text{NO}_2^- \) ligands in transition metal compounds.\(^3\) As we have discussed for these compounds in more detail previously,\(^8\) the \( \delta(\text{NO}_2) \) mode is typically insensitive to the bonding geometry of \( \text{NO}_2 \), occurring at 817–863 cm\(^{-1}\), but the \( \nu_a(\text{NO}_2) \) mode is very sensitive to this bonding geometry. The \( \nu_a(\text{NO}_2) \) mode has a frequency of 1171–1225 cm\(^{-1}\) for chelating isomers and 1306–1392 cm\(^{-1}\) for nitro isomers.\(^3,14,17\) IRAS detects only one peak in the 1120–1220 cm\(^{-1}\) range that must be due to \( \nu_a(\text{NO}_2) \) and no feature that can be assigned to \( \nu_s(\text{NO}_2) \). Therefore, because of the strict dipole selection rule in IRAS (compared to HREELS) we show conclusively that chemisorbed \( \text{NO}_2 \) is bonded in an \( \text{O}_2\text{O}^-\) chelating geometry with \( \text{C}_2\text{v} \) symmetry on \( \text{Au}(111) \), confirming the previous assignment made by using HREELS. The small peak at 1903 cm\(^{-1}\) is due

<table>
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<td>1280</td>
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**Figure 2.** IRAS spectra after \( \text{NO}_2 \) exposures on a \( \text{Au}(111) \) surface at 86 K. All of the spectra were collected at 86 K.

**Figure 3.** IRAS spectra obtained following: (a) 1 ML \( \text{NO}_2 \) dosed on \( \text{Au}(111) \) at 86 K; (b) annealing the surface in (a) to 172 K for 30 s; (c) annealing the surface in (a) to 184 K for 30 s; (d) dosing 1 ML \( \text{NO}_2 \) at 185 K. All of the spectra were collected at 86 K.
to the formation of a very small amount of N₂O₃ by reaction of residual NO in the chamber with chemisorbed NO₂.

A pure N₂O₃ monolayer can be readily made from the pure chelating NO₂ monolayer on Au(111) by NO exposure to the adlayer at 120 K. All of the peaks in the IRAS spectrum in Figure 4 can be assigned to N₂O₃. The strongest peak at 1898 cm⁻¹ is due to the ν(N=O) mode, and the peaks at 1273, 1184, and 804 cm⁻¹ are due to the νₐ(NO₂), νₜ(NO₂), and δ(NO₂) modes, respectively. We propose that adsorbed N₂O₃ is bonded to the surface with Cₐ symmetry using one oxygen atom, in a monodentate fashion, with its O₂NN̄ bond perpendicular to the Au(111) surface. First, the νₐ(NO₂) and νₜ(NO₂) peaks have comparable intensity in the gas phase, and we observed comparable intensity of the νₐ(NO₂) and νₜ(NO₂) modes for the chemisorbed species. The surface dipole selection rule should strongly attenuate the νₜ(NO₂) peak if a chelating O₂NŌ-geometry were formed, and this does not occur. The observation of IR intensity ratios of the other bands different from those in gas-phase N₂O₃ indicates that the adsorbed species is oriented and that this orientation is not with the molecular plane parallel with the surface. Furthermore, the very strong intensity of the ν(N=O) mode is consistent with this dynamic dipole nearly perpendicular to the surface. When this monodentate N₂O₃ adlayer is heated to 185 K, chelating NO₂ appears again on the surface following the breaking of the N–N bond in N₂O₃. This is consistent with an N—N bond dissociation energy of 42 kJ/mol.⁸ We can now point out that the strong ν(N=O) peak of pure adsorbed N₂O₃ shows that the amount of N₂O₃ coadsorbed with chelating NO₂ in Figure 3 is very small indeed.

Since NO is not adsorbed on the Au(111) surface even at 105 K,⁸ this reaction likely occurs via an Eley—Rideal mechanism.¹⁹ Chelating NO₂ on the Au(111) surface may exist as a surface-bound radical, with an unpaired electron on the N atom (if the hybridization of the gas-phase molecule is maintained), and the radical—radical coupling reaction with NO (also a radical with the unpaired electron on the N atom) would readily occur. The following schematic illustrates the proposed bidentate NO₂ and monodentate N₂O₃ species formed on Au(111).

In all these IRAS studies, we did not observe any evidence for nitrite—N₂O₄ or NO²NO₃⁻ species formed from NO₂ exposures on Au(111). Koch et al.¹⁶ did not observe these species either when they studied NO₂ adsorption on gold foil at 80 K.

3.2. Reactions of H₂O with Preadsorbed NO₂, N₂O₃, and N₂O₄ on Au(111). Water interacts very weakly with the Au(111) surface, TPD of H₂O on Au(111) does not resolve the desorption of any strongly bound, chemisorbed state, and no decomposition occurs.⁷,²⁰ Consistent with these reports, our TPD spectra show only a single narrow H₂O desorption peak, ranging from 153 to 165 K as the coverage increases.

Although NO₂ and H₂O adsorb molecularly and reversibly when adsorbed separately, coadsorption leads to reactions. Those reactions that lead ultimately to the deposition of oxygen adatoms on the surface are the easiest to monitor, because oxygen adatoms recombine on Au(111) and desorb as O₂ at 520–545 K leaving a clean surface.²¹,²² Figure 5 shows O₂ TPD spectra that we used to monitor these reactions for a variety of coadsorption conditions. All of the exposures of both H₂O and NO₂ were carried out with the crystal at 86 K.

Figure 4. IRAS spectra obtained after (a) 1 ML NO₂ dosed on Au(111) at 185 K to give a pure monolayer of chelating chemisorbed NO₂, (b) NO exposure on a Au(111) surface precovered by the chelating NO₂ monolayer at 120 K to form a pure N₂O₃ monolayer, and (c) annealing the formation in (b) to 185 K for 30 s. All of the spectra were collected at 86 K.

Figure 5. O₂ TPD spectra after predosing NO₂ on Au(111) at 86 K followed by H₂O exposures at the same temperature: (a) 1 ML H₂O dose after 0.5 ML NO₂; (b) 6 ML H₂O dose after 0.5 ML NO₂; (c) 0.5 ML H₂O dose after 1 ML NO₂; (d) 6 ML H₂O dose after 1 ML NO₂; (e) 1 ML H₂O dose after 5 ML NO₂; (f) 1 ML H₂O dose after 7.5 ML NO₂; (g) 4.5 ML H₂O dose after 7.5 ML NO₂; (h) 4.5 ML H₂O dose after 10 ML NO₂.
Only 1% in the mass spectrum cracking pattern, and HNO$_3$ does not produce HONO as an ion fragment. The other three H$_2$O desorption peaks at 174, 209, and 222 K arise either from interactions of H$_2$O with adsorbed N$_2$O$_3$ or from cracking of higher molecular weight products. Since the gas-phase N$_2$O$_3$ mass spectrum does not give a fragment ion of $m/e = 32$, the peak at 143 K in O$_2$ TPD must be assigned to cracking from HNO$_2$ or HONO (or possibly some other unknown species). The O$_2$ peaks at 174, 209, and 222 K also arise from cracking of the products. In NO TPD, the peaks at 143, 174, and 222 K can be assigned to cracking from N$_2$O$_4$, HNO$_3$, and other products. The long “trailing” of the NO desorption trace with a peak at 350–430 K is unusual and is likely to indicate that the decomposition of intermediates that finally produce oxygen adatoms on Au(111) cause reaction-rate-limited NO desorption over a wide temperature range. In NO$_2$ TPD, the peak at 143 K is mainly due to cracking from unreacted N$_2$O$_4$ and the two higher desorption NO$_2$ peaks at 174 and 222 K arise from cracking of other products. In addition, the NO$_3$ TPD spectra also have a desorption profile that extends to quite high temperatures, including a peak at 350–430 K. This high-temperature NO$_3$ desorption is also reaction-rate limited and is similarly produced from the decomposition of intermediates that finally generate oxygen adatoms on Au(111).

In other studies, we found that the oxygen formation reaction was highly dependent on the crystallinity of the ice when N$_2$O$_4$ reacts with ice films on Au(111). Figure 7a shows that this phenomena was also observed in the experiments in which H$_2$O was exposed on N$_2$O$_4$ films. Figure 7a, trace iii, shows that a substantial amount of O$_2$ was produced in TPD when 7.5 ML NO$_2$ (pure N$_2$O$_4$) was predosed on Au(111) followed by dosing 1 ML H$_2$O at 86 K. In Figure 7a, trace ii, a predosed 7.5 ML NO$_2$ film at 86 K was annealed to 115 K for 30 s and then 1 ML H$_2$O was dosed on the film at 86 K. Under the conditions of Figure 7a, trace ii, about the same amount of O$_2$ was produced as that in Figure 7a, trace iii. Consistently, IRAS shows in Figure 2 that the NO$_2$ multilayer formed on Au(111) at 86 K is pure N$_2$O$_4$ and subsequently annealing to 115 K does not change the chemical state of N$_2$O$_4$. In contrast, Figure 7a, trace i, shows that no O$_2$ was produced in TPD when a 7.5 ML NO$_2$ film was formed on Au(111) at 113 K and followed by dosing 1 ML H$_2$O on the Au(111) at 113 K. This result clearly demonstrates that the crystallinity of the deposited ice clusters is a crucial factor for oxygen formation.

Previous IRAS studies showed that amorphous ice was formed when H$_2$O was dosed on Au(111) at 86 K, and this amorphous ice had non-hydrogen-bonded “free OH” groups. These “free OH” groups were shown to have strong reactivity for oxygen formation when N$_2$O$_4$ reacts with preadsorbed ice films, and “free OH” groups also show greater reactivity in other reactions compared to fully hydrogen-bonded crystalline ice. Annealing amorphous ice to 115 K or dosing H$_2$O at the same temperature produces crystalline ice and a loss in reactivity for oxygen formation since all of the “free OH” groups disappear because of crystallization that forms fully hydrogen-bonded ice species.

In contrast to the oxygen formation pathway, acid formation reactions occur regardless of the NO$_2$ exposures, dosing sequence, or crystallinity of H$_2$O in the coadsorbed layer. The reactions during TPD depicted in Figure 6 are very complicated, but we tentatively assign the peaks in the low-
studies. NO 2 exposures on Au(111) at 185 K produce a pure symmetry. Exposing this chemisorbed NO 2 monolayer on Au-

4. Conclusions

IRAS confirms the bonding geometries of NO 2 , N 2 O 3 , and N 2 O 4 adlayers on Au(111) deduced in previous HREELS studies. NO 2 exposures on Au(111) at 185 K produce a pure monolayer of chemisorbed, O,O'-chelating NO 2 with C 2v symmetry. Exposing this chemisorbed NO 2 monolayer on Au-(111) at 120 K to gas-phase NO leads to a monolayer of adsorbed N 2 O 3 that is bonded to the surface through one oxygen and has C 1 symmetry. This conclusion about the monodentate bonding of N 2 O 3 clarifies the ambiguity that was left in the previous HREELS determination. Large NO 2 exposures on Au-(111) at 86 K produce crystalline N 2 O 4 multilayers with a preferential orientation of the N–N bond perpendicular to the Au(111) surface.

Two reaction paths are found when preadsorbed layers of nitrogen oxides (NO 2 , N 2 O 3 , and N 2 O 4 ) on Au(111) react with ice clusters formed by postdosing H 2 O on these surfaces at low temperatures. One path is associated with HONO and HNO 3 formation. This reaction channel proceeds regardless of the water exposure temperature (which controls the crystallinity and concentration of “free OH” groups of the ice clusters formed) and the size of the NO 2 exposures. The other reaction channel forms oxygen adatoms on the Au(111) surface during heating, and this pathway occurs only at the interface between amorphous ice clusters and N 2 O 4 in films deposited on Au(111). Conditions that form crystalline ice strongly inhibit this reaction. Also, two other adsorbed nitrogen oxides species, i.e., chelating NO 2 and N 2 O 3 , that are normally observed following NO 2 exposures on Au(111) at 86 K cannot react with amorphous ice to form oxygen on Au(111). These results are consistent with those of our previous studies of nitrogen oxides from NO 2 exposures reacting with amorphous ice films predeposited on Au(111). These observations support our proposed mechanism for the formation of oxygen adatoms on Au(111) in which nitrite–N 2 O 3 , a reactive precursor, is formed by interactions between “free OH” groups of amorphous ice and N 2 O 4 and then this species is converted to nitrosium nitrate(NO + 3 NO 3 −), which produces oxygen adatoms on the surface following thermal decomposition.

These facile reactions between N 2 O 3 and H 2 O, along with the new structure–reactivity relationships established, are important to chemical foundations for a number of technologies, ranging from energetic materials to atmospheric chemistry.

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References and Notes