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

Jiang Wang and Bruce E. Koel*

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482

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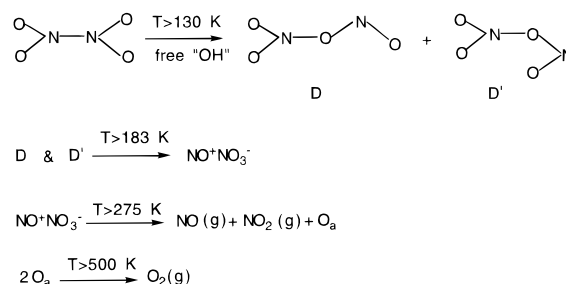
Adsorption or bonding geometries of pure adlayers of several N_xO_y species, i.e., nitrogen dioxide (NO₂), dinitrogen trioxide (N₂O₃), and dinitrogen tetroxide (N₂O₄), on Au(111) were determined by utilizing infrared reflection–absorption spectroscopy (IRAS). Dosing NO₂ on Au(111) at 85 K produced, in 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 O,O'-chelating geometry with C_{2v} symmetry. A monolayer of adsorbed N₂O₃ was produced by exposing the pure, chelating NO₂ adlayer to NO(g). The adsorbed complex with N₂O₃ has C_s 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 N₂O₄ 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.¹ Also, many different metastable N_xO_y intermediates² 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 coordination compounds³ and on metal surfaces.^{4,5} 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).^{6,7} 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 (ONO–NO₂) and nitrosonium nitrate (NO⁺NO₃[−]), and we proposed that N₂O₄ was responsible for the formation of oxygen adatoms as shown in the following mechanism.⁷



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)⁸ and Au(poly)⁹ 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 postdosed water to form ice films.

* To whom correspondence should be addressed.

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_2O_3 , and N_2O_4 adlayers on Au(111). We also obtain new information on the reacting species in condensed films of $\text{NO}_2 + \text{H}_2\text{O}$ that lead to oxygen formation on the Au(111) surface. Pure N_2O_3 and chemisorbed, chelating NO_2 monolayers do not react with amorphous ice to form oxygen on Au(111). Only N_2O_4 multilayer films produce oxygen adatoms in these reactions, and the results are identical to those obtained by reacting N_2O_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 2×10^{-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 adsorbates 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_2O 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_2O) was used after degassing

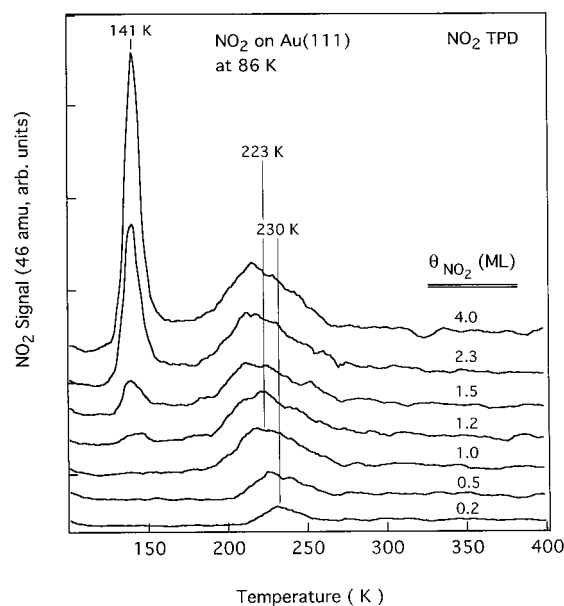


Figure 1. NO_2 TPD spectra following NO_2 exposures on Au(111) at 86 K.

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 $\sim 150^\circ\text{C}$ under NO_2 pressure for 30 min.

Adsorbate coverages herein are referenced to $\Theta = 1\text{ ML}$ 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 $\Theta_{\text{NO}_2} = 1\text{ ML}$ (or 4.2×10^{14} molecules/ cm^2).⁸ The H_2O 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 (1.0×10^{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_2O_3 , and N_2O_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 $\text{NO}_2/\text{Au}(111)$ 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_2O_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-(poly) 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_2O_4 multilayers was estimated to be 35 kJ/mol.⁸

Chemisorbed NO_2 on Au(111) has been assigned as an O,O'-nitrito surface chelate with C_{2v} 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 $\nu_a(\text{NO}_2)$ and symmetric $\nu_s(\text{NO}_2)$ NO_2 stretching modes. Interaction with the Au(111) surface could markedly decrease the energies of

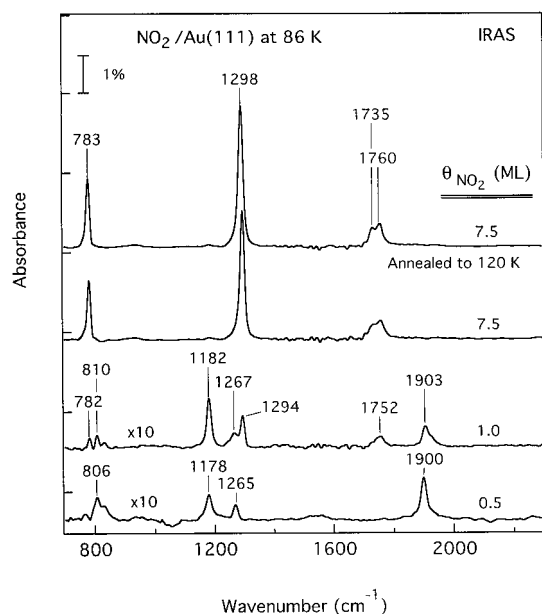


Figure 2. IRAS spectra after NO₂ exposures on a Au(111) surface at 86 K. All of the spectra were collected at 86 K.

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 NO₂ gas-phase IR spectrum.¹³ For example, the NO₂ group in Ni(α -picoline)₂(NO₂)₂¹⁴ has $\Delta[\nu_a(\text{NO}_2) - \nu_s(\text{NO}_2)] = 73$ 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 NO₂ exposures on 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 data⁸ very well. At 0.5 ML NO₂ coverage, a mixture of chemisorbed NO₂ and N₂O₃ exists on Au(111). N₂O₃ is formed by reaction of chemisorbed NO₂ with residual NO⁸ in the background that arises from decomposition of NO₂ in the UHV chamber. Chemisorbed NO₂ 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 upright O,O'-chelating geometry with C_{2v} symmetry.⁸ Two peaks due to N₂O₃ are seen at 1900 and 1265 cm⁻¹ that arise from NO stretching, $\nu(\text{NO})$, and NO₂ asymmetric stretching, $\nu_a(\text{NO}_2)$, modes, respectively. The other two peaks from N₂O₃ appear at 1178 and 806 cm⁻¹ due to the $\nu_s(\text{NO}_2)$ and $\delta(\text{NO}_2)$ modes, which overlap with the same modes of chelating NO₂. At 1 ML NO₂ coverage, the adsorbed species are chelating NO₂, N₂O₃, and N₂O₄. The peaks at 1182 and 810 cm⁻¹ are due to chemisorbed chelating NO₂. The peaks at 1903, 1267, 1182, and 810 cm⁻¹ are from N₂O₃. The peaks at 1760, 1735, 1294, and 783 cm⁻¹ are due to the $\nu_a(\text{NO}_2)$, $\nu_s(\text{NO}_2)$, and $\delta(\text{NO}_2)$ modes, respectively, of N₂O₄.^{7,8,15,16} When the NO₂ coverage is 7.5 ML, only bands due to N₂O₄ were observed. Annealing

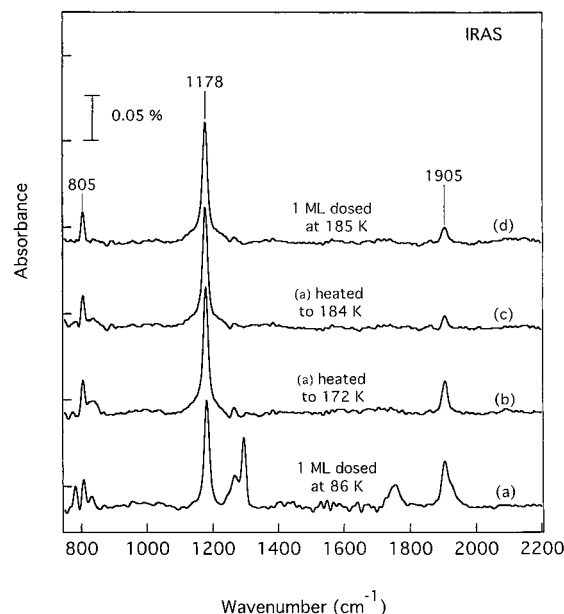


Figure 3. IRAS spectra obtained following: (a) 1 ML NO₂ dosed on Au(111) at 86 K; (b) annealing the surface in (a) to 172 K for 30 s; (c) annealing the surface in (a) to 184 K for 30 s; (d) dosing 1 ML NO₂ at 185 K. All of the spectra were collected at 86 K.

this multilayer to 120 K does not change the IRAS spectra. This multilayer film can be described as pure crystalline N₂O₄ with a preferential orientation of the N—N bond almost perpendicular to the 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 N₂O₄ surface layer, we also wanted to obtain pure NO₂ and N₂O₃ layers. These were made by the procedure outlined in Bartram et al.,⁸ and our IRAS spectra for chemisorbed NO₂ are shown in Figure 3. The pure, chemisorbed monolayer of NO₂ can be made by dosing NO₂ on Au(111) at 185 K or by dosing a NO₂ monolayer at 86 K and then heating to 185 K. Peaks at 1179 and 804 cm⁻¹ are characteristic for chelating NO₂⁻ 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 NO₂, occurring at 817–863 cm⁻¹, but the $\nu_s(\text{NO}_2)$ mode is very sensitive to this bonding geometry. The $\nu_s(\text{NO}_2)$ 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 $\nu_s(\text{NO}_2)$ and no feature that can be assigned to $\nu_a(\text{NO}_2)$. Therefore, because of the strict dipole selection rule in IRAS (compared to HREELS) we show conclusively that chemisorbed NO₂ is bonded in an O,O'-chelating geometry with C_{2v} symmetry on Au(111), confirming the previous assignment made by using HREELS. The small peak at 1903 cm⁻¹ is due

TABLE 1: Vibrational Frequencies (cm⁻¹) and Assignments of Adsorbed NO₂, N₂O₃, and N₂O₄ on Au(111) Surfaces

mode	NO ₂ /Au(111) NO ₂ monolayer		N ₂ O ₃ /Au(111) N ₂ O ₃ monolayer		N ₂ O ₄ /Au(111) N ₂ O ₄ multilayer		
	HREELS ⁸	IRAS	HREELS ⁸	IRAS	HREELS ⁸	IRAS ¹⁶	IRAS
$\nu(\text{O}_2\text{N}-\text{NO})$			250				
$\rho(\text{O}_2\text{NNO})$			450–650		440		
$\delta_s(\text{NO}_2)$	800	805	800	806	770	785	783
$\nu_s(\text{NO}_2)$	1180	1178	1180	1182	1280	1301	1298
$\nu_a(\text{NO}_2)$	1180		1270	1272	1755	1750	1735, 1760
$\nu(\text{NO})$			1890	1897			

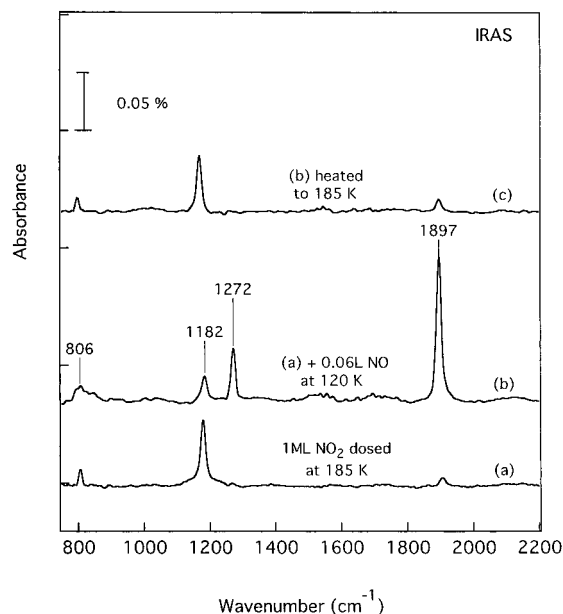


Figure 4. IRAS spectra obtained after (a) 1 ML NO_2 dosed on Au(111) at 185 K to give a pure monolayer of chelating chemisorbed NO_2 , (b) NO exposure on a Au(111) surface precovered by the chelating NO_2 monolayer at 120 K to form a pure N_2O_3 monolayer, and (c) annealing the surface in (b) to 185 K for 30 s. All of the spectra were collected at 86 K.

to the formation of a very small amount of N_2O_3 by reaction of residual NO in the chamber with chemisorbed NO_2 .

A pure N_2O_3 monolayer can be readily made from the pure chelating NO_2 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 N_2O_3 . The strongest peak at 1898 cm^{-1} is due to the $\nu(\text{N}=\text{O})$ mode, and the peaks at 1273, 1184, and 804 cm^{-1} are due to the $\nu_a(\text{NO}_2)$, $\nu_s(\text{NO}_2)$, and $\delta(\text{NO}_2)$ modes, respectively. We propose that adsorbed N_2O_3 is bonded to the surface with C_s symmetry using one oxygen atom, in a monodentate fashion, with its $\text{O}_2\text{NN}=\text{O}$ bond perpendicular to the Au(111) surface. First, the $\nu_a(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$ peaks have comparable intensity in the gas phase, and we observed comparable intensity of the $\nu_a(\text{NO}_2)$ and $\nu_s(\text{NO}_2)$ modes for the chemisorbed species. The surface dipole selection rule should strongly attenuate the $\nu_a(\text{NO}_2)$ peak if a chelating O, O' -geometry were formed, and this does not occur. The observation of IR intensity ratios of the other bands different from those in gas-phase N_2O_3 ¹⁸ 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 $\nu(\text{N}=\text{O})$ mode is consistent with this dynamic dipole nearly perpendicular to the surface. When this monodentate N_2O_3 adlayer is heated to 185 K, chelating NO_2 appears again on the surface following the breaking of the N–N bond in N_2O_3 . This is consistent with an N–N bond dissociation energy of 42 kJ/mol.⁸ We can now point out that the strong $\nu(\text{N}=\text{O})$ peak of pure adsorbed N_2O_3 shows that the amount of N_2O_3 coadsorbed with chelating NO_2 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 NO_2 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 NO_2 and monodentate N_2O_3 species formed on Au(111).

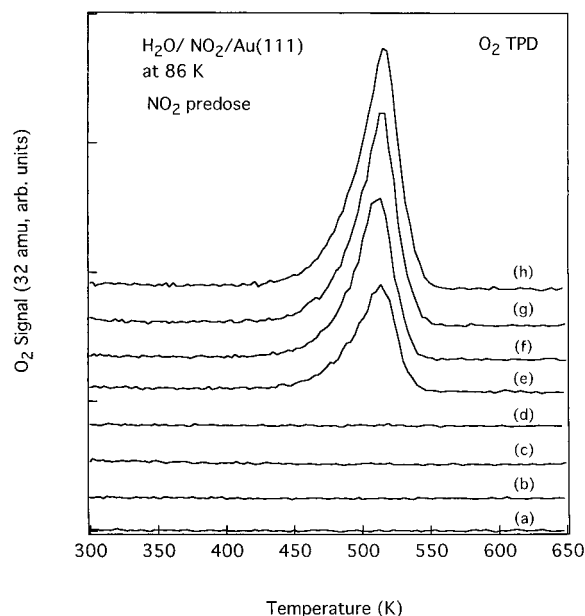
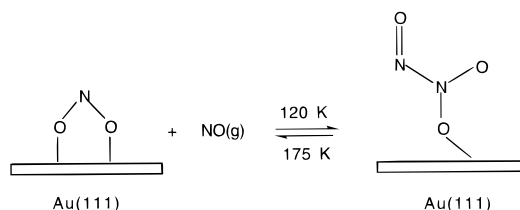


Figure 5. O_2 TPD spectra after predosing NO_2 on Au(111) at 86 K followed by H_2O exposures at the same temperature: (a) 1 ML H_2O dose after 0.5 ML NO_2 ; (b) 6 ML H_2O dose after 0.5 ML NO_2 ; (c) 0.5 ML H_2O dose after 1 ML NO_2 ; (d) 6 ML H_2O dose after 1 ML NO_2 ; (e) 1 ML H_2O dose after 5 ML NO_2 ; (f) 1 ML H_2O dose after 7.5 ML NO_2 ; (g) 4.5 ML H_2O dose after 7.5 ML NO_2 ; (h) 4.5 ML H_2O dose after 10 ML NO_2 .



In all these IRAS studies, we did not observe any evidence for nitrite– N_2O_4 or NO^+NO_3^- species formed from NO_2 exposures on Au(111). Koch et al.¹⁶ did not observe these species either when they studied NO_2 adsorption on gold foil at 80 K.

3.2. Reactions of H_2O with Predesorbed NO_2 , N_2O_3 , and N_2O_4 on Au(111). Water interacts very weakly with the Au(111) surface, TPD of H_2O 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 H_2O desorption peak, ranging from 153 to 165 K as the coverage increases.

Although NO_2 and H_2O 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 O_2 at 520–545 K leaving a clean surface.^{21,22} Figure 5 shows O_2 TPD spectra that we used to monitor these reactions for a variety of coadsorption conditions. All of the exposures of both H_2O and NO_2 were carried out with the crystal at 86 K. The deposition of amorphous ice occurs at this low surface temperature.^{7,23,24} O_2 desorption only results when the NO_2 preexposure was in the multilayer range forming a pure N_2O_4 film. The amount of oxygen formation saturates for NO_2 preexposures exceeding 10 ML. For NO_2 preexposures in the submonolayer range, forming a NO_2 and N_2O_3 precovered Au(111) surface, parts a and b of Figure 5 show that no oxygen was produced

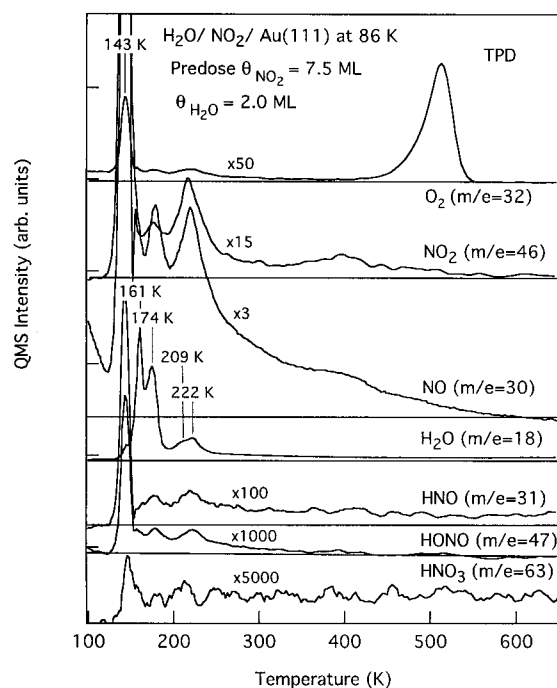


Figure 6. TPD spectra for several detected gas-phase products formed during heating in TPD after predosing 7.5 ML NO₂ on Au(111) at 86 K followed by a 2 ML H₂O exposure at the same temperature.

for 1–6 ML H₂O postdoses. This indicates that NO₂ and N₂O₃ are not responsible for oxygen formation. Moreover, parts c and d of Figure 5 show that no oxygen is produced when different postexposures of H₂O were dosed on the adlayer formed from a 1 ML NO₂ exposure on Au(111). This NO₂ dose forms a mixture of NO₂, N₂O₃, and N₂O₄ covering the surface. This result implies that interactions (hydrogen bonding) between N₂O₄ clusters and amorphous ice clusters are critical for oxygen deposition and coadsorbed NO₂ and N₂O₃ can block this interaction. These results are consistent with our observations that only N₂O₄ multilayer films react with amorphous ice clusters precovering the Au(111) surface and that the maximum amount of oxygen produced is about 0.5 ML.^{6,7} This independence on the dosing sequence indicates that the Au surface plays little role in forming the initial intermediates that lead to oxygen formation and these are formed at the interface between N₂O₄ and amorphous ice.

Other products in addition to O₂ were liberated into the gas phase during heating in TPD after H₂O was exposed on an NO₂ precovered surface. For 2 ML H₂O exposed on a 7.5 ML NO₂ precovered Au(111) surface at 86 K, Figure 6 shows that signals in the QMS during TPD were observed at $m/e = 63, 47, 31, 46, 30, 18$, and 32. These masses ostensibly monitor HNO₃, HONO, HNO, NO₂, NO, H₂O, and O₂, respectively. No evidence was observed in TPD for other possible reduction products such as H₂, N₂, NH₃, N₂O, and NH₂NH₂. We propose that HONO and HNO₃ are produced from these coadsorbed layers under UHV conditions below 145 K. The gas-phase HNO₃ mass spectrum shows a parent peak ($m/e = 63$) that is only 1% in the mass spectrum cracking pattern, and HNO₃ does not produce HONO as an ion fragment.²⁵ It is uncertain whether HNO is a reaction product because the HONO mass spectrum is unknown and HNO could be a cracking fragment of HONO. In contrast to the oxygen formation pathway, acid formation reactions occur regardless of the NO₂ exposures, dosing sequence, or crystallinity of H₂O in the coadsorbed layer.

The reactions during TPD depicted in Figure 6 are very complicated, but we tentatively assign the peaks in the low-

temperature range as follows. The peak at 161 K in H₂O TPD is assigned to unreacted water because the desorption temperature is the same as that of multilayer H₂O. The other three H₂O desorption peaks at 174, 209, and 222 K arise either from interactions of H₂O with adsorbed N₂O₄ or from cracking of higher molecular weight products. Since the gas-phase N₂O₄ mass spectrum does not give a fragment ion of $m/e = 32$, the peak at 143 K in O₂ TPD must be assigned to cracking from HNO₃ or HONO (or possibly some other unknown species). The O₂ 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 N₂O₄, HNO₃, and other products. The long “tailing” 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 NO₂ TPD, the peak at 143 K is mainly due to cracking from unreacted N₂O₄ and the two higher desorption NO₂ peaks at 174 and 222 K arise from cracking of other products. In addition, the NO₂ TPD spectra also have a desorption profile that extends to quite high temperatures, including a peak at 350–430 K. This high-temperature NO₂ desorption is also reaction-rate limited⁷ 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 N₂O₄ reacts with ice films on Au(111).^{6,7} Figure 7a shows that this phenomena was also observed in the experiments in which H₂O was exposed on N₂O₄ films. Figure 7a, trace iii, shows that a substantial amount of O₂ was produced in TPD when 7.5 ML NO₂ (pure N₂O₄) was predosed on a Au(111) followed by dosing 1 ML H₂O at 86 K. In Figure 7a, trace ii, a predosed 7.5 ML NO₂ film at 86 K was annealed to 115 K for 30 s and then 1 ML H₂O was dosed on the film at 86 K. Under the conditions of Figure 7a, trace ii, about the same amount of O₂ was produced as that in Figure 7a, trace iii. Consistently, IRAS shows in Figure 2 that the NO₂ multilayer formed on Au(111) at 86 K is pure N₂O₄ and subsequently annealing to 115 K does not change the chemical state of N₂O₄. In contrast, Figure 7a, trace i, shows that no O₂ was produced in TPD when a 7.5 ML NO₂ film was formed on Au(111) at 113 K and followed by dosing 1 ML H₂O 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 H₂O was dosed on Au(111) at 86 K,⁷ and this amorphous ice had non-hydrogen-bonded “free OH” groups.^{23,26} These “free OH” groups were shown to have strong reactivity for oxygen formation when N₂O₄ reacts with preadsorbed ice films, and “free OH” groups also show greater reactivity in other reactions compared to fully hydrogen-bonded crystalline ice.^{23,26,27} Annealing amorphous ice to 115 K or dosing H₂O 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.^{7,23,26} We propose that the strong hydrogen bonding between N₂O₄ and the highly polar “free OH” groups on the amorphous ice surface plays a crucial role in breaking the N–N bond (where D(O₂N–NO₂) = 53 kJ/mol⁸) and stabilizing polar products and intermediates such as ONO–NO₂ and NO⁺NO₃[–].

The reactivity of two other forms of nitrogen oxides, chelating chemisorbed NO₂ species and a pure monolayer of N₂O₃, with

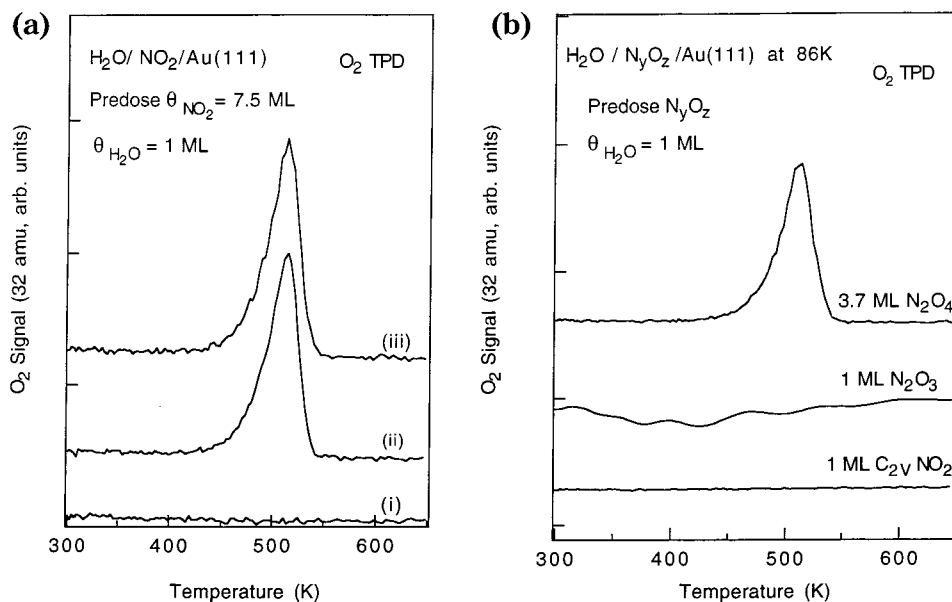


Figure 7. (a) O₂ TPD spectra probing requirements for generating surface oxygen: (i) 7.5 ML NO₂ predosed on Au(111) at 113 K followed by 1 ML H₂O exposure at the same temperature; (ii) 7.5 ML NO₂ predosed on Au(111) at 86 K, then annealed to 115 K for 30 s, followed by dosing 1 ML H₂O on the film at 86 K; (iii) 7.5 ML NO₂ predosed on Au(111) at 86 K followed by 1 ML H₂O exposure at the same temperature. (b) O₂ TPD spectra probing the extent of oxygen formation on Au(111) for the reaction of amorphous ice clusters formed by 1 ML H₂O exposures on preadsorbed films of (bottom) chelating NO₂ monolayer, (middle) N₂O₃ monolayer, and (top) N₂O₄ multilayer.

postdosed amorphous ice clusters on Au(111) at 86 K was also studied by TPD. The O₂ TPD spectra in Figure 7b show that no O₂ was produced either in reactions between chelating NO₂ or pure N₂O₃ and amorphous ice. Therefore, only N₂O₄ can react efficiently with amorphous ice to eventually oxidize the Au surface, and coadsorbed N₂O₃ and chelating NO₂ block the interaction of “free OH” groups with N₂O₄ to inhibit oxygen formation at low NO₂ exposures.

Comparing these results with our previous studies of N₂O₄ reacting with preadsorbed amorphous ice films,⁷ we find exactly the same results—acid formation and oxygen formation occur via two separate reaction pathways proceeding under different conditions. Acid-forming reactions are sensitive to neither the NO₂ exposure nor the crystallinity of the ice, but oxygen formation occurs only when amorphous ice is available and NO₂ exposure is in the multilayer range (to form pure N₂O₄). This demonstrates that the same oxygen formation mechanism is operating independent of the dosing sequence of NO₂ and H₂O. We further proved in this study that N₂O₄ is the only nitrogen oxide (of those investigated) that can (ultimately) produce oxygen by reacting with amorphous ice. This represents strong support for our proposed mechanism in which N₂O₄ first isomerizes and forms NO⁺NO₃[−], which finally decomposes at higher temperatures to form atomic oxygen on Au(111) during TPD.

Finally, the whole area of how N_xO_y interacts with water is important in the atmosphere. These studies reveal new information about fundamental interactions between N_xO_y and water (ice), for example, extending previous fundamental studies of N₂O₅ and ice.^{28–30}

4. Conclusions

IRAS confirms the bonding geometries of NO₂, N₂O₃, and N₂O₄ adlayers on Au(111) deduced in previous HREELS studies. NO₂ exposures on Au(111) at 185 K produce a pure monolayer of chemisorbed, O,O′-chelating NO₂ with C_{2v} symmetry. Exposing this chemisorbed NO₂ monolayer on Au(111) at 120 K to gas-phase NO leads to a monolayer of

adsorbed N₂O₃ that is bonded to the surface through one oxygen and has C_s symmetry. This conclusion about the monodentate bonding of N₂O₃ clarifies the ambiguity that was left in the previous HREELS determination. Large NO₂ exposures on Au(111) at 86 K produce crystalline N₂O₄ 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 (NO₂, N₂O₃, and N₂O₄) on Au(111) react with ice clusters formed by postdosing H₂O on these surfaces at low temperatures. One path is associated with HONO and HNO₃ 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 NO₂ 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 N₂O₄ 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 NO₂ and N₂O₃, that are normally observed following NO₂ 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 NO₂ 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—N₂O₄, a reactive precursor, is formed by interactions between “free OH” groups of amorphous ice and N₂O₄ and then this species is converted to nitrosonium nitrate(NO⁺NO₃[−]), which produces oxygen adatoms on the surface following thermal decomposition.

These facile reactions between N_xO_y and H₂O, 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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