

# Chemisorbed Oxygen on Au(111) Produced by a Novel Route: Reaction in Condensed Films of NO<sub>2</sub> + H<sub>2</sub>O

Jiang Wang, Michael R. Voss, Harald Busse, and Bruce E. Koel\*

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

Received: February 5, 1998; In Final Form: April 24, 1998

We report a facile, low-temperature reaction between condensed-phase NO<sub>2</sub> and H<sub>2</sub>O that leads ultimately to the formation of a large concentration ( $\theta_0 = 0.42$  monolayers) of adsorbed oxygen adatoms on a Au(111) surface. This reaction represents a novel route to generate surface oxygen on Au that can be utilized in fundamental studies of oxidation catalysis over Au such as low-temperature CO oxidation and the operation of Au converter tubes used in redox chemiluminescence detectors for atmospheric NO<sub>x</sub>. Also, this reaction may be relevant to heterogeneous processes occurring on ice particles in stratospheric clouds. This reaction is not specifically catalyzed by the Au(111) surface or by the defects present on the Au surface, and so this reaction may have some general utility for facile oxidation of unreactive surfaces.

## Introduction

Some time ago, we reported that low-temperature coadsorption of H<sub>2</sub>O and NO<sub>2</sub> on Au(111) led to new peaks in the thermal desorption spectra of these two molecules and led to the formation of oxygen adatoms at the surface.<sup>1</sup> We have carefully reinvestigated this chemistry, which we had found difficult to reliably reproduce earlier, in order to define the conditions for surface oxygen formation and to investigate the mechanism of such a reaction. This intriguing chemistry is of interest for a number of reasons. The interaction of oxygen with transition metal surfaces has received significant attention, particularly with regard to the role of chemisorbed oxygen in oxidation reactions catalyzed on these surfaces. Higher selectivity in oxidation catalysis might be achieved by using a less reactive metal catalyst, such as Au, if reactive oxygen can be made available on the gold surface. The adsorption and reactions of organic molecules such as methanol, formic acid, formaldehyde, acetylene, and ethylene have been studied on clean and oxidized Au(110)<sup>2,3</sup> and Au(111).<sup>1</sup> In general, organic molecules show no reactivity on clean Au surfaces but can be oxidized when coadsorbed with oxygen adatoms. Outka et al.<sup>2,3</sup> found that methanol was activated by 0.25 monolayers (ML) of oxygen adatoms and oxidized to form methyl formate, H<sub>2</sub>O, H<sub>2</sub>, and CO<sub>2</sub>. Formaldehyde was oxidized to HCOOH, H<sub>2</sub>O, and CO<sub>2</sub>. Formic acid and acetylene were oxidized to H<sub>2</sub>O and CO<sub>2</sub>. Ethylene is the only one of these molecules that does not react with oxygen adatoms on Au(110). Also, recently, gold has been found to be an effective component in the Au/TiO<sub>2</sub> catalyst for the water-gas shift reaction.<sup>4</sup> However, fundamental studies on Au surfaces have long been hampered by the extremely small dissociative sticking coefficient of O<sub>2</sub> under UHV conditions; i.e., exposure of O<sub>2</sub> on the Au(111) surfaces does not result in chemisorption of any measurable amount of adsorbed oxygen.<sup>5</sup>

Previously, studies of O/Au(111) had to resort to high-pressure and high-temperature exposure to O<sub>2</sub>, conditions that are known to cause the segregation of impurities to the Au surface, to dosing O<sub>2</sub> in the presence of a hot filament,<sup>6</sup> or to using O<sub>3</sub>,<sup>7</sup> which is clean but is potentially hazardous to use.

Therefore, it would be useful to discover a more convenient method to cleanly produce surface oxygen on Au under UHV conditions for use in fundamental studies of oxidation reactions on Au. In this Letter, we report on characterization of a novel reaction between coadsorbed NO<sub>2</sub> and H<sub>2</sub>O, which conveniently and reliably generates surface atomic oxygen on Au(111) surfaces. For conditions described herein, oxygen coverages from 0 to ~0.42 ML oxygen adatoms can be produced. A more detailed report discussing the reaction mechanism involving the intermediates nitrite-N<sub>2</sub>O<sub>4</sub> and nitrosonium nitrate (NO<sup>+</sup>NO<sub>3</sub><sup>-</sup>) will be published elsewhere.<sup>8</sup>

## Experimental Method

These studies were carried out in a UHV chamber equipped with a double-pass cylindrical mirror analyzer (CMA) for Auger electron spectroscopy (AES), reverse-view 4 grid optics for low-energy electron diffraction (LEED), a UTI 100C quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD), a Mattson Galaxy 6020 FTIR spectrometer for reflection-absorption infrared spectroscopy (RAIRS), an ion gun for sputtering, and gas, dosing facilities. The system base pressure was  $2 \times 10^{-10}$  Torr.

TPD measurements were made with the sample surface in line-of-sight to the QMS ionizer and using a low, linear heating rate of 3.5 K/s. A screen biased by -55 V was placed between the QMS ionizer and the sample to suppress low-energy electrons coming out of the QMS.<sup>9</sup> AES was used to check the cleanliness of the surface and measure the coverage of atomic oxygen. Spectra were recorded using an incident beam energy of 3 kV and a modulation voltage of 6 V<sub>P-P</sub>. A 0.2  $\mu$ A beam current was used to minimize electron-induced desorption.

The Au(111) sample (ca. 10 mm diameter  $\times$  2 mm thickness) was mounted tightly under tension between two 0.015 in. tungsten wires that were imbedded in two grooves along the crystal edges. These two wires were spot-welded to thick Ta rods directly attached to a liquid N<sub>2</sub>-cooled Cu block. The sample could be cooled to 85 K and resistively heated to 1000 K. The temperature was measured by a chromel-alumel thermocouple firmly placed directly into a hole in the edge of

\* To whom correspondence should be addressed.

the Au crystal. The Au(111) surface was cleaned by repeated sputtering–annealing cycles using Ar<sup>+</sup> ion sputtering at room temperature (10 min, 500 V, 1  $\mu$ A) at an incident angle of 45° and annealing at 973 K for 10 min. The cleanliness and structure of the surface were checked by AES and LEED. Sharp spots characteristic of good ordering were always observed after annealing. Usually, a (1  $\times$  1) LEED pattern was seen, but sometimes a pattern due to a reconstructed surface structure, Au(111)-( $\sqrt{3} \times \sqrt{3}$ ),<sup>10</sup> was seen.

Deionized water (H<sub>2</sub>O) was used after degassing via several freeze–pump–thaw cycles. NO<sub>2</sub> was used as received (Matheson, 99.9%). To minimize reactions of NO<sub>2</sub> in the doser gas lines, stainless steel and gold-plated gaskets were utilized, and the entire dosing manifold gas line was initially passivated at ~150 °C under NO<sub>2</sub> pressure for 30 min.

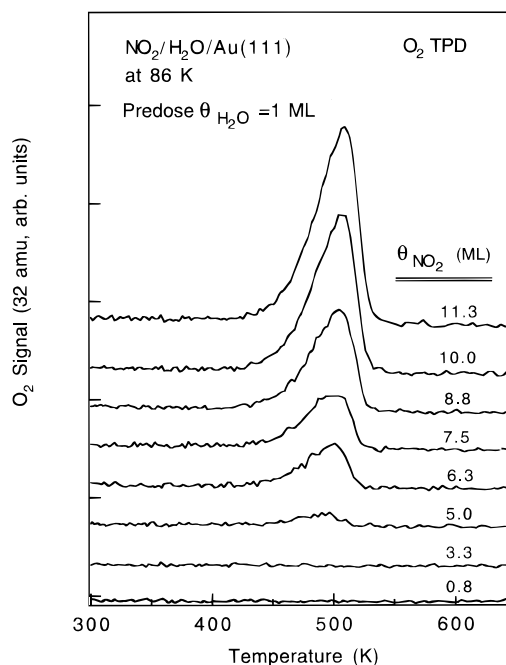
## Results and Discussion

NO<sub>2</sub> adsorption on Au(111) single-crystal and polycrystalline gold surfaces is completely reversible, and no decomposition was detected in previous studies in our group.<sup>11–13</sup> On Au(111), there are two NO<sub>2</sub> desorption states in TPD with peak desorption temperatures of 230 and 143 K. The high-temperature peak is due to the chemisorbed monolayer of NO<sub>2</sub>, revealed by both HREELS<sup>11</sup> and FTIR<sup>13</sup> to be mostly composed of chelating NO<sub>2</sub>. The desorption activation energy for this species is 14 kcal/mol. As the exposure increases, the low desorption temperature peak grows in owing to the formation of a physisorbed multilayer of NO<sub>2</sub>. This exists as a pure dimer of NO<sub>2</sub>, N<sub>2</sub>O<sub>4</sub>. On Au (poly) surfaces, there is another NO<sub>2</sub> TPD peak at 325 K due to molecular adsorption at defect sites.<sup>12</sup>

H<sub>2</sub>O adsorption on Au(111) has been studied previously<sup>14</sup> and was also reinvestigated by us as a reference for subsequent coadsorption reactions. TPD spectra show only one desorption peak even after very high exposures, indicating that H<sub>2</sub>O on Au(111) is very weakly held, nucleating clusters even in the “monolayer” regime, and it clearly shows zero-order desorption kinetics. H<sub>2</sub>O desorption occurs over the range of 155–165 K, depending on the coverage of H<sub>2</sub>O. These factors make a coverage determination of H<sub>2</sub>O on Au(111) very difficult. To roughly estimate the H<sub>2</sub>O concentration, TPD experiments were performed utilizing “background dosing” where the H<sub>2</sub>O pressure could be measured with an ion gauge. Since the sticking probability of H<sub>2</sub>O is unity on a cold surface at 86 K,<sup>14,15</sup> we can use the H<sub>2</sub>O pressure to determine the number of H<sub>2</sub>O molecules adsorbed on the surface for a given background dose. We estimate that this result is within a factor of 3 of the correct value based on the typically encountered errors in determining the actual H<sub>2</sub>O pressure at the Au(111) surface. The coverage of H<sub>2</sub>O on the surface after exposures using a directed beam were obtained by comparison of the subsequent TPD area with that following TPD after background dosing. The monolayer equivalent coverage of H<sub>2</sub>O on Au(111) was calculated to be one-half of the H<sub>2</sub>O/Pt(111) bilayer coverage determined by XPS.<sup>16</sup> This coverage on Au(111) could be obtained by a 1 L background exposure.

Even though the adsorption of NO<sub>2</sub> and H<sub>2</sub>O are completely reversible when adsorbed separately on Au(111), coadsorption leads to reaction. We have previously reported that new NO<sub>2</sub> and H<sub>2</sub>O peaks in TPD are observed,<sup>1</sup> and here we focus on the most interesting feature, the appearance of O<sub>2</sub> desorption.

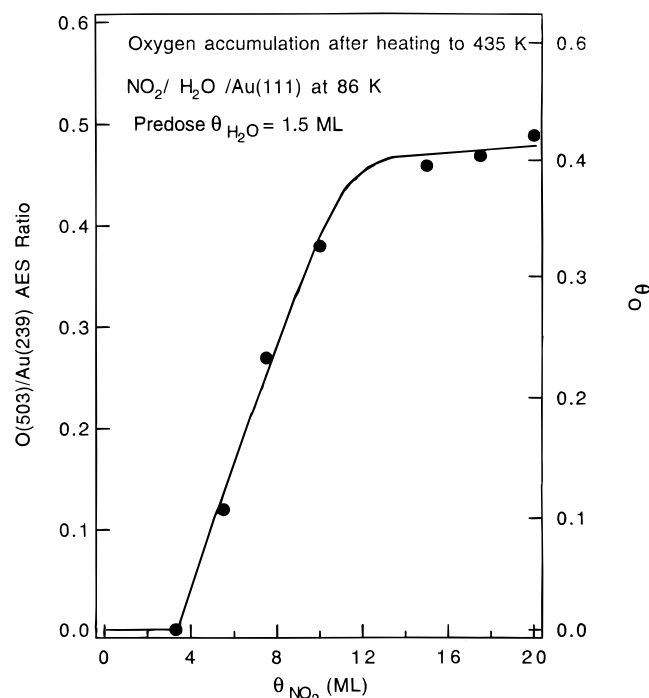
Figure 1 shows several TPD spectra of O<sub>2</sub> after initially dosing 1 ML H<sub>2</sub>O on Au(111) at 86 K followed by dosing NO<sub>2</sub> at the same temperature. As the NO<sub>2</sub> exposure was increased to more than 3.3 ML, desorption of O<sub>2</sub> was observed in a peak



**Figure 1.** O<sub>2</sub> TPD spectra following NO<sub>2</sub> dosed on a Au(111) surface at 86 K precovered by 1 ML H<sub>2</sub>O at the same temperature.

at 517 K. This peak saturated when the NO<sub>2</sub> coverage was more than 10 ML. In previous work, exposure of Au(111) to O<sub>3</sub> at 300 K generates an atomic oxygen adlayer that desorbs as molecular O<sub>2</sub> in TPD over the range of 515–545 K as the oxygen coverage increases.<sup>17</sup> Thus, the oxygen species generated by coadsorption of NO<sub>2</sub> and H<sub>2</sub>O can be identified as atomic oxygen by the desorption temperature of O<sub>2</sub> in Figure 1. The appearance of the O<sub>2</sub> TPD peak corresponds to the strongest interaction between N<sub>2</sub>O<sub>4</sub> and H<sub>2</sub>O, which is demonstrated by the formation of an additional high-temperature desorption peak at 214 K in the corresponding TPD spectra of H<sub>2</sub>O.<sup>8</sup> Tolbert et al.<sup>18</sup> also observed a desorption peak at high temperature in the TPD of H<sub>2</sub>O when they studied the reaction of N<sub>2</sub>O<sub>5</sub> with ice surfaces. They attributed this high-temperature peak to hydrated N<sub>2</sub>O<sub>5</sub>. A strong interaction between N<sub>2</sub>O<sub>4</sub> and H<sub>2</sub>O appears to be a key factor in surface oxygen formation. For the monolayer of NO<sub>2</sub>, a relatively weak interaction between water and nitrogen oxides was observed, which gives a desorption peak at 195 K in the water TPD spectra, and no surface oxygen was formed. We monitored a number of other QMS signals during TPD, and we also detected HNO<sub>3</sub> and HONO as desorbed products under all conditions.

Experiments were carried out to quantify the surface oxygen coverage using an initial dose of 1.5 ML H<sub>2</sub>O on Au(111) at 86 K followed by NO<sub>2</sub> exposures on the surface at the same temperature. This coadsorbed layer was then heated to 435 K to remove weakly adsorbed species and decompose any precursors to get an oxygen-covered Au(111) surface. After the sample was cooled to 86 K, the O/Au ratio was measured by AES. Figure 2 shows these oxygen coverages generated by NO<sub>2</sub> + H<sub>2</sub>O coadsorption. The left ordinate axis is the AES peak-to-peak height ratio of the O(KLL) 519 eV signal to the Au(MNN) 239 eV signal, and the right-hand axis is given as oxygen monolayers. These data are consistent with Figure 1 (even though the H<sub>2</sub>O coverage is 1.5 ML), showing that there is no oxygen formed at NO<sub>2</sub> coverages below a thin multilayer (3.3 ML) and that oxygen formation reaches saturation at NO<sub>2</sub> exposures of more than 10 ML. This saturation coverage of atomic oxygen on Au(111), with an O/Au AES ratio of 0.47



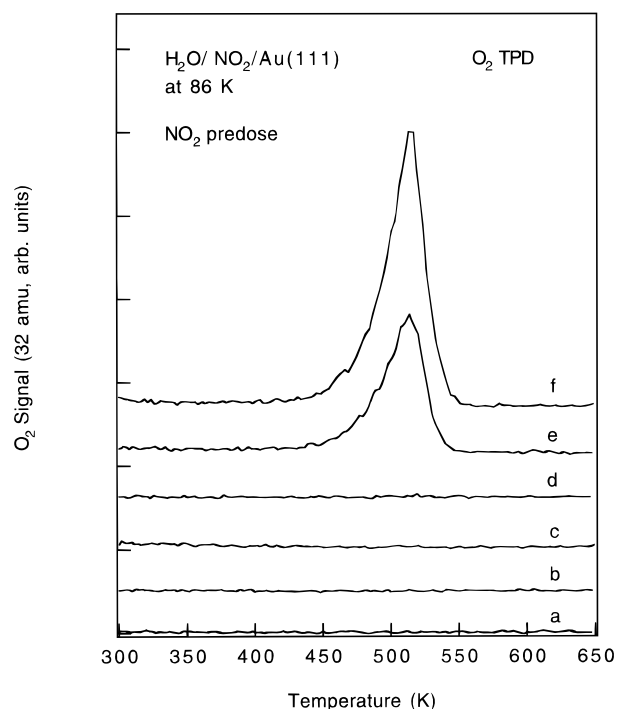
**Figure 2.** Surface oxygen coverage determined by AES using the peak-to-peak height ratio of the O (519 eV) signal to the Au (239 eV) signal. The initial dose of H<sub>2</sub>O was 1.5 ML in all cases with increasing subsequent NO<sub>2</sub> exposures. The relationship between the O/Au AES ratio and the oxygen coverage was determined by studies of O<sub>3</sub>/Au(111).<sup>17</sup>

corresponds to  $\theta_0 = 0.42$  ML. The coverage was determined by calibration of the O/Au ratio with that of atomic oxygen formed by O<sub>3</sub> decomposition on Au(111),<sup>17</sup> and it is also consistent with the O/Au ratio of a chelating NO<sub>2</sub> monolayer on Au(111) with  $\theta_{\text{NO}_2} = 0.4$  ML.<sup>11</sup>

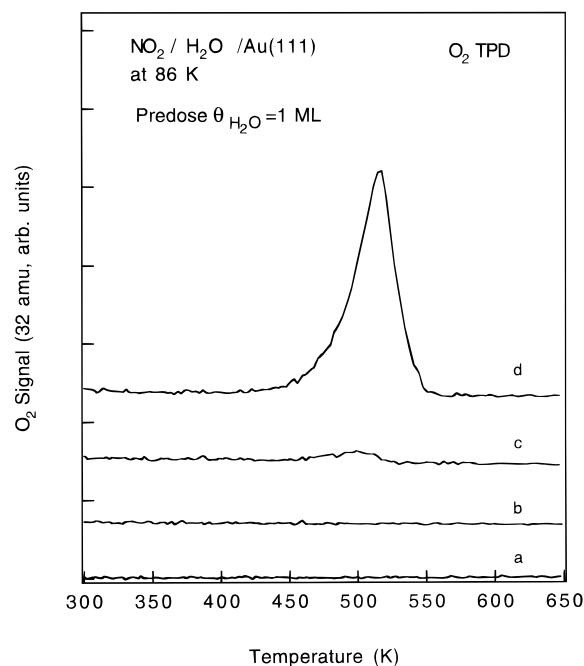
To further characterize this reaction, we also carried out TPD studies after predosing NO<sub>2</sub> and then postdosing H<sub>2</sub>O on Au(111) at 86 K. Figure 3a–d shows that for submonolayer and monolayer NO<sub>2</sub> precoverages, independent of the amount of H<sub>2</sub>O dosed, there was no O<sub>2</sub> desorption detected in TPD. In contrast, a substantial amount of O<sub>2</sub> desorption was observed after dosing H<sub>2</sub>O on top of an NO<sub>2</sub> multilayer, as shown in Figure 3e,f. The independence of the reactivity on the dosing sequence and unique reaction selectivity for multilayer NO<sub>2</sub> indicates that oxygen formation reactions (or formation of oxygen-generating precursors) occur at the interface between the N<sub>2</sub>O<sub>4</sub> and H<sub>2</sub>O clusters and have little to do with the Au(111) surface.

To further probe effects of the Au(111) surface on oxygen formation, we conducted reactions on a Au(111) single crystal with a high concentration of defects as characterized by desorption of NO<sub>2</sub> in TPD at 325 K. No oxygen was desorbed in TPD when we dosed multilayer H<sub>2</sub>O and NO<sub>2</sub> on this defective surface at 110 K. Surprisingly, TPD of H<sub>2</sub>O still showed just one H<sub>2</sub>O desorption peak at the same temperature as the desorption of H<sub>2</sub>O from defect-free Au(111). This result indicates that defects on Au(111) do not promote oxygen formation. These experiments also led us to see that the dosing temperature was an important parameter.

The crucial influence of dosing temperature on oxygen generation is shown by the TPD experiments in Figure 4. Figure 4d shows that a substantial amount of O<sub>2</sub> was produced in TPD when we predosed 1 ML H<sub>2</sub>O on Au(111) at 86 K followed by dosing 7.5 ML NO<sub>2</sub> at the same temperature. However, when



**Figure 3.** O<sub>2</sub> TPD spectra after predosing NO<sub>2</sub> on Au(111) at 86 K followed by H<sub>2</sub>O exposure at the same temperature. (a) 1 ML H<sub>2</sub>O dose after 0.5 ML NO<sub>2</sub>, (b) 6 ML H<sub>2</sub>O dose after 0.5 ML NO<sub>2</sub>, (c) 0.5 ML H<sub>2</sub>O dose after 1 ML NO<sub>2</sub>, (d) 6 ML H<sub>2</sub>O dose after 1 ML NO<sub>2</sub>, (e) 1 ML H<sub>2</sub>O dose after 7.5 ML NO<sub>2</sub>, and (f) 4.5 ML H<sub>2</sub>O dose after 7.5 ML NO<sub>2</sub>.



**Figure 4.** O<sub>2</sub> TPD spectra after several experiments to probe the requirements for generating surface oxygen. (a) 0.03 L of (NO<sub>2</sub> + H<sub>2</sub>O) premixed in the gas line at room temperature and dosed on Au(111) at 86 K; (b) 7.5 ML NO<sub>2</sub> dosed at 110 K that was precovered by 1 ML H<sub>2</sub>O dosed at the same temperature; (c) identical to that in (b) except that the dosing temperature was 86 K and the predosed H<sub>2</sub>O layer was annealed to 115 K prior to NO<sub>2</sub> dosing. (d) 7.5 ML NO<sub>2</sub> dosed on Au(111) at 86 K that was precovered by 1 ML H<sub>2</sub>O at the same temperature.

we exposed the same amount of NO<sub>2</sub> on a surface that was formed by dosing 1 ML H<sub>2</sub>O on Au(111) at 86 K, followed by annealing the surface to 113 K, only a tiny amount of O<sub>2</sub> was

produced (Figure 4c). Furthermore, no O<sub>2</sub> desorption was detected when we dosed 1 ML H<sub>2</sub>O on Au(111) at 110 K and then exposed 7.5 ML NO<sub>2</sub> at the same temperature (Figure 4b). These results demonstrate that the physical state of the H<sub>2</sub>O plays a key role in the eventual formation of surface oxygen, and amorphous ice clusters formed at these low temperatures could be an active phase associated with surface oxygen formation. Amorphous ice, characterized by "free OH" species, has been demonstrated to be more reactive than crystalline ice for acetone adsorption, along with HCl and ClONO<sub>2</sub> decomposition, by Roberts and co-workers.<sup>19,20</sup> In addition, when we dosed 0.03 L of a premixed (H<sub>2</sub>O + NO<sub>2</sub>) gas using a directed beam doser to Au(111) at 86 K, no oxygen was found as shown in Figure 4a. This indicates that oxygen formation does not depend on HNO<sub>2</sub> or HNO<sub>3</sub> intermediates because both HNO<sub>2</sub> and HNO<sub>3</sub> should have been dosed on the Au(111) surface. It is well-known that HNO<sub>2</sub> and HNO<sub>3</sub> are formed when gaseous NO<sub>2</sub> and H<sub>2</sub>O are mixed at room temperature.

The results of other related experiments, including FTIR studies and a discussion of the reaction mechanism, will be reported elsewhere.<sup>8</sup> Briefly, we concluded that N<sub>2</sub>O<sub>4</sub> in thick films in the presence of free OH groups of amorphous ice isomerize to the nitrite (ONO–NO<sub>2</sub>) isomer, which converts to nitrosonium nitrate (NO<sup>+</sup>NO<sub>3</sub><sup>–</sup>). This species decomposes below 400 K to generate atomic oxygen on the surface.

## Conclusions

Even though H<sub>2</sub>O and NO<sub>2</sub> do not react on Au(111) under UHV conditions when adsorbed separately, coadsorption leads to reaction. Under certain conditions, reaction leads eventually to the formation of oxygen adatoms. We have found that surface concentrations of atomic oxygen up to 0.42 ML can be readily produced on Au(111) surfaces by a reaction of coadsorbed H<sub>2</sub>O and NO<sub>2</sub> at dosing temperatures below 100 K. The

requirements for surface oxygen formation are dosing temperatures below 100 K and NO<sub>2</sub> multilayers. The dosing sequence (either NO<sub>2</sub> or H<sub>2</sub>O first) and defects on the Au(111) surface do not appreciatively affect the oxygen yield, indicating that this reaction probably occurs at the interface between amorphous ice and N<sub>2</sub>O<sub>4</sub>.

**Acknowledgment.** This work was supported by the Army Research Office.

## References and Notes

- (1) Lazaga, M. A.; Parker, D. H.; Kastanas, G. N.; Koel, B. E. In *Catalytic Selective Oxidation*; ACS Symposium Series 523; Oyama, S. T., Hightower, J. W., Eds.; American Chemical Society: Washington, DC, 1993; p 90.
- (2) Outka, D. A.; Madix, R. J. *J. Am. Chem. Soc.* **1987**, *109*, 1708.
- (3) Outka, D. A.; Madix, R. J. *Surf. Sci.* **1987**, *179*, 361.
- (4) Sakurai, H.; Ueda, A.; Kobayashi, T.; Haruta, M. *Chem. Commun.* **1997**, 271.
- (5) Pireaux, J. J.; Chtaib, M.; Delrue, J. P.; Thiry, P. A.; Liehr, M.; Caudano, R. *Surf. Sci.* **1984**, *141*, 211.
- (6) Asult, A. G.; Madix, R. J. *Surf. Sci.* **1986**, *169*, 347.
- (7) Parker, D. H.; Koel, B. E. *J. Vac. Sci. Technol.* **1990**, *A8* (3), 2585.
- (8) Wang, J.; Koel, B. E. Submitted to *Surf. Sci.*
- (9) Xu, C.; Koel, B. E. *Surf. Sci. Lett.* **1993**, *292*, L803.
- (10) Koestner, R. J. Ph.D. Thesis, University of California, Berkeley, 1982.
- (11) Bartram, M. E.; Koel, B. E. *Surf. Sci.* **1989**, *213*, 137.
- (12) Wickham, D. T.; Banse, B. A.; Koel, B. E. *Catal. Lett.* **1990**, *6*, 163.
- (13) Wang, J.; Koel, B. E. Submitted to *J. Phys. Chem.*
- (14) Kay, B. D.; Lykke, K. R.; Creighton, J. R.; Ward, S. J. *J. Chem. Phys.* **1989**, *91*, 5120.
- (15) Xu, C.; Koel, B. E. Unpublished work.
- (16) Wagner, F. T.; Moylan, T. E. *Surf. Sci.* **1987**, *182*, 125.
- (17) Saliba, N.; Parker, D. H.; Koel, B. E. *Surf. Sci.*, in press.
- (18) Tolbert, M. T.; Rossi, M. J.; Golden, D. M. *Science* **1988**, *240*, 1019.
- (19) Schaff, J. E.; Roberts, J. T. *J. Phys. Chem.* **1994**, *98*, 6900.
- (20) Graham, J. D.; Roberts, J. T. *J. Phys. Chem.* **1994**, *98*, 5974.