# METAL/ELECTROLYTE SURFACE CHEMISTRY: THE ADSORPTION OF NITRIC ACID AND WATER ON Ag(110)

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The adsorption of  $HNO_3/H_2O$  mixtures on Ag(110) was investigated to learn more about the chemistry of the metal/electrolyte interface. The experiments were performed in ultrahigh vacuum (UHV) using thermal desorption spectroscopy (TDS), low energy electron diffraction (LEED), and electron stimulated desorption ion angular distribution (ESDIAD) over temperatures of 80-650 K and coverages of 0-10 monolayers (ML). As this is the first known study of HNO3 in UHV, the mass spectrometer cracking pattern for HNO<sub>3</sub> is here reported. HNO<sub>3</sub> adsorbs irreversibly on the clean surface at 80 K and loses its acidic proton to form an adsorbed surface nitrate (NO<sub>2</sub>) below 150 K. The saturation amount of adsorbed NO<sub>2</sub> is  $0.4 \pm 0.1$  ML for which adsorption occurs in either a normal or split  $c(2 \times 2)$  structure. NO<sub>3</sub> is stable on the surface up to 450 K beyond which it decomposes directly to gaseous NO2 and NO and adsorbed atomic oxygen. NO<sub>3</sub> decomposition is first order with an activation energy  $E_a = 151 \pm 4 \text{ kJ mol}^{-1}$  and a pre-exponential factor of  $A = 10^{15.4 \pm 0.4}$  s<sup>-1</sup>. NO<sub>3</sub> stabilizes adsorbed H<sub>2</sub>O by about 8 kJ mol<sup>-1</sup> and is hydrated by as many as three H<sub>2</sub>O molecules. Multilayers of HNO<sub>3</sub>/H<sub>2</sub>O desorb at 150-220 K and show evidence of extensive hydrogen bonding and hydration interactions. No evidence for HNO<sub>3</sub>-induced corrosion or other surface damage was detected in any of these experiments.

### 1. Introduction

Many electrochemical and corrosion processes are governed by events occurring at the solid/liquid interface, the molecular details of which are not well understood. This system is inherently complex as it contains, in addition to the substrate, solvent molecules, anions, cations, reactant or product species involved in surface reactions, and a large potential drop [1]. The fundamental chemical and physical interactions between electrolyte and substrate can be probed by ultrahigh vacuum (UHV) modeling experiments [2,3] in which adsorption and surface reactions of electrolyte components on a model electrode are studied under well defined conditions. These experiments depart from electrochemistry only in the low temperatures required for water adsorption (80–180 K) and the inability to control the potential drop at the interface.

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0039-6028/89/\$03.50 © Elsevier Science Publishers B.V. (North-Holland Physics Publishing Division) UHV modeling provides the most basic information regarding solvent-ionsubstrate interactions and therefore complements the more traditional electrochemical research being carried out by other groups [4]. Most UHV adsorption studies to date have involved adsorbates relevant to heterogeneous catalysis so relatively little is known about electrolyte surface chemistry at the molecular level.

Previous UHV modeling studies have investigated the coadsorption of either a protic solvent ( $H_2O$ ) or an aprotic solvent ( $CH_3CN$ ) with electropositive (Cs) and electronegative (Br, O) species on Cu(110) and Ag(110) [2,3,5-8]. The electropositive and electronegative species were chosen to represent adsorbed cations and anions. In general there are strong interactions between the solvent and coadsorbed ions which take the form of surface solvation [3]. The number of solvent molecules interacting with the adsorbed model ion ranges from one to six.

Wagner and co-workers performed UHV modeling studies for coadsorbed HF and  $H_2O$  on Pt(111) [9] and coadsorbed CO and  $H_2O$  on Rh(111) and Pt(111) [10]. They observed direct evidence for adsorbed hydronium ions  $(H_3O^+)$  produced by HF dissociation in the hydrogen bonded network of HF and  $H_2O$  on Pt(111) at 100 K. The possible importance in electrocatalysis of CO-H<sub>2</sub>O interactions was demonstrated by the existence of hydrophilic adsorption (intermixed CO and  $H_2O$ ) on Rh(111) versus hydrophobic adsorption (separate CO and  $H_2O$  domains) on Pt(111).

There have been relatively few other surface science studies of inorganic acids adsorbed on metals. Hubbard's research group has extensively studied ordered halide overlayers on Pt(111) and Ag(111) electrodes by emersion from solutions of HCl, HBr, or HI ([11–14], and references therein). They observed a variety of ordered structures depending on electrode potential and electrolyte concentration. Zei et al. [15], recently studied Au(111) electrodes emersed from  $H_2SO_4$  solutions and observed ordered, two-dimensional  $H_2SO_4$  adlayers following emersion. These studies were all performed at room temperature and neither higher nor lower temperature regimes were systematically investigated.

There remains a strong need to study  $H_2O$  interactions with coadsorbed anions. First, many anomalous electrochemical effects are often attributed to anions adsorbed from the electrolyte [1]. The anion is said to be specifically adsorbed in that it is in direct contact with the surface, but still maintains part of its hydration shell. Many electrolytes have polynuclear anions (NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, etc.) and the interactions between H<sub>2</sub>O and these species have never been studied. Second, it is of interest to see how H<sub>2</sub>O interactions with polynuclear anions may differ from atomic anions. Recent calculations [16,17] suggest that some differences may occur since a larger anion may be able to prevent its charge from being locally screened by the metal electrons.

In this study the models for electrolyte and electrode are a  $HNO_3/H_2O$ 

mixture and a Ag(110) surface, respectively. To our knowledge this is the first study of nitric acid adsorption in UHV. Aqueous solutions of nitric acid are commonly used electrolytes and have a reasonable vapor pressure [18] enabling them to be admitted to the vacuum chamber as a vapor. The Ag(110) surface was chosen since its surface chemistry is well understood [19]. The clean surface is essentially chemically inert, but adsorbed atomic oxygen promotes a wide variety of surface reactions depending on the reactant.

Nitric acid adsorption also leads into the surface chemistry of nitrogen oxides. The adsorption of NO<sub>2</sub> on Ag(111) was recently studied with high resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS) by Outka et al. [20]. They observed formation of a surface nitrate (NO<sub>3</sub>) by reaction of NO<sub>2</sub> and O with the latter coming from either a small amount of NO<sub>2</sub> dissociation on the surface or by direct addition of oxygen. Adsorbed NO<sub>3</sub> exhibited  $C_{2v}$  symmetry with bonding to the surface occurring through only one of the oxygen atoms. Surface nitrate was reported to decompose to its atomic constituents at temperatures below 500 K.

Nitric oxide adsorption on silver has been studied by several groups. Lambert and co-workers [21,22] found that adsorption on Ag(110) and Ag(111) was molecular for temperatures above 300 K, whereas Behm and Brundle observed both molecular and dissociative chemisorption at 25 K with the latter producing  $N_2O$  and O at 125 K [23]. The dynamics of NO scattering from Ag(111) have also been extensively studied [24,25].

We studied HNO<sub>3</sub> adsorption on Ag(110) with TDS, low energy electron diffraction (LEED), and electron stimulated desorption ion angular distribution (ESDIAD) over the temperature range of 80 to 650 K. HNO<sub>3</sub> adsorption on Ag(110) leads directly to a surface nitrate at temperatures below 200 K. The properties of NO<sub>3</sub> from HNO<sub>3</sub> are similar to NO<sub>3</sub> from NO<sub>2</sub> and O [20], though some distinct differences exist. Surface nitrate decomposes at temperatures above 450 K to yield gaseous NO<sub>2</sub> and NO in approximately a 2:1 ratio. The decomposition kinetics for NO<sub>3</sub> on Ag(110) were also measured. Attractive interactions were evident between NO<sub>3</sub> and H<sub>2</sub>O and complex hydrations interactions were seen for multilayers of HNO<sub>3</sub> and H<sub>2</sub>O in the temperature range 150–220 K.

## 2. Experimental

The experiments were performed in a stainless steel UHV chamber (fig. 1) equipped with turbomolecular and titanium sublimation pumps. A base pressure of better than  $1 \times 10^{-10}$  Torr was achieved after bakeout at 150 °C for 24 h.

The Ag(110) crystal was cut to within  $\pm 0.5^{\circ}$ , mechanically polished, electropolished [26], and cleaned in vacuum by 40 min cycles of 500 eV Ar<sup>+</sup>



Fig. 1. Schematic of ultrahigh vacuum chamber.

bombardment followed by annealing to 800 K. This produced a clean surface after approximately 150 h of sputtering as determined by a sharp  $(1 \times 1)$ LEED pattern and the absence of impurity induced thermal desorption features after exposure to H<sub>2</sub>O at 80 K [27]. The temperature was measured with a chromel-alumel thermocouple mounted in a hole in the side of the crystal. The sample was mounted on an *XYZ*-rotary manipulator with facilities for liquid nitrogen cooling and resistive heating.

Gases and condensible vapors were dosed through a stainless steel gas handling system with facilities for five noncondensible gases and two condensible vapors. The doser, shown in fig. 2, consisted of two independent gas lines ending in glass microcapillary arrays, a shutter capable of blocking the line of sight between either one or both doser lines and the sample, an electric heater for outgassing the doser, and a thermocouple (not shown). It was mounted on a linear transfer mechanism to bring it to within 2 mm of the sample for dosing. Gas flow in the doser was controlled by either a variable leak valve for noncondensibles or a 0.1 mm diameter stainless steel construction for condensibles.

Thorough passivation of the doser was required to prevent reaction of  $HNO_3$  with the doser walls. This was accomplished by operating the doser in a pseudo-differentially pumped manner. That is,  $HNO_3$  was allowed to flow



Fig. 2. Schematic of doser used for dosing noncondensible gases and acid vapors.

through the doser with the shutter in front of the outlet for at least 15 min before adsorption. The background pressure was  $3 \times 10^{-10}$  Torr while HNO<sub>3</sub> was flowing through the doser. Exposures could then be accurately controlled by opening and closing the shutter.

The Ag(110) sample at 80 K was exposed to gaseous mixtures of HNO<sub>3</sub> and  $H_2O$  via the condensible (vapor) doser. Two different mixtures of HNO<sub>3</sub> and  $H_2O$  were used in this work. One was simply the vapor above the azeotropic mixture (68 wt% HNO<sub>3</sub>). The other came from a more concentrated mixture prepared by adding  $H_2SO_4$  (which binds  $H_2O$  in the liquid phase) to the 68 wt% HNO<sub>3</sub> in a 3:2 ratio by volume [28]. Since the flow conditions in the doser correspond to Knudsen diffusion, the dosing mixture which actually impinges on the sample surface is more dilute in HNO<sub>3</sub>. The actual compositions of the doser mixtures were found to be 15 mol% HNO<sub>3</sub> for the vapor above the azeotrope and 85 mol% HNO<sub>3</sub> for the concentrated vapor (see appendix).

Thermal desorption spectra were measured with a Balzers QMG-112 quadrupole mass spectrometer with a 90° off-axis detector. The ionization energy was approximately 93 eV and the ionizer was located about 12 cm away from, and in line of sight with, the sample. The heating rate for TDS was 7 K s<sup>-1</sup> and was constant over the range 100-800 K. Data were recorded either in an analog fashion with an X-Y recorder or digitally with a personal computer running software capable of recording up to 100 masses in a single run [29].

Coverages were determined by TDS and are expressed in units of monolayers where 1 ML is defined as the number of topmost metal atoms for this surface ( $8.45 \times 10^{14}$  cm<sup>-2</sup>). The total coverage  $\theta_T$  is the sum of the HNO<sub>3</sub> and H<sub>2</sub>O coverages

$$\theta_{\rm T} = \theta({\rm HNO}_3) + \theta({\rm H}_2{\rm O}). \tag{1}$$

Measurement of  $\theta(\text{HNO}_3)$  and acid concentrations is discussed in the appendix, while  $\theta(\text{H}_2\text{O})$  was determined as follows. The mass spectrometer signal was first calibrated for O<sub>2</sub> (m/e = 32) by correlating the known LEED patterns [30] for atomic oxygen [ $p(n \times 1)$ , n = 2-9] at coverages  $\theta(\text{O}) = 1/n$ with the O<sub>2</sub> TDS area at 580 K. We observed LEED patterns for n = 2-8providing an oxygen calibration accurate to  $\pm 8\%$ . The H<sub>2</sub>O and O<sub>2</sub> calibrations are related through the stoichiometry of the reaction (all species are adsorbed unless otherwise indicated)

$$OH + OH \rightarrow H_2 O_{gas} + O, \tag{2}$$

which occurs at 300 K on Ag(110). The details of this calibration method have been discussed previously [27].

The LEED and ESDIAD optics used in these experiments were identical to those described by Madey and Yates [31] and consisted of two hemispherical grids, one flat grid, two microchannel plates, and a phosphor fluorescent screen. The typical electron current to the sample was 10-20 nA. For temperature dependent measurements the sample was annealed to the desired temperature and allowed to cool to about 100 K before the pattern was photographed.

## 3. Results

### 3.1. Mass spectrometer cracking pattern for HNO<sub>3</sub>

The mass spectrometer cracking pattern for 85 mol% HNO<sub>3</sub> is given in table 1. To our knowledge there are no similar data in the literature with which

Table 1 Mass spectrometer signals for 85 mol% HNO<sub>3</sub>

m/e	Ion	Relative intensities		
		HNO <sub>3</sub> from doser	HNO <sub>3</sub> /Ag(110) <sup>a)</sup>	
14	N <sup>+</sup>	16	12	
15		5	6	
16	$O^+$	29	24	
17	$OH^+$	19	29	
18	$H_2O^+$	6	16	
28	-	2	3	
30	NO <sup>+</sup>	100	100	
31	HNO <sup>+</sup>	0	19	
46	$NO_2^+$	60	85	
47	$HNO_{2}^{+}$	0	15	
63	$HNO_{3}^{+}$	1	1	

<sup>a)</sup> HNO<sub>3</sub> desorbing from multilayers of 85% HNO<sub>3</sub> on Ag(110) at 150 K.

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to compare these results. The data are normalized with the most intense signal (m/e = 30) assigned the value of 100. The three peaks for m/e = 30, 46, and 63 in a 100:60:1 ratio characterize the nitric acid. Note that no signal was detected for m/e = 31, 47, 62 (NO<sub>3</sub>), 81 (HNO<sub>3</sub> · H<sub>2</sub>O), or 99 (HNO<sub>3</sub> · 2H<sub>2</sub>O) indicating the absence of gaseous nitric acid hydrates and possible products of reaction between HNO<sub>3</sub> and the doser walls. Also, no signals were detected which could be ascribed to N<sub>2</sub>, N<sub>2</sub>O, N<sub>2</sub>O<sub>4</sub>, or N<sub>2</sub>O<sub>5</sub> in any of the work reported here.

### 3.2. Nitric acid adsorption on Ag(110)

The mass spectrometer signal for multilayers of 85% HNO<sub>3</sub> desorbing from Ag(110) at 150 K is also listed in table 1. There is good agreement between adsorbed and gaseous HNO<sub>3</sub> with the exception of increased signals for masses 31, 46, and 47. This indicates that some HNO<sub>2</sub> was formed, though the presence of extra NO<sub>2</sub> and HNO cannot be confirmed since the cracking pattern for HNO<sub>3</sub> is unknown.

Thermal desorption spectra showing the major products for 85% and 15%  $HNO_3$  are shown in fig. 3. Multilayer  $HNO_3$  desorption occurred at 150 K for 85%  $HNO_3$  and 165 K for 15%  $HNO_3$  as seen in the curves for masses 30, 46, and 63. Small  $HNO_3$  desorption features were also observed at 185 and 207 K for both mixtures. Some additional NO desorbed in low temperature peaks at 120 and 150 K for the 15% mixture. The  $H_2O$  desorption spectra are discussed in section 3.4.

Above room temperature desorption occurred only at 505 K for NO (m/e = 30) and NO<sub>2</sub> (m/e = 46) and 580 K for O<sub>2</sub> (m/e = 32). The NO<sub>2</sub> peak was similar in shape and peak position to the NO peak, but a factor of ten smaller. As discussed in the appendix a significant portion of the 505 K peak for mass 30 is due to NO<sub>2</sub>. Oxygen desorption occurred at the normal temperature for recombinative desorption of atomic oxygen [30]. After heating beyond 600 K, the Ag(110) surface was clean and well ordered as shown by a sharp  $p(1 \times 1)$  LEED pattern.

Thermal desorption spectra for HNO<sub>3</sub> (m/e = 63) as a function of coverage of the 85% mixture are shown in fig. 4. No desorption of the parent molecule was detected for total coverages  $\theta_T = 0.16$  ML or less. For  $\theta_T = 0.32$  ML, HNO<sub>3</sub> desorbed at 141 and 185 K, with the latter already saturated. A new peak at 150 K was seen for  $\theta_T = 0.65$  ML which grew with increasing HNO<sub>3</sub> coverage to become the dominant peak at 0.97 ML and higher total coverages.

The coverage dependences for masses 30 and 32 for both acid mixtures are shown in fig. 5. Small peaks for mass 30 were seen at 145 K and 170 for  $\theta_T = 0.16$  ML of 85% HNO<sub>3</sub>. These peaks can be attributed to a small amount of HNO<sub>3</sub> desorption; HNO<sub>3</sub> was not observed in fig. 4 for this coverage because of its weak signal form mass 63 (see table 1). The dominant signal for mass 30 for this low coverage occurred at 505 K showing that at low coverages most, if not all, adsorbed HNO<sub>3</sub> decomposes through a high temperature pathway yielding the high temperature NO, NO<sub>2</sub>, and O<sub>2</sub> peaks. This is borne out by the curve for  $\theta_T = 0.86$  ML for 15% HNO<sub>3</sub> [ $\theta$ (HNO<sub>3</sub>)  $\approx 0.13$  ML] in which almost no signal for m/e = 30 occurred at low temperature combined with an appreciable amount of NO at 505 K.

The high temperature NO and O<sub>2</sub> peaks grew together with increasing coverage and saturated at a total coverage of about 0.7 ML as shown in fig. 5a. Though not shown, the NO<sub>2</sub> desorption peak at 505 K also grew with the NO peak, but was always a factor of ten less. Both the NO and NO<sub>2</sub> peaks at 505 K grew to saturation without changing temperature indicating first-order desorption behavior. Essentially the same results were obtained for 15% HNO<sub>3</sub> with saturation occurring at  $\theta_T \approx 2.6$  ML (fig. 5b).

The mass 30 signal at low temperature and high coverage of 85% HNO<sub>3</sub> can be attributed entirely to the cracking fragment of desorbing HNO<sub>3</sub> (compare



Fig. 3. Survey of thermal desorption spectra following adsorption of 2 ML of 85% HNO<sub>3</sub> (a) and 4.3 ML of 15% HNO<sub>3</sub> (b) on Ag(110) at 80 K.



Fig. 3. Continued.

fig. 4). Clearly evident is the appearance of the 150 K peak at  $\theta_T = 0.73$  ML which at higher coverages eventually obscures the lower temperature peak. The 150 K peak ultimately shifted to 165 K at  $\theta_T = 6$  ML and is identified as multilayer HNO<sub>3</sub> desorption since it did not saturate.

The low temperature behavior of mass 30 was more complex for 15% HNO<sub>3</sub>. Initially a peak appeared at 135 K and split into two peaks at 125 and 145 K for  $\theta_T = 3.4$  ML. These features cannot be assigned to desorbing HNO<sub>3</sub> and therefore represent desorbing NO. The NO may have been present initially as a contaminant produced by reaction with the doser walls. Nonetheless, the features at 160 and 185 K and the higher temperature shoulder at about 210 K can all be attributed to desorbing HNO<sub>3</sub>. As the coverage was increased still further, the peak at 160 K continued to grow, but a new peak at 180 K appeared at  $\theta_T = 6.0$  ML. The 180 K peak was the only one not to saturate so it can be identified as multilayer desorption.



Fig. 4. HNO<sub>3</sub> desorption as a function of initial total coverage of 85% HNO<sub>3</sub> adsorbed on Ag(110) at 80 K.

# 3.3. Identification of adsorbed NO<sub>3</sub>

Fig. 6 shows the integrated TDS signals for the high temperature NO and  $O_2$  peaks for both acid mixtures as a function of coverage. The graphs show raw data in the form of TDS area (in units of Coulombs measured at the electron multiplier output) versus exposure time. A single curve is drawn through both the NO and  $O_2$  points as a guide to the eye. Both curves show a nearly linear increase in area with increasing exposure and turn over monotonically to a saturation value at about 2 min for 85% HNO<sub>3</sub> and about 4 min for 15% HNO<sub>3</sub>.

At saturation the respective amounts of desorbing  $O_2$ , NO, and NO<sub>2</sub> were determined to be 0.26, 0.14, and 0.23 ML (see appendix). Thus, there was almost twice as much NO<sub>2</sub> than NO. An atom balance over all species desorbing at high temperature yields a ratio of N:O of  $1:3.0\pm0.7$  where almost all of the error comes from the mass spectrometer sensitivities and cracking fractions, each assumed to be  $\pm 10\%$ . Thus, the stoichiometry of the

adsorbate present between 220 and 450 K is  $NO_3$  and all other  $NO_x$  species can be ruled out except  $N_2O_5$ , which is unlikely in any event.

TDS measurements in which  $H_2O$  was used as a chemical probe for adsorbed atomic oxygen further examine the chemical structure of the adsorbate. The experiment is outlined in fig. 7. Curve a shows  $H_2O$  and O desorption following coadsorption of just  $H_2O$  and O on Ag(110) at low temperature. The peaks labeled  $\beta$ ,  $\gamma$ , and  $\delta$  are due to interactions or reactions of  $H_2O$  with atomic oxygen [27,32]. In particular, the  $\delta$  peak results from reaction (2). Thus, the  $\delta$  TDS state is an indicator of atomic oxygen on Ag(110); atomic oxygen reacts with  $H_2O$  to form OH which in turn disproportionates to yield the  $\delta$  state.

When 85% HNO<sub>3</sub> was adsorbed at 100 K and heated to 300 K (fig. 7b),  $H_2O$  desorption occurred in a single peak at 180 K. The absence of both the  $\gamma$ 



Fig. 5. NO desorption as a function of initial total coverage of 85% HNO<sub>3</sub> (a) and 15% HNO<sub>3</sub> (b) adsorbed on Ag(110) at 80 K. The high temperature O<sub>2</sub> desorption behavior is also shown for 85% HNO<sub>3</sub> (a).



and  $\delta$  states confirms that no atomic oxygen formed by the reaction NO<sub>3</sub>  $\rightarrow$  NO<sub>3-x</sub> + x O

was present to temperatures as high as 185 K. That is, no decomposition of the NO<sub>3</sub> moiety occurred. The sample was allowed to cool to 100 K and more H<sub>2</sub>O was readsorbed. The resulting TDS (curve c) shows H<sub>2</sub>O desorbing at 150 K, due to H<sub>2</sub>O on the clean surface, and at 180 K. Again, no NO<sub>3</sub> decomposition occurred up to 300 K. This experiment was repeated for successively higher annealing temperatures and it was found that annealing temperatures between 450 and 465 K were required for the  $\delta$  state to be observed (curve d). At this temperature some NO and NO<sub>2</sub> desorption already occurs. The shift in peak temperature of the  $\delta$  state in fig. 7d is consistent with changes in the peak temperature which occur with coverage [27]. The conclusion is that adsorbed atomic oxygen, produced by reaction (3), does not appear until the HNO<sub>3</sub> covered surface is heated to at least 450 K and is strong evidence that the adsorbate is, in fact, NO<sub>3</sub>.

(3)



Fig. 6. Growth of the 505 K NO and the 580 K O<sub>2</sub> TDS peaks as a function of exposure for 85% HNO<sub>3</sub> (a) and 15% HNO<sub>3</sub> (b) on Ag(110). The raw data are in the form of TDS area versus exposure time. The error bars apply to TDS area. These curves also show the coverage of surface nitrate (NO<sub>3</sub>) as a function of total coverage (see appendix for further details).

Additional evidence for the stability of NO<sub>3</sub> to 450 K was obtained by coadsorbing HNO<sub>3</sub> and isotopic oxygen (<sup>18</sup>O). None of the label appeared in the NO or NO<sub>2</sub> desorption at 505 K indicating that atomic oxygen cannot exchange or react with the nitrogen containing intermediate. This intermediate cannot be a mixture NO or NO<sub>2</sub> since both desorb below room temperature [20].

Both the chemical probe and isotope exchange experiments show independently that subsequent to  $HNO_3$  adsorption and heating to at least 220 K, all nitrogen and oxygen atoms are bound in a molecular adsorbate of stoichiome-



Fig. 7. Use of  $H_2O$  adsorption as a chemical probe for atomic oxygen on Ag(110). (a)  $H_2O$  and  $O_2$  desorption following coadsorption of  $H_2O$  with atomic oxygen on Ag(110) at 100 K. (b)  $H_2O$  desorption following adsorption of 0.08 ML of 85% HNO<sub>3</sub> at 100 K. The sample was heated only to 300 K during the TDS measurement and allowed to cool to 100 K.  $H_2O$  was then readsorbed and the subsequent thermal desorption spectrum is shown in (c). (d)  $H_2O$  desorption after heating the sample with 0.25 ML of 85% HNO<sub>3</sub> to 465 K, cooling to 100 K, and readsorbing  $H_2O$ . The  $\beta$ ,  $\gamma$ , and  $\delta$  peaks indicate that atomic oxygen was formed during the anneal to 465 K.

try NO<sub>3</sub>. The saturation NO<sub>3</sub> coverage is  $0.4 \pm 0.1$  ML (see appendix) and the adsorbate is stable up to 450 K as shown by (1) the chemical probe experiment and (2) the c(2 × 2) LEED pattern observed at 220–450 K (see section 3.5). This finding is consistent with Outka et al. [20], who showed NO<sub>3</sub> to be stable to at least 385 K.

#### 3.4. $H_2O$ desorption and interaction with $NO_3$

The coverage dependence for  $H_2O$  desorption for both acid mixtures is shown in fig. 8. Here the two different compositions produce very different spectra. For the concentrated mixture (fig. 8a)  $H_2O$  desorbed initially in a peak at 190 K for  $\theta_T = 0.16$  ML. At higher coverages, the primary desorption peak was at 185 K with a shoulder at 190-220 K. Both of these features continued to grow up to  $\theta_T = 3$  ML. A lower temperature peak at 145 K



Fig. 8.  $H_2O$  desorption as a function of initial total coverage of 85% HNO<sub>3</sub> (a) and 15% HNO<sub>3</sub> (b) on Ag(110) at 80 K.

appeared at  $\theta_T = 0.65$  ML which shifted to higher temperature and grew without bound with increasing coverage. The 145–150 K peak therefore represents H<sub>2</sub>O desorption from multilayers of the acid mixture.

The 190 K peak can be attributed to  $H_2O$  interacting with adsorbed NO<sub>3</sub> as this was the only feature present at coverages sufficiently low for all HNO<sub>3</sub> to adsorb irreversibly. The 185 K peak and the high temperature shoulder represent water interacting with HNO<sub>3</sub> adsorbed either directly on the surface or within the first few layers. The appearance of these features corresponds to those at 185 and 210 K for HNO<sub>3</sub> (figs. 4 and 5a). Similarly, the 150 K peak appeared at about the same coverage as the 150 K peak for HNO<sub>3</sub>.

The higher water content of 15% HNO<sub>3</sub> enables more details of the  $H_2O-NO_3$  interaction to be learned (fig. 8b). The curves for the two lowest coverages correspond to an exposure regime in which all HNO<sub>3</sub> adsorbs irreversibly to form NO<sub>3</sub> (see fig. 6b). Water interacting directly with NO<sub>3</sub> desorbed at 182 and 190 K for  $\theta_T = 0.86$  and 1.7 ML, respectively. These



Fig. 9. Total amount of  $H_2O$  adsorbed as a function of exposure of 85% HNO<sub>3</sub> and 15% HNO<sub>3</sub>. The  $H_2O$  coverage was determined from the total TDS peak area calibrated for  $H_2O$ . Both curves are plotted for a common abscissa of exposure time. Conversion of exposure time to total coverage is discussed in the appendix.

peaks were already saturated since additional water desorption occurred at about 150 K. The ratio of  $H_2O: NO_3$  (i.e., the hydration number for  $NO_3$ ) was constant at approximately 3:1 as determined by the area under the 182–190 K  $H_2O$  peaks and fig. 6b.

The complex hydration chemistry of HNO<sub>3</sub> [28] is apparently manifested by the complex H<sub>2</sub>O TDS behavior for higher coverages of 15% HNO<sub>3</sub>. Desorption peaks at 160 and 185 K for  $\theta_T = 2.6$  ML can be related to the HNO<sub>3</sub> peaks at similar temperature and coverage. With increasing coverage the dominant desorption peak changes from 167 K at 5.2 ML, to 163 K at 6.9 ML, to 180 K at 7.7 ML. The 167 K peak actually diminished in intensity with increasing coverage and was completely absent at 13 ML (not shown). The 163 K peak saturated at 85 ML, while the 180 K peak was the only one not to saturate.

Fig. 9 shows the total amount of desorbing water as a function of total coverage for both acid mixtures. A straight line was found for 15% HNO<sub>3</sub>, whereas the data for 85% HNO<sub>3</sub> showed some curvature at low exposures. The latter indicates that some excess water was formed by a surface reaction as discussed in section 4.1.

# 3.5. LEED and ESDIAD results

Adsorption of either acid mixture at 80-100 K was apparently random since no LEED or ESDIAD patterns indicative of preferential order were observed. The LEED pattern was either  $p(1 \times 1)$  with a high background or just a high background when many multilayers were adsorbed. The ESDIAD signal was a broad, intense central spot of ions emitted with random trajectories.

Fig. 10 shows LEED patterns obtained for adsorption of 85% HNO<sub>3</sub> at 80 K and annealing to the indicated temperatures. The surface nitrate coverage was at or near saturation. A  $p(3 \times 2)$  pattern evolved after annealing to 180 K to desorb excess HNO<sub>3</sub> and H<sub>2</sub>O (fig. 10b). This pattern corresponds to about 0.2 ML H<sub>2</sub>O for a ratio of H<sub>2</sub>O: HNO<sub>3</sub> of roughly 1:2. The missing



Fig. 10. LEED patterns for HNO<sub>3</sub> adsorbed on Ag(110) for an incident beam energy of 110 eV.
(a) Clean surface; p(1×1). (b) Adsorption of 1 ML of 85% HNO<sub>3</sub> at 80 K and annealed to 180 K; p(3×2). (c) Same sample as (b) but further annealed to 200 K; split c(2×2). (d) Adsorption of 0.7 ML of 85% HNO<sub>3</sub> at 80 K and annealed to 225 K; c(2×2).

[(1/2)n, m] (n, m = integers) spots indicate a glide plane symmetry in the [001] direction since the incident electron beam was off-normal and the scattering plane was along the [001] direction [33]. In the absence of other information (primarily vibrational spectra), a unique real space interpretation cannot be determined.

Upon further heating to 200 K a  $c(2 \times 2)$  pattern with all spots split along the [110] direction was observed (fig. 10c). This was often observed for saturation NO<sub>3</sub> coverages, though occasionally a normal  $c(2 \times 2)$  was detected as shown in fig. 10d. The ESDIAD signal decreased dramatically once the multilayers were desorbed and was essentially too weak to photograph. The  $c(2 \times 2)$  pattern (split or normal) remained as the temperature was increased to approximately 450 K coinciding with the onset of NO<sub>3</sub> decomposition and subsequent NO and NO<sub>2</sub> desorption. The  $p(n \times 1)$  patterns characteristic of atomic oxygen appeared upon annealing to 500 K and remained with increasing temperature until all oxygen had desorbed. After removal of the O<sub>2</sub> TDS state at 580 K, a sharp  $p(1 \times 1)$  pattern was again observed.

## 4. Discussion

### 4.1. Adsorption and reaction of HNO<sub>3</sub>

Nitric acid adsorption at low temperature followed by heating to 200 K is a direct route to surface nitrate on Ag(110). One question which arises concerns the fate of H in HNO<sub>3</sub>. We detected H<sub>2</sub> desorption for both 85% and 15% HNO<sub>3</sub> which was similar in peak position and shape to the H<sub>2</sub>O desorption shown in fig. 8. Follow-up experiments showed, however, that 75%-100% of that signal was due to H<sub>2</sub> being displaced from the chamber walls by H<sub>2</sub>O and/or HNO<sub>3</sub> desorbing from the sample. This unfortunate anomaly is apparently a result of prolonged HNO<sub>3</sub> dosing. Our experiments did show conclusively that all hydrogen containing species desorbed from the surface below 200 K.

There was no evidence for surface damage following  $HNO_3$  adsorption. LEED patterns indicative of well defined surface periodicity were observed at 180 K with  $HNO_3$  present and after desorption of all adsorbed species at temperatures in excess of 600 K.

A small amount of HNO<sub>3</sub> was reduced to HNO<sub>2</sub> by the Ag(110) surface as seen by both HNO<sub>2</sub> (table 1) and excess H<sub>2</sub>O desorption (fig. 9 - 85% HNO<sub>3</sub>). In general, reactions of nitric acid with metals can take the form

$$2 M + n NO_3^{-} + 3n H^+ \rightarrow 2 M^{n+} + n HNO_2 + n H_2O, \qquad (4)$$

where M is the metal and n its valency [28]. For the case of silver (n = 1) we can write

$$2 * + 3 HNO_3 \rightarrow 2 * NO_3 + HNO_2 + H_2O_3$$
 (5)

where two NO<sub>3</sub> species have been added to each side of eq. (4) and \* represents an adsorption site. Comparison of these two reactions implies that HNO<sub>3</sub> reduction may be mediated by adsorbed ions (H<sup>+</sup> and NO<sub>3</sub><sup>-</sup>), though further studies are needed to verify this point. We expect that HNO<sub>3</sub> would dissociate to H<sup>+</sup> and NO<sub>3</sub><sup>-</sup> similar to HF which forms H<sup>+</sup> and F<sup>-</sup> when coadsorbed with H<sub>2</sub>O on Pt(111) [9].

The close relationship between HNO<sub>3</sub> and H<sub>2</sub>O desorption shown in figs. 3, 4, and 8 is evidence that the two species from one hydrogen bonded network on the surface and desorption occurs as the network is thermally disrupted. This is not unexpected since nitric acid forms at least six hydrates in solution: HNO<sub>3</sub>  $\cdot$  (H<sub>2</sub>O)<sub>n</sub> (n = 1/2, 1, 3/2, 3, 6, and 15) [28].

## 4.2. Adsorption and decomposition of $NO_3$ on Ag(110)

Understanding the chemisorption of NO<sub>3</sub> is the first step in relating chemisorption with electrosorption. The TDS and LEED results show that the saturation coverage of NO<sub>3</sub> is  $0.4 \pm 0.1$  ML and adsorption occurs in a  $c(2 \times 2)$  or split  $c(2 \times 2)$  structure. Both of these findings are consistent with the existence of some degree of lateral repulsive interactions in the NO<sub>3</sub> adlayer as would be expected if it were ionic. For example, strong lateral repulsive interactions have been observed for the ionic form of adsorbed Cs on Ag(110) [5]. A  $c(2 \times 2)$  LEED pattern for a total coverage less than 0.5 L can occur for repulsive interactions. Binder and Landau [34,35] have shown that an adsorbate with repulsive nearest neighbor interactions can form a  $c(2 \times 2)$ structure for coverages as low as 0.35 ML – well within the error limits of this measurement.

We attribute the splitting in the  $c(2 \times 2)$  structure to antiphase domains of NO<sub>3</sub>. The splitting is in the [110] direction indicating that the mismatch is also in this direction (along the rows). That all spots are split is evidence that the lattice vector between domains is not integrally related to the substrate [36]. The only way this can occur is if adsorption occurs on different sites, namely, one phase could be adsorbed in atop sites with another being in bridge sites. Thus, there are at least two adsorption sites for NO<sub>3</sub> on Ag(110) with similar binding energies, though they cannot yet be identified.

The decomposition kinetics for NO<sub>3</sub> were determined by analysis of the 505 K TDS peak for m/e = 30. The reaction peak is well modeled by the equation  $r = A \exp(-E_a/RT) \sigma(NO_3)$ , (6)

where r is the reaction rate,  $A = 10^{15.4 \pm 0.4} \text{ s}^{-1}$ ,  $E_a = 151 \pm 4 \text{ kJ mol}^{-1}$ , and  $\sigma(\text{NO}_3)$  is the absolute coverage of NO<sub>3</sub> in units consistent with r. The reaction is first order in  $\sigma$  (NO<sub>3</sub>) as determined by plots of ln r versus ln  $\sigma(\text{NO}_3)$  at constant temperature; the slope was unity to within 10% for three different temperatures. The apparent activation energy  $E_a$  was calcu-

lated by an isosteric analysis in which  $\ln r$  was plotted versus 1/T at constant coverage [37]. The reported value is based on 18 TDS curves analyzed at 5 different coverages. The pre-exponential factor A was then determined by setting  $r_p$ , the calculated reaction rate at the peak temperature and coverage  $(T_p \text{ and } \sigma_p)$ , equal to the measured rate. A final check was made by calculating the entire TDS peak from eq. (6); the model peak was in very good agreement with the measured peak.

The mechanism proposed for  $NO_3$  decomposition is reaction (7) combined with either one of (8) or (9),

$$NO_3 \rightarrow NO_2 + O \rightarrow NO_{2(gas)} + O, \tag{7}$$

$$NO_2 \rightarrow NO + O \rightarrow NO_{(gas)} + O,$$
 (8)

$$NO_3 \rightarrow NO + 2 O \rightarrow NO_{(gas)} + 2 O,$$
 (9)

with (7) rate limiting at all coverages. Our reasons for this are (1) the reaction is first order in NO<sub>3</sub> coverage and well modeled with kinetic parameters reasonable for surface reactions and (2) coadsorption of  $N(^{16}O)_3$  with <sup>18</sup>O showed none of the label appearing in either the NO or NO<sub>2</sub> peaks at 505 K. A mechanism in which NO<sub>3</sub> decomposes to its atomic constituents and recombines to form NO and NO<sub>2</sub> can be ruled out since it would violate the law of microscopic reversibility. Furthermore, if decomposition did go straight to atoms, then some N<sub>2</sub> should desorb at 505 K in contradiction to our findings.

Since NO<sub>2</sub> is the predominant decomposition product, NO production by either (8) or (9) occurs only slightly slower than (7). If either rate were very different than (7), then the peak shapes for masses 30 and 46 would be considerably different and the former could not be modeled with an expression as simple as (6) since it is composed of both NO and NO<sub>2</sub>.

The value of  $E_a$  reported here is in good agreement with an earlier estimate of 163 kJ mol<sup>-1</sup> for NO<sub>3</sub> decomposition on Ag(110) [20]. Observation of the decomposition products NO<sub>2</sub> and NO is expected since these are produced by nitric acid treatment of metals with positive reduction potentials [38]. Thermal decomposition of bulk AgNO<sub>3</sub> has also been studied [39]. There is little agreement regarding the stability of AgNO<sub>3</sub> with reported decomposition temperatures ranging from 480 to 800 K. Decomposition of NO<sub>3</sub> on Ag(110) is more in line with the lower temperature. For decomposition at 800 K an apparent activation energy was reported to be  $59 \pm 8$  kJ mol<sup>-1</sup> [40] – much lower than our result.

Our findings for surface nitrate are generally consistent with those of Outka et al. [20], in which NO<sub>3</sub> was formed from coadsorbed NO<sub>2</sub> and O on Ag(110). On the basis of high resolution electron energy loss spectroscopy (HREELS), they proposed that NO<sub>3</sub> is bound with only one oxygen atom in direct contact with the surface. Comparison of our work with their shows, however, that the

 $NO_3$  species may not be the same for the two situations. In the former study nitrate decomposition was identified by an NO desorption peak at 530 K in reasonable agreement with ours at 505 K. They attributed this peak to atomic recombination of N and O in contrast to the direct  $NO_3$  decomposition mechanism in steps (7)–(9). They also measured a broad NO desorption feature extending from 300 to 500 K and exceeding the 530 K NO peak in intensity, and  $NO_3$  decomposition occurred without production of  $NO_2$ .

We do not believe their results to be in error since we could reproduce them by either (1) adsorbing NO<sub>2</sub> directly or (2) dosing HNO<sub>3</sub> from an unpassivated doser. The latter apparently yields NO<sub>2</sub> by reaction of HNO<sub>3</sub> with the doser walls. The most likely explanation at this point is that NO<sub>3</sub> produced directly from HNO<sub>3</sub> is somehow different than NO<sub>3</sub> from NO<sub>2</sub> and O. Clearly, more research is required to account for these differences.

### 4.3. Interactions among coadsorbed $NO_3$ and $H_2O$

The low coverage  $H_2O$  desorption spectra in figs. 7b, 7c and 8 show that  $H_2O$  is stabilized by NO<sub>3</sub>.  $H_2O$  directly associated with adsorbed NO<sub>3</sub> desorbed in a peak ranging from 180 to 190 K as opposed to 150 K for the clean surface. The NO<sub>3</sub>-induced stabilization is estimated to be 8 kJ mol<sup>-1</sup> according to this difference in desorption temperatures. The NO<sub>3</sub> hydration number of 3 implies that  $H_2O$  interacts directly with NO<sub>3</sub> in the form of a surface solvation reaction [3]

$$NO_3 + 3 H_2O \rightarrow NO_3 \cdot (H_2O)_3. \tag{10}$$

For comparison, a  $p(3 \times 2)$  LEED pattern was observed for Br hydration on Cu(110) and Ag(110) with the hydration number being 1 [3,6], whereas  $c(2 \times 2)$ ,  $p(4 \times 3)$ , and  $c(4 \times 4)$  patterns were observed for Cl hydration on Ag(110) with hydration numbers ranging from 1–10 [41]. The LEED patterns for hydrated halides illustrate the importance of substrate interactions in these systems. That no LEED pattern was detected for the NO<sub>3</sub> · (H<sub>2</sub>O)<sub>3</sub> phase shows that hydration is essentially a direct interaction between H<sub>2</sub>O and NO<sub>3</sub>, most probably hydrogen bonding.

## 5. Summary and conclusions

Nitric acid adsorption has been studied for the first time in UHV. The mass spectrometer cracking pattern for HNO<sub>3</sub> is here reported. Adsorption of HNO<sub>3</sub> on clean Ag(110) is a direct route to surface nitrate. The saturation coverage of NO<sub>3</sub> is  $0.4 \pm 0.1$  ML with adsorption occurring in a c(2 × 2) or split c(2 × 2) structure. Nitrate decomposition is first order and occurs at temperatures greater than 450 K to give gaseous NO<sub>2</sub> and NO in a ratio of roughly 2:1. Excess oxygen remains on the surface and desorbs as  $O_2$  above 550 K. Surface nitrate formed by reacting  $NO_2$  with O on Ag(110) is apparently different than  $NO_3$  produced directly by  $HNO_3$ ; the exact differences are a topic for further study.

Stabilization of adsorbed  $H_2O$  by  $NO_3$  is evidence for some form of attractive interaction between the two species. As many as three water molecules can interact with each  $NO_3$  species. The adsorption properties of  $NO_3$  are consistent with it possessing some degree of ionicity, though exactly how much remains to be shown.

The details of the  $HNO_3/H_2O$  adlayer were also investigated at low temperature. Multilayer adsorption leads to an extensive hydrogen bonded network over the surface in which a rich degree of hydration chemistry occurs.

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### Appendix. Measurement of coverages and dosing fluxes

In TDS the coverage of species i is given by

$$\boldsymbol{\theta}(\mathbf{i}) = s_{\mathbf{i}}^{n} / c_{\mathbf{i}}^{n}, \tag{11}$$

where  $s_i^n$  is the integrated TDS signal for m/e = n for species i (C) and  $c_i^n$  is the calibration for m/e = n for species i (C/ML). The calibration factor for  $O_2$  (m/e = 32) was  $8.2 \pm 0.7 \times 10^{-9}$  C/ML. At saturation the integrated  $O_2$ TDS area was  $2.3 \times 10^{-9}$  C (fig. 6a) so the maximum amount of  $O_2$  desorbing at 580 K was  $\theta(O_2)_{sat} = 0.26$  ML. The calibration factors for NO and NO<sub>2</sub> can be calculated from the O<sub>2</sub> factor according to

$$c_{\rm NO}^{30} = r_{\rm NO}^{30} c_{\rm O_2}^{32},\tag{12}$$

$$c_{\rm NO_2}^{46} = f_{\rm NO_2}^{30} r_{\rm NO_2}^{30} c_{\rm O_2}^{32},\tag{13}$$

where  $r_i^n$  is the relative sensitivity for m/e = n of species i relative to  $O_2$ ,  $r_{NO}^{30} = 1.47$ ,  $r_{NO_2}^{30} = 0.33$  [42,43], and  $f_{NO_2}^{30}$  is the ratio of masses 30/46 for

 $NO_2 = 2.70$  [43-45]. From (12) and (13) the calibration factor for NO is  $1.2 \times 10^{-8}$  C/ML and for NO<sub>2</sub> it is  $1.0 \times 10^{-9}$  C/ML. Fig. 6a and the 10:1 ratio of the 505 K TDS peaks for masses 30/46 are used to determine the saturation amount of NO<sub>2</sub>

$$s_{\rm NO_2}^{46} = s_{\rm T}^{30} / 10 = 2.3 \times 10^{-10} \, {\rm C},$$
 (14)

where the subscript T refers to the total TDS signal for m/e = 30. When this is substituted into eq. (11) with n = 46, we find  $\theta(NO_2)_{sat} = 0.23$  ML. To find the saturation amount of NO we note that

$$s_{\rm NO}^{30} = s_{\rm T}^{30} - s_{\rm NO_2}^{30} = s_{\rm T}^{30} \left( 1 - f_{\rm NO_2}^{30} / 10 \right) = 1.7 \times 10^{-9} \, \rm C, \tag{15}$$

where eq. (14) was used in deriving the last term. From eq. (11) with n = 30, we find that  $\theta(NO)_{sat} = 0.14$  ML.

Since all desorbing NO and NO<sub>2</sub> come from adsorbed NO<sub>3</sub>, the saturation coverage of NO<sub>3</sub> is 0.14 + 0.23 = 0.37 ML as given by an N atom balance. This is but a rough estimate; the error limits are  $\pm 0.1$  ML. The NO<sub>3</sub> saturation coverage value sets the left ordinates in figs. 6a and 6b and, from the initial slopes of these curves, we determine the HNO<sub>3</sub> arrival rates to be 0.41 and 0.13 ML/min for the 85% and 15% mixtures, respectively.

The arrival rate for  $H_2O$  is found from the slopes of the linear portions of the curves in fig. 9. For the 85% and 15% mixtures the rates were 0.13 and 0.74 ML/min, respectively. The total dosing fluxes are just the sum of the individual components, eq. (1). These values are 0.49 and 0.74 ML/min for the 85% and 15% mixtures and were used to set the lower abscissas in fig. 6 and both abscissas in fig. 9. The acid concentration is simply the ratio of acid arrival rate to the total dosing flux. This yields 85% and 15% HNO<sub>3</sub> when rounded to the nearest 5%.

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