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In Situ Ambient Pressure Studies of the Chemistry of NO₂ and Water on Rutile TiO₂(110)

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The adsorption of NO₂ on the rutile TiO₂(110) surface has been studied at room temperature in the pressure range from $\sim 10^{-8}$ torr to 200 mtorr using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). Atomic nitrogen, chemisorbed NO₂, and NO₃ were formed, each of which saturates at pressures below $\sim 10^{-6}$ torr NO₂. Atomic nitrogen originates from decomposition of the NO_x species. For pressures of up to 10^{-3} torr, no significant change in the NO_x surface species occurred, suggesting that environmentally relevant conditions with typical NO₂ partial pressures in the 1–100 ppb range can be modeled by ultrahigh vacuum (UHV) studies. The chemisorbed surface species can be removed by *in situ* annealing in UHV: all of the NO_x species disappear around 400 K, whereas the N 1s signal associated with atomic nitrogen diminishes around 580 K. At higher pressures of NO₂ ($p(\text{NO}_2) \geq 10^{-6}$ torr), physisorbed NO₂ and adsorbed water, which was likely due to displacement from the chamber walls, appeared. The water coverage grew significantly above $\sim 10^{-3}$ torr. Concurrently with co-condensation of water and NO₂, the population of NO₃ species grew strongly. From this, we conclude that the presence of NO₂ and water leads to the formation of multilayers of nitric acid. In contrast, pure water exposure after saturation of the surface with 200 mtorr NO₂ did not lead to a growth of the NO₃ signals, implying that HNO₃ formation requires weakly adsorbed NO₂ species. These findings have important implications for environmental processes, since they confirm that oxides may facilitate nitric acid formation under ambient humidity conditions encountered in the atmosphere.

Introduction

Oxide surfaces represent a major fraction of the surfaces on earth in the form of soils and urban materials such as concrete, and they are present as aerosol particles in the atmosphere. They are believed to play an important role in the fate of environmental pollutants, such as toxic organics, sulfur oxides, and nitrogen oxides, which are mostly of anthropogenic origin.^{1–3} Such pollutants cause severe problems like smog and acid rain and are also a human health hazard.⁴

Heterogeneous reactions of NO_x ($x = 1, 2$) present in the atmosphere, which is mainly derived from combustion of fossil fuels,⁵ may play key roles in determining pollution levels in the atmosphere. Emissions of NO_x from car exhausts range from 0.015 to 0.8 g NO_x/km.⁶ For diesel engines operating under urban driving conditions, NO₂ accounts for 35–70% of total gas emissions. Therefore, the need arises for more efficient destruction of NO_x in exhaust gases (DeNO_x processes).¹ In order to reduce the adverse health effects of NO₂ in urban regions, the World Health Organization suggested that maximum concentrations should not exceed the Specific Guideline Value of 23 ppb (corresponding

to ca. 45 $\mu\text{g}/\text{m}^3$ or a partial pressure of ca. 10^{-5} torr)⁷ in the annual mean.

Under ambient conditions, NO₂ reacts with water to form HNO₃, through both gas-phase and surface-mediated processes. HNO₃ may then be deposited onto oxide particles.⁸ HNO₃ may also be formed *in situ* on tropospheric surfaces, for instance, via the heterogeneous hydrolysis of NO₂,^{8–12} and may be removed by dry or wet deposition¹³ or decomposition to nitrogen. Reactions on oxide surfaces, thus, may provide routes for NO₂ remediation and may play a role in the balance of NO_x in the atmosphere.

Several model studies of the reactions occurring on oxides under ambient conditions have been reported under low pressure (ultrahigh vacuum) conditions and conclude that HNO₃ and HONO form from the reaction of NO₂ with H₂O. On Gobi desert sand (primarily an aluminosilicate), the thermochemical reaction of monomeric NO₂ with hydroxyls and H adatoms formed from H₂O dissociation lead to HNO₃ and HONO formation, respectively.¹² The desorption of NO₂ after exposure of the sand to H₂O multilayer and monolayer doses indicated decomposition of HNO₃ at temperatures up to 500 K.¹² Also, photochemical

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HONO formation has recently been reported on rutile and anatase TiO₂ particles.¹⁴

In this work, we set out to probe the effects of pressure on the reactions of NO₂ on TiO₂(110). Nitrogen dioxide reacts under vacuum conditions to form a mixture of adsorbed NO₂, NO₃, and atomic nitrogen on metal oxides, such as MgO(100),^{15–17} ZnO(0001)/Zn,¹⁸ TiO₂(110),¹⁹ CeO₂,¹⁶ and Zn_xMg_{1–x}O(100),¹⁵ and on thin alumina films deposited on NiAl(100).^{20–22} The chemistry of NO₂ on metal oxide surfaces is relatively complex because of the fact that multiple species may form. Although the radical character of free NO₂ is located mainly on the nitrogen atom, the surface species identified bond to oxides primarily via the oxygen atoms. Further, density functional theory (DFT) calculations of various conceivable NO_x structures on TiO₂ suggest that chemisorbed NO₂ and NO₃ structures are not significantly charged.¹⁹ Even when bonding to Ti at oxygen vacancy sites, the charge density transfer to the NO_x species was found to be smaller than 0.5 e[–].

Herein, we bridge several decades of pressure (10^{–8} torr to 200 mtorr) to determine if there are significant changes in the intermediates formed on the TiO₂(110) surface at higher pressures, and to probe the effects of ambient water on the reactivity of NO₂ on a model oxide surface, since the possible effect of pressure has been suggested.¹ We make a direct comparison of previous ultrahigh vacuum (UHV) studies on vacuum-reduced rutile TiO₂(110)¹⁹ to higher pressure regimes on the same surface. We have chosen the rutile TiO₂(110) surface because it has been widely studied as a model system and because it becomes conducting after vacuum reduction and, therefore, amenable to investigation with the tools of surface science. The vacuum reduction leads to oxygen vacancies, which can also be created by Ar⁺ sputtering or by e[–] bombardment.^{23,24}

By using ambient pressure X-ray photoelectron spectroscopy (AP-XPS),²⁵ we show that NO₂ exposure at room temperature leads to saturation of the TiO₂ with chemisorbed NO₃, NO₂, and atomic nitrogen. Annealing an NO₂ saturated surface subsequently leads to decomposition of all NO_x species and disappearance of atomic N. At NO₂ pressures above ~10^{–5} torr, water is displaced from the chamber walls and accumulates on the TiO₂. Concurrently, features attributed to HNO₃ accumulation on the surface grow. In contrast to the coadsorption, exposing a surface saturated with strongly bound NO_x species to increasing pressures of water only leads to buildup of the water signals. This is directly related to corresponding processes under environmentally relevant conditions.^{8–11}

Experimental Methods

All X-ray photoelectron experiments were performed at beamline 9.3.2 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory.²⁶ The endstation (base pressure initially ~5 × 10^{–9} torr, rising to ~4 × 10^{–8} torr after high-pressure NO₂ exposure) consists of a sample preparation chamber with a sputter gun and an analytical chamber, which is also equipped with a quadrupole mass spectrometer.

The sample was mounted via tantalum clips to a ceramic button heater. Type K thermocouple wires, glued into a small hole in the crystal (Ceramabond 503, Aremco Inc.), were used to measure temperature. A slightly reduced rutile (110) single crystal with a light blue tint was previously prepared by cycles of Ar⁺ sputtering (1.5 keV) and subsequent annealing to 900 K. The surface was cleaned *in situ* by repeated cycles of Ar⁺ sputtering (1.5 keV) followed by annealing to the technically achievable temperature of ~700 K in vacuum. Its cleanliness was monitored with survey scans (up to 800 eV) and C 1s spectra.

The spectra for the various regions (C 1s, N 1s, O 1s, and Ti 2p) were recorded using different photon energies such that these core level photoelectrons all had similar kinetic energies (KEs; 240 eV) and, thus, similar escape depths.²⁷ Our estimated probe depth was roughly four TiO₂ monolayers (ca. 11 Å) for all elements (except in the survey scans). This experimental configuration also minimized variation in the transmission of the electron optics, rendering quantitative analysis more reliable.

Peak areas were quantified so as to establish the relative O 1s to N 1s peak areas as a means of identifying specific species. Least square fits were performed for all spectra choosing appropriate parameters for the Voigt profiles and allowing the binding energy (BE) of identified species to shift within small intervals. The obtained ratios are in good agreement with the theoretical values derived from ionization cross sections calculated at the Hartree–Fock level.²⁸

To minimize the effects of attenuation by multilayers and physisorbed NO₂ at higher pressures, we analyzed the O 1s and N 1s peak areas of surface species relative to the O 1s bulk signal, which we assumed should remain constant. After correction for attenuation, the signal of bridging oxygen stayed roughly constant throughout our experiments. The coverages of N-species were estimated using the relative ionization cross sections of N and O.²⁸ Inelastic scattering backgrounds in the experimental data have been subtracted using Tougaard function baseline fits.^{29,30} All recorded spectra have been normalized to the beam current, and in order to correct for small work function changes of the analyzer and sample the energy scales have been referenced such that the bulk O 1s signal is detected at a BE of 530.5 eV (full width at half-maximum, FWHM ≈ 1.5 eV).³¹

A significant shoulder at ~1.1–1.6 eV higher BE (~531.8 eV) is attributed to surface bridging oxygen species^{32,33} which was characterized previously using angular resolved XPS.³⁴ The peak area is consistent with the value of ~10% (1/3 of the surface oxygens are 2 coordinated bridging oxygens, whereas the rest have 3 Ti neighbors as in the bulk) expected for our measurement geometry (using a monolayer thickness of 3.2 Å)²⁴ and kinetic energy. Although there is some discrepancy about this state as some groups did not resolve/observe it^{19,35} or assign it to other

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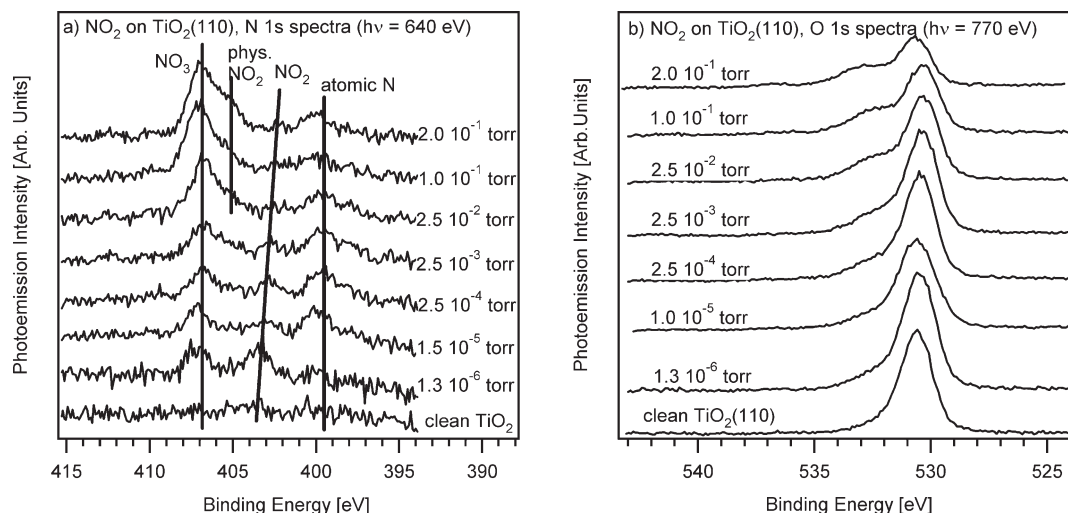


Figure 1. Ambient pressure X-ray photoelectron spectra of the N 1s and O 1s regions following exposure of vacuum-annealed TiO₂(110) to NO₂ at 300 K. All spectra are stacked from the bottom to the top in sequence of increasing pressures. The primary energies are indicated in the corresponding graphs.

species including acidic bridging hydroxyls,^{31,36} hydrocarbon contaminations,^{31,36} or oxygens adjacent to vacancies,^{23,31,36} we point out that even the maximum expectable concentration of bridging hydroxyls (i.e., roughly twice the concentration of surface oxygen vacancies, ca. 20%) would not account for the observed intensity. Since this signal remains unchanged during NO₂ or H₂O exposure, we cannot rule out a contribution by OH, but it does not appear to affect our reactivity.

The Ti 2p_{3/2} peak at 459.3 eV for Ti⁴⁺ on the clean surface had a constant spin–orbit splitting of 5.7 eV and fit to a 3/2 (FWHM ≈ 1.4 eV) and 1/2 (FWHM ≈ 2.2 eV) area ratio of ~0.27. At the beginning of each exposure experiment, a small low BE shoulder on the Ti⁴⁺ 2p_{3/2} peaks was visible at ~458.8 eV, which is usually assigned to Ti³⁺ species at oxygen vacancies and sputter defects. It typically amounted to ~10% but disappeared quickly upon NO₂ exposure. Such surface oxygen vacancies remain after “bulk-assisted” reoxidation of the sputtered surface at temperatures above 700 K, which leads to preferential diffusion of excess surface Ti into the bulk until the surface stoichiometry of Ti:O = 1:2 is almost restored.³⁷ In the temperature range between ~400 and ~700 K, the diffusion of point defects involves both Ti interstitials and oxygen vacancies and is much slower, which causes the surface reoxidation to remain incomplete.³⁷

The C 1s data showed only very weak traces of C contamination at ~289 eV that decreased over the course of the experiments.³¹ In the survey scans, we also observed a slight segregation of Ca, which is a typical impurity of TiO₂.³⁸ We used the intensity of this Ca peak and the theoretical ionization cross sections as functions of the KE to correct for the corresponding O 1s component at ~531.9 eV. Although very small at UHV conditions, the CaO amount grew to almost 6% of the bulk O 1s signal during high-pressure exposure. Since the KE of the electrons from this state in the surveys is much larger, the CaO detected is partially from subsurface layers (up to ~7 TiO₂ layers).

Only minimal radiation damage occurred in our experiments. At high pressures, we observed slight decreases of the O 1s and N 1s signals (<~5% over a period of 48 min) assigned to NO₂ and NO₃, which we attribute to radiation-induced processes, but were recovered once the sample position was changed. Once the gas background was pumped down to the low 10^{−8} torr range, however, the N 1s peak of atomic N was found to grow significantly (~35% increase) at the expense of the NO_x signals over

a period of up to 2 h. This did not occur if the sample was left to sit without beam exposure. Since this was primarily due to beam effects, the sample was displaced by small distances parallel to its surface during the experiments to avoid extensive beam damage.

Results and Discussion

Exposure of the TiO₂(110) Surface to Elevated NO₂ Pressures. Several different N-containing species are formed from the reaction of NO₂ on the freshly prepared, vacuum-annealed TiO₂-(110) surface at room temperature, in agreement with previous studies under UHV conditions (Figure 1). The N 1s binding energies are assigned to atomic nitrogen (399.5 eV), NO₂ (402.3–403.1 eV), and NO₃ (407.0 eV), consistent with previous literature values.¹⁹

Two pressure regimes are apparent in our experiments: a low NO₂ pressure regime below ~10^{−5} torr and a higher pressure regime, which is distinguished by the appearance of H₂O. At partial pressures in the range from ~10^{−8} to ~10^{−5} torr, peaks corresponding to atomic N, NO₃, and NO_x (assigned to chemisorbed NO₂) are observed and saturate quickly, indicating that there is no difference in chemical behavior in this pressure region, that is, no “pressure gap” over 5 orders of magnitude in pressure.

Chemisorbed NO₃ is identified by the N 1s and O 1s (Figure 1a and b, respectively) components at binding energies of 407.0 and 532.5 eV (O 1s/N 1s peak area ratio of 3:1; Figure 2 shows an example of fitted data), in agreement with prior work.¹⁹ Our assignment of the peaks at 403.1 and 533.0 eV to chemisorbed NO₂ is based on the binding energies and the O 1s/N 1s peak area of roughly 2:1.¹⁹ While the N 1s BE of the NO₃ species is constant with pressure, the N 1s peak of NO₂ shifts to lower binding energies. In the O 1s data, there is also a slight binding energy shift in the bulk oxygen peak due to a slight band bending caused by adsorption.³⁹ According to our quantitative analysis, both the strongly bound NO₃ and NO₂ species saturate at pressures of ~10^{−6} torr with coverages of ca. ~0.1–0.2 ± 0.1 monolayer (ML) each (Figure 3; Table 1). The peak at 399.5 eV (~399 eV¹⁹) is attributed to atomic nitrogen formed from NO₂ decomposition,¹⁹ which saturates at a coverage of ca. 0.2 ± 0.1 ML in the low-pressure regime.

Only at pressures above 10^{−3} torr are substantial changes observed, when the signals of the NO₃-containing species (adsorbed NO₃ and HNO₃) increase dramatically and concomitantly with

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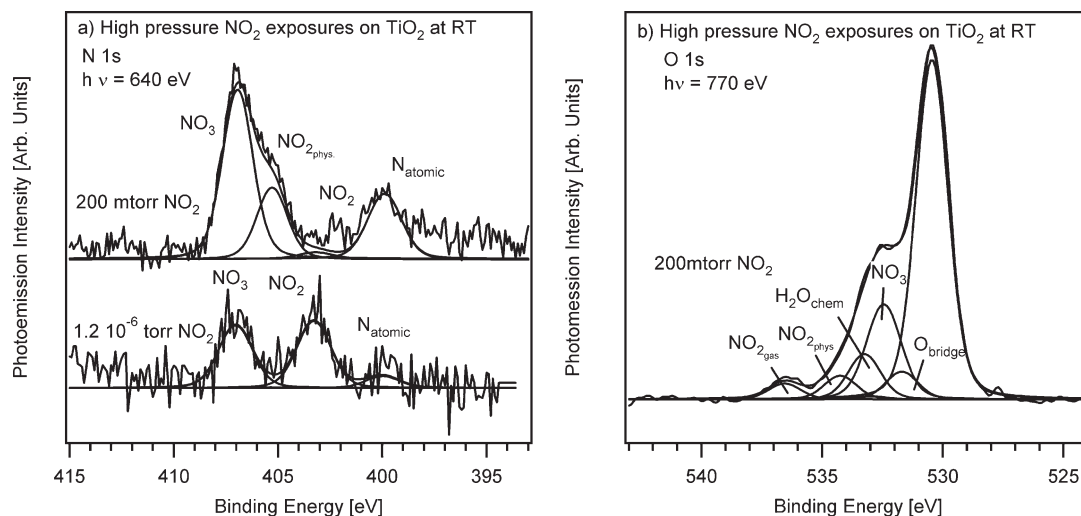


Figure 2. Examples of (a) N 1s and (b) O 1s data fits for exposure of the clean TiO₂(110) sample to 1.2×10^{-6} torr ((a) only) and 200 mtorr NO₂, respectively, at room temperature (after Tougaard baseline correction).

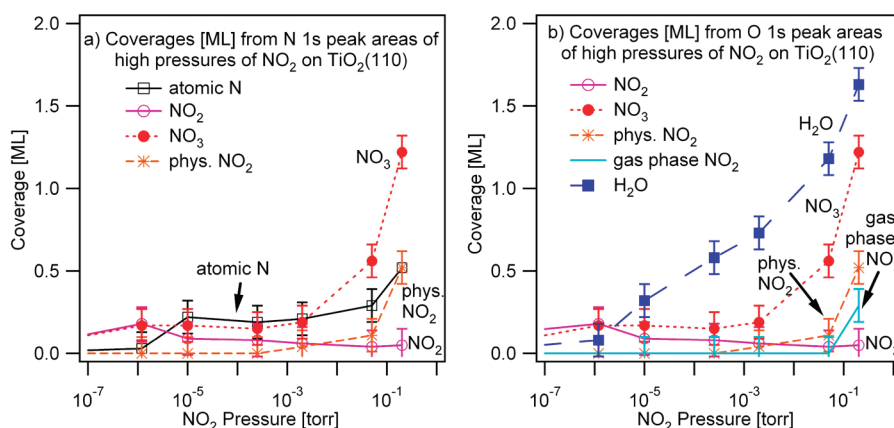


Figure 3. Estimated coverages of various species based on the (a) N 1s and (b) O 1s components for high-pressure exposures of NO₂ on TiO₂(110) at room temperature. The peak areas were obtained from least-squares fits with Voigt functions after attenuation correction. Error bars have been estimated from the average residual noise (rms). Chemisorbed NO₃ (in the literature, sometimes referred to as “nitrates”) corresponds to filled circles, NO₂ (“nitrites”) to empty circles, atomic nitrogen to empty squares, and adsorbed H₂O to filled squares.

Table 1. Estimated Coverages [ML] of Various Species Based on the (a) N 1s and (b) O 1s Components for High-Pressure Exposures of NO₂ on TiO₂(110) at Room Temperature^a

surface species	pressure [torr]						
	1.2×10^{-6}	1.0×10^{-5}	2.5×10^{-4}	1.0×10^{-3}	2.2×10^{-2}	1.1×10^{-1}	2.0×10^{-1}
atomic N	0.0	0.2	0.2	0.2	0.3	0.3	0.5
chem. NO ₂	0.2	0.1	0.1	0.1	0.0	0.1	0.1
chem. NO ₃ and HNO ₃	0.2	0.2	0.2	0.2	0.6	0.9	1.2
phys. NO ₂	0.0	0.0	0.0	0.0	0.1	0.2	0.5
gas phase NO ₂	0.0	0.0	0.0	0.0	0.0	0.0	0.3
chem. H ₂ O	0.1	0.3	0.6	0.7	1.2	1.1	1.6

^a The coverages of the surface species were quantified by taking the bridging oxygen O 1s signal as a reference (for details, please see the Experimental Methods section), which remained constant within ~5% after correction for the gas phase attenuation. The peak areas were obtained from least-squares fits with Voigt functions after attenuation correction.

H₂O (Figure 3, Table 1). The source of the H₂O is displacement by NO₂ from the chamber walls,⁴⁰ which is an unavoidable complication in high-pressure experiments.

Therefore, at these higher pressures, we are probing the effect of gaseous water codosed with NO₂. Water adsorbs on the TiO₂ substrate and is detected based on the appearance of the

characteristic O 1s component at ~533.5 eV.³¹ Although signals in the range of 532.9–534 eV have also been attributed to top-hydroxyls in other studies,^{31,32,34,35} we rule these species out since bridging oxygen vacancies necessary for H₂O dissociation³¹ are already healed at this pressure. As shown in Figure 3b, the O 1s signal of adsorbed water increases slowly to ~0.7 ML in the range of 10⁻⁵–10⁻³ torr total pressure.

Importantly, physisorbed and gas-phase NO₂ or the dimer, N₂O₄, are also observed at higher NO₂ pressure simultaneously

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with the exponential increase of the NO₃ signals. Above 2.5×10^{-2} torr, a shoulder appears on the N 1s and O 1s peaks at 405.4 and 534.3 eV (ratio 1:2), respectively, which is probably physisorbed N₂O₄ via comparison to earlier IRAS studies,⁴¹ but it cannot be distinguished from NO₂ by our XPS experiments. At pressures of 200 mtorr of NO₂, a very weak but distinguishable signal of gas phase NO₂/N₂O₄ is measured at 537.6 eV.

At 10^{-3} torr of NO₂, the total surface coverage in the mixed phase of species bound directly to the substrate (N_{atomic}, NO₂, NO₃, and H₂O) sums up to ~ 1.3 ML. Above this threshold pressure, the amounts of adsorbed H₂O and NO₃ on the TiO₂-(110) surface increase rapidly: their coverages are estimated at notably high levels of ~ 1.6 and ~ 1.2 ML, respectively, at 200 mtorr. With this, the total surface coverage surprisingly exceeds 2 ML. It is therefore likely that the NO₃ species in excess of the saturation coverage found at the lower pressures are not strongly chemisorbed to the substrate.

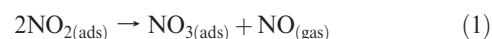
Therefore, we propose that condensed HNO₃, which is stabilized by H-bonding to the surface species or coadsorbed water, is formed at higher pressures. The BEs of the N 1s and O 1s signals of HNO₃ coincide within the detector resolution with those of chemisorbed NO₃; however, an independent confirmation using other spectroscopic techniques will be necessary. Although it is easily conceivable that water molecules and NO_x species may be coadsorbed in the same unit cell, the large amount, > 1 ML, of NO₃ species on the surface at 200 mtorr cannot be expected given the fact the binding of this species would most likely involve one bridging oxygen per nitrate according to recent DFT calculations.¹⁹ We also considered islanding of NO₃ species or surface restructuring due to water coadsorption, but this would not account for the increase of the NO₃ signals and its reversible nature as explained in the next section.

We propose that HNO₃ forms when multilayers of H₂O condense on the surface with physisorbed NO₂, in analogy to the formation of H₂SO₄ from co-condensed SO₃/H₂O multilayers in UHV.⁴² We do not attribute this to adsorption of HNO₃ formed in the gas phase because exposure of a NO₂ saturated surface to water does *not* yield NO₃. If there were reactions on the chamber walls, nitric acid should likewise form under these circumstances. Nitric acid formation has also been reported on other oxides, that is, quartz and borosilicate glass surfaces.⁹ Since surface oxygen vacancies required for H₂O dissociation are healed by NO₂ decomposition at these pressures,³¹ it is unlikely that HNO₃ formation occurs only via attack of surface hydroxyls as proposed by Gustafsson et al.¹²

In order to estimate the water partial pressure in the background, we invoked the Langmuir adsorption model and used the adsorption enthalpy of -75 kJ/mol determined for a H₂O monolayer.³¹ We have limited this rough estimate to the low-pressure/monolayer saturation regime above which HNO₃ formation or deposition starts. Assuming that there is no effect due to the presence of NO_x species other than site blocking, we obtain a water partial pressure of ca. 10^{-6} torr for the formation of 0.6 ML H₂O_(ads) as estimated from XPS at $p(\text{NO}_2) = 2.5 \times 10^{-4}$ torr. At $p(\text{NO}_2) = 1 \times 10^{-5}$ torr, a water partial pressure of ca. 5×10^{-7} torr would be required to form 0.3 ML H₂O_{ads}. Thus, the water partial pressure in this regime trails the NO₂ partial pressure by ca. 2 orders of magnitude, which indicates that HNO₃ buildup starts above water partial pressures of ca. 10^{-5} torr (total pressures of 10^{-3} torr).

Atomic nitrogen persists on the surface at higher pressures, up to 0.2 torr, and even grows substantially to almost 0.5 ML, which suggests that bulk defects from deeper layers can be drawn out in such highly oxidizing atmospheres.^{43–45} Previous UHV studies at room temperature reported significantly lower atomic N coverages that diminished at higher NO₂ exposures, possibly due to a reoxidation by NO_x species.¹⁹ Also, beam damage contributed slightly to the growth of the signal due to atomic N (see Experimental Methods section). Indeed, surface oxygen vacancies, which are characterized by peaks at 1.3 eV lower BE than the Ti 2p bulk peaks (ca. 10%),²³ are healed by exposure to even the lowest NO₂ pressures in the beginning of the experiment as concluded from the disappearance of these components (see Experimental Methods section). Thus, it is likely that a migration of Ti interstitials from the subsurface region occurs,^{43–45} although other possibilities such as decomposition at step sites or migration of bulk oxygen vacancies (Henderson reported oxygen vacancy migration simultaneously to Ti interstitial diffusion starting at ~ 400 K³⁷) may not be ruled out based on the XPS results. This migration may lead to the formation of new TiO_x features, including particles and strands, and roughening of the surface, which could form new, more reduced sites for decomposition at higher pressures.^{44,45}

Overall, our observations agree well with the behavior of NO₂ on rutile single crystals of TiO₂(110)¹⁹ and MgO(100),¹⁷ where formation of chemisorbed NO₃ from a disproportionation of NO₂ in UHV conditions was suggested:



The NO₃ species are stable up to temperatures well above 400 K, but the NO will likely desorb immediately at room temperature since it adsorbs only very weakly on TiO₂(110).⁴⁶ By using the desorption activation barrier of ca. 32 kJ/mol obtained by assuming a frequency factor of 10^{13} Hz⁴⁷ and using the measured desorption temperature of NO from TiO₂(110) of 127 K,⁴⁶ we estimated from a Langmuir isotherm that the surface NO will be negligible at room temperature for NO₂ pressure of up to 200 mtorr (< 0.005 ML) even if large amounts of it would be produced by reactions on the chamber walls.

On dry γ -Al₂O₃, nitrates and nitrites are formed initially in roughly equal amounts,²² but nitrites begin to convert into nitrates at higher NO₂ doses. By reaction with hydroxyls, NO₂ is suggested to form nitrates on the surface as implied by Fourier transform infrared (IR) experiments.²² Strongly bound NO_x species were not affected by exposure to water as shown in IR experiments. In contrast, NO₂ forms only nitrites on θ -Al₂O₃/NiAl(100) at temperatures below ~ 180 K, whereas at higher temperatures nitrates are also detected by XPS.²⁰ Furthermore, small amounts of atomic nitrogen with a BE around ~ 397 eV are noticeable at temperatures between 80 and 750 K, but these features have not been assigned by Ozensoy et al.²⁰ The binding energies of the N 1s core levels are in agreement with the work of Rodriguez et al.¹⁹ and our assignments.

When NO₂ and water are condensed on aluminum oxide films, Ozensoy et al. determined that mixed phases of nitrates and

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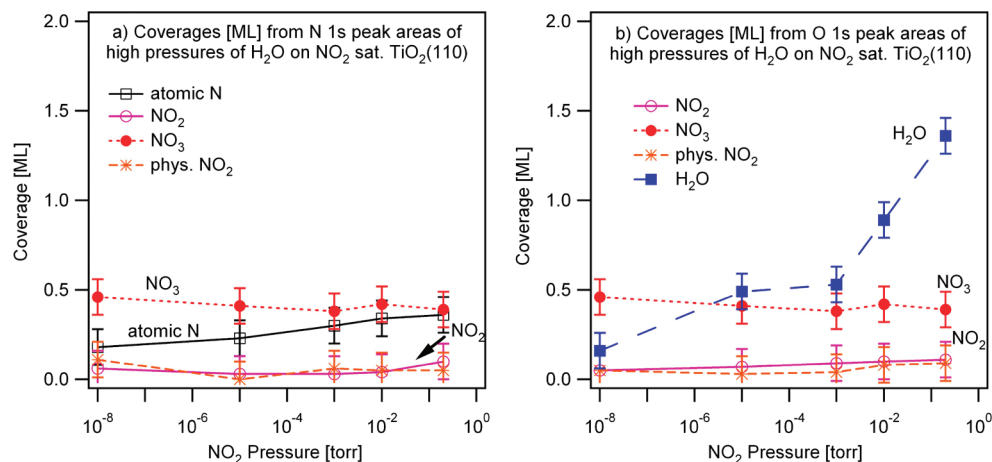


Figure 4. Estimated coverages of various species based on the (a) N 1s and (b) O 1s components for high-pressure exposures of H₂O on TiO₂(110) saturated with 200 mtorr NO₂ at room temperature. Chemisorbed NO₃ corresponds to filled circles, NO₂ to empty circles, atomic nitrogen to empty squares, and adsorbed H₂O to filled squares. Note that the coverage of NO₃ is slightly increased at 0.4–0.5 ML during this experiment. Also, a slow increase of the atomic N species on the surface is detected due to beam damage.

nitrites were present based on temperature programmed desorption and X-ray photoelectron studies.²¹ Though water may dominate the surface by blocking sites on the oxide surface at higher exposures, chemisorbed NO_x species are still evolved in temperature programmed reaction experiments. However, since this group performed water exposures at very low pressures, no further comparison can be made.

Exposure of the NO₂ Saturated TiO₂(110) Surface to Elevated H₂O Pressures. After the pump-down from 200 mtorr NO₂ to a pressure of $\sim 4 \times 10^{-8}$ torr, the reversibly bonded species formed at elevated NO₂ pressures were no longer present. Importantly, the strong excess of the NO₃ signals, the peaks of physisorbed NO₂, and the O 1s peak due to adsorbed water all disappear. Essentially, all species present are the same as those under lower pressure conditions. For example, toward the end of the pump-down process, the coverages of chemisorbed NO₂ and NO₃ decreased to 0.2 ± 0.1 ML for NO₂ and 0.4 ± 0.1 ML for NO₃, close to the amounts observed in the low-pressure range. The NO₃ signal was also observed in subsequent experiments to remain slightly elevated, around 0.4 ML, after saturation at 200 mtorr NO₂. The N 1s signal of atomic N remained at 0.5 ± 0.1 ML.

Upon increasing the H₂O pressure stepwise to test the effect of higher humidities on the NO_x adsorbate layers, however, we found no significant change (Figure 4). Increasing H₂O pressures up to 200 mtorr at room temperature left the strongly chemisorbed NO₃ and NO₂ as well as the atomic N species unaffected. As mentioned above, a similar behavior was reported for NO₂ and H₂O coadsorption on alumina surfaces under UHV conditions.^{21,22} The surface concentrations of strongly adsorbed NO₃ and NO₂ species did not change significantly for H₂O pressures between 10^{-5} torr and 200 mtorr aside from a minor decrease due to beam damage, which led to a simultaneous increase of atomic nitrogen. In contrast to our experiments on NO₂ exposure in which we observed a strong increase of the water signal in the O 1s XPS spectrum, the amount of water detected here is considerably smaller ($\sim 66\%$ of the amount detected for 200 mtorr NO₂ is measured for 200 mtorr of water here). This is consistent with previous findings⁹ that the presence of nitric acid stabilizes water in HNO₃–H₂O complexes. Since no HNO₃ was formed from the strongly bound NO₂ and NO₃ species in this experiment, the coverage of adsorbed water remained smaller. This is indirect evidence of the buildup of HNO₃ species during the exposure to high NO₂ pressures.

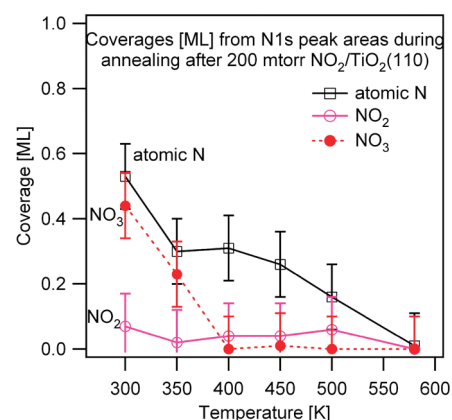


Figure 5. Estimated surface coverages from the N 1s components of the NO_x species during annealing of a TiO₂(110) sample that has been saturated with 200 mtorr NO₂ at room temperature (and then pumped down to 4×10^{-8} torr). The peak areas were obtained from least-squares fits with Voigt functions after attenuation correction.

Thermal Decomposition of a TiO₂(110) Surface Saturated with 200 mtorr NO₂. On a different surface prepared with 200 mtorr NO₂, we probed the thermally induced decomposition and desorption of NO_x species (Figure 5). During annealing, we observed a quick drop of the signals attributed to surface NO₃ until complete disappearance occurred at ~ 400 K. In independent temperature programmed reaction spectroscopy (TPRS) studies performed in our lab,⁴⁸ we found that the decomposition of NO₃ species is accompanied by a small NO₂ evolution peak (Figure 6). Taking into account different heating rates in both experimental sets, the temperature of the desorption maximum of NO₂, 450 K, is in good agreement with that observed here.

Thus, the disappearance of NO₃, of which small traces were still observed up to 500 K in UHV experiments,¹⁹ can be understood as a decomposition of the NO₃ and subsequent desorption of NO₂ according to eq 2:



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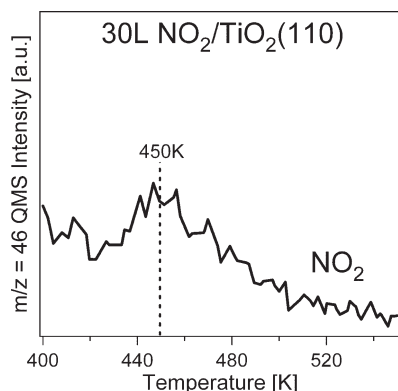


Figure 6. NO_2 evolution due to surface NO_3 decomposition as observed in independent TPRS experiments. A NO_2 multilayer (~ 30 L) was adsorbed at ~ 130 K on a clean, vacuum-reduced $\text{TiO}_2(110)$ surface. A linear heating rate of ~ 2.1 K/s was employed. For further details regarding the experimental procedure, please see ref 49.

The NO_2 signal, in contrast, starts off at a very small value just above the detection threshold. Given the noise of our raw data, it is hard to judge whether a significant change of its surface coverage occurs during the annealing experiments. However, since the NO_2 generated during NO_3 decomposition desorbs below 400 K, no buildup of chemisorbed NO_2 on the terraces is expected. In addition, the atomic nitrogen signal decreases more gradually until it disappears entirely by ~ 580 K. It may be reoxidized to NO or NO_2 by surface oxygen adatoms or oxygen from the bulk of the substrate or diffuse as a dopant into deeper layers.

Our experiments demonstrate the critical roles that oxides may play in the atmospheric chemistry of pollutants. Our work shows only minor differences across the pressure gap in the formation of NO_3 , NO_2 , and atomic nitrogen species observed *in situ* at ambient pressures, corresponding well with UHV results. We suggest that metal oxides may affect atmospheric NO_2 concentrations in multiple ways: metal oxides may facilitate HNO_3 formation in the presence of ambient moisture,^{8–11} and they may act as a sorbent promoting the adsorption and decomposition of NO_2 as suggested previously.

Conclusions

In situ AP-XPS experiments have been carried out in the pressure range from 10^{-8} torr to 200 mtorr, with the aim of investigating the pressure gap and reactivity of NO_2 on rutile $\text{TiO}_2(110)$. Furthermore, we have studied the effect of higher humidity on the reactivity of NO_2 at low and high water partial pressures.

At room temperature and low pressures, only chemisorbed NO_3 and NO_2 are formed, saturating the surface. Their coverages

remain constant between $\sim 10^{-5}$ torr and 10^{-3} torr. Moreover, atomic nitrogen species evolving from decomposition of surface NO_x species build up to a sizable level of ca. 0.2 ML. The formation of atomic nitrogen increases significantly at 200 mtorr NO_2 and leads to coverages of up to 0.5 ML, which is much too large to be accounted for by a simple healing of bridging oxygen vacancies and suggests that decomposition involves reduced bulk defects such as Ti interstitials, which are drawn out in highly oxidizing atmospheres.

Annealing in vacuum of a surface that had been exposed to 200 mtorr NO_2 results in the disappearance of the chemisorbed NO_3 and NO_2 species around 400 K. Since the surface coverage of atomic nitrogen remained constant up to this temperature, the adsorbed NO_3 and NO_2 species must have decomposed to free NO_2 , which desorbed subsequently. The atomic nitrogen started to decrease above 400 K until it diminished entirely around 580 K.

Importantly, coexposure to NO_2 at pressures above $\sim 10^{-3}$ torr leads to the formation of nitric acid on the saturated surface. This is facilitated by the readsorption of water, which was displaced from the chamber walls and observed at NO_2 pressures above $\sim 10^{-5}$ torr. Above $\sim 10^{-3}$ torr of NO_2 , XPS indicated a sharp increase in the surface water coverage and the appearance of physisorbed $\text{NO}_2/\text{N}_2\text{O}_4$. This coincides with a strong increase in the N 1s and O 1s signals assigned to surface NO_3 , which far exceeds the coverage of bridging oxygen atoms on the surface (> 1 ML). Therefore, we propose that this is a buildup of HNO_3 in the $\text{H}_2\text{O}/\text{NO}_2$ multilayer. Since exposing a surface previously saturated with 200 mtorr NO_2 to increasing pressures of water (also up to 200 mtorr) did not lead to significant changes in the NO_3 , NO_2 , or atomic nitrogen signals, we conclude that the formation of HNO_3 requires the presence of physisorbed NO_2 and H_2O , while the chemisorbed NO_2 and NO_3 species saturating the surface are not reactive.

In summary the pressure gap between high-pressure *in situ* conditions and UHV is rather subtle in this example, further emphasizing the continued importance of UHV fundamental studies. While the formation and decomposition of the chemisorbed NO_3 and NO_2 species correspond well with previous UHV studies, the only major differences are attributed to the increased formation of atomic N from bulk defects. The formation of HNO_3 on the sample is caused by the simultaneous coadsorption of water and indicates that oxide surfaces can facilitate its formation under ambient humidity conditions encountered in the atmosphere by condensing the reactants.

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