Adsorption and Oxidation of NO₂ on Anatase TiO₂: Concerted Nitrate Interaction and Photon-Stimulated Reaction

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ABSTRACT: The catalytic and photon-induced oxidation of NO₂ on anatase TiO₂ has been studied and compared with the surface nitrate species obtained after adsorption of HNO₃. Using a combination of in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), density functional theory (DFT), and temperature-programmed desorption (TPD), it is shown that identical products are obtained in all reaction systems but that their formation rates differ significantly. The surface reaction products are identified as combinations of surface–NO₃⁻ species, where NO₂ bonds to the lattice oxygen, and freely adsorbed NO₃⁻ ions. These products can be obtained either by dissociative adsorption of HNO₃ or by catalytic/photocatalytic oxidation of NO₂, which is facilitated by UV light. A concerted reaction mechanism is unraveled that involves reorientation of bidentate nitrate that pushes out a neighboring protonated lattice oxygen to form a surface–NO₃⁻ species and a terminal OH group. The thermal stability of these surface species has been studied by means of TPD and simultaneous in situ DRIFTS measurements that reveal a main desorption peak (m/z = 46) at around 430 °C, which is attributed to concerted nitrate desorption through pentoxide (N₂O₅) formation. A weaker and broader TPD peak is found at about 185 °C and is attributed to desorption of nitrate species bonded in a compressed configuration. The experimental results can be explained by the changing stability of the identified nitrate products, which depends strongly on the surface chemical environment and the surface coverage. The DFT results show that the stabilization of intermediate NO₃ adsorbates and the final nitrate reaction products occurs through a bifunctional charge exchange mechanism that is mediated by the TiO₂ crystal. In particular, a stable surface–NO₃⁻ and NO₃⁻ ion pair configuration has been identified. This mechanism explains both the thermal and photoinduced oxidation of NO₂ and their thermal stability and different formation rates, yielding high photoinduced oxidation reaction rates. Our results provide insights into the structure and chemical stability of nitrate surface products on TiO₂ particles and their formation mechanism, which is important for understanding their catalyzed transformation into the harmful compounds HONO and N₂O during continued UV light illumination.

KEYWORDS: NO₂, TiO₂, photoadsorption, density functional theory, infrared spectroscopy, thermal desorption spectroscopy

1. INTRODUCTION

Adsorption and photoreaction of small molecules on TiO₂ are important in atmospheric chemistry and industrial and environmental applications. Nitrogen dioxide (NO₂) is an inorganic air pollutant that has a negative impact on human health, animal life, and the environment. It is released in the form of NO₂ gas (NO and NO₂) during natural events such as volcanic eruptions, lightning strikes, and forest fires. Currently, however, anthropogenic emissions from combustion processes, transport, and industry are the dominating sources.

Under sunlight illumination, NO₂ undergoes photolysis and is converted to NO and atomic oxygen, O(¹P), which further reacts with molecular oxygen to produce tropospheric ozone. This is one of the main components of photochemical smog—a combination of toxic chemicals that forms during reactions between NOₓ and volatile organic compounds (VOCs)—and it can be damaging to the lungs and respiratory system. The other two main components of photochemical smog are peroxyacetyl nitrate (PAN), which is more damaging to plants than ozone, and nitric acid (HNO₃). NO has low solubility in water and can thus readily spread throughout the whole respiratory system. In contrast, the negative health effects of NO₂ are related to its dissolution in moisture and the associated formation of HNO₃. In the atmosphere, the formation of nitric acid primarily occurs through reactions between NO₂ and ozone or NOₓ and OH radical (at night and in the daytime, respectively) which lead to the formation...
of nitric acid aerosols.\textsuperscript{9} It has also been suggested that nitrate can form through reactions of NO\textsubscript{2} at the surface of mineral dust particles.\textsuperscript{10} This nitrate formation occurs most prominently on TiO\textsubscript{2} minerals and is therefore believed to play a significant role in the geochemical oxidation of NO\textsubscript{x} gases, even though TiO\textsubscript{2} is a minor component of mineral dust.\textsuperscript{3} Consequently, since nitrate formation on TiO\textsubscript{2} surfaces offers a route toward “deNO\textsubscript{X}ification” of the atmospheric environment, it has attracted considerable research interest as an environmental remediation technology.\textsuperscript{11}

The photoinduced and thermal oxidations of NO\textsubscript{2} on TiO\textsubscript{2} have both been studied extensively.\textsuperscript{12,13,10,14−22} During thermal oxidation, it has been suggested that NO\textsubscript{2} undergoes a disproportionation reaction, where two NO\textsubscript{2} molecules react and form NO\textsubscript{3} and NO\textsubscript{+}.\textsuperscript{12−14} This was later challenged when the estimated ratio between the amount of consumed NO\textsubscript{2} and generated NO was found to be 3:1 rather than 2:1.\textsuperscript{20} Instead, another mechanism was suggested in which two types of nitrate species are formed; one where NO\textsubscript{3} is freely adsorbed at Ti\textsuperscript{4+} sites and one where it is bound to a O\textsuperscript{2−} lattice ion, forming a surface NO\textsubscript{3} species.\textsuperscript{20,22} In contrast, the suggested photochemical reaction mechanism on TiO\textsubscript{2} appears simpler: viz., NO\textsubscript{3} reacts with a photoproduced OH\textsuperscript{+} radical and forms NO\textsubscript{3}− and H\textsuperscript{+}.\textsuperscript{15} Since NO\textsubscript{3}− undergoes photolysis under UVC illumination, NO\textsubscript{3} is replenished but can also be further transformed into the more harmful compounds HONO and NO\textsubscript{2}.\textsuperscript{16−19} This reversible reaction process has been identified as a “reNO\textsubscript{X}ification” pathway, and the use of TiO\textsubscript{2} for photocatalytic deNO\textsubscript{X}ification has been questioned for this reason.\textsuperscript{17,18,23} This creates a precarious situation, since TiO\textsubscript{2} is currently implemented in several technical applications, such as functional building materials and several environmental air remediation technologies.\textsuperscript{24} It is therefore important to understand the reaction mechanisms for nitrate formation on TiO\textsubscript{2}, and in particular the adsorbate structure and chemical stability of the nitrate reaction products.

In this study, the products obtained after catalytic and photocatalytic oxidations of NO\textsubscript{2} on TiO\textsubscript{2} have been compared with the surface products obtained after adsorption of HNO\textsubscript{3}, using operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), temperature-programmed desorption (TPD), and density functional theory (DFT). We model reactions initiated by the presence of photexcited electrons by adding a ground-state electron to the system. As we have previously shown,\textsuperscript{25} the presence of a localized negative charge (added to the model system in the DFT calculation but obtained though photoexcitation in reality) influences the surface reactivity and molecular adsorption. The combined experimental and theoretical results provide a detailed description of the nitrate reaction products that are formed during both the thermal and photochemical oxidation of NO\textsubscript{2} on TiO\textsubscript{2}. The two most commonly exposed surface facets, namely the (101) and (001) surfaces, have been examined, and the results show that indirect, surface-mediated charge transfer governs nitrate formation.

2. EXPERIMENTAL SECTION

Anatase TiO\textsubscript{2} nanoparticles (powder grade Hombikat UV100, Sachtleben Chemie GmbH, Duisburg, Germany) was used in all measurements. Previous studies have shown that these particles exhibit truncated-bipyramidal crystal shapes, but with a rounded morphology exposing appreciable fractions of both (101) and (001) surfaces.\textsuperscript{26,27} The average crystal size of these particles was determined to be 9.0 ± 0.3 nm by XRD, using the Scherrer equation. A pretreatment annealing step at 400 °C was applied before experiments, which decreases the amorphous content in the powder sample.\textsuperscript{26} More information about the XRD measurements and Scherrer analysis can be found in the Supporting Information of our previous publications.\textsuperscript{25,28}

DRIFTS measurements were performed using a vacuum-pumped FTIR spectrometer (Vertex 80v, Bruker Optik GmbH, Ettingen, Germany) equipped with an HgCdTe detector and a custom-modified Praying Mantis DRIFT accessory, equipped with a high-temperature reaction chamber (HVC-DRM-5, Harrick Scientific Inc., NY, USA) that enabled simultaneous UV illumination of the sample and a mass spectrometry analysis of the desorbing products. A tunable UV LED light source (FCS-LED, Prizmatix) was used and operated at 365 nm to give an intensity of 15 mW/cm\textsuperscript{2} at the sample position, as measured by a thermopile detector (PM160T, Thorlabs, NJ, USA). A controlled gas flow through the powder sample bed was enabled using mass flow controllers (Bronkhorst High-Tech BV, The Netherlands) that were set to give a total gas flow rate of 100 mL/min.

Repetitive DRIFT spectra were measured in situ and averaged over 120 scans at 1 min intervals, except in the TPD experiments, where DRIFT spectra were acquired every 12 s from an average of 20 scans, giving a temperature resolution of 3 °C during a heating rate of 15 °C/min. All DRIFT spectra were measured at a resolution of 4 cm\textsuperscript{-1}.

Prior to each experiment, the sample was heated in synthetic air (Air Liquide, purity 99.9999%) at 400 °C for 15 min in order to remove carbonous impurities from the surface and subsequently cooled in synthetic air to 20 °C. The TiO\textsubscript{2} samples thus prepared are dehydroxylated. Two background spectra were subsequently measured at 20 °C: one for use during monitoring of the surface reaction (120 scans) and one for use during the TPD measurement (20 scans). The former was performed in a flow of HNO\textsubscript{3} vapor (concentration 69% in research grade solution) or NO\textsubscript{2} gas (50 ppm, 98% purity), mixed in synthetic air. HNO\textsubscript{3} was added to the synthetic air flow by passing the gas through the nitric acid reservoir, which was kept at a fixed temperature of 75 ± 0.2 °C, thereby admitting 7 vol % HNO\textsubscript{3} and 9 vol % H\textsubscript{2}O to the synthetic air flow. The adsorption of HNO\textsubscript{3} was stopped after 45 min, when the signals were saturated, while the oxidation reactions with NO\textsubscript{2} (both with and without UV illumination) were conducted for 3 h.

For TPD measurements, a quadrupole mass spectrometer (QME 125-2, Pfeiffer Vacuum, Germany), connected to a 10 m long narrow nonactivated silica capillary column, was employed. The capillary opening was placed slightly above the sample surface in the DRIFTS reaction cell, and its other end was mounted with a graphite-ferrule-sealed Swagelok feed-through to a directed gas inlet in the ultrahigh-vacuum chamber (base pressure \(7.5 \times 10^{-11}\) mbar, rising to about \(10^{-6}\) mbar during measurements) to the cross-beam ionization source in the mass spectrometer (MS). The sample was heated from 20 to 500 °C at a rate of 15 °C/min. The reported TPD spectra depict mass/charge (m/z) ratios of 46 (NO\textsubscript{2}+) since HNO\textsubscript{3} and NO\textsubscript{3}− are both decomposed into NO\textsubscript{2} in the MS ionization source.\textsuperscript{19} No effluent NO\textsubscript{2} gas was detected from the surface reactions above the S/N limit of the setup. The estimated temperature resolution during the TPD measurements was 1.75 °C. The time delay that arises due to diffusion...
of gas through the capillary tube was accounted for by calibrating the spectrometer using CO. All TPD spectra are presented as normalized intensity values with the strongest signal in each measurement being normalized to 1.

3. SIMULATIONS

DFT calculations were performed using the Vienna ab initio simulation package (VASP, 5.4.4) and the generalized gradient approximation (GGA) functional suggested by Perdew et al. A Hubbard-like $U$ correction term ($U = 3.5$ eV) was applied to account for the on-site Coulomb interactions of the Ti d electrons, as proposed by Dudarev et al. The latter is a commonly used methodology to treat localized charges in metal oxide systems, and it has been recommended specifically for studies of redox catalytic reactions on TiO$_2$. The $U$ potential applied here has also been recommended for TiO$_2$ based on a linear response analysis performed on a defective TiO$_2$(101) slab. To account for the valence-core interactions, pseudopotentials were generated using the projected augmented wave (PAW) method proposed by Blochl et al. The valence states of Ti, O, and N atoms were modeled using 4, 6, and 5 electrons, respectively. All calculations of the electronic wave function were performed at the Γ point and with a kinetic energy cutoff of 546 eV.

For the construction of TiO$_2$(101) (2 × 3) and TiO$_2$(001)-1 × 1 (2 × 2) supercells, totals of 192 and 162 atoms were used, respectively. These contained 4 and 3 stoichiometric TiO$_2$ layers with 64 and 54 TiO$_2$ units in each slab, respectively. The bottom two layers were kept fixed during the ionic relaxations, and a minimum vacuum gap of 15 Å was used to separate the slabs in the direction of the surface normal. For calculations of adsorption energy as a function of coverage and adsorbate distance, two elongated stab structures were used that contained twice the number of atoms in the surface plane and half the number of bulk layers. The ionic relaxation was performed using the conjugant gradient algorithm available in VASP and carried out until all forces were lower than 0.01 eV/Å. Transition-state calculations were performed using the climbing nudge elastic band method (cNEB) by Henkelman et al. Seven images were used in all cases.

The finite differences method was used to calculate the vibrational frequencies, using a step length of 0.015 Å and allowing only the atoms that were part of the adsorbates to move. To make the calculated vibrational frequencies more directly comparable to the experiment, all frequencies were shifted downward by 24 cm$^{-1}$, which corresponds to the difference between calculated and experimental frequencies of the symmetric and asymmetric vibrational modes in NO$_2$ and HNO$_3$, respectively. While the TiO$_2$(001)-1 × 4 reconstructed surface is generally agreed to be the thermodynamically preferred surface termination obtained after annealing under vacuum, for nanoparticles under atmospheric conditions subjected to mild annealing, we expect (001) surfaces to be present, which is the initial structure in most reported studies of as-prepared particles. Finally, the Redhead formula was used to estimate desorption temperatures from calculated binding energies and the experimental temperature ramping rate 15 °C/min.

4. RESULTS AND DISCUSSION

4.1. Operando DRIFTS and TPD. Figure 1a shows DRIFT spectra obtained after adsorption of HNO$_3$, photo-oxidation of NO$_2$, and adsorption of NO$_2$ on the anatase TiO$_2$ nanoparticles. It is evident that the spectra appear almost identical in all three cases, with the exception of the peak at 1360 cm$^{-1}$ that appears after HNO$_3$ adsorption. This peak is due to adsorption of nitric acid on the reaction cell windows and is also formed in varying amounts after the NO$_2$ reaction, but to a much smaller extent (see dotted curve in Figure 1a). The remaining peaks, located at 1612, 1585, 1492, 1302, and 1249 cm$^{-1}$, have previously been observed after oxidation of NO$_2$ on TiO$_2$ and can be attributed to surface nitrate.

A minor peak is observed at around 1180 cm$^{-1}$ after adsorption of NO$_2$ (dotted curve in Figure 1a), which can be attributed to nitrite species, confirming that the TiO$_2$ samples are largely dehydroxylated, since the nitrates are suggested to bond to OH surface groups. In the thermal NO$_2$ oxidation reaction, it has been argued that a combination of surface--NO$_3^-$ species and freely adsorbed NO$_3$ is obtained. Hitherto, the formation of mixed surface--NO$_3^-$ and freely adsorbed NO$_3^-$ species has not been reported to occur for photoinduced NO$_2$ reactions on TiO$_2$ or upon adsorption of HNO$_3$. The identical IR absorption characteristics in Figure 1a suggest, however, that the same surface products are obtained in all three cases.

The inset in Figure 1a shows the kinetics of the nitrate formation following HNO$_3$ and NO$_2$ adsorption at 20 °C in synthetic air, as well as NO$_2$ photoadsorption under the same conditions, as measured by operando DRIFTS. It should be
noted that the concentration of HNO$_3$ in the gas feed was significantly higher than the concentration of NO$_2$, which explains the steeper HNO$_3$ uptake curve. It is also evident that the thermal NO$_2$ oxidation reaction at 20 °C following adsorption is slow and that the nitrate formation does not reach saturation during the 3 h exposure time. The rate constants were determined by fitting the data to a pseudo-first-order reaction kinetics model, and the integrated area of the saturated photo-oxidized NO$_2$ spectrum was used to define 1 monolayer (ML) coverage. The results show that the photocatalytic reaction was 10 times faster than the thermal oxidation, with the corresponding rate constants $k_{\text{photo}} = 0.018$ ML s$^{-1}$ and $k_{\text{thermal}} = 0.0016$ ML s$^{-1}$, respectively. A similar enhancement of SO$_2$ adsorption has been shown to occur during UV illumination on anatase TiO$_2$. This observation could therefore suggest a similar electron-stimulated mechanism for the enhancement of the NO$_2$ adsorption. However, as we show below, the NO$_3$ system accommodates charges very differently compared to SO$_2$ and results in a different adsorption process.

Figure 2. Operando DRIFTS spectra recorded during TPD measurements. The peaks at 1492 and 1302 cm$^{-1}$ (see Figure 1a) are strongly reduced after the first TPD peak at around 185 °C and then gradually disappear at increasing temperature. The other peaks, situated at 1612, 1585, and 1249 cm$^{-1}$, disappear after the second TPD peak at around 430 °C. The signal measured at 1360 cm$^{-1}$ is obtained from adsorbed HNO$_3$ on the reaction cell windows.

Figure 3. (a) Reaction diagram for the conversion of NO$_3^-$ into s-NO$_3^-$ on TiO$_2$(001) and TiO$_2$(101) following reaction 2a. The energy is plotted on the same scale in both graphs, and the inset figures illustrate the structures associated with each reaction coordinate. (b) Suggested reaction pathway for thermal and photoinduced oxidation of NO$_2$, illustrated on the TiO$_2$(001) surface. Color scheme: O, red; Ti, blue; N, green; H, pink.
Figure 1b shows TPD spectra \((m/z = 46)\) obtained after adsorption of \(\text{HNO}_3\), photo-oxidation of \(\text{NO}_2\), and oxidation of \(\text{NO}_2\). From the TPD spectra, it is possible to distinguish two desorption peaks around approximately 185 and 430 °C. The exact position of the peaks differs slightly, which can be attributed to the different surface coverages (see the inset in Figure 1a) and adsorbate–adsorbate interactions, as we discuss below. Since \(m/z = 46\) is the only detected mass, it can be concluded that the nitrates desorb from the surface either in the form of neutral \(\text{NO}_2^+\) molecules or as molecules that decompose into \(\text{NO}_2\) during the ionization process in the mass spectrometer. The normalized intensity indicates the relative...
Table 1. Adsorption Energies and Calculated Vibrational Frequencies of the N–O Modes of HNO₃ and Its Dissociative Adsorption Nitrate Products on the TiO₂(101) and TiO₂(001) Surfaces

<table>
<thead>
<tr>
<th>TiO₂ surface</th>
<th>adsorbate</th>
<th>( E_{ads} (\text{eV}) )</th>
<th>( \nu (\text{O–N–O}) ) (cm(^{-1}))</th>
<th>( \nu (\text{O–N–O}) ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(101)</td>
<td>NO₃⁻ + H⁺</td>
<td>−2.39</td>
<td>1521</td>
<td>1097</td>
</tr>
<tr>
<td>(101)</td>
<td>s-NO₃⁻</td>
<td>−2.12</td>
<td>1615</td>
<td>1153</td>
</tr>
<tr>
<td>(101)</td>
<td>dimer (NO₃⁻/s-NO₃⁻) + OH⁻ + H⁺</td>
<td>−2.29 alt.², −1.95</td>
<td>1522/1627</td>
<td>1105/1140</td>
</tr>
<tr>
<td>(101)</td>
<td>dimer (NO₃⁻/s-NO₃⁻)</td>
<td>−1.90³</td>
<td>1522/1624</td>
<td>1096/1143</td>
</tr>
<tr>
<td>(001)</td>
<td>NO₃⁻H⁺</td>
<td>−2.71</td>
<td>1596</td>
<td>1247</td>
</tr>
<tr>
<td>(001)</td>
<td>s-NO₃⁻ + OH⁻</td>
<td>−2.54</td>
<td>1485</td>
<td>1298</td>
</tr>
<tr>
<td>(001)</td>
<td>dimer (NO₃⁻/s-NO₃⁻) + OH⁻ + H⁺</td>
<td>−2.75 alt.², −2.33</td>
<td>1590/1507</td>
<td>1245/1282</td>
</tr>
<tr>
<td>(001)</td>
<td>dimer (NO₃⁻/s-NO₃⁻)</td>
<td>−2.51³</td>
<td>1593/1495</td>
<td>1245/1289</td>
</tr>
<tr>
<td>(001)</td>
<td>1 ML</td>
<td>−1.90⁶</td>
<td>1614/1659</td>
<td>1160/1171</td>
</tr>
<tr>
<td>(001)</td>
<td>0.5 ML</td>
<td>−1.43⁴</td>
<td>1612, 1585, 1492</td>
<td>1249, 1302</td>
</tr>
<tr>
<td>expstl</td>
<td></td>
<td></td>
<td>1160/1171</td>
<td></td>
</tr>
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</table>

\(^{a}\)Experimental frequencies are shown in the bottom row for comparison. \(^{b}\)Calculated relative to a free HNO₃ molecule in the gas phase; i.e., corresponding to a dissociative adsorption of HNO₃ unless otherwise specified. \(^{c}\)Calculated relative to free NO and NO₂ molecules in the gas phase. \(^{d}\)Calculated relative to free NO and NO₂ molecules in the gas phase and an elongated slab structure containing twice as many surface atoms but a reduced number of bulk layers.

The fraction of desorbing species at each temperature; the high-to-low TPD area ratio is about 5:1 in all cases, showing that the majority of nitrate species desorb recombinatively above 400 °C and are strongly bonded to the TiO₂ surface.

Figure 2 shows operando DRIFT spectra measured during the TPD measurements at intervals of 100 °C. Since the developments of the DRIFT spectra and the TPD profiles are very similar in all reaction systems, there is good reason to believe that the obtained reaction products are the same in all cases, albeit with different relative coverages. The DRIFT spectra acquired at different temperatures can be used to identify the desorbing species. The IR bands situated at 1612, 1585, and 1249 cm⁻¹ are identified as the desorbing species. The IR bands situated at 1492 cm⁻¹ (about 20% of the total concentration). The other main IR peaks, situated at 1612, 1585, and 1248 cm⁻¹, disappear at around 430 °C.

4.2. Identification of Nitrate Species. In a previous study it was shown that HNO₃ dissociates on the (101) surface, leaving the proton to a nearby bridging oxygen with almost no barrier to produce NO₃⁻(ads) + H⁺(ads), forming a monodentate surface nitrate species, which can transform to a bidentate configuration via an activated process involving a rotation of the nitrate. This bidentate configuration is very similar to the most stable adsorption configuration for the (101) surface identified in this work (see Figure 3a). We find that the same type of mechanism also can occur on the (001) surface, again with a small barrier (0.03 eV; see Figure S2). We write the dissociative adsorption (including the rotation-motion of the nitrate molecule) as

\[
\text{HNO}_3 \rightarrow [\text{NO}_3^- \cdots \text{H}^+](\text{ads})
\]

(1a)

The “…” sign signifies that the two species are associated in a surface complex. These complexes could break apart as a result of proton hopping following the reaction:

\[
[\text{NO}_3^- \cdots \text{H}^+](\text{ads}) \rightarrow \text{NO}_3^-(\text{ads}) + \text{H}^+(\text{ads})
\]

(1b)

The calculated energies of this reaction are very small: 0.07 and 0.03 eV for the (101) and (001) surfaces, respectively. The complexes can also undergo a conversion into strongly bonded nitrate adsorbates in a concerted motion where the free oxygen atom on adsorbed NO displaces the neighboring hydroxide ion (H⁺(ads)) into a terminal OH⁻(ads) as follows:

\[
[\text{NO}_3^- \cdots \text{H}^+](\text{ads}) \rightarrow [\text{s-NO}_3^- \cdots \text{OH}^-](\text{ads})
\]

(2a)

Reaction diagrams, including transition states, for the two surfaces are shown in Figure 3a. This reaction pathway is energetically much more favorable than any mechanism involving Ti–O bond breaking. The reaction barriers are 0.69 and 0.92 eV for (101) and (001), respectively. They are both significantly smaller than the adsorption energy and may be thermally activated, and s-NO₃⁻ is expected at high coverage (see Figure 4). The complexes could break apart as a result of proton hopping in a way analogous to that for [NO₃⁻…H⁺](ads).

\[
[\text{s-NO}_3^- \cdots \text{OH}^-](\text{ads}) \rightarrow \text{s-NO}_3^-(\text{ads}) + \text{OH}^-(\text{ads})
\]

(2b)

The adsorption energies and calculated vibrational frequencies of the NO₃⁻ and s-NO₃⁻ adsorbates are shown in Table 1. Corresponding values obtained for HNO₃ are shown in the Supporting Information, together with reported vibrational frequencies of isolated NO₂ and NO₃ molecules and complexes and previously reported data of adsorbed nitrate and nitrite on TiO₂ nanoparticles. The assignment of spectra is not straightforward, since possible interaction with both hydrogen and surface hydroxyls formed upon HNO₃ dissociation. The temperature-resolved DRIFTS data give more insight into the origin of the absorbance bands and will be discussed in more detail below. However, the calculated bands associated with s-NO₃⁻ and species agree reasonably well with experimental DRIFT spectra and show that both NO₃⁻ and surface-NO₃⁻ are formed during adsorption of HNO₃. In particular, the broad bands measured around 1500 and 1300 cm⁻¹ can largely be attributed to high-coverage structures of NO₃⁻. The NO₃⁻ on TiO₂(101), while the peaks at 1612, 1585, and 1249 cm⁻¹ can be largely attributed to s-NO₃⁻ and NO₃⁻ on TiO₂(001). Given the close resemblance of the DRIFT spectra of thermally and photo-oxidized NO₂ it is reasonable that the same nitrate products are formed in those cases as well.

4.3. NO₂ Oxidation and Photo-oxidation. Upon NO₂ adsorption on TiO₂, it has been suggested that NO₃⁻ and NO⁺ are formed through a disproportionation reaction (reaction 3).

Sivachandiran et al. reported that only about one-
third of the reacted NO₃ molecules were converted to NO₂ and therefore suggested that NO⁺ is further transformed into surface-NO₂⁻ and subsequently surface-NO₃ as

\[ 2\text{NO}_2(ads) \rightarrow \text{NO}_3^- + \text{NO}^+(ads) \]  

\[ \text{NO}^+(ads) + \text{O}^{2-}(surf) \rightarrow \text{s-NO}_2^- \]  

\[ \text{s-NO}_2^- + \text{NO}_2(ads) \rightarrow \text{s-NO}_3^- + \text{NO(gas)} \]  

\[ 3\text{NO}_2(ads) + \text{O}^{2-}(surf) \rightarrow \text{NO}_3(ads) + \text{s-NO}_3^- + \text{NO(gas)} \]

where the overall reaction process is summarized in reaction 6. The same authors later suggested that s-NO₃ transforms into freely adsorbed NO₃⁻ through creation of an oxygen vacancy, which eventually would lead to the formation of two NO₃⁻ species that bind in either monodentate or bidentate configurations. This was suggested to explain the appearance of two TPD peaks, which were measured at 177 °C and T > 307 °C, since these adsorbates were expected to desorb at different temperatures. According to our calculations, the different binding energies of monodentate and bidentate NO₃⁻ can not, however, explain this large temperature difference (see Figure S1 in the Supporting Information). Instead, we here propose that bidentate NO₃⁻ coordinated to Ti⁴⁺ sites is formed together with s-NO₃⁻ by a different disproportionation reaction (reaction 7) by direct interaction of NO₂ with lattice O²⁻ ions and that NO₂ subsequently reacts with NO⁺ as follows (see Figure 3b):

\[ 2\text{NO}_2(ads) + \text{O}^{2-}(surf) \rightarrow \text{s-NO}_3^- + \text{NO}_2^-(ads) \]  

\[ 2\text{NO}_2(ads) \rightarrow \text{NO}_3^- (ads) + \text{NO}^+(ads) \]  

\[ \text{NO}_2^-(ads) + \text{NO}^+(ads) \rightarrow \text{NO}_3(ads) + \text{NO(gas)} \]  

\[ 3\text{NO}_2(ads) + \text{O}^{2-}(surf) \rightarrow \text{NO}_3^- (ads) + \text{s-NO}_3^- + \text{NO(gas)} \]

Reaction 7 has previously been suggested by Mikhaylov et al., who argued that it would occur spontaneously on TiO₂ during adsorption of NO₂. Since this process should be facilitated by the presence of photoexcited charges (discussed further below), it is likely that it would be enhanced by UV illumination. We argue, however, that it is reasonable to assume that the formation of NO₃⁻ and NO also could occur by a more direct disproportionation reaction, where an oxygen atom is transferred from NO₂ to NO₃⁻ as follows:

\[ 2\text{NO}_2(ads) + \text{O}^{2-}(surf) \rightarrow \text{s-NO}_3^- + \text{NO}_2^-(ads) \]  

\[ \text{NO}_2^-(ads) + \text{NO}_2(ads) \rightarrow \text{NO}_3^- (ads) + \text{NO(gas)} \]  

\[ 3\text{NO}_2(ads) + \text{O}^{2-}(surf) \rightarrow \text{NO}_3^- (ads) + \text{s-NO}_3^- + \text{NO(gas)} \]

Reaction 13 (or 10) yields the same 3:1 NO₂:NO stoichiometry as the proposed reaction of NO₂ with surface OH groups on hydroxylated TiO₂ particles. Importantly, however, the reaction with the surface O²⁻ anion (reaction 11 (or 7)), critically affects the nitrate—nitrate interaction. Figure 3b illustrates reactions 11 and 13, where two NO₂ molecules initially bond to the TiO₂ surface and form s-NO₃⁻ and NO₂⁻ and where a third NO₂ molecule subsequently oxidizes the NO₂⁻ adsorbate into NO₃⁻ and is thereby converted to NO. The resulting s-NO₃⁻ and NO₃⁻ nitrate species stabilize each other by acting as electron donors and electron acceptors, respectively, and the same is true for the initially adsorbed NO₂ molecules. As we show below, this becomes evident when studying the surface—NO₃⁻ and NO₂⁻ adsorbates individually on the clean TiO₂ surface.

Figure 4 summarizes the results for the most favorable configurations on the (001) and (101) anatase surfaces at different adsorbate coverages. Upon adsorption and conversion of HNO₃ into s-NO₃⁻ and OH⁻ the terminal OH⁻ captures an electron and thereby provides a hole that stabilizes s-NO₃⁻ (reaction 2a).

Conversely, the hydrogen can act as an electron donor (eqs 1a and 1b). Similarly, we find that neighboring s-NO₃⁻ and NO₃⁻ nitrate dimers stabilize each other when placed close to each other on adjacent rows to minimize repulsive O—O interactions originating from the nitrate adsorbates (Figure 4b). It is not possible to place the nitrate species sufficiently close on the same row, since this leads to a large increase in repulsive O—O interactions. For the same reason, the nitrate adsorption energy increases (becomes less negative) when the coverage increases (Figure 4c). A distinct difference can be found for the (001) and (101) surfaces, however. While particularly stable dimer configurations can be found on the (001) surface at low coverage, similar stable configurations cannot be accommodated on the (101) surface. This is explained by the larger distance between s-NO₃⁻ and NO₃⁻ nitrate dimers when they are placed on adjacent rows on the (101) surface, which is dictated by the (101) surface crystal structure. Instead, Eads is rather insensitive to coverage on the (101) surface and even slightly decreases (becomes more negative) up to about 0.5 ML on the (101) surface. Note that what we here define as 1 ML also includes compressed nitrate structures that bind in less favorable configurations and in the experiments give rise to the low-temperature TPD peak. In contrast, according to DFT calculations, what can be defined as full coverage of a well-ordered and stable nitrate structure occurs at 0.5 ML.

Concluding that indirect substrate-mediated charge redistribution governs nitrate adsorption, we can now understand the enhanced photoadsorption of nitrates seen in Figure 1. On the clean TiO₂ surface, a hole can be created by removing an electron from the system, which increases the stability of the s-NO₃⁻ structure, making the adsorption strongly exothermic (see charge redistribution for the TiO₂(001) adsorption system in Figure S3 in the Supporting Information).

Similarly, the NO₂⁻ adsorption energy is more than 10 times higher on the clean TiO₂(001) surface when an electron has been added to the system. The same trend is found on the (101) surface. In particular, Eads decreases for s-NO₃⁻ from being endothermic to exothermic, from +0.31 to −1.96 eV on (101) when adding a hole, and from −0.16 to −2.28 eV on (001). Eads for NO₂⁻ decreases from −0.2 to −1.54 eV on (101) when adding an electron and from −0.15 to −1.75 eV on (001). We note here the difference between HNO₃ adsorption and oxidation of NO₂. For NO₂ adsorption and oxidation, NO₂⁻ must be stabilized to enable formation of NO₃⁻. In contrast, when NO₂⁻ is formed by dissociative adsorption of HNO₃, it is stabilized by the hydrogen atom (eqs 1a and 1b). NO₂ oxidation thus mimics the situation during UV illumination, when excited electron—hole (e−−h⁺) pairs...
are created through interband absorption in TiO$_2$. It therefore seems plausible that the pathway depicted in Figure 3b, reactions 11-13, can explain both the oxidation and photo-oxidation of NO$_2$ on TiO$_2$ and that the presence of photoexcited charges facilitates the initial adsorption process. This is what was seen in the inset of Figure 1a in the dramatic enhancement of nitrate formation during photoadsorption and can be explained by the enhanced NO$_3^-$ adsorption shown as the intermediate step in Figure 3b.

### 4.4. Desorption of Nitrate Species

The main desorption peak at around 430 °C is associated with the disappearance of the distinct IR bands at 1612, 1585, and 1249 cm$^{-1}$, which can be associated with s-NO$_3^-$ and NO$_3^-$ species on TiO$_2$(001) based on their calculated frequencies and adsorption energies (Table 1). The NO$_3^-$ ion is unlikely to desorb as a neutral species, and it is reasonable to expect a recombination desorption, i.e., a second-order desorption process, of the dimer-like NO$_3^-$ and -NO$_3^-$ products, since they stabilize each other. In Figure 3b, the stabilization of two nitrate species occurs spontaneously by a concerted mechanism whereby an electron from s-NO$_3^-$ is transferred to a neighboring NO$_3^-$ through the TiO$_2$ slab (see Figure S3b in the Supporting Information). This indirect, substrate-mediated NO$_3^-$ and s-NO$_3^-$ interaction can be viewed as a net adsorbate--adsorbate attraction and could explain why the high-temperature TPD peak is shifted to higher temperatures for photo-oxidized NO$_2$ and HNO$_3$ in comparison to thermally oxidized NO$_2$, which has a lower coverage in our experiments (Figure 1a, inset). The desorption can occur in several ways: for instance, by decomposition of NO$_3^-$ to NO$_2$(g) and Tl$^{4+}$=O$^-$(ads). Another possibility, promoted by the nitrate stabilization found in this work, could be a combination of NO$_3^-$ and s-NO$_3^-$ into a neutral N$_2$O$_5$ molecule (dissociates into NO$_3^-$ in the mass spectrometer), a reaction analogous to N$_2$O$_3$ formation on aerosols. Another possibility is that a neutral NO$_3^-$ molecule desorbs from s-NO$_3^-$, such that the remaining hole stimulates the simultaneous recombination of two NO$_3^-$ into an N$_2$O$_5$ and a surface adatom. Other possibilities to compensate for the charge neutralization in the system upon nitrate desorption could also involve hydroxyls, not only for the nitrate-covered surfaces obtained from adsorption of HNO$_3$ to photo-oxidized NO$_2$ and thermally oxidized NO$_2$, which again indicates that adsorbate--adsorbate interactions are important. In contrast to the indirect substrate-mediated dimer stabilization mechanism governing the 430 °C desorption, the low-temperature desorption can be explained by the electrostatic repulsion between neighboring nitrates, which destabilizes the adsorbates at increasing surface coverage. Figure S4 depicts the calculated desorption temperature for different nitrate configurations, explicitly showing that they are destabilized if they are placed on the same row where repulsive O=O interaction occurs, mimicking a kinetically “frozen” high coverage surface. The same behavior is seen in Figure 4c, where the adsorption energy rapidly decreases (becomes less negative) as the coverage increases from 0.5 to 1 ML on the (101) surface. Above 200 °C the loss of IR absorption peaks at around 1500 and 1300 cm$^{-1}$ is due to desorption of nitrate from (101) surface facets. First, we note that the nitrate species do not exhibit the same pronounced (indirect) attractive interaction on the (101) surface (Figure 4b) and thus bond much more weakly. Our calculations indicate that s-NO$_3^-$ on the (101) surface adsorbs in unfavorable configurations at 1 ML and that this significantly influences the calculated vibrational frequencies. This is manifested in the calculated vibrational frequencies at different nitrate coverage in Table 1, where it is seen that the vibrational modes on the (101) surface are very sensitive to the local environment (configuration and coverage) but occurs in the same range as those that disappear above 200 °C. We therefore attribute the decrease at around 1500 and 1300 cm$^{-1}$ to loss of nitrate on (101), and “kinetically” restricted nitrate structures on both facets, yielding N$_2$O$_3$ desorption, such as those shown in Figure S4.

### 5. CONCLUSIONS

We have shown that identical surface products are obtained from the catalytic and photocatalytic oxidation of NO$_2$ on TiO$_2$ and that these are identical with the surface nitrates obtained after adsorption of HNO$_3$. By combining in situ DRIFTS and TPD experiments with DFT calculations, the nitrate species have been identified as a combination of a terminal OH group and NO$_3^-$ ions. These stabilize each other by donating charge in opposite directions, and they are also strongly influenced by the surface chemical environment. The charge compensation mechanism responsible for the formation of stable nitrate dimers also explains the enhanced nitrate formation rate upon band-gap illumination, where the photogenerated charges stabilize the intermediate NO$_3^-$ adsorbates. The formation of surface--NO$_3^-$ was found to occur by a concerted reorientation of the bidentate nitrate and concomitant movement of the neighboring protonated lattice oxygen to form a terminal OH group, which may be a generally relevant mechanism at low NO$_2$ or HNO$_3$ coverages for a larger class of metal oxide systems. In most practical applications, but also under vacuum, adsorbed oxygen at the surface readily becomes protonated in the presence of H(ads) species at the surface, leading to the formation of OH(ads) species. Thus, our results strongly suggest that the most likely species which mediate the transfer of oxygen from/to lattice positions in the surface are those considered in the paper, namely the various NOx species and OH groups, even in excess oxygen.

Our findings are important for the development of TiO$_2$ as an atmospheric deNOxification catalyst, especially since...
surface nitrate has been shown to be further transformed into the more harmful gases HONO and N₂O during continued UV illumination. Given the general nature of the proposed reaction pathways, we believe that the presented results could be of value for continued investigations of similar surface reactions on wider classes of metal oxide particles.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.2c03334.

Calculated bonding configurations, calculated adsorption energies, reaction pathway for the monodentate to bidentate transformation of the nitrate species, recombining desorption temperatures of monodentate and bidentate NO₃ on the TiO₂(001) surface, calculated spin-polarized charge density during bonding of NO₂ and NO, together with NO, on the TiO₂(001) surface, and calculated desorption temperature for N₂O₃ from NO₃ and s-NO₃ (PDF)

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