Chemical and photochemical reactions on mineral oxide surfaces in gaseous and liquid phases: environmental implications of fate, transport and climatic impacts of mineral dust aerosol

Gayan Randika S. Rubasinghe

University of Iowa

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CHEMICAL AND PHOTOCHEMICAL REACTIONS ON MINERAL OXIDE SURFACES IN GASEOUS AND LIQUID PHASES: ENVIRONMENTAL IMPLICATIONS OF FATE, TRANSPORT AND CLIMATIC IMPACTS OF MINERAL DUST AEROSOL

by

Gayan Randika S Rubasinghe

An Abstract

Of a thesis submitted in partial fulfillment of the requirements for the Doctor of Philosophy degree in Chemistry in the Graduate College of The University of Iowa

July 2011

Thesis Supervisors: Professor Vicki H. Grassian
ABSTRACT

Mineral dust aerosols emitted from the Earth crust during various natural and anthropogenic processes continuously alter the chemical balance of the atmosphere via heterogeneous processes and thus, impact on the global climate. Understanding of heterogeneous chemistry and photochemistry on mineral dust has become vital to accurately predict the effect of mineral dust loading on the Earth’s atmosphere. Here, laboratory measurements are coupled with model studies to understand heterogeneous chemistry and photochemistry in the atmosphere with the specific focus on reactions on mineral oxide surfaces.

Heterogeneous uptake of gas phase HNO$_3$ on metal oxides, oxyhydroxides and carbonates emphasized binding of nitric acid to these mineral surfaces in different modes including monodentate, bidentate and bridging under dry conditions. It is becoming increasingly clear that the heterogeneous chemistry, including uptake of HNO$_3$, is a function of relative humidity (RH) as water on the surface of these particles can enhance or inhibit its reactivity depending on the reaction. All the studied model systems showed a significant uptake of water with the highest uptake by CaCO$_3$. Under humid conditions, two water solvated nitrate coordination modes were observed that is inner-sphere and outer-sphere, which differ by nitrate proximity to the surface.

Photochemical conversion of nitric acid to gas phase N$_2$O, NO and NO$_2$ through an adsorbed nitrate intermediate under different atmospherically relevant conditions is shown using transmittance FTIR and XPS analysis. Photochemistry of adsorbed nitrate on mineral aerosol dust may be influenced by the presence of other distinct gases. This thesis converses formation of active nitrogen, NO$_x$ and N$_2$O, and chlorine, ClO$_x$, species
in the presence of co-adsorbed trace gases that could potentially regulate the peak concentration and geographical distribution of atmospheric ozone. Here we report formation of atmospheric N$_2$O, from the photodecomposition of adsorbed nitrate in the presence of co-adsorbed NH$_3$ via an abiotic mechanism that is favorable in the presence of light, relative humidity and a surface. Estimated annual production of N$_2$O over the continental United States from this new reaction pathway is ~5% of total U.S. anthropogenic N$_2$O emissions. Not only NH$_3$ but also gaseous HCl react with adsorbed nitrate to activate “inert” N and Cl reservoir species through adsorbed nitrate under different atmospherically relevant conditions.

Mineral dust aerosol is a major source of bioavailable iron to the ocean with an annual deposition of ~ 450 Tg of dust into the open ocean waters. In this study, we report enhanced Fe dissolution from nano scale Fe-containing minerals, i.e. α-FeOOH, beyond the surface area effects. We further report with clear evidence that aggregation impacts on dissolution. Proton-promoted dissolution of nanorods is nearly or completely quenched in the aggregated state. Acid type, oxyanions and light are several other key factors responsible for regulating for iron dissolution. The work reported in this thesis provides insight into the heterogeneous chemistry and photochemistry of mineral dust aerosol under different atmospherically relevant conditions.
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Thesis Supervisors: Professor Vicki H. Grassian
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Gayan Randika S Rubasinghege

has been approved by the Examining Committee
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Gregory R. Carmichael
To my wife, Achala De Silva,
who has been by my side every giant step
I have made in my life
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ABSTRACT

Mineral dust aerosols emitted from the Earth crust during various natural and anthropogenic processes continuously alter the chemical balance of the atmosphere via heterogeneous processes and thus, impact on the global climate. Understanding of heterogeneous chemistry and photochemistry on mineral dust has become vital to accurately predict the effect of mineral dust loading on the Earth’s atmosphere. Here, laboratory measurements are coupled with model studies to understand heterogeneous chemistry and photochemistry in the atmosphere with the specific focus on reactions on mineral oxide surfaces.

Heterogeneous uptake of gas phase HNO$_3$ on well characterized metal oxides, oxyhydroxides and carbonates emphasized binding of nitric acid to these surfaces in different modes including monodentate, bidentate and bridging under dry conditions. It is becoming increasingly clear that the heterogeneous chemistry, including uptake of HNO$_3$, is a function of relative humidity (RH) as water on the surface of these particles can enhance or inhibit its reactivity depending on the reaction. All the studied model systems showed a significant uptake of water with the highest uptake by CaCO$_3$. Quantitative analysis of water uptake indicated formation of multilayers of water over these reactive surfaces. Under humid conditions, two water solvated nitrate coordination modes were observed that is inner-sphere and outer-sphere, which differ by nitrate proximity to the surface.

Photochemical conversion of nitric acid to gas phase nitrous oxide, nitric oxide and nitrogen dioxide through an adsorbed nitrate intermediate under different atmospherically relevant conditions is shown using transmittance FTIR and XPS
analysis. The relative ratio and product yields of these gas phase products change with relative humidity. Photochemistry of adsorbed nitrate on mineral aerosol dust may be influenced by the presence of other distinct gases in the atmosphere making it complicated to understand. This thesis converses formation of active nitrogen, NO\textsubscript{x} and N\textsubscript{2}O, and chlorine, ClO\textsubscript{x}, species in the presence of co-adsorbed trace gases, that could potentially regulate the peak concentration and geographical distribution of atmospheric ozone. Here we report formation of atmospheric N\textsubscript{2}O, from the photodecomposition of adsorbed nitrate in the presence of co-adsorbed NH\textsubscript{3} via an abiotic mechanism that is favorable in the presence of light, relative humidity and a surface. Estimated annual production of N\textsubscript{2}O over the continental United States is 9.3\textsuperscript{+0.7/-5.3} Gg N\textsubscript{2}O, ~5\% of total U.S. anthropogenic N\textsubscript{2}O emissions. Not only NH\textsubscript{3} but also gaseous HCl react with adsorbed nitrate to activate “inert” N and Cl reservoir species, yielding NOCl, NO\textsubscript{x}, Cl and Cl\textsubscript{2}, through adsorbed nitrate under different atmospherically relevant conditions.

Mineral dust aerosol is a major source of bioavailable iron to the ocean with an annual deposition of ~ 450 Tg of dust into the open ocean waters. In this study, we report enhanced Fe dissolution from nano scale Fe-containing minerals, i.e. \alpha-FeOOH, beyond the surface area effects that can be attributed to the presence of more reactive sites on specific crystal planes exposed. We further report with clear evidence that aggregation impacts on dissolution. Proton-promoted dissolution of nanorods is nearly or completely quenched in the aggregated state. Acid type, presence of oxyanions and light are several other key factors responsible for regulating for iron dissolution. The work reported in this thesis provides insight into the heterogeneous chemistry and photochemistry of mineral dust aerosol under different atmospherically relevant conditions.
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CHAPTER 1
INTRODUCTION

The atmosphere is an important part of what makes Earth livable. The quality of the air that living organisms breathe, the nature and level of pollutants, visibility and atmospheric esthetics, and even climate are dependent upon chemical phenomena that occur in the atmosphere. However, it has long been assumed that the Earth’s atmosphere, mainly composed of nitrogen (N₂), 78%, oxygen (O₂), 21%, and several noble gases of fixed concentrations, is a large unchangeable reservoir. This long held view was first cast into doubt in 1952 with London experiencing an extended period of incredibly high particulate levels, now referred to as London Smog. The particulate concentrations, 5-19 times greater than modern regulatory standards, led to the deaths of more than 4000 people during the two week episode and over 12,000 in the 3 months following.¹⁻³ Several decades later, the recurrent phenomenon of the ozone hole due to polar stratospheric ozone losses finally shattered the earlier view of fixed atmosphere and highlighted the importance of trace gases and aerosol particles those are often have highly variable concentrations.⁴

The many trace gases and aerosols that reside throughout the atmosphere are continuously altered by chemical, physical and dynamic processes. Thus, the atmosphere serves as a giant gaseous reaction chamber encircling the Earth. These gases and aerosols are more concentrated near the surface. For example, approximately 60% of the mass of the atmosphere resides below the summit of Mount Everest, and 99% below 30 km altitude.⁵ The work reported in this thesis focuses on the regions of the Earth’s
atmosphere below 30 km, which have the strongest influence on life, including the troposphere and stratosphere. The troposphere is the lowermost layer of the atmosphere and extends from the surface up to 10 to 17 km, depending on season and latitude.

Figure 1.1 Schematic of the major processes contributing to atmospheric aerosols. This figure shows examples of the natural and anthropogenic processes producing gases and particles in the atmosphere. Subsequent processes can transform and age these particles as they are transported through the atmosphere. Adapted from ref. 7.
1.1 Atmospheric Aerosol

The term “atmospheric aerosols” encompasses a wide range of particles having different compositions, sizes, shapes and optical properties depending on their origin and subsequent atmospheric processing. Atmospheric particles are generally divided according to their sources. Figure 1.1, which has been adapted from Prather et al., is a schematic of the major processes contributing to atmospheric aerosols. A large fraction of primary aerosols is natural in origin, including wind-driven processes such as the resuspension of dust, sea salt and volcanic ash. Conversely, human induced emissions, i.e., coal combustion, biomass burning, and vehicle emissions, are having a significant effect on the atmosphere.

Table 1.1. Estimated annual emissions, lifetimes, mass loadings and optical depths of major aerosol types.

<table>
<thead>
<tr>
<th>Aerosol Type</th>
<th>Total Emission (Tg / Yr)</th>
<th>Lifetime (day)</th>
<th>Mass Loading (Tg)</th>
<th>Optical depth @ 550 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Median (Range)</td>
<td>Median (Range)</td>
<td>Median (Range)</td>
<td>Median (Range)</td>
</tr>
<tr>
<td>Sea Salt</td>
<td>6000 (2000 – 12000)</td>
<td>0.4 (0.03 – 1.1)</td>
<td>6 (3 – 13)</td>
<td>0.030</td>
</tr>
<tr>
<td>Dust</td>
<td>1600 (700 – 4000)</td>
<td>4.0 (1.3 – 7)</td>
<td>20 (5 – 30)</td>
<td>0.032</td>
</tr>
<tr>
<td>POM</td>
<td>100 (50 – 140)</td>
<td>6.2 (4.3 – 11)</td>
<td>1.8 (0.5 – 2.6)</td>
<td>0.019</td>
</tr>
<tr>
<td>BC</td>
<td>11 (8 – 20)</td>
<td>6.5 (5.3 – 15)</td>
<td>0.2 (0.05 – 0.5)</td>
<td>0.004</td>
</tr>
<tr>
<td>Sulfate</td>
<td>190 (100 – 230)</td>
<td>4.1 (2.6 – 5.4)</td>
<td>2.0 (0.9 – 2.7)</td>
<td>0.034</td>
</tr>
</tbody>
</table>


Note: Statistics are based on results from 16 models examined by Aerosol Comparisons between Observations and Models (AeroCom) project. POM = particulate organic matter; BC = black carbon; Sulfate = sulfate from SO2 oxidation.
Estimated total annual emission of aerosol particles or particulate matter in the atmosphere is on the order of 3000 to 8000 Tg.\(^1\) Aerosol loading, or the amount of it in the atmosphere, is usually quantified by mass concentration or by optical measure, aerosol optical depth (AOD).\(^2\) Table 1.1 represents estimated source strengths, lifetimes and amounts for major aerosol types, based on an aggregate of emission estimates and global model simulations. As seen in Figure 1.1, secondary aerosol particles are formed from chemical and photochemical reactions of gas phase species that are directly emitted into the atmosphere by forming new particles or condensing on existing particle surfaces.

1.1.1 Mineral Dust Aerosol

Mineral dust aerosol contributes to one of the largest mass fractions of total aerosol emissions as it has been estimated in Table 1.1 and by other researchers that between 1000 - 4000 Tg of these aerosols are emitted annually.\(^3-5\) Large dust events, in the form of windblown soils, originate from arid and semiarid regions, with the largest contribution from the “dust belt” that extends from North Africa, over Middle East and Central and South Asia, to China.\(^6\) Large-scale dust events are typically characterized by dust loadings of more than 500 $\mu$g/m\(^3\),\(^7\) visibility of less than a kilometer\(^8\) and particle sizes ranging from 0.01 to 40 $\mu$m in diameter.\(^9,10\) One would expect most of the Earth’s dust emissions to originate from desert regions. Although the exact amount is difficult to quantify, an estimated 20% to 50% of global dust emissions are believed to be anthropogenic in origin.\(^11,12\) It is expected that the annual dust loading will continue to increase due to the fact that arid and semiarid regions of the globe expand with escalating levels of deforestation, land usage, and wind erosion. For an example, approximately
15% of the land in China is occupied by deserts but human activities have expanded these deserts at an estimated rate of 1560 km\(^2\)/year.\(^{23}\) As a result of this on-going desertification, mineral aerosol at Barbados has shown a two to four fold increase since the late 1960’s.\(^{24}\)

As seen in Table 1.1, these dust particles have a life time of days to weeks, with larger particles being removed rather quickly through gravitational settling, and submicron dust particles potentially remaining in the atmosphere up to several weeks, allowing them to be transport globally.\(^{25,26}\) As discuss in Zhang et al.,\(^{27}\) 30% of dust emissions from Chinese deserts are believed to be re-deposited into the deserts while 20% may be transported over regional scales and the remaining dust emissions, 50%, may be transported long distances over the Pacific Ocean and can even reach Canada and the western coast of the United States.\(^{26,28-30}\) Although the current sources, emissions and concentrations of mineral dust aerosol are well documented, many of the effects of mineral aerosol in the atmosphere remain unclear.\(^{31}\)

1.1.2 Mineralogy of Dust Aerosol

The composition of mineral dust aerosol is extremely diverse and the exact mineralogy depends on the source region. In general, mineral dust is comprised largely of crustal species including quartz, mica, metal oxides, carbonates (calcite and dolomite), sulfates (gypsum) and clay minerals, with the dust being a complex mixture of particles and particle aggregates.\(^{32-36}\) Thus, reactivity is expected to vary based on the chemical composition and physical properties of individual minerals.\(^{37}\) Oxide minerals represent an important and reactive component of mineral dust aerosol. According to the elemental
compositions of four authentic dust samples given in Table 1.2, iron and aluminum (or their oxides) represent a major fraction of the reactive component of mineral dust.

Table 1.2  Average chemical composition of mineral dust particles from four source regions.

<table>
<thead>
<tr>
<th>Element</th>
<th>China Loess</th>
<th>Saharan Sand</th>
<th>Inland Saudi Arabian Sand</th>
<th>Coastal Saudi Arabian Sand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>46</td>
<td>69</td>
<td>53</td>
<td>31</td>
</tr>
<tr>
<td>Ca</td>
<td>17</td>
<td>2</td>
<td>3</td>
<td>39</td>
</tr>
<tr>
<td>Al</td>
<td>17</td>
<td>15</td>
<td>22</td>
<td>7</td>
</tr>
<tr>
<td>Fe</td>
<td>7</td>
<td>5</td>
<td>9</td>
<td>3</td>
</tr>
<tr>
<td>Mg</td>
<td>6</td>
<td>3</td>
<td>7</td>
<td>13</td>
</tr>
<tr>
<td>K</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>Na</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>


Iron oxides are a significant fraction of the Earth’s crust and, as such, a major component of mineral dust aerosol in the atmosphere, contributing 6 – 9% by mass in clay aggregates.\(^{38, 39}\) Recent studies demonstrated that iron oxides in mineral aerosols occur as hematite (\(\alpha-\text{Fe}_2\text{O}_3\)), goethite (\(\alpha-\text{FeOOH}\)) and maghemite (\(\gamma-\text{Fe}_2\text{O}_3\)) which are transferred into the atmosphere as a result of wind and volcanic activity.\(^{39}\) In addition, these are introduced to the atmosphere as fly ash from power plants, combustion exhaust,
and from industrial operations. Aluminum and aluminum silicates contribute ~8% by mass to the total dust burden in the atmosphere. The most common form of crystalline aluminium oxide, also known as alumina, is corundum that is the alpha phase of Al_2O_3. In terms of its crystallography, corundum adopts a trigonal Bravais lattice with a space group of R-3c. Alumina also exists in other phases, namely $\gamma$-, $\delta$-, $\eta$-, $\theta$-, and $\chi$-alumina.$^{40}$ Each has a unique crystal structure and properties.

Metal oxides mixed with clay minerals are most likely to be transported long distances due to the fact that they are generally the smaller component of terrestrial soil, with grain sizes of less than 2 $\mu$m in diameter. Given that alumina and iron oxides can actively participate in chemical and photochemical reactions during the atmospheric transport, the studies reported in this thesis focus on understanding various aspects of reactions between atmospheric gases and mineral dust aerosols using above metal oxides as proxies for mineral aerosols.

1.2 Climatic Impacts of Mineral Dust Aerosols

Mineral aerosols have significant effects on climate by impacting both the global radiative energy budget and the chemical balance of the atmosphere via several mechanisms.$^{41}$ (a) scattering and absorbing solar radiation; (b) scattering, absorbing and emitting thermal radiation; and (c) acting as a cloud condensation nuclei.$^{42-44}$ The first two mechanisms are called the “direct climatic effects” and relate to the optical properties of particles based on their size, shape and chemistry. The third mechanism is called the “indirect climatic effect”. If the incoming solar radiation is absorbed or scattered before reaching the Earth, it will have a negative radiative effect. Conversely, outgoing long-
wavelength radiation from the Earth can be absorbed by particulate matter and a positive effect on the radiation budget. Figure 1.2(a) displays current estimates and uncertainty ranges of radiative forcing from natural and anthropogenic sources in 2005 relative to the pre-industrial climate.\textsuperscript{45} Greenhouse gases, such as water (H\textsubscript{2}O), carbon dioxide (CO\textsubscript{2}), methane (CH\textsubscript{4}), O\textsubscript{3} and dinitrogen oxide (N\textsubscript{2}O), absorb terrestrial infrared (IR) radiation followed by re-radiation back to the Earth’s surface, resulting in global warming. In contrast, aerosol influences are not yet quantified adequately as scientific understanding is designated as “Medium – Low” and “Low” for direct and indirect climatic forcing, respectively.\textsuperscript{41, 46, 47} Moreover, the IPCC AR4 report (2007) concluded that uncertainties associated with changes in earth’s radiation budget due to anthropogenic aerosols make the largest contribution to the overall uncertainty in radiative forcing of climate changes among the factors assessed over the industrial period (Figure 1.2(b)).

Mineral dust aerosols have shown a significant impact on the chemical balance of the atmosphere due to the fact that aerosols have been found to act as reaction sites and carriers for many condensed and adsorbed species. For an instance, it has been shown that the majority of reactions involving the conversion of SO\textsubscript{2} to SO\textsubscript{4}\textsuperscript{2-} occur on the surface of the aerosol particle. In addition, it has been observed that variations in gas phase concentrations of nitrogen oxide species, ozone and hydroxyl radicals with varying mineral dust loadings in the atmosphere.\textsuperscript{48} Therefore interactions between trace gases and mineral dust particle surfaces not only may led to change the gas phase compositions in the atmosphere, but also may lead to the modification of the optical constants and thermodynamic properties of the surface, that in turn may affect the radiative balance, leading to climatic forcing.
Figure 1.2  Radiative forcing (RF) of climate between 1750 and 2005.

(a) Global average RF estimates and uncertainty ranges in 2005, relative to the pre-industrial climate. Typical geographical extent of the forcing (spatial scale) and the assessed level of scientific understanding (LOSU) are also given.

(b) Probability distribution functions for anthropogenic and greenhouse gas RFs. Adapted from IPCC 2007 (ref. 45).
Biogeochemical cycles are also impacted by mineral dust aerosols. For an example, surface chemistry and photochemistry of iron oxides under ambient conditions plays a crucial role in a number of environmental processes, such as the role of hematite, $\alpha$-Fe$_2$O$_3$, which is present in the atmosphere and is also an important nutrient source for ocean life. In the atmosphere, the reactions between Fe-containing mineral dust aerosols and pollutant gases have been identified as an important mechanism for increasing the amount of bioavailable iron through the reduction of Fe(III) to Fe(II). This process is proposed to occur in a thin aqueous layer coating the iron oxide surface. Therefore as environmental interfaces, thin film of water adsorbed on iron oxide and other oxide surfaces, will play an important role in the chemistry and the adsorption of molecules on oxide surfaces under ambient conditions of pressure and relative humidity.

1.3 Heterogeneous Chemistry and Photochemistry on Mineral Dust

Landmark studies by Solomon and others attributed the formation of the ozone hole to heterogeneous chemistry occurring between trace gases and small ice particulates, or polar stratospheric clouds, as we call it today. Prior to this realization, atmospheric studies had mainly focused on understanding the homogeneous chemistry of the atmosphere. With the beginning of failing to explain the atmospheric processes using atmospheric models, included only homogeneous chemistry, there was an increased push to study heterogeneous interactions in the atmosphere. Today, convincing evidence from field, laboratory, and modeling has shown that heterogeneous reactions with mineral dust alter the chemical composition of the atmosphere, especially the lower troposphere. Conversely, during these atmospheric processes, the physiochemical properties of the
dust particle, especially the surface properties, are subjected to change that may have a significant impact on the surface chemistry.\textsuperscript{57}

Figure 1.3 Cartoon representation of the life cycle of dusts represented in terms of emissions, long-range transport of dust where important yet in some cases poorly understood chemical and physical processes occur and subsequent deposition into aquatic and terrestrial ecosystems. These “aged” dust particles can then undergo deposition into aqueous and terrestrial ecosystems with very different physicochemical properties than the freshly emitted particles. Adapted from ref. 57.

Figure 1.3 shows a cartoon drawing of the life cycle of an atmospheric dust particle, adopted from Rubasinghege et al.,\textsuperscript{58} in terms of emission, transport, and deposition into aqueous and terrestrial ecosystems as a modified “aged” dust particle. The focus here is on the important yet sometimes poorly understood physical and chemical heterogeneous processes, especially the involvement of sun. Laboratory studies on the heterogeneous chemistry of mineral dust aerosol in the past 10 years have focused mainly on the night time chemistry of the dust.\textsuperscript{56} This can in some ways be regarded as being representative of only “half” the story. Short wavelengths (< 290 nm) radiation is
absorbed in the stratosphere and upper troposphere, but a significant solar actinic flux reaches the Earth’s surface. The actinic flux in the troposphere in the UV region, 300 – 400 nm, is on the order of 1013 quanta cm$^{-2}$ s$^{-1}$. Photon energies in this region (300 – 400 kJ/mol) are sufficient to initiate a number of direct photochemical processes involving adsorbates on the dust particle surface. Given that photochemistry dominates the day time gas phase chemistry of the atmosphere, and new light induced pathways continue to be discovered, along with the realization that the surface and near surface regions of particles catalyze and promote reactions that perturb the composition of the troposphere, one can pose the question, “what is the role of heterogeneous photochemistry in the troposphere? and, furthermore, how does the day time chemistry of mineral dust aerosol differ from night time chemistry?” Although these solar initiated reactions may be of significance in the atmosphere, little is known about photochemical reactions involving mineral dust aerosol.

1.4 Reactivity of Nitric Acid with Mineral Dust Aerosol

In this thesis, the focus will be the chemical and photochemical reactivity of nitric acid, HNO$_3$, with the metal oxide surfaces, in the presence and absence of co-adsorbed water, and different other co-adsorbed species, including HCl and NH$_3$. The nitrogen oxides are of great interest in the Earth’s troposphere due to their relationship to O$_3$ concentrations and thus the greenhouse effect. These nitrogen species are released into the atmosphere mainly in the form of NO, which is then readily oxidized to NO$_2$, and those are collectively known as NO$_x$ (NO + NO$_2$). The principle sources of NO$_x$ are biomass burning and fossil fuel combustion from vehicles, which results in approximately half of the global concentration. A summary of several important
reactions involving nitrogen oxides is provided in Figure 1.4, which is adapted from Schuttlefield et al.\textsuperscript{62}

![Figure 1.4](image)

Figure 1.4  Schematic of a reaction scheme of important gas phase chemistry and photochemistry involving nitrogen oxides in the troposphere. Potential heterogeneous reactions on mineral dust surfaces are shown by dashed lines. Adapted from ref. 61.

\( \text{NO}_x \) reacts catalytically to produce ozone and OH radicals, the main tropospheric oxidant, and is removed from the atmosphere through conversion to nitric acid. The well-
known sinks of atmospheric nitric acid is wet and dry deposition that leaves an atmospheric mixing ratio of HNO₃ ~ 10 ppbv. But, in polluted areas this value can be substantially higher. Often the ratio of HNO₃ to NOₓ is over predicted in modeling studies by a factor of ~ 5 to 10, which is thought to be largely due to over prediction of the HNO₃ concentration used in the models that results from a reaction pathway that has been unaccounted for.

In the atmosphere, nitrogen oxides readily react with particulate matter (e.g. mineral dust and sea salt aerosol) to yield adsorbed nitrate. Valuable information regarding the chemical speciation, as the coordination of products adsorbed on the surface, has been obtained using FTIR spectroscopy. Several surface species have been proposed following the adsorption of nitrogen oxides on metal oxide surfaces which include nitrate (NO₃⁻), nitrite (NO₂⁻) and nitrosyl (NO⁺). In this thesis, transmission FTIR spectroscopy is combined with collaborative quantum chemical calculations to further the understanding of nitrate adsorbed on metal oxide surfaces in the presence and absence of several co-adsorbed species, including water, chloride and ammonia.

For decades, it was thought that nitrate is the end product of NOₓ oxidation, with removal via wet and dry deposition. However, with the observation of active photochemistry of nitrate in snow packs, and the subsequent studies on the reactive oxides of nitrogen such as HONO, NO, and NO₂ generated in this process, particulate nitrate may, in fact, be a reservoir rather than a sink for gas phase nitrogen oxides in the atmosphere. It has been shown that in solution and in snow packs, nitrate ion can undergo the following reactions upon photolysis at 305 nm under acidic conditions.
\[
\text{NO}_3^- + H^+ \rightarrow \text{NO}_2 + \text{OH}^*
\] (1.1)

\[
\text{NO}_3^- \rightarrow \text{NO}_2^- + \text{O}(^3\text{P})
\] (1.2)

The nitrite ion formed in reaction (1.2) can then undergo further photolysis \((\lambda_{\text{max}} = 354 \text{ nm})\) to yield,

\[
\text{NO}_2^- + H^+ \rightarrow \text{NO} + \text{OH}^*
\] (1.3)

Not only are the nitrogen species that are formed reactive, but the resulting formation of OH radical and O\((^3\text{P})\) are both highly reactive in the gas and aqueous phase relevant to the atmosphere\(^{41, 85}\) Thus, in this thesis the potential changes in the photochemical activity of surface adsorbed nitrate on metal oxide surfaces, particularly on alumina surface, are discussed.

1.5 Water Uptake on Mineral Dust

A large fraction of the mineral dust particles contain hydrosopic components and thus their radiative influence tends to be a strong function of atmospheric water content, as measured by changes in relative humidity (RH). Under humid conditions, atmospheric water vapor readily adsorbs to dust particle and dissociates resulting a hydroxyl terminated on the dust particle surface\(^{86}\). Adsorbed water is then hydrogen bonded to these hydroxyl groups in equilibrium with water vapor forming a thin water layer over the particle surface which potentially modify the surface properties.

In the presence of surface adsorbed water, reactions with trace atmospheric gases can be both enhanced and inhibited\(^{87-89}\). For an example, the surface activity of atmospheric mineral dust China Loess changes its reactivity towards SO\(_2\) with changing relative humidity\(^{90, 91}\). Under dry conditions, China Loess mainly adsorbs SO\(_2\), but in the
presence of co-adsorbed water, under humid conditions, SO$_2$ hydrolysis leads to the formation of H$_2$SO$_3$. Furthermore, the kinetics of the heterogeneous hydrolysis of N$_2$O$_5$ was recently measured on quartz and the uptake coefficient was found to increase by a factor of four as the relative humidity increased.\textsuperscript{92} Similarly, Mashburn et al. reports that as the relative humidity increased the uptake coefficient and HNO$_3$ content all increased. Reaction rates were seen to increase by an order of magnitude or more at higher relative humidity compared to dry conditions.\textsuperscript{93} Moreover, it has been shown that co-adsorbed water molecules readily solvate adsorbed nitric acid species on the aluminum oxide surface forming inner and outer sphere complexes.\textsuperscript{94} According to all of the studies discussed above, relative humidity plays a significant role in the reactivity of mineral dust aerosol and its potential implications in the atmosphere. In this thesis, water uptake on mineral dust components will be quantified in order to fully understand its impact on surface chemistry and photochemistry of mineral dust aerosol.

1.6 Synopsis of Dissertation Chapters

The study of atmospheric chemistry includes three scientific approaches: (a) field measurements of aerosol particles; (b) laboratory studies focused on the behavior of the physiochemical properties of model systems representative of atmospheric aerosols; and (c) model analysis that including gas phase chemistry, photochemistry and heterogeneous chemistry, and optical properties so that models can be effectively predict important global climate impacts of mineral dust aerosols. Direct field measurements provide information about aerosol particles in the atmosphere including composition, size and concentration. In the laboratory, conditions can be carefully controlled to isolate specific
heterogeneous interactions and focus on well-defined experimental variables. The objective of this research was to aid understanding of heterogeneous chemistry and photochemistry in the troposphere with the specific focus on reactions on mineral oxide surfaces through laboratory measurements and selected atmospheric model studies.

Multiple experimental techniques were involved in the investigation of the reactions of trace atmospheric gases with selected mineral oxide surfaces, including alumina and iron oxides. These experimental methods include FT-IR spectroscopy, both transmission and attenuated total reflection (ATR)-FTIR spectroscopy, as well as the use of a quartz crystal microbalance, X-Ray Diffraction, and Scanning Electron Microscopy. In addition to these techniques, several other complementary collaborative techniques were used to help with characterization of samples. In some instances, the coupling of these techniques allowed for both qualitative and quantitative measurements. The experimental and theoretical methods that were used for the research discussed in this thesis are described in detail in Chapter 2.

Transmission and ATR-FTIR spectroscopy was used to investigate nitric acid adsorption in the presence and absence of co-adsorbed water, and water uptake and phase transitions as a function of relative humidity. The nitrate experiments were combined with quantum chemical calculations in a collaborate effort. The water adsorption experiments using ATR-FTIR spectroscopy were combined with a quartz crystal microbalance in order to quantitatively measure the amount of water taken up on atmospherically relevant insoluble particles as a function of relative humidity. Atmospheric modeling were combined with nitrate photochemistry, particularly in the presence of co-adsorbed ammonia experiments, in a collaborate effort. The coupling of
techniques will also be outlined in Chapter 2 and also where appropriate throughout the thesis.

In Chapter 3, bulk and surface properties of several types of mineral oxides, including $\alpha$-Fe$_2$O$_3$, $\alpha$-FeOOH, $\gamma$-Fe$_2$O$_3$ and $\gamma$-Al$_2$O$_3$, are characterized using a variety of techniques. For these well-characterized mineral oxides, data from transmission FTIR was used to investigate nitric acid. Previous literature data on nitric acid on mineral oxides will be reviewed. These data provided valuable information, in terms of understanding different chemisorption and physisorption modes of nitric acid on mineral oxide surfaces, kinetics, monolayer coverage and more. Measurements from transmission FTIR and ATR-FTIR spectroscopy coupled with quartz crystal microbalance (QCM) were quantified to investigate water uptake on mineral oxides as a function of relative humidity. Furthermore, phase transition of adsorbed nitric acid species as a function of relative humidity was investigated following the same techniques. Although nitric acid and water uptake is found to be variable and dependent on type of the mineral oxide, it is shown that nitric acid bind to the mineral oxide surfaces in different modes including monodentate, bidentate and bridging under dry conditions whereas under humid condition, solvation of adsorbed products is observed with the formation of inner and outer sphere complexes. These variations in nitric and water uptake and different binding modes of nitric acid will be explored with a discussion of atmospheric implications.

HNO$_3$ uptake on mineral dust has been conventionally thought of as a removal mechanism for nitrogen species in the atmosphere. However, this is not a complete picture of dust nitrate chemistry only part of the story. Therefore, in Chapter 4, we focus on potential reaction pathways and mechanisms to bring the adsorbed nitrate back to the
gas phase including photochemistry of adsorbed nitrate, under different relative humidity conditions. The photochemistry of adsorbed nitrate on dry alumina surfaces, a proxy for mineral dust, using broadband irradiation ($300 < \lambda < 700$ nm) and narrow band pass ($\lambda \sim 310$ nm) was studied in detail under different experimental conditions. Because the molecular and electronic structure of adsorbed nitrate changes in the presence of co-adsorbed water, the role of adsorbed water in the broadband photolysis of adsorbed nitrate on alumina surfaces was also examined. The photochemistry of adsorbed nitrate was monitored with transmission FTIR spectroscopy. The experimental results showed that adsorbed nitrate readily undergoes photochemical reaction to yield several nitrogen-containing gas phase and surface-bound products and that co-adsorbed water changes both the initial photolysis rate and the gas phase product distribution.

In Chapter 5, the focus is on understanding the effect of co-adsorbed gas phase ammonia, NH$_3$, on photochemistry of adsorbed nitrate. From previous studies, it was known that ammonium nitrate, NH$_4$NO$_3$, is formed from reactions involving nitrogen oxides and ammonia. NH$_4$NO$_3$ is also a common component of ambient particles that is transported across the globe. Besides, 41.8 Tg of solid ammonium nitrate is applied to agricultural fields as a N amendment each year. Therefore it is important to investigate photochemistry of ammonium nitrate, both in pure form and coated on mineral dust particles surfaces, under different environmental conditions. Transmission FTIR studies revealed formation of nitrous oxide, N$_2$O, as the major gas phase product via an abiotic mechanism upon irradiation of NH$_4$NO$_3$. N$_2$O is a potential greenhouse gas and currently believed to be the single most important ozone depleting substance. After several isotopic studies, a new reaction mechanism for the abiotic formation of N$_2$O, for the first time,
was successfully proposed which will be discussed in details during this chapter. In addition, annual production of N\textsubscript{2}O from atmospheric aerosols and surface fertilizer application over the continental United States from this abiotic pathway is estimated from results of an annual chemical transport simulation with the Community Multiscale Air Quality model (CMAQ).

Gaseous hydrochloric acid, HCl, levels reaching concentrations of a few parts per billion (ppbv) have been measured in polluted air and in some indoor settings. Direct emissions include garbage burning, incineration of municipal and medical wastes, burning of biomass, agricultural products and coal, and industrial processes, e.g., semiconductor and petroleum manufacturing. Natural sources in air include volcanic eruptions and reactions of sea salt and organochlorine compounds. The effect of gas phase HCl on chemistry and photochemistry of nitric acid adsorbed onto mineral oxide dust particle surfaces will be discussed in Chapter 6. Mixing of wind blown dust with sea salt, having lots of chloride ions, also can lead to a different heterogeneous chemistry on the mineral oxide surface. The transmission FTIR studies coupled with XPS analysis of reacted samples confirmed a new product formation on the particle surface along with formation of several gas phase species, including NOCl, NO\textsubscript{2}, NO and N\textsubscript{2}O. Due to the fact that NOCl and NO\textsubscript{2} are photoactive in the UV/Visible region of the solar spectrum, upon irradiation here we observed a surface mediated Cl activation and formation of gas phase NO. Higher levels of labile Cl and NO\textsubscript{x} yield to lower levels of atmospheric ozone. The information revealed in this work will be used to explain continuous production of active Cl and N species in the atmosphere so as to explain observed incessant ozone depletion.
Iron dissolution in Fe-containing dust aerosol can be linked to source material (mineral or anthropogenic), mineralogy, and iron speciation. All of these factors need to be incorporated into atmospheric chemistry models if these models are to accurately predict the impact of Fe-containing dusts into open ocean waters. In Chapter 7 and 8, we combine dissolution measurements along with spectroscopy and microscopy to focus on nanoscale size effects in the dissolution of Fe-containing minerals in low-pH environments and the importance of acid type, including HNO₃, H₂SO₄, and HCl, on dissolution. All of these acids are present in the atmosphere, and dust particles have been shown to be associated with nitrate, sulfate, and/or chloride. These measurements were done under light and dark conditions so as to simulate and distinguish between daytime and nighttime atmospheric chemical processing. Chapter 7 primarily focuses on effect of particle size and particle aggregation on iron dissolution. The results from the experiments discussed in this chapter highlight the dependence of iron dissolution on particle aggregation and aggregation state, whether it is a tide aggregation or not. Furthermore, it discusses the complexity involve in iron dissolution especially when nano particles get in to the picture. In Chapter 8, the main focus is to investigate the effect of light, acid type, and polyatomic oxyanions present in the medium. Both photon induced reductive iron dissolution and mode of anion binding are found to play significant roles in the dissolution of α-FeOOH under different experimental conditions. This chapter will explore more on these important, yet unconsidered, factors in the atmospheric processing of iron-containing mineral dust aerosol.

General conclusions are given in Chapter 9 along with the major points of this thesis highlighting significant ideas that will contribute to a better understand of the
heterogeneous chemistry and photochemistry of the atmosphere. Collectively, the results presented here provide insight into the heterogeneous reactivity of mineral dust aerosol under different environmental conditions.
The scope of the research presented in this thesis was done using a number of different experimental methods and techniques to investigate laboratory studies of physicochemical characterization of source materials and atmospheric processing of mineral oxides. The use of both macroscopic and molecular level studies as complementary data sets allowed for better understanding of the surface chemistry and adsorption process at the surface. In this chapter, these experimental techniques and methods are discussed in detail. These techniques include Fourier Transform Infrared (FTIR) spectroscopy, both transmission and attenuated total reflection (ATR)-FTIR spectroscopy, quartz crystal microbalance (QCM) measurements, X-Ray diffraction (XRD), and scanning electron microscopy (SEM). In addition to these techniques, several other complementary techniques that were used in this dissertation research in collaboration with other scientists are also briefly discussed.

2.1 Fourier Transform Infrared (FTIR) Spectroscopy

Infrared (IR) spectroscopy is by far the single most useful technique for the analysis of both gas phase and surface. IR spectroscopy provides data on the composition and structure of surface compounds, the nature of bonds formed between adsorbed molecules and the surface, and the existence of various types of surface and gas phase compounds. A vibrational spectrum reflects both the properties of molecules and characteristic features of separate chemical bonds.
Figure 2.1  Transmission FTIR experimental setup.
(a) Schematic of the IR cell; 1. tungsten grid sample holder jaws 2. direction of incident light; 3. aluminum holder for the IR windows; 4. O-rings; 5. IR window; 6. stainless steel holder for the IR window; 7. stainless steel cube 8. holes for clamping the Tungsten grid sample holder; 9. toward the glass handling system (gas inlet/outlet).

(b) Schematic of the gas handling system.
2.1.1 Transmission FTIR Spectroscopy: Experimental Setup

Transmission FTIR spectroscopy was used in a number of experiments to investigate formation of new gas phase species and different metal oxide surfaces in equilibrium with different atmospherically relevant gases. Infrared spectra were collected using a single beam FTIR spectrometer, Mattson Research Series (RS – 10000), equipped with a liquid nitrogen-cooled narrowband Mercury Cadmium Telluride (MCT) detector. Typically, a total of 250 scans were acquired at an instrument resolution of 4 cm\(^{-1}\) over the spectral range from 800 to 4000 cm\(^{-1}\). A commercially available air dryer (Balston 75-62) was used to purge the spectrometer and the internal compartment to minimize H\(_2\)O and CO\(_2\) concentrations in the purge air. An infrared cell made from a stainless steel cube was placed in the sample compartment of the spectrometer. The stainless steel infrared cell was coated with Teflon in order to avoid HNO\(_3\) decomposition. A schematic of this infrared cell is shown in Figure 2.1(a). Depending on the reactant gas of being used, either two Ge or BaF\(_2\) windows (Janos Technology Inc.) were placed into two Teflon coated stainless steel holders and were sealed by O-rings to the IR cell. The Teflon coated infrared cell is a cube of 7 cm in all dimensions along the outside, with a total inner volume of 197 ± 2 mL.

The IR cell was designed in such a way that both the gas phase and the surface could be studied simultaneously. Approximately 5-15 mg of oxide powder was pressed onto half of a tungsten grid. The other half was left uncoated and was used to measure the infrared spectrum of the gas phase. The grid is held in place by sample holder jaws of the infrared cell, which are also Teflon coated. The infrared cell sits on a linear translator inside the internal compartment of the spectrometer so that the position of IR cell can be
changed with respect to the infrared beam path. The half of the grid coated with the oxide powder yields spectral features associated with the oxide surface and surface adsorbates as well as gas phase spectral features, whereas the uncoated half of the grid only yields information about the gas phase. The infrared cell was connected through a Teflon tube to a gas-handling system (volume; $V = 1216 \pm 4$ mL). The gas handling system consists of a 6-port manifold that is connected to reagent gases, a two-stage vacuum system and two absolute pressure transducers (MKS instruments) that operate in two different ranges from 0.001 to 10.00 Torr and from 0.1 to 1000 Torr. A schematic of this setup is shown in Figure 2.1(b). The vacuum system consists of a turbo molecular pump and a mechanical pump that is used to evacuate the system down to a final pressure of around $1 \times 10^{-6}$ Torr.

In transmission FTIR experiments, in order to obtain spectra of both surface species and the gas phase species present, single beam spectra of the oxide powder in the presence of the gas or after exposure to a reactant gas are referenced to those prior to exposure. Thus, information about adsorbed surface species can be obtained by using spectral subtraction of the gas phase spectrum under identical conditions. All IR spectra were recorded at 296 K unless otherwise indicated.

2.1.2 Transmission FTIR Spectroscopy: Photochemical Studies

The transmission FTIR experiments described in Section 2.1.1 was slightly modified for photochemical experiments. Above all, a 500 Watt mercury arc lamp (Oriel, model no. 66033) was used as a broadband light source that contained ultra-violet, visible, and infrared light. The optical path length of the light from the arc lamp to the
Figure 2.2 Schematic of the optical path of the light from the mercury arc lamp the infrared cell sitting inside the FTIR spectrometer. The sample is irradiated for certain time intervals after which spectra are then recorded of the gas phase and the oxide surface.
infrared cell and a graphical representation of these modifications are shown in Figure 2.2. Following sample preparation and reactive gas introduction, the valve connecting the FTIR cell to the mixing chamber was closed, letting the gas phase products accumulate inside the cell as the surface was irradiated. The unwanted infrared light was removed with a water-filled filter. Samples were irradiated with either the full broadband irradiation (sans infrared light) or with the use of long-pass filters ($\lambda < 300$ nm, Oriel filter no. 59425) to cut off higher energy wavelengths of light. The intensity of the broadband light source, reaching to the sample inside the custom-made IR cell, was measured using a solar cell (model EI-100, Optical Energy Technologies). Irradiance of the lamp output was measured using a spectroradiometer (model RPS900-R, International Light Technologies). According to these measurements, mineral oxide surface, placed inside the IR cell, receives broadband light approximately equal to one solar constant.

During the photolysis, infrared spectra of both gas phase and surface were recorded with a single-beam Mattson RS-10000 spectrometer in a similar fashion described in section 2.1.1. To investigate surface-mediated post irradiation processes, the light source was turned off and IR spectra (25 scans, 4 cm$^{-1}$ resolution) were immediately collected of the gas phase every 3 min for 2 h.

2.1.3 Attenuated Total Reflectance (ATR) - FTIR Spectroscopy: Flow Cell Reactive System

Another powerful analytical tool for molecularly probing gas-solid and gas-liquid interfaces during in situ reactions of metal oxides and other mineral surfaces for the last two decades is ATR-FTIR spectroscopy. The ability to molecularly probe in real time the
Figure 2.3  Modified ATR-FTIR used to study water and reactive gas uptake. 
(a) Schematic of the IR cell. 
(b) Measurements of the ATR-FTIR cell.
solid-liquid interface has real advantages over other spectroscopic techniques, especially other IR techniques because of the strong absorption of water. This requires that the sample of interest be placed onto an internal reflection element (IRE).

The incident IR beam is introduced above the critical angle, defined as

\[ \theta_c = \sin^{-1}(n_2/n_1) \]

where \( n_1 \) and \( n_2 \) are the real part of the refractive indexes of the sample and crystal, respectively, allowing for the beam to be internally reflected. When the beam is reflected, it creates an evanescent wave that exponentially decays into the sample. From which, the radiation can be absorbed by a sample that is placed in direct contact with the IRE. This evanescent wave produces a limited penetration depth of the infrared radiation on the order of 1 \( \mu \text{m} \).\(^{95, 96}\) The absorbance is proportional to the path length, which is similar to transmission infrared spectroscopy, however, in the case of ATR-FTIR spectroscopy, the effective path length, \( b' \), is equal to the number of reflections of the IR beam times the penetration depth, i.e.

\[ b' = N \times d_p \]

\[ \text{Eq: 2.1} \]

where \( N \) is the number of reflections and \( d_p \) is the penetration depth per reflection. The penetration depth, \( d_p \), is given as

\[ d_p = \frac{\lambda_1}{2 \pi n_1 (\sin^2 \theta - n_{21}^2)^{\frac{1}{2}}} \]

\[ \text{Eq: 2.2} \]

where \( \lambda \) is the wavelength of IR radiation, \( \theta \) is the angle of incidence and \( n_{21} \) is equal to \( n_2/n_1 \) and \( \lambda_1 = \lambda_{\text{vacuum}}/n_1 \).\(^{97-99}\) The small penetration depth and short path length allow for infrared absorption measurements of a strongly adsorbing medium such as those seen for infrared measurements of aqueous solutions.\(^{96}\)
A modified version of the above mentioned commercially available ATR horizontal liquid cell apparatus (Pike Technology) was used in gas phase adsorption studies. The modified cell is shown in Figure 2.3. The optics attachment and bottom portion of the liquid cell (Pike Technology) were placed inside the internal compartment of the spectrometer. The top placed of the commercial liquid cell was replaced with a Teflon lid which contained four openings for a relative humidity sensor (Honeywell, HIH-3602-L), a temperature sensor and two remaining for the air inlet and outlet flow.

The modified horizontal ATR cell was coupled to a flow system as shown in Figure 2.4. In water uptake experiments, the exact humidity of the air was controlled by mixing dry and wet air to reach the desired relative humidity as measured by the RH sensor. The dry air passes through Hydro-purge filters (Altech Associates, Inc.) before adjusting the RH that removes moisture, oil and organics. The flow rate was kept constant using flow meters throughout the entire system. In all the experiments, once the relative humidity was increased, it was allowed to stabilize and equilibrated for 20 to 60 minutes. The relative humidity was then recorded from the relative humidity sensor in the modified ATR-FTIR chamber as well as the mixing chamber by a custom built digital readout.

The flow reactive system was used to investigate water uptake by different mineral oxides as well as the kinetics of the uptake of different gases on the surface of metal oxides. The latter study involves mixing of dry air with treated air that passes through the reactant gas bubbler. The concentration of the gas was controlled by the use of two mass flow controllers (MFC) (MKS Instruments) having a range of 100 sccm (standard cubic centimeters per minute). By controlling the flow of dry air through one
Figure 2.4  Schematic of the ATR-FTIR and quartz crystal microbalance experimental setup.
MFC and the flow of treated air from the other MFC, the concentration of the gas can be determined. The effect of water on the kinetics of the uptake of these gases on the surface of the mineral oxide was investigated by using both the relative humidity flow and the treated air flow setup simultaneously.

In all of these experiments, a thin film of the sample was prepared by suspending the mineral oxide in high purity water (Fisher, Optima). The suspension was poured into the horizontal cell and water was allowed to evaporate overnight under the dry air purge of the internal compartment. This allowed for a uniform dispersion of particles on the IRE (AMTIR, Ge or ZnSe). The total sample mass deposited on the IRE was ~ 35 mg spread over the 7.3 cm by 0.7 cm area of the IRE. Infrared spectra were obtained using a single beam Thermo Nicolet FTIR spectrometer, equipped with a liquid-nitrogen-cooled narrow-band mercury cadmium telluride (MCT) detector. The FTIR spectrometer optics and the internal compartment were purged using a commercial air dryer (Balston 75-60). Typically 500 scans were acquired at an instrument resolution of 4 cm⁻¹ over the spectral range between 650 or 830 and 4000 cm⁻¹ depending on the frequency cutoff of the ATR-FTIR internal reflection element that was used. Spectra reported are referenced to the ATR-FTIR element without any sample present and under dry conditions (< 5 %).

2.1.4 ATR-FTIR spectroscopy in the Aqueous Phase: Surface Adsorption Studies

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was also used to compare the adsorption of acid anions and polyatomic oxyanions on two different particle sizes of an iron containing mineral goethite, α-FeOOH. These studies were carried out as complementary experiments in an investigation of iron dissolution at
low pH environments. Here, a 1.5 mL suspension of a 2 g/L FeOOH in Optima water was placed on a AMTIR horizontal ATR cell (Pike Technologies, Inc.) using a Nicolet Thermo Electron FTIR spectrometer (Nexus 670, Madison, WI) and allowed to dry overnight creating a thin film that evenly coated the crystal. The crystal was flushed with a delicate stream of water to rinse any loosely bound particles. For each concentration, acid anion solution at constant pH values was added every ten minutes to the ATR flow cell to allow time for equilibration of the solution with the thin film. The solution was added until equilibrium was reached which was correlated to the time when the integrated peak area remained constant over time. The concentration for the acid anion solution investigated was 100 mM. Solution phase experiments were also conducted in the absence of the goethite layer.

2.2 Quartz Crystal Microbalance (QCM) Measurements

The amount of water and reactive gas uptake on mineral oxide surfaces was measured with the quartz crystal microbalance (QCM) that was also in parallel with an ATR-FTIR system to simultaneously measure the uptake with spectroscopic techniques (Figure 2.4).

The QCM measures the frequency of vibration at piezoelectric point for the crystal in the instrument as humid air flows over the sample. The change in the frequency can be related to the mass of water or reactive gas uptake from the air passing through on the sample when the mass loading is less than 2% of the crystal frequency by the Sauerbrey equation,

\[ \Delta f = -C_f \times \Delta m \]

Eq: 2.3
where $\Delta f$ is the change in frequency (Hz), $\Delta m$ is the change in mass ($\mu g/cm^2$) related to the change in frequency, and $-C_f$ is the sensitivity factor is a constant for a 5 MHz AT-cut quartz crystal (56.6 Hz.$\mu g^{-1}.cm^{-2}$).100,101 The QCM measurements yield important quantitative data that along with the analyses provided by ATR-FTIR spectroscopy provides for a better understanding of adsorbed species on atmospherically relevant particles.

In these experiments, water and reactive gas adsorption on mineral oxide particles were quantified using a commercial 5 MHz quartz crystal microbalance flow cell with a 1” inch diameter gold/Cr polished quartz crystal (QCM200, Stanford Research Systems). In sample preparation, oxide power, approximately 10 to 25 mg, was first suspended in water and then the suspension was sprayed onto the QCM crystal using a glass atomizer. This method created a uniform thin film of particles covering the entire active area of the balance. The entire QCM system was placed inside a custom-made Teflon box that was designed to protect the flow cell from air currents which could affect the stability of these measurements.

The frequency of the coated QCM was then recorded and subtracted from the baseline frequency (5 ± 0.1 MHz) with no sample present. This gave the exact mass of the sample before starting the RH measurements. After the sample was dried overnight (< 5 % RH), the QCM was zeroed to $\Delta f = 0$ so that the change in mass measured was only due to the mass of water or reactive gas taken up by the sample as a function of gas pressure. The relative humidity or reactive gas was allowed to stabilize and equilibrate for approximately 30 minutes, depending on the sample. Multiple experiments were
preformed on the same sample as well as repeat experiments on different samples in order to average the effect of time dependence of the uptake results.

2.3 Quantitative Iron Dissolution Measurements: Batch Reactor Studies to Investigate Processing of Iron Oxyhydroxide

Atmospheric processing of iron oxyhydroxide at low pH environments was investigated to understand the role of particle size, pH, aggregation, light and acid type in proton-promoted iron dissolution using a set of batch reactor studies. These experiments were carried out in a custom-made glass reactor using synthesized nanoscale particles (nanorods) of α-FeOOH and particles with micron dimensions (microrods). Experimental protocol followed during the synthesis of these particles is discussed in the section 2.6.4. Reactor design, shown in Figure 2.5, has been described previously.\textsuperscript{102}

Briefly, the reaction vessel had a capacity of 70 mL and was stirred using a magnetic stir bar. The vessel had a quartz window with an area of 12.5 cm\textsuperscript{2} mounted on top that permitted deoxygenated experiments and was to allow for reactions to proceed under atmospheric conditions. In experiments performed under deoxygenated conditions, suspensions were purged with N\textsubscript{2} for \~10 min prior to the experiment begin, and during experiment the headspace of the reaction vessel was purged to maintain positive N\textsubscript{2} pressure. The ionic medium used for dissolution experiments was 5 mM NaClO\textsubscript{4}. The sample loading was maintained 0.2 g\textperiodcentered L\textsuperscript{−1} of α-FeOOH in solutions of HNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4}, and HCl. The pH was monitored with a glass electrode standardized with pH buffer solutions. Experiments were performed at pH 1 and 2 and were adjusted with HCl as necessary. At pH 2, nanorod and microrod suspensions were stable, and the particles
were fairly well dispersed. The temperature was kept constant (298 ± 1 K) through use of a water jacket integrated to the reaction vessel. These experiments were conducted in the presence and absence of light.

Over time, samples were periodically removed from the reactor using a disposable syringe that was connected to 10 cm of Teflon tubing. Aliquots (1 mL) were collected after passing through a 0.2 μm PTFE filter (Expertek) and immediately acidified with 40
μL of 5 M HCl to preserve the sample for iron analysis. At each sampling event, enough sample volume was taken to allow for analysis of dissolved Fe(II) and total dissolved iron. All dark and light experiments were conducted in triplicate with average measurements reported. Reported errors represent one standard deviation.

2.4 Complementary Physical and Chemical Characterization Techniques

2.4.1 Scanning Electron Microscopy

A Hitachi S-4000 SEM-EDX system was used to collect scanning electron microscopy (SEM) images. Particles were sprinkled onto tape that was attached to an aluminum stub. An accelerating voltage of 15 kV was used to obtain the images shown. The bulk elemental compositions as well as the bulk morphology of the mineral oxides were acquired with a Hitachi S-3400N SEM-EDX system. Particles were sprinkled onto carbon tape that was attached to a carbon stub. An accelerating voltage of 15 kV was used to obtain bulk elemental compositions with a limit of detection of 1 wt % in the bulk (1 x 10^{23} atoms).

2.4.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) was used as a characterization tool to examine size and morphology of the mineral oxide particles. TEM stubs were prepared by with carbon coatings on 400 mesh copper stubs. Carbon was deposited onto a small, clean piece of mica which was removed into a water bath by surface tension. Blank copper TEM grids were placed on wire-mess table and the water was siphoned out until the carbon film was deposited on the blank TEM grids. The grids were again dried
overnight and stored in a desiccator to maximize shelf life. Sample preparation for TEM analysis included sonicating a dilute suspension of the sample in water or methanol for 20-30 minutes and dropping a portion onto TEM stub with a pipette. Once the droplet was dry, TEM analysis was performed.

2.4.3 Powder X-ray Diffraction

Crystalline structure and composition of bulk powder samples were determined using (XRD) analysis. Dry powder samples were placed in the XRD sample holder, and the surface of the powder was smoothed with a razor until flush with the rim of the holder. A Siemens D5000 X-ray diffractometer with Cu Kα target and nickel filter was used to collect the XRD powder patterns between angles of 2θ from 10° and 90°.

2.4.4 BET Surface Area Measurements

The surface area of the mineral oxide powders were measured by BET surface area analysis. Relative pressures, \( \frac{P}{P_o} \), of inert gases are introduced into a calibrated sample cell that allows the adsorption of the inert gas, \( \text{N}_2 \) in the current studies, to be measured, \( W \). The cross section of the \( \text{N}_2 \) molecule is known and total surface area can be calculated. The total surface area is divided by the sample mass to give a surface area per unit mass. The specific surface area of each metal oxide was determined from seven-point \( \text{N}_2 \)-BET adsorption isotherm measurements performed on a Quantachrome 4200e surface area analyzer by the following equation (Eq. 2.4) in the limited linear range of the BET isotherm,

\[
\frac{1}{W((P_o / P) - 1)} = \frac{1}{W_mC} + \frac{C-1}{W_mC} \left( \frac{P}{P_o} \right) \quad \text{Eq: 2.4}
\]
where $W_m$ is the weight of adsorbate constituting one monolayer of coverage and $C$ is a constant. Plotting $1/W((P_o/P)-1)$ versus $(P/P_o)$ allows for determination of $W_m$ and $C$ by the slope and intercept of the linear fit. The sample preparation for surface area analysis is minimal. Prior to analysis, samples were degassed overnight at temperatures that would not change the materials’ properties.

2.4.5 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a powerful surface sensitive technique which uses x-rays to eject core electrons, an electron from a higher energy level, then relaxes down to a lower energy state and simultaneously releases a photoelectron which has a characteristic binding energy. Since the mean free path of electrons in the solid usually on the order of 10nm, XPS inherently probes the surface and near-surface region of the material but penetration depth can also be adjusted.

The kinetic energy of the electron is typically measured but it can be related to the binding energy. This relationship given by the Einstein equation, to a first approximation, can be written as:

$$E_B = h\nu - E_K$$  \hspace{1cm} Eq: 2.5

where $E_B$ is the binding energy referenced to vacuum level and $E_K$ is the kinetic energy of the electron. Furthermore, the binding energy can shift up to a 1-2 eVs depending on the chemical environment of the atom. Thus, XPS can yield information about the elements present on the surface, the oxidation state of the elements and surface functional groups present (e.g. hydroxyl groups on oxide surfaces). A custom-designed Kratos Axis Ultra
X-ray photoelectron spectroscopy system (Manchester, UK) was used to investigate the bare and reacted surfaces of the metal oxide particles. The experimental setup for reactions and analysis have been previously described in detail. Briefly, the powder samples were pressed onto indium foil which was placed on either a stainless steel bar or copper stub for analysis. The samples were placed into the XPS analysis chamber, which had a pressure that was maintained in the $10^{-9}$ Torr range during analysis. Charging was prevented by using low energy electrons to neutralize the samples. Wide energy range survey scans were acquired using the following instrumental parameters: energy range from 1200 to -5 eV, pass energy of 160 eV, step size of 1 eV, dwell time of 200 ms, and an x-ray spot size of $\sim 700 \times 300 \mu m$. The data collected were analyzed using CasaXPS data processing software.

2.5 Reagents and Materials

2.5.1 Metal Oxide, Oxyhydroxide and Carbonate Powders

Commercially available Fe$_2$O$_3$, Al$_2$O$_3$ and CaCO$_3$ powders were used in these experiments. The source materials used in this research represent different reactive components of mineral dust aerosol. Iron oxides, including Hematite ($\alpha$-Fe$_2$O$_3$, 99.9%) and maghemite ($\gamma$-Fe$_2$O$_3$, 98%), and corundum ($\alpha$-Al$_2$O$_3$, 98%) were purchased from Alfa Aesar. Iron oxyhydroxide, geothite ($\alpha$-FeOOH) was synthesized according to the method described in section 2.3.1. Gamma phase of alumina ($\gamma$-Al$_2$O$_3$, 98%) was purchased from Degussa and OMYA is the manufacture of calcium carbonate (CaCO$_3$, 98%) used in these experiments. All the surface areas were measured using a Quantachrome Nova 1200 Multipoint BET apparatus. X-ray diffraction of the powders
confirmed the crystalline phases of the metal oxides presented here. A Hitachi S-4000 scanning electron microscope was used to acquire images of Fe₂O₃, Al₂O₃ and CaCO₃ particles. Sample imaging was done using a working distance of 12 mm, with an emission current of 10 mA and an accelerating voltage of 15 KV.

2.5.2 Clays

Three different clay minerals, montmorillonite, kaolinite and illite were used as proxies for soil particles. These clay samples were received from several different sources. Kaolinite, KGa-1b, from Washington county in Georgia, and illite, IMt-1, from Silver Hill, Montana, were also obtained from the Source Clay Repository. Samples of montmorillonite, SWy-2 and SAz-1, from Crook County in Wyoming and from Apache county in Arizona respectively, were obtained from the Source Clay Repository (Clay Mineral Society). All of the powdered samples were used as is with the exception of illite which was obtained in the form of a rock. The illite sample was processed into a powder using a mortar and pestle and then a wiggle-l-bug.

2.5.3 Salts

Sodium chloride (Certified ACS) was purchased from Fisher, while NH₄NO₃ (98.0%, ACS), and Ca(NO₃)₂ (ACS, greater than 99.0 %) were purchased from Alfa Aesar. Ferric nitrate nonahydrate [Fe(NO₃)₃·9H₂O; 98%], sodium bicarbonate (NaHCO₃, 99.5%), and potassium hydroxide (KOH) were purchased from Sigma Aldrich and used for iron oxy hydroxide (α-FeOOH) synthesis.
2.5.4 Synthesis of Iron Oxyhydroxide

Two primary particle sizes of goethite were synthesized. The larger particles, referred to as microrods, were synthesized according to Schwertmann and Cornell.\textsuperscript{104} Briefly, 180 mL of 5 M KOH was rapidly added to 100 mL of 1 M Fe(NO$_3$)$_3$. The mixture was diluted with distilled water to a final volume of 2 L and was then held in a closed polyethylene flask at 70 °C for 60 h. Goethite nanoparticles, referred to as nanorods, were synthesized according to a modified version of the method provided by Burleson and Penn for goethite synthesis from ferrihydrite,\textsuperscript{105} in which 1 L of 0.48 M NaHCO$_3$ solution was added dropwise (rate of approximately 4.5 mL/min) to an equal volume of 0.4 M Fe(NO$_3$)$_3$ that was being vigorously stirred. During this titration, the pH of the ferric nitrate solution increased from approximately 1.0 to 2.4. The resulting suspension was then microwaved to boiling, immediately cooled to ~ 20 °C using an ice bath, and purified via dialysis for three days according to the details provided in Anschutz and Penn.\textsuperscript{106} Conversion of the resulting ferrihydrite particles to goethite was accomplished by first raising the pH to 12 using 5 M KOH and then heating the resulting suspension at 90 °C for 24 h. In all instances, goethite particles were purified via three cycles of water washes and centrifugation. Particles were then freeze-dried, ground by mortar and pestle and passed through a 150 μm or 45 μm sieve for microrods and nanorods, respectively.

2.5.5 Liquid and Gas Reagents

Distilled H$_2$O (Optima grade) was purchased from Fisher Scientific and was degassed prior to use. Dry gaseous nitric acid was taken from the vapor of a 1:3 mixture
of concentrated HNO₃ (70.6% HNO₃, Mallinckrodt) and 95.9% H₂SO₄ (Mallinckrodt).

¹⁴NH₃ (99.99%) and ¹⁵NH₃ (98%) isotopes of gaseous ammonia were used in photolysis experiments of coated ammonium nitrate over alumina particles. In iron dissolution experiments, solutions of 0.1 N (pH 1) and 0.01 N (pH 2) were prepared from concentrated HNO₃ (70.6% HNO₃, Mallinckrodt), H₂SO₄ (95.9% H₂SO₄, Mallinckrodt), and HCl (37.6% HCl, Fisher). Measurements of dissolved Fe(II) and total dissolved iron were performed with 1,10-phenanthroline (≥99%) and hydroxylamine hydrochloride (98%) which were purchased from Sigma Aldrich and ammonium acetate (98.5%, Fisher) and glacial acetic acid (99.7%, EMD).
CHAPTER 3
SPECTROSCOPIC AND MICROSCOPIC INVESTIGATION OF NITRIC ACID AND WATER ADSORPTION ON METAL OXIDE, OXYHYDROXIDE AND CARBONATE PARTICLES

3.1 Abstract

In the atmosphere, metal oxides, oxyhydroxides and carbonates contribute to a major fraction of mineral dust aerosol and are often used as proxies in studies to understand the chemical behavior of dust particles. In this study, transmission FTIR is used to investigate adsorbed nitrate on several selected metal oxides (α-Fe₂O₃, γ-Fe₂O₃, α-Al₂O₃ and γ-Al₂O₃), a metal oxyhydroxide (α-FeOOH) and a carbonate (CaCO₃) at 296K. The experimental results suggest that HNO₃ is molecularly and irreversibly adsorbed onto these particle surfaces and vibrational frequencies can be assigned to different modes of coordination (monodentate, bidentate and bridging) of the nitrate ion to the surface in the absence of co-adsorbed water. For these well-characterized proxies, ATR-FTIR spectroscopy is combined with quartz crystal microbalance (QCM) mass measurements to investigate water uptake as a function of relative humidity (RH). Based on BET isotherm analysis for water adsorption, extent of water uptake greatly depends on the type, cryptography and particle size of the dust component. Among the studied samples, CaCO₃ showed the highest water uptake in all the RHs while iron oxide showed a greater affinity towards water adsorption compared to alumina especially at lower RHs.

In the presence of co-adsorbed water, adsorbed nitrates become solvated and displaced from the direct coordination to the surface. Water uptake on nitrate-coated
remained similar for alumina samples compared to uncoated surfaces, however, for iron oxides, oxyhydroxide and calcium carbonate, the shape of the adsorption isotherm changed for nitrate coated particles with an increased amount of water uptake at a given RH. Furthermore, subsequent uptake of HNO₃ and water on CaCO₃ particles yield micropuddles or small islands of Ca(NO₃)₂ (aq) on the particle surface. Thus adsorbed water plays an important and multi-faceted role in the chemical reactivity of surface adsorbed species on mineral dust. In the current study, experimental IR spectra are combined with quantum chemical calculations for a better assignment of the vibrational frequencies and to confirm adsorbed complexes. Differences in spectral features due to nitrate adsorption and amendment in the nitrate iron environment in the presence of co-adsorbed water will be discussed in detail.

3.2 Introduction

Among many crustal species found in mineral dust aerosol, metal oxides, oxyhydroxides and carbonates play a significant role in determining the chemical behavior of the dust particle, especially the heterogeneous chemistry and photochemistry. Iron Oxides are a significant fraction of the Earth’s crust and, as such, a major component of mineral dust aerosol in the atmosphere, contributing 6 – 9% by mass in clay aggregates.⁵⁸,⁵⁹ Recent studies demonstrated that iron oxides in mineral aerosols occur as hematite (α-Fe₂O₃) and maghemite (γ-Fe₂O₃) whereas the major oxyhydroxide form is the goethite (α-FeOOH) which are transferred into the atmosphere as a result of wind and volcanic activity.⁵⁹ In addition, these are introduced to the atmosphere as fly ash from power plants, combustion exhaust, and from industrial operations.
Earth crust is comprised of ~8% by mass of aluminum oxides in the form of, mainly, corundum (α-Al₂O₃), aluminum silicate clays, i.e. kaolinite, illite and montmorillonite. Besides, aluminas have had some form of chemical and industrial use throughout history. For little over a century corundum has been the most widely used and known of the aluminas. Today, in the industry, emerging metastable aluminas, including the γ, δ, η, θ, κ, β, and χ polymorphs, have been growing in important. In particular, γ-alumina has received wide attention, with established use as a catalyst and catalyst support, and growing application in wear abrasives, structural composites, and as part of burner systems in miniature power supplies. The carbonate component of the mineral dust can comprise as much as 30% of the total mineral dust aerosol. Carbonate minerals such as calcite (CaCO₃) and dolomite (CaMg(CO₃)₂) are thought to be the reactive components of mineral dust aerosol and a reactive component of carbonate containing structures including monuments, statues and buildings. Once these different forms of metal oxides, oxyhydroxides and carbonates from various natural and anthropogenic origins are emitted to the atmosphere, they easily become part of the atmospheric dust aerosol and potentially contribute to alter the chemical balance of the atmosphere and global climate. Especially, as these particles are transported through the atmosphere, they react with nitrogen oxides including NOₓ, HNO₃ and N₂O₅.

Ozone in the troposphere is produced by a complex series of chemical and photo chemical reactions in which NOₓ (NO + NO₂) plays a major role with a nonlinear relationship to ozone concentration. Therefore, the peak ozone level in the lower atmosphere is highly affected by the amount of NOₓ present. Recent atmospheric model studies have reported that the HNO₃ to NOₓ ratio has deviated by a factor of
5 – 10, especially during the spring and summer when the dust storms in Asia are prevalent.\textsuperscript{115, 116} Moreover, HNO\textsubscript{3} concentration is over-predicted in atmospheric chemistry models. One possible reason for this inconsistency may potentially be due to ignorance of important chemical processes involving the heterogeneous denitrification in the lower atmosphere. Frequently, they are neglected in atmospheric model studies, due to the fact that higher uncertainties are associated with the rates of heterogeneous processes.

In previous studies, it has been found that gas phase nitric acid is neutralized by reacting with mineral aerosols to form particulate nitrate\textsuperscript{88, 114} and more than 40\% of total atmospheric nitrate is associated with mineral dust aerosol.\textsuperscript{111} Several surface species have been proposed following the adsorption of nitrogen oxides on metal oxide surfaces including species like nitrate (NO\textsubscript{3}\textsuperscript{−}), nitrite (NO\textsubscript{2}\textsuperscript{−}) and nitrosyl (NO\textsuperscript{+}).\textsuperscript{66, 70, 117, 118} Therefore, information from the recent model studies and field observations suggest that mineral oxides, oxyhydroxides and carbonates present in mineral aerosol could act as a reactive surface towards HNO\textsubscript{3} acid, thus, influencing the trace atmospheric gas budget through heterogeneous reactions.\textsuperscript{111, 119} Although, a detailed understanding of the coordination of adsorbed nitrate ion is currently unknown.

HNO\textsubscript{3} concentrations appear to be connected to the surface area of aerosol particles and their water uptake capacities. Under humid conditions, atmospheric water vapor readily adsorbs to dust particle and dissociates resulting a hydroxyl terminated on the dust particle surface.\textsuperscript{86} Adsorbed water is then hydrogen bonded to these hydroxyl groups in equilibrium with water vapor forming a thin water layer over the particle surface which potentially modify the surface properties. Besides, it is becoming
increasingly clear that the heterogeneous chemistry of mineral dust aerosol is a function of relative humidity (RH) as water on the surface of the mineral dust particles can enhance or inhibit its reactivity depending on the reaction. Mashburn et al. reports that as the relative humidity increased the uptake coefficient and HNO₃ content all increased. Reaction rates were seen to increase by an order of magnitude or more at higher relative humidity compared to dry conditions. Moreover, it has been shown that co-adsorbed water molecules readily solvate adsorbed nitric acid species on the aluminum oxide surface forming inner and outer sphere complexes. Thus, it is important to quantify and understand the water uptake by these different mineral surfaces and its potential implications in the atmosphere.

In this study, a complete investigation was carried out to understand the heterogeneous reactions of HNO₃ and water on above metal oxide, oxyhydroxide and carbonate particles. These separate systems are chemically much simpler than mineral aerosol found in the atmosphere but still they provide some insight into adsorption mechanisms as well as the fate of adsorbed species in heterogeneous atmospheric chemistry. Transmission FTIR spectroscopy is used to investigate the adsorption of HNO₃ on mineral particles. For the nitrate ion, the degenerate ν₃ vibrational mode, the most intense band in the infrared spectrum, splits into multiple bands upon adsorption due to both a decrease in the nitrate ion symmetry and different modes of coordination (monodentate, bidentate and bridging) to the surface. It was noted previously that the spectrum of adsorbed nitrate in the presence of co-adsorbed water shows similarities to the spectrum of nitrate ion in aqueous solution suggesting that the nitrate ion is solvated on the surface. In addition, X-ray photoelectron spectroscopy (XPS) is
used to confirm the uptake of HNO₃ on studied mineral surfaces. ATR-FTIR spectroscopy is combined with quartz crystal microbalance (QCM) mass measurements to investigate water uptake on pure and nitrate coated mineral surfaces as a f(RH). Here, quantum chemical calculations are used to model vibrational frequencies of the nitrate ion adsorbed on an alumina surface in the presence and absence of co-adsorbed water. These values are compared against experimental data to aid in the assignment of the complex spectra and the coordination of nitrate to aluminum oxide surfaces in the presence and absence of co-adsorbed water.⁹⁴

3.3 Experimental Methods

3.3.1 Characterization of Source Materials

The sources of all the materials, α-Fe₂O₃, γ-Fe₂O₃, α-Al₂O₃, γ-Al₂O₃, α-FeOOH and CaCO₃, and reagents used in this study are listed in Chapter 2.6. Mineral samples were characterized using a variety of techniques, including surface area measurements, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), X-Ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). A detailed description of the experimental setups and techniques used in this chapter are discussed in Chapter 2.

3.3.2 Transmission FTIR for HNO₃ Adsorption Studies

Transmission FTIR spectroscopy was used to measure the vibrational spectra of several selected metal oxides (α-Fe₂O₃, γ-Fe₂O₃, α-Al₂O₃ and γ-Al₂O₃), oxyhydroxide (α-FeOOH) and carbonate (CaCO₃) surfaces in equilibrium with gas-phase HNO₃. For
\( \gamma \)-Fe\(_2\)O\(_3\), \( \gamma \)-Al\(_2\)O\(_3\) and CaCO\(_3\) samples, transmission FTIR spectroscopy was also used to study the nitrated surfaces in the presence of co-adsorbed water. The experimental setup for these experiments is described in detail in Chapter 2.1.1.

3.3.3 XPS Studies for HNO\(_3\) Uptake

XPS spectra were collected using a custom-designed Kratos Axis Ultra X-Ray photoelectron spectrometer with a monochromatic Al K\(_\alpha\) X-Ray source which has been previously described in chapter 2. The samples were pressed onto indium foil and mounted on a copper stub for analysis. The stub was placed in a custom made reaction chamber which was attached to the mixing chamber of the transmission FTIR and treated with HNO\(_3\) following the same protocol used in transmission FTIR measurements. Then treated sample was introduced into the XPS analysis chamber, which had a pressure that was maintained in the 10\(^{-9}\) Torr range during analysis. Charging was prevented by using low energy electrons to neutralize the samples. Wide energy range survey scans were acquired using the following instrumental parameters: energy range from 1200 to -5 eV, pass energy of 160 eV, step size of 1 eV, dwell time of 200 ms, and an x-ray spot size of \( \sim \) 700 x 300 \( \mu \)m. The data collected were analyzed using CasaXPS data processing software.

3.3.4 ATR-FTIR Coupled with QCM for Water Uptake Studies

A detailed description of the experimental setups and techniques used in water uptake studies are discussed in Chapter 2, with a detailed description of the ATR-FTIR experimental setup in Chapter 2.1.3 and QCM setup in Chapter 2.2. Briefly, a thin film of
the insoluble sample was prepared by placing the particles in high purity water (Fisher, Optima) followed by a 15 min sonication to break the aggregations. The suspension was poured into the horizontal cell; the water was allowed to evaporate overnight under the dry air purge (< 5 % RH) in the modified ATR-FTIR. This procedure allowed for a uniform dispersion of particles and good contact of the particle surface with the IRE. The total sample mass deposited on the IRE was between 35 to 50 mg. Spectra reported were referenced to the ATR-FTIR element without any sample present and under dry conditions (< 5 %).

Water adsorption on proxies for mineral dust was quantified using a commercial 5 MHz quartz crystal microbalance flow cell (QCM200, Stanford Research Systems) in parallel with the ATR-FTIR spectrometer as previously described in the literature. In brief, the powder samples were first suspended in water and a uniform thin film of particles covering the entire active area of the balance was obtained by spraying the suspension onto the QCM crystal using a glass atomizer. Typical sample weights were on the order of 15 to 22 µg over the 0.4 cm² active area of the crystal. The exact mass of the sample before starting the RH measurements was calculated by subtracting the frequency of the coated QCM from the baseline frequency with no sample present. Each relative humidity was allowed to stabilize and equilibrate for approximately 30 minutes and QCM data was collected. QCM measures the change in frequency of the crystal that can directly be related to the mass of water taken up by the sample deposited on to the quartz crystal microbalance. The relationship between the change in frequency and the change in mass is given by the Sauerbrey equation:

\[ \Delta f = -C_f \times \Delta m \]  
\[ \text{Eq: 3.1} \]
where $\Delta f$ is the change in frequency (Hz), $\Delta m$ is the change in mass ($\mu g/cm^2$), and $C_f$ is the sensitivity factor, $56.6 \, Hz\cdot \mu g^{-1} \cdot cm^{-2}$, for the 5 MHz AT-cut quartz crystal used in this study.

3.3.5 Quantum Chemical Calculations

Both energy optimization and vibrational frequency calculations for binuclear alumina cluster models were performed using Spartan ‘04 and Spartan ’06 for Windows (version 1.0.3 and 1.0.1, respectively) software packages$^{123,124}$ using B3LYP hybrid DFT level of theory with a 6-31G(d) basis set. A detail description of complementary quantum chemical calculations can be found in Ref. 24.

3.4 Results

3.4.1 Physical and Chemical Characterization of Source Material

Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, X-Ray powder diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area measurements, X-Ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to characterize both bulk and surface properties of the six different source materials used in this study.

SEM images for representative metal oxide, oxyhydroxide and carbonate samples are shown in Figure 3.1. These images show that these samples are different from each other in shape and variable in size. As discussed in Hudson et al. the irregular shaped $\mathrm{CaCO_3}$, $\alpha$-$\mathrm{Fe_2O_3}$ and $\alpha$-$\mathrm{Al_2O_3}$ particles have shape factors, $\chi$, ranging from 1.2-1.3 where $\chi=1$ is a sphere.$^{125}$ The shape factors for $\gamma$-$\mathrm{Fe_2O_3}$ and $\gamma$-$\mathrm{Al_2O_3}$ were $\sim1$ suggesting
Figure 3.1 Representative SEM images of individual particles of (a). CaCO$_3$ (b) $\alpha$-FeOOH and (c). $\alpha$-Fe$_2$O$_3$. Representative TEM images of individual particles of (d). $\gamma$-Fe$_2$O$_3$ (e). $\gamma$-Al$_2$O$_3$ and (f). $\alpha$-Al$_2$O$_3$. 
more spherical shaped particles. α-FeOOH showed a clear rod shape with a diamond or rhomboidal basic structure. The results of the surface area measurements and particle size, along with the source of the material, are reported in Table 3.1. It can be seen from Table 3.1 that the surface areas of the studied source material fall in the range between 23 ± 2 and 101 ± 5 m²/g and the particle size of these materials ranges from 13 ± 2 nm to little over one micron. These surface areas are used to calculate the coverages of adsorbed nitric acid and water on these different samples in terms of monolayers that is discussed in further detail (*vide infra*).

Table 3.1. Particle size and surface area measurements of the source material.

<table>
<thead>
<tr>
<th>Oxide sample</th>
<th>Commercial Source</th>
<th>Average Particle size (nm)</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe₂O₃</td>
<td>Alfa Aesar</td>
<td>310 (± 22)</td>
<td>23 (± 2)</td>
</tr>
<tr>
<td>γ-Fe₂O₃</td>
<td>Alfa Aesar</td>
<td>110 (± 34)</td>
<td>50 (± 3)</td>
</tr>
<tr>
<td>α-FeOOH</td>
<td>Synthetic</td>
<td>1006 (± 55) x 25 (± 6)</td>
<td>39 (± 2)</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>Degussa</td>
<td>13 (± 4)</td>
<td>101 (± 5)</td>
</tr>
<tr>
<td>α-Al₂O₃</td>
<td>Alfa Aesar</td>
<td>220 (± 40)</td>
<td>12.4 (± 2)</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>OYMA</td>
<td>1214 (± 202)</td>
<td>10.1 (± 0.4)</td>
</tr>
</tbody>
</table>

Information about crystallinity, phases, and the presence or absence of impurities can be read from an X-Ray powder diffraction analysis. No impurities were detected in any of the commercial or synthesized samples. X-ray diffraction patterns were consistent
with that expected for respective standards of each sample, with patterns for nanoparticles, especially in gamma alumina, exhibiting line broadening as is typically observed with decreasing particle size. XPS was used to obtain surface elemental compositions for each of the studied samples and to identify any surface impurities. Representative XPS wide energy range survey scans for the two iron oxides and iron oxyhydroxide are shown in Figure 3.4, along with the high resolution XPS scans for the reacted samples. For iron oxide and oxyhydroxide samples Fe and O were determined to make up the majority of all of the elements whereas in alumina samples it was Al and O (not shown). In above five samples, elemental carbon was detected in trace level indicating presence of carbonate as a result of exposure to atmospheric CO₂. No other surface impurities were detected in XPS in any of the six samples.

ATR-FTIR spectroscopy can also provide insights into the surface chemical and physical properties of the source material. Figure 3.2 displays the ATR-FTIR spectra of each of the source minerals after overnight drying at < 5 % RH. Surface characterization with ATR-FTIR spectroscopy showed more pronounced differences in the OH stretching region (3000 – 3500 cm⁻¹) and in the surface phonon modes (~ 1000 cm⁻¹). With the exception of CaCO₃, all the other five samples showed strong absorbance for surface OH groups even after overnight drying. This IR feature is more structured in α-FeOOH, γ-Fe₂O₃ and γ-Al₂O₃ surfaces. The distinct absorption bands at 3489 and 3661 cm⁻¹ in the spectrum for α-FeOOH arise from surface O-H groups of higher coordination (doubly and triply coordinated) and singly coordinated surface hydroxyl groups respectively.¹²⁶, ¹²⁷ Similar surface features are observed for γ-Fe₂O₃ and γ-Al₂O₃ at 3616 and 3687 cm⁻¹ respectively. These additional hydroxyl groups on the mineral surface are suspected to
Figure 3.2  ATR-FTIR spectra are shown for all the clay minerals investigated in this study under dry conditions (< 5 % RH). (a). CaCO₃. (b). α-FeOOH (c). α-Fe₂O₃ (d). γ-Fe₂O₃ (e). γ-Al₂O₃ and (f). α-Al₂O₃.
play an important, if not dominant, role in adsorption reactions.

Strong absorptions observed near or below 1000 cm$^{-1}$ arise from lattice vibrations or phonon modes. In iron oxide samples, $\alpha$-Fe$_2$O$_3$ and $\gamma$-Fe$_2$O$_3$, peaks around 1010 & 732 and 1024 & 769 cm$^{-1}$ can be assigned to Fe-O stretch. In alpha and gamma phases of alumina samples, IR absorptions corresponding to Al-O stretch can be observed at 893 and 732 cm$^{-1}$ respectively. According to previous investigations by Cambier,$^{128,129}$ the bands observed at 881 and 791 cm$^{-1}$ for $\alpha$-FeOOH can be assigned to the bending modes of the bulk hydroxyl groups in ($\delta$OH) and out ($\gamma$OH) of the (001) plane. In CaCO$_3$ sample, the most intense bands at 714, 878 and 1436 cm$^{-1}$ and are assigned to the fundamental vibrational modes, $\nu_2$, $\nu_3$ and $\nu_4$, of the carbonate ion in bulk calcite.$^{95,130-132}$ Weaker bands at 1794 and 2514 cm$^{-1}$ are due to combination modes. The frequencies of the vibrational bands observed in this study are in good agreement with literature values.

3.4.2 Transmission FTIR Spectroscopy and XPS Investigation of HNO$_3$ Adsorption

The adsorption of nitric acid on metal oxides, oxyhydroxides and carbonates particles was studied under dry conditions, i.e., in the absence of water vapor. FTIR spectra following the reaction of HNO$_3$ on these mineral particles, at 296 K, as a function of HNO$_3$ exposure by increasing the pressure from 0.050 to 1.70 Torr for a period of 30 min are shown in Figure 3.3 and 3.5. The assignments of the vibrational bands of nitric acid adsorbed on these particles are given in Table 3.2 and 3.3. The experiments were done using the method previously described by Goodman et al.$^{88}$ Briefly, the each sample was loaded into the infrared cell and evacuated to $10^{-7}$ Torr overnight. A known pressure of HNO$_3$ was added into the infrared cell containing the mineral particles for
25 min. Absorbance spectra of HNO₃ adsorbed on these oxide particles were obtained by referencing the sample spectrum after HNO₃ was introduced into the infrared cell to the background spectrum prior to HNO₃ adsorption. Gas phase absorption bands measured through the blank grid could then be subtracted from the spectrum in order to obtain a spectrum of adsorbed HNO₃ only. Gas phase HNO₃ was then evacuated from the infrared cell and another spectrum was recorded and referenced to the background spectrum. The next highest pressure of HNO₃ was then added into the infrared cell containing mineral sample. Spectra were collected in the presence and upon evacuation of gas-phase HNO₃. This procedure was repeated until the surface becomes saturated.

3.4.2.1 Iron Oxides and Oxyhydroxides

With the addition HNO₃, several new absorption bands were appeared between 900 and 2000 cm⁻¹ and grow in intensity increasing pressure up to 1.70 Torr, as seen in Figure 3.3. The absorption bands in the region from 1200 to 1650 cm⁻¹ are assigned to the degenerate ν₃ mode of nitrate ion coordinated to the surface in different bonding configurations. Upon coordination, the symmetry of the nitrate ion decreases from D₃h symmetry to C₂ᵥ, and the degenerate ν₃ vibrational mode splits into two peaks, one to higher and one to lower frequency (ν₃,high and ν₃,low). As previously discussed in the literature, the difference in frequency (Δν₃) between ν₃,high and ν₃,low depends on the coordination mode and the distortion of the nitrate ion from D₃h symmetry.¹¹⁷,¹³³ The ν₁ vibrational mode, only Raman active for free nitrate ion, becomes IR active upon a decrease in symmetry and is seen at ~1050 cm⁻¹.
Figure 3.3  Transmission FTIR spectra of HNO₃ adsorption on (a) $\gamma$-Fe₂O₃ and (b) $\alpha$-Fe₂O₃ and (c) $\alpha$-FeOOH in the spectral range extending from 900 to 2000 cm⁻¹. All the bottom spectra refer to spectra recorded in the presence of nitric acid as a function of increasing pressure ranging from 0.050 to 1.7 Torr. Gas phase nitric acid absorption bands have been subtracted from those spectra shown. “Evacuated” refers to the spectra recorded after evacuation of gas phase HNO₃ used in these experiments.
Table 3.2. Assignment of vibrational frequencies of adsorbed products following the adsorption of HNO₃ on α-Fe₂O₃, γ-Fe₂O₃, α-Al₂O₃, γ-Al₂O₃ and α-FeOOH.  

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<th>α-Fe₂O₃</th>
<th>α-FeOOH</th>
<th>γ-Al₂O₃</th>
<th>α-Al₂O₃</th>
<th>Calculated frequencies for alumina</th>
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</table>

The assignments are based on literature references.  b n.o. = not observed below oxide coordinated nitrate absorption bands.  c Ref. 88, 1177, 120, 137-140
There is little change in the spectrum upon evacuation of gas phase nitric acid. In the HNO₃ acid “evacuated” spectrum, most of the absorption bands between 900 and 2000 cm⁻¹ remain in the surface spectrum. Disappearance of absorption bands at ~1674, 1336, and 1265 cm⁻¹ can be easily identified when a difference spectrum is taken, for a particular HNO₃ pressure, by subtracting the gas phase evacuated spectrum from spectrum recorded in the presence of gas-phase HNO₃. Similar vibrational frequencies have been observed for molecularly adsorbed nitric acid on SiO₂.⁸⁸ The νₐ(O-N-O) stretch, observed in present work at 1674 cm⁻¹, is shifted from that of the gas phase reported in the literature by -30 cm⁻¹.¹³⁴ A similar shift of -25 cm⁻¹ was calculated at B3LYP/6-311+G(d) level of theory by Thompson et al. for HNO₃ molecule bonded to Si(OH)₄ cluster via hydrogen bonding with a calculated binding energy of -35.50 kJ mol⁻¹.¹³⁵ Therefore, these bands can be attributed to molecularly adsorbed HNO₃. Although the absorption bands for molecularly adsorbed HNO₃ and oxide-coordinated nitrate overlap, this is clearly visible in the absorption band at ~1680 cm⁻¹. Thus, the results imply that HNO₃ reacts with iron oxides and mainly form oxide-coordinated nitrate which is irreversible, and some weakly adsorbed HNO₃.

The absorption bands for γ-Fe₂O₃ have been reported in previous studies in our laboratory and are assigned to the degenerate modes of oxide coordinated monodentate, bidentate and bridging nitrate which has been split into two bands because of loss of symmetry upon adsorption.⁸⁸ Similarly, in α-Fe₂O₃ and α-FeOOH, the bands around 1615, 1564, 1540, 1330, 1290, 1270 cm⁻¹ and the broad adsorption band around 1040 cm⁻¹ can be assigned to ν₃ and ν₁ vibrational modes of adsorbed monodentate, bidentate and bridged nitrate ion.¹¹⁷ It should be noted that in the case of α-FeOOH,
Figure 3.4 XPS analysis of nitric uptake on iron oxides and oxyhydroxides (a) Survey XPS of α-Fe₂O₃ (top panel), γ-Fe₂O₃ (middle panel), α-FeOOH (bottom panel) before reacting with HNO₃ (b) High resolution XPS in the N1s region of α-Fe₂O₃ (top panel), γ-Fe₂O₃ (middle panel), α-FeOOH (bottom panel). In each panel of high resolution XPS, bottom - prior to exposure to HNO₃ and top – exposed to 1 Torr of HNO₃.
weak absorption band at 1414 cm$^{-1}$ may be due to partially-solvated nitrate on Fe-hydroxylated cluster.$^{94}$ As will be discussed in the following section, absorption bands due to water-solvated nitrate become more intense in the presence of gas phase water vapor (Relative humidity $> 10\%$).

In XPS studies, the sample was pressed onto indium foil attached to a copper stub and then it was placed inside the custom made glass reaction chamber connected to the mixing chamber of the transmission FTIR and evacuated overnight. Following evacuation, oxide sample was equilibrated with $\sim$1 Torr of HNO$_3$ for 30 min and evacuated for 12 hours. Then stub with the treated sample was introduced to the XPS analysis chamber. The results from the XPS analysis for $\gamma$-Fe$_2$O$_3$, $\alpha$-Fe$_2$O$_3$ and $\alpha$-FeOOH are shown in Figure 3.4. The survey spectra (Figure 3.4(a)) for $\gamma$-Fe$_2$O$_3$, $\alpha$-Fe$_2$O$_3$ and $\alpha$-FeOOH show photoelectron peaks at 708, 525, 285, 95, 56 and 23 eV which can be assigned to Fe2p, O1s, C1s, Fe3s, Fe3p and O2s respectively. High resolution XPS data, after exposure to HNO$_3$ acid, is shown in Figure 3.4(b). For all the three iron samples one additional surface species was observed with a binding energy of 407 eV. This can be assigned to nitrate (N1s) on the surface. This assignment supports the results obtained from transmission FTIR. Further analysis was done by curve fitting to identify the speciation of N compounds on the surface.

It was determined from volumetric measurements that under dry conditions, the saturation coverage of nitric acid on $\alpha$-Fe$_2$O$_3$, $\gamma$-Fe$_2$O$_3$ and a-FeOOH were 2.32 (± 0.12) x $10^{14}$, 4.46 (± 0.26) x $10^{14}$ and 1.05 (± 0.08) x $10^{14}$ molecules-cm$^{-2}$, respectively. The higher adsorption capacities can be attributed to higher surface area and the smaller particle size.
Figure 3.5  Transmission FTIR spectra of HNO₃ adsorption on (a). α-Al₂O₃ and (b). γ-Al₂O₃ and (c). CaCO₃ in the spectral range extending from 900 to 2000 cm⁻¹. All the bottom spectra refer to spectra recorded in the presence of nitric acid as a function of increasing pressure ranging from 0.050 to 1.7 Torr. Gas phase nitric acid absorption bands have been subtracted from those spectra shown. “Evacuated” refers to the spectra recorded after evacuation of gas phase HNO₃ used in these experiments. In Figure c, asterisks in the spectra indicate losses due to surface carbonate absorptions.
3.4.2.2 Alumina

The transmission FTIR spectra of the aluminum oxides, \(\alpha\)-Al\(_2\)O\(_3\) and \(\gamma\)-Al\(_2\)O\(_3\) exposed to HNO\(_3\) at 296 K are shown in Figure 3.5(a) and (b), respectively. Similar to iron oxides, upon adsorption of HNO\(_3\) on the aluminum oxide particles several new absorption bands appear between 900 and 2000 cm\(^{-1}\), and grow in intensity as the nitric acid pressure increases. These spectra are broad and complex suggesting there are several different adsorbed products on the surface. The results shown in previous studies by Miller et al. and Baltrusaitis et al. aid in the assignments of the vibrational frequencies for \(\alpha\)-Al\(_2\)O\(_3\) and \(\gamma\)-Al\(_2\)O\(_3\).\(^{117, 121, 136}\) The bands between 1500 – 1630 cm\(^{-1}\) and 1250 – 1330 cm\(^{-1}\) assigned to \(\nu_3,\text{low}\) and \(\nu_3,\text{high}\) vibrational modes of adsorbed nitrate coordinated to the aluminum oxide surface with different coordinations (See Table 3.2). In particular, the absorption bands at 1328 and 1539 and at 1330 and 1538 cm\(^{-1}\) were assigned to the monodentate coordination of nitrate on \(\alpha\)-Al\(_2\)O\(_3\) and \(\gamma\)-Al\(_2\)O\(_3\), respectively. For the bidentate coordination, absorption bands at 1304 and 1564 cm\(^{-1}\) are assigned for \(\alpha\)-Al\(_2\)O\(_3\) whereas it was 1303 and 1572 cm\(^{-1}\) for \(\gamma\)-Al\(_2\)O\(_3\). The absorption bands at 1264 and 1633 cm\(^{-1}\) and 1265 and 1625 cm\(^{-1}\) were assigned to the bridged coordination of nitrate for \(\alpha\)-Al\(_2\)O\(_3\) and \(\gamma\)-Al\(_2\)O\(_3\), respectively. These assignments are made from previous literature assignments.\(^{117, 120, 136-140}\)

Upon analysis of the “evacuated” spectra, there is little change in the spectrum upon evacuation of gas phase nitric acid with the exception of a loss in intensity of the absorption band at approximately 1680 cm\(^{-1}\) for both the alumina surfaces. As discussed in the previous section, absorption bands with these vibrational frequencies have been observed for molecularly adsorbed nitric acid.\(^88, 136\) There are some additional absorption
bands in the spectra with vibrational frequencies of 1486 and 1485, and 1421 cm$^{-1}$ for $\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$, respectively. Based on results shown in Seisel et al. for HNO$_3$ on Saharan dust, absorption bands around at 1485 cm$^{-1}$ can be assigned to ion coordinated nitrate.$^{136,141}$

A higher surface coverage for HNO$_3$ adsorption, $6.58 \pm 0.38 \times 10^{14}$ molecules$\cdot$cm$^{-2}$, was recorded from $\gamma$-Al$_2$O$_3$ compared to $\alpha$-Al$_2$O$_3$ and iron samples studied. It was only $1.48 \pm 0.13 \times 10^{14}$ molecules$\cdot$cm$^{-2}$ for $\alpha$-Al$_2$O$_3$.

### 3.4.2.3 Calcium Carbonate

Transmission FTIR spectra following HNO$_3$ adsorption on the surface of calcium carbonate as a function of nitric acid pressure are shown in Figure 3.5(c). Losses of surface calcium carbonate can be observed in the IR spectra as nitric acid reacts with the surface and the corresponding IR bands are marked with a asterisk on the Figure. Several new absorption features grow in as a f(HNO$_3$ pressure). These new features can be assigned to the presence of two surface species, adsorbed nitrate and carbonic acid (H$_2$CO$_3$). New absorption bands associated with adsorbed nitrate are seen at 745 ($\nu_4$), 816 ($\nu_2$) and 1045 cm$^{-1}$ ($\nu_1$) 1302 cm$^{-1}$($\nu_3$) and remain in the spectrum even after the evacuation of the gas phase. The vibrational assignment for adsorbed nitrate and carbonic acid are summarized in Table 3.3. These bands are in good agreement with previous studies for nitrate absorptions.$^{87,88,133,142}$ The intensity of the symmetric stretching vibration at 1045 cm$^{-1}$, an infrared inactive mode for the nitrate ion with D$_{3h}$ symmetry, suggests that the nitrate ion is in an asymmetric environment. Based on structures of similar compounds, the nitrate ion can be proposed to have a bidentate
The formation of carbonic acid is also evident by the appearance of absorption bands at 687, 839, 1022 and 1688 cm\(^{-1}\) and assignment of vibrational frequencies are given in Table 3.3. The condensed form of carbonic acid has a C=O vibration at 1705 cm\(^{-1}\) and in adsorbed carbonic acid, the C=O vibration is at lower wavenumber 1688 cm\(^{-1}\). This indicates that the C=O bond in adsorbed carbonic acid is interacting with nearby ions on the surface.

The surface eventually saturates with adsorbed nitrate and carbonic acid, as evidenced by the lack of any increase in the absorption bands as the exposure and pressure are further increased. The surface coverage from volumetric measurements for
nitric acid on calcium carbonate was determined to be $2.84 \pm 0.34 \times 10^{14}$ molecules cm$^{-2}$.

3.4.3 ATR-FTIR and QCM Studies of H$_2$O Uptake on Metal Oxides, Oxyhydroxides and Carbonates

Water adsorption on $\gamma$-Fe$_2$O$_3$, $\alpha$-Fe$_2$O$_3$, $\alpha$-FeOOH, $\alpha$-Al$_2$O$_3$, $\gamma$-Al$_2$O$_3$ and CaCO$_3$ was investigated as a function of relative humidity. Figure 3.6(a–f) are representative ATR-FTIR difference spectra of water adsorption on above mineral surfaces. The spectra show changes in the 3400 - 3600 cm$^{-1}$ and 1600 to 1700 cm$^{-1}$ as a function of increasing RH from $<$ 5 % to $\sim$ 80 % RH. These bands are assigned to the stretching ($\nu_{\text{OH}}$) and bending ($\delta_{\text{OH}}$) modes of water respectively,$^{143}$ and grow in as the RH is increased. The structure in the O-H stretch suggests that water is in a more structured environment similar to that of the structure of ice. It can be seen from these spectra that the stretching region for $\gamma$-Fe$_2$O$_3$, shown in Figure 3.6(a), is more structured than that of other studied samples. Especially at higher relative humidities, the O–H stretching band for $\gamma$-Fe$_2$O$_3$ splits into two bands with centers at 3553 and 3115 cm$^{-1}$. Based on evidence from pervasive studies, this may indicate that $\gamma$-Fe$_2$O$_3$ is reacting with gas phase water to form $\gamma$-[Fe(O)OH].$^{144}$ Minor structural features in the $\nu_{\text{OH}}$ absorption can be observed for $\alpha$-Al$_2$O$_3$ and $\alpha$-FeOOH.

In O–H stretching region of CaCO$_3$, a broad absorption band grows in. At low relative humidity this band has distinct structure. The three distinct features in this broad band appear in the spectra at 3247, 3372 and 3596 cm$^{-1}$. These features grow as the RH increases. At the higher RH ($>$45% RH), as the coverage of molecularly adsorbed water
Figure 3.6 ATR-FTIR spectra of water absorption on (a) $\gamma$-Fe$_2$O$_3$ (b) $\alpha$-Fe$_2$O$_3$ (c) $\alpha$-FeOOH (d) $\alpha$-Al$_2$O$_3$ (e) $\gamma$-Al$_2$O$_3$ and (f) CaCO$_3$ as a function of relative humidity from 0 to 80 % RH. Each Spectrum was referenced to the appropriate clean surface spectrum prior to exposure to water vapor. Gas phase absorptions were then subtracted from the spectrum.
increases, these features become less distinct giving way to one broader band centered around 3372 cm\(^{-1}\). According to the literature, at low relative humidity, it appears that two-dimensional islands of water present on the surface indicating formation of an ordered “ice-like” structure with its characteristic frequency at 3247 cm\(^{-1}\) that is close to the frequency found for solid water.\(^{145}\) At higher relative humidity, it appears that the water molecules start to cluster together to form liquid-like water and would explain the loss of distinct peaks in the O–H stretching region and the growth of a broadband centered near 3372 cm\(^{-1}\). To support this argument, the bending mode absorption band also exhibits similar changes, as a function of relative humidity.

In previous studies infrared absorption integrated band intensities were used to quantify the water uptake where several assumptions made in this type of analysis. This study uses data from QCM measurements to quantify the amount of water taken up by the mineral samples. Representative QCM measurements are shown in Figure 3.7(a–f) for \(\gamma\)-Fe\(_2\)O\(_3\), \(\alpha\)-Fe\(_2\)O\(_3\), \(\alpha\)-FeOOH, \(\alpha\)-Al\(_2\)O\(_3\), \(\gamma\)-Al\(_2\)O\(_3\) and CaCO\(_3\). The change in frequency, \(\Delta f\), was recorded as the RH was both increased and decreased. For some cases, i.e. \(\alpha\)-Al\(_2\)O\(_3\), the QCM data in Figure 3.7 shows there is hysteresis in the water uptake, as they never dry out to the original frequency and deviates beyond the slight drift in frequency over time by the QCM (\(\sim \pm 0.1\) µg/cm\(^2\)). This can be due to presence of higher amounts of water, dissociated or undissociated, coordinated with metal centers of the mineral surface. Since \(\Delta f\) is initially taken as zero after overnight drying of the mineral studied on the QCM at RH < 5 \%, that allows for the change in frequency to be converted directly into the mass of the water taken up as a \(f(RH)\). The calculated mass of water at each specific relative humidity can be converted into coverage by using the total
Figure 3.7  Water uptake on mineral samples was monitored as a f(RH) with a QCM. Representative QCM measurements are shown for (a). $\gamma$-Fe$_2$O$_3$ (b). $\alpha$-Fe$_2$O$_3$ (c) $\alpha$-FeOOH (d). $\alpha$-Al$_2$O$_3$ (e). $\gamma$-Al$_2$O$_3$ and (f). CaCO$_3$. The change in frequency can be related to the mass according to Equation 3.1.
Figure 3.8  QCM measured water uptake on (a) $\gamma$-Fe$_2$O$_3$ (b) $\alpha$-Fe$_2$O$_3$ (c) $\alpha$-FeOOH (d) $\alpha$-Al$_2$O$_3$ (e) $\gamma$-Al$_2$O$_3$ and (f) CaCO$_3$. These data are plotted in terms of monolayers (ML) adsorbed as a f(RH). The reference point ($\Delta f = 0$) is taken as the 0 % RH point after overnight drying for all samples. 1 ML = $10^{15}$ molecules·cm$^{-2}$.
surface area of each sample deposited onto the QCM. This is done by multiplying the mass of the studied sample, measured with the QCM, by the specific BET surface area measured for each mineral sample. A monolayer (ML) is taken as $1 \times 10^{15}$ water molecules·cm$^{-2}$.\textsuperscript{146} The QCM data, for all of the studied minerals, was plotted in terms of “monolayer” coverage and shown in Figure 3.7. Data from multiple sets of experiments are included in every plot for each sample. Based on the results shown in Figure 3.7, all of the minerals take up water significantly with the highest for CaCO$_3$ and the lowest for $\alpha$-Al$_2$O$_3$.

Compared to metal oxides and oxyhydroxide, carbonate minerals are thought to have higher surface charge density at the interface.\textsuperscript{147} The presence of this high surface charge is due to the existence of a thin and highly structured electric double layer at the carbonate solution interface. This electric double layer has a high capacitance capability that makes it able to accommodate high charge densities. This very high surface charge is compensated by the dissociative adsorption of water on the surface. According to previous studies by Stipp and Hochella, when a CaCO$_3$ surface exposed only to ambient air or water vapor, strongly chemisorbed hydroxyl groups are formed on the surface that remain on the surface even under ultra-high vacuum conditions.\textsuperscript{148, 149} X-ray photoelectron spectroscopy (XPS) established the presence of CO$_3$H$^-$ and OH$^-$ groups on the surface.\textsuperscript{148, 149} Due to its hydrophilic nature, the Ca(OH)(CO$_3$H) surface layer can readily adsorb more water from the atmosphere. Thus, formation of these surface bond species can be the reason for the observed higher water uptake in CaCO$_3$. 

3.4.4 Transmission FTIR Spectroscopy Studies of Water uptake on Metal Oxide and Carbonate Particles Coated with a Nitrate layer

Water adsorption on metal oxide and carbonate particles, $\gamma$-Fe$_2$O$_3$, $\gamma$-Al$_2$O$_3$ and CaCO$_3$ saturated with HNO$_3$ were also investigated by transmission FTIR spectroscopy described in Chapter 2.1.1. Changes in the spectrum of nitrate ion in the presence of water and changes in the uptake of water when the nitrate ion is adsorbed on the mineral surface were also studied. In these experiments, each sample was exposed to HNO$_3$ (1.7 Torr) for thirty minutes such that the surface is saturated. The gas phase HNO$_3$ was then evacuated over night to get rid of any weakly bond species which yielded a layer of adsorbed nitrate over the particle surface. This “nitrated” surface was then exposed to different RHs ranging from 5 to 80% RH. The transmission FTIR spectra of “nitrated” $\gamma$-Fe$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ particles as a function of relative humidity are shown in Figure 3.9. The assignments of the vibrational frequencies, from the FTIR spectra shown in Figure 3.9, of the adsorbed nitrate products are given in the Table 3.2. These assignments are made from previous literature assignments.$^{117, 120, 137-140}$

With the increase of RH, there is the growth of a band at approximately 1640 cm$^{-1}$ and 1630 cm$^{-1}$, for $\gamma$-Fe$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ which is due to the bending mode of adsorbed water. In addition, there are changes in the adsorbed nitrate ion spectrum in the $\nu_3$ region. At the lower relative humidity values (%RH < 20), absorptions due to monodentate, bidentate and bridged nitrate species, as well as several new bands are observed as the relative humidity is increased. At higher relative humidity, these new intense absorption bands begin to dominate the spectra with frequencies at ~1406 and 1340 cm$^{-1}$ for both $\gamma$-Fe$_2$O$_3$ and $\gamma$-Al$_2$O$_3$. These two bands are assigned to the $\nu_3$ mode of
Figure 3.9  Transmission FTIR spectra shown in the spectral range extending from 900 to 2000 cm\(^{-1}\) of “nitrated” (a) $\gamma$-Al\(_2\)O\(_3\) and (b) $\gamma$-Fe\(_2\)O\(_3\) as a function of increasing water vapor pressures.
adsorbed water-solvated nitrate. The smaller splitting (~ 65 cm\(^{-1}\)) in the frequencies of the \(v_3\) band, compared to dry condition, implies a decrease in the distortion of the molecular ion from \(D_{3h}\) symmetry in the presence of co-adsorbed water.

At this relative humidity, it was been determined that multiple layers of adsorbed water (ca. 2 ML) would be present on both the surface. Previous spectroscopic studies as well as the reactivity studies implies that water is not evenly distributed on the surface even above 1 ML and that there are “bare” or “open” sites at high relative humidity.\(^{93}\) According to Xu et. al., there can be isolated O-H groups, or O-H groups not hydrogen bonded to adsorbed water even at 50 % RH on hydrated surfaces.\(^{150}\) Thus, from the spectroscopic data and multilayer calculations, for nitrate adsorption on metal oxide surfaces, \(\gamma\)-Fe\(_2\)O\(_3\) and \(\gamma\)-Al\(_2\)O\(_3\), it would appear that nitrate is not completely solvated by water molecules on the surface even at the higher relative humidities.

The influence of adsorbed water on the surface chemistry of calcium carbonate with HNO\(_3\) was further investigated. The spectra shown in Figures 3.10(a) were recorded of the calcium carbonate surface following successive cycles of HNO\(_3\) exposures followed by H\(_2\)O vapor exposures. As discussed earlier, for the first exposure of HNO\(_3\) to the surface, adsorbed nitrate and carbonic acid are formed. The HNO\(_3\) pressures used in the study are high enough such that the surface saturates. After the surface is saturated, the same surface is exposed to water vapor and then the infrared cell is evacuated before collecting a spectrum. It can be seen that the carbonic acid bands, easiest seen for the band near 1685 cm\(^{-1}\), go away in the spectra with the addition of water to the surface. Further subsequent addition of HNO\(_3\) on the same surface shows that carbonic acid is formed on the surface again. This continues to happen in successive exposure of HNO\(_3\)
Figure 3.10 (a) Transmission FTIR spectra of subsequent exposures of HNO₃ and water on CaCO₃ particles. All the spectra are recorded after evacuation of the exposure gas. (b) Representative SEM images of CaCO₃ particles before (left) and after (right) the reaction with HNO₃ and water. (c) Pictorial cartoon representation of the formation of micropuddles (small islands) following the reaction of HNO₃ and water on CaCO₃ particle surface.
followed by water vapor exposure.

Figure 3.10(b) shows representative SEM images of CaCO$_3$ particles before and after the exposure to HNO$_3$ followed by H$_2$O. It can be clearly seen that CaCO$_3$ surface has been subjected to dissolution during the exposure along with the formation of small islands (white dots) on the surface. Figure 3.10(c) is a pictorial cartoon of island formation of micropuddles of calcium nitrate following water adsorption. Thus, these results indicate formation of a single layer of nitrate adsorption which in the presence of water leads to ionic mobility and the subsequent formation of islands of calcium nitrate. The mechanism involved in the formation of these new structures on the surface will be conversed in detailed in the Discussion section.

3.4.5 Quantum Chemical Calculations

Quantum chemical calculations were carried out at B3LYP/6-31+G(d) level of theory to verify the structures of adsorbed nitrate in the presence and absence of co-absorbed water. Vibrational frequencies were calculated for six different cluster models of adsorbed nitrate corresponding to different modes of bonding to the surface, as shown in Figure 3.11. Cluster models 3.11(a) to (d) represent monodentate, bidentate, (O-O)-bridged and O-bridged coordinated nitrate structures. The calculated characteristic degenerate $\nu_3$ and $\nu_1$ frequencies for these cluster models are given in Table 3.2. Additionally, calculated vibrational frequencies are computed and compared with experimental values. Calculated vibrational frequencies were scaled by the appropriate scaling factor of 0.9632. The experimental values are in a good agreement with the frequencies for cluster models 3.11(a), (b) and (c), thus confirming the assignment of
Figure 3.11 Energy minimized structures for four cluster models \([\text{Al}_2(\text{OH})_3(\mu-\text{OH})(\text{NO}_3^-)]^-\) optimized at B3LYP/6-31+G(d) level of theory. Atoms of different elements are highlighted with different colors: metal sites, green; oxygen, red; hydrogen, blue; nitrogen, purple. Structures include, (a) monodentate (b) bidentate (c) & (d) bridged (e) inner-sphere coordinated and (f) outer-sphere coordinated nitrated on alumina surface. Structural parameters as well as vibrational frequencies calculated at the same level of theory are given in Table 3.2.
adsorbed nitrate with different modes of coordination to the surface in the absence of co-
adsorbed water.

For solvated nitrate complexes, vibrational frequencies were calculated for the
nitrate ion bonded to an aluminum atom in the presence of eleven water molecules, inner-
sphere coordination (Figure 3.11(e)) and for the nitrate ion not directly bonded to an
aluminum atom in the presence of eleven water molecules, outer-sphere coordination
(Figure 3.11(f)). Eleven water molecules were picked due to fact that several layers of
water in the cluster models closely mimic the experimentally observed values of 2-4 ML
of adsorbed water on aluminum oxides at the higher relative humidity. Thus from
calculated vibrational frequency analysis, both inner and outer sphere models of nitrate
ion to the aluminum oxide surfaces can be inferred.

3.5 Discussion on Reaction Mechanisms

In HNO₃ adsorption on metal oxide and oxyhydroxide particles, the majority of
the adsorption is irreversible, in that upon evacuation of the gas phase, adsorbed products
remain. The results from γ-Fe₂O₃, γ-Al₂O₃ and α-Al₂O₃ are comparable with the previous
studies. In the case of α-Fe₂O₃, α-Al₂O₃ and α-FeOOH, they showed a significant
reactivity towards HNO₃ through heterogeneous adsorption, but the coverage calculations
highlight relatively less reactivity compared to γ-Fe₂O₃ and γ-Al₂O₃. Given the
importance to particle size effect, larger particle size and less surface area are the primary
courses for the lower adsorption ability of the α-Fe₂O₃, α-Al₂O₃ and α-FeOOH. In
previous studies, following reaction sequence has been proposed for the reactive
uptake of nitric acid on oxide and oxyhydroxide particles which is confirmed by the current study.

\[
HNO_3(g) \rightarrow [HNO_3(a)] \rightarrow H^+(a) + NO_3^-(a) \quad \text{Eq: 3.1}
\]

or

\[
HNO_3(g) + M-OH \rightarrow [M-OH_2]^+ + NO_3^-(a) \quad \text{Eq: 3.2}
\]

where M is the metal ion. In the presence of water, the adsorbed water layer solvates nitrate on the surface, in which water act as another medium for the dissociation reaction.

\[
[M-OH_2]^+ + NO_3^-(a) + H_2O(a) \rightarrow M-OH + H_3O^+ + NO_3^-(aq) \quad \text{Eq: 3.3}
\]

or via direct deprotonation

\[
HNO_3(g) + H_2O \rightarrow H_3O^+ + NO_3^-(aq) \quad \text{Eq: 3.4}
\]

When a “dry” carbonate surface, without any pre-adsorbed water, is exposed to HNO3, surface reacts with HNO3 yielding Ca(NO3)2 and carbonic acid via,110,111

\[
CaCO_3(s) + 2HNO_3(g) \rightarrow Ca(NO_3)_2(a) + H_2CO_3(a) \quad \text{Eq: 3.5}
\]

Under humid conditions, water is readily adsorbed on CaCO3 surface and dissociate to yield a surface with (OH)(CO3H) according to the reaction given in Eq: 3.6.132,148

\[
CaCO_3(s) + H_2O(g) \rightarrow Ca(OH)(CO_3H) \quad \text{Eq: 3.6}
\]
In the literature, it is proposed that a weakly adsorbed water layer or a thin water film grows on the Ca(OH)(CO$_3$H) surface. This water layer appears to grow as a function of relative humidity in a structured two-dimensional array similar to what has been observed on other surfaces. At higher relative humidities, above $\sim$ 50% RH, a three-dimensional water layer forms.\textsuperscript{145} When this “wet” surface is exposed to HNO$_3$, the reaction yields Ca(OH)(NO$_3$) as the end product via,\textsuperscript{95}

$$\text{Ca(OH)(CO}_3\text{H}) + \text{HNO}_3(\text{g}) \rightarrow \text{Ca(OH)(NO}_3\text{)(a)} + \text{H}_2\text{CO}_3(\text{a})$$  \hspace{1cm} \text{Eq: 3.7}

The role of adsorbed water in the reaction of HNO$_3$ on calcium carbonate particles involves increased ionic mobility and surface segregation. In subsequent exposures of HNO$_3$ and water on CaCO$_3$ particles (Figure 3.10(a)), during the first step HNO$_3$ reacts with CaCO$_3$ surface under dry conditions, as given in Eq. 3.5 (or 3.7, if pre-adsorbed is present), and results in a passivation layer. Water adsorption on passivation layer yields an aqueous layer and this layer is a result of the deliquescence of calcium nitrate at approximately 10% RH.\textsuperscript{152} Besides, this results in the dissociation of carbonic acid leaving Ca(OH)(NO$_3$) on the surface and increase the mobility of the surface ions via,

$$\text{H}_2\text{CO}_3(\text{s}) + \text{H}_2\text{O(}\text{g}) \rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O(}\text{s})$$ \hspace{1cm} \text{Eq: 3.8}

The ions from remaining Ca(OH)(NO$_3$) segregate to form micropuddles in the presence of adsorbed water. Upon evacuation of water vapor, these micropuddles form an amorphous solid with trapped water, as shown in Figure 3.10(b). Formation of the amorphous calcium nitrate solid allows extra sites to be available for further uptake of HNO$_3$ onto the surface.
3.6 Conclusions

This study was done to address the question of whether denitrification by metal oxides, oxyhydroxides and carbonates would be significant to reduce the HNO₃ acid in the atmosphere and to understand the uptake of water by these mineral surfaces and the effect of co-adsorbed water on HNO₃ adsorption. Adsorbed nitrate, following exposure of mineral particle surfaces to HNO₃, in the presence and absence of co-adsorbed water, was investigated by transmission FTIR and quantum chemical calculations. The laboratory studies showed that studied particles can adsorb HNO₃ at a significant level and this can be considered as a reactive uptake on these particle surfaces. Under dry conditions (%RH < 1), there are at least three different coordination modes of adsorbed nitrate, including monodentate, bidentate and bridging. In the literature, the assignment of vibrational frequencies for these oxide coordinated nitrate structures have been previously discussed for different metal oxides, including some of the oxides studied here (γ-Fe₂O₃, γ-Al₂O₃ and α-Al₂O₃). The results obtained in this study were in good agreement with the literature. Besides, here, we compare the calculated frequencies for different cluster models to provide additional insight into these structures.

All the oxides, oxyhydroxides and carbonates used in this investigation showed a significant water uptake with the highest uptake by CaCO₃. Monolayer calculation indicated formation of multilayers of water over these reactive surfaces which can change the reactivity of the particle surface. The large amounts of water adsorbed, especially for CaCO₃ and γ-Fe₂O₃, provides additional evidence for the importance of water uptake on these mineral components of dust and the role it may play in the atmosphere. Water alone was found to reversibly adsorb on the surface of calcium carbonate, resulting in a thin
water film, which exhibits a two-dimensional layer growth mode prior to three-dimensional growth.

Under humid conditions, on metal oxide and oxyhydroxide surfaces, co-adsorbed water was found to have an effect on local bonding of the nitrate ion, as well as geometry and vibrational frequencies. Both experimental and computational work showed there can be two water solvated nitrate coordination modes that is inner-sphere and outer-sphere, which differ by nitrate proximity to the surface. The reaction of nitric acid on the surface of calcium carbonate forms calcium nitrate, with the concurrent formation of carbonic acid that decomposes to carbon dioxide in the presence of water. Water was found to play a role in the uptake of HNO₃ on calcium carbonate due to the fact that co-adsorbed water increases the ionic mobility of adsorbed ions on the surface, leading to the formation of micropuddles of calcium nitrate. The formation of these new structures exposed additional sites on the calcium carbonate surface that allows for an increase in the uptake of these gases onto the surface. Thus, adsorbed water significantly influences the uptake of most trace gases, including nitrogen oxides, onto aerosol dust components in the atmosphere.

This study shows further evidence regarding the important role that adsorbed nitrate and co-adsorbed water play in the surface chemistry and surface reactivity of metal oxides, oxyhydroxides and carbonates under environmentally relevant conditions of temperature and relative humidity.
3.7 Acknowledgement

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CHAPTER 4

DAYTIME AND NIGHTTIME CHEMISTRY OF ADSORBED NITRATE ON γ-ALUMINA PARTICLE SURFACES: EFFECT OF MOLECULAR OXYGEN, RELATIVE HUMIDITY AND PARTICLE SURFACE

4.1 Abstract

Mineral dust aerosol is indisputably an important component of the Earth’s atmosphere and provides a reactive surface for heterogeneous photochemistry to occur. These reactions can alter concentrations of key trace atmospheric gases as well as change the physicochemical properties of the dust particles. Nitrogen oxides, including nitrogen dioxide and nitric acid, react with mineral dust particles in the atmosphere to yield adsorbed nitrate. Although nitrate ion is a well known chromophore in natural waters, little is known about the surface photochemistry of nitrate adsorbed on mineral particles. In this study, nitrate adsorbed on aluminum oxide, a model system for mineral dust aerosol, is irradiated with broadband (λ > 300 nm) and narrowband pass (λ = 310 ± 2 nm) radiation as a function of relative humidity (RH) in the presence of molecular oxygen. Upon irradiation with broadband light, the nitrate ion readily undergoes photolysis to yield nitrogen-containing gas phase products, including NO₂, NO and N₂O, with NO being the major product. The relative ratio and product yields of these gas phase products change with relative humidity, with N₂O production being highest at the higher relative humidities. With 310 nm narrowband pass, NO₂ was the major gas phase product and there was no NO production. Information from wavelength dependence photolysis was used to derive a detail reaction scheme for the photolysis of adsorbed nitrate on
aerosol dust particles. Furthermore, an efficient dark reaction readily converts the major NO product into NO$_2$ during post-irradiation. Photochemical processes on mineral dust aerosol surfaces have the potential to impact the chemical balance of the atmosphere, yet little is known about these processes. In this study the impact that adsorbed nitrate photochemistry may have on the renoxification of the atmosphere is discussed.

4.2 Introduction

Mineral dust is a reactive component of the tropospheric aerosol.\textsuperscript{56, 111} It is now widely recognized that reactions on mineral dust aerosol impact both the chemical balance of the atmosphere and the physicochemical properties of the particles which, in turn, can change the climate impact of these particles. In the atmosphere, surface adsorbed nitrate on particulate matter, e.g. mineral dust and sea-salt aerosol, comes from heterogeneous reaction of gas phase nitrogen oxides including NO$_2$ and HNO$_3$ with these particles.\textsuperscript{56, 153} NO$_x$ (NO + NO$_2$) represents the major gas phase nitrogen containing anthropogenic pollutant, produced as a result of automobile and industrial fuel combustion.\textsuperscript{154} In the lower atmosphere, these nitrogen oxides participate in a complex series of chemical and photochemical reactions to produce tropospheric ozone in a non-linear relationship with respect to the ozone concentrations. Therefore, peak ozone levels are affected by the amount of NO$_x$ present in the gas phase which depends on the ground base emissions and subsequent reactions in the lower atmosphere.\textsuperscript{88, 114, 155} Moreover, as noted above, atmospheric nitric acid, the main reservoir species in the NO$_x$ cycle\textsuperscript{114} can readily react with particulate matter in the atmosphere to yield adsorbed nitrate.\textsuperscript{88} Thus
understanding all processes that impact NO\(_x\) and reservoir species such as HNO\(_3\) is important in atmospheric chemistry and air quality.

Oxide minerals represent an important and reactive component of mineral dust aerosol. Given that aluminum oxides and aluminum silicates contribute \(\sim 8\%\) by mass to the total dust burden in the atmosphere,\(^{156-158}\) aluminum oxides can be used as model systems to begin to understand various aspects of nitrogen oxide reactions on mineral dust aerosol. Several experimental and theoretical studies have shown that heterogeneous uptake of nitric acid on aluminum oxide and aluminosilicates yields a chemisorbed nitrate layer on the particle surface.\(^{88, 93, 156, 159, 160}\) Vibrational frequencies of adsorbed nitrate have been assigned and interpreted using quantum chemical calculations of binuclear alumina cluster models.\(^{156}\) Under humid conditions, atmospheric water vapor readily adsorbs to oxide particles and dissociates resulting in a hydroxyl terminated surface.\(^{161}\) Adsorbed water can hydrogen bond to these hydroxyl groups in equilibrium with water vapor. It has been shown that co-adsorbed water molecules readily solvate adsorbed nitrate ions on the aluminum oxide surface forming inner and outer sphere complexes.\(^{156}\)

Although, nitric acid adsorption and water uptake on aluminum oxide surfaces have been previously well studied, much less is known about the photochemistry of adsorbed nitrate on these particle surfaces. Given that photochemistry dominates the daytime gas phase chemistry of the atmosphere, and new light induced pathways continue to be discovered,\(^{162}\) there is whole lot of information available in the literature to realize that the surface and near surface regions of particles catalyze and promote reactions that perturb the composition of the troposphere. In natural waters, nitrate is an important chromophore\(^{83, 163}\) with an absorption in the solar region of the spectrum at 302 nm (\(\varepsilon = \ldots\))
7.2 M$^{-1}$·cm$^{-1}$) attributed to the n to $\pi^*$ electronic transition. Excitation of this transition results in the photochemical production of nitrogen dioxide and nitrite ion under acidic conditions.$^{82, 84, 164, 165}$

Here we present surface photochemical mechanisms identified in laboratory studies. The current study involves broadband ($\lambda > 300$ nm) photolysis of nitrate adsorbed on aluminum oxide particles, proxies for dust aerosol, to yield several gas phase nitrogen oxides, including N$_2$O, NO and NO$_2$. This reaction is potentially significant as it defines a route for the renoxification of the atmosphere whereby nitric acid, usually considered a reservoir species that, once associated with particulate matter such as dust, is removed from the atmosphere and becomes a source of NO$_x$ (NO$_x$ = NO + NO$_2$). We also focus our attention on the gas phase products that form in this reaction upon narrowband photolysis (310 ± 2 nm) of adsorbed nitrate, near the wavelength maximum of the first electron transition (n $\rightarrow$ $\pi^*$), to better understand the potential role of nitrate photochemistry on mineral dust and to derive a possible reaction mechanism or pathway that involves in photochemistry of adsorbed nitrate on aerosol particles. Besides the important ramifications of this photochemical reaction converting nitrate into NO$_x$ and N$_2$O, another interesting point of this study is that the product distribution dependent on the ambient conditions, i.e. relative humidity and the presence of molecular oxygen. Here we expand on this initial investigation and more thoroughly investigate the relative humidity dependence of the reaction products and kinetics. In addition, we present a study of a surface-mediated dark reaction converting NO to NO$_2$ during post-irradiation. The new reaction pathways explored in this chapter will lead to explain and predict concentrations of key gas phase constituents under a variety of environmental conditions.
4.3 Experimental Methods

4.3.1 Sources of the Oxide Powders and Reagents

Commercially available $\gamma$-Al$_2$O$_3$ (Degussa, Aluminum oxide C) with a surface area of 101 ± 4 m$^2$.g$^{-1}$ was used in these experiments. The surface area was determined using a Quantachrome Nova 4200e multipoint BET apparatus. Dry gaseous nitric acid was taken from the vapor of a 1:3 mixture of concentrated HNO$_3$ (70.6% HNO$_3$, Mallinckrodt) and 95.9% H$_2$SO$_4$, (Mallinckrodt). Distilled H$_2$O (Fisher, Optima grade) was degassed prior to use.

4.3.2 Transmission FTIR Spectroscopy

Photochemistry of adsorbed nitrate was monitored via transmission FTIR spectroscopy. The experimental setup for these experiments is described in detail in Chapter 2.1.1. and 2.1.2. Briefly, the infrared cell consists of a stainless steel cube with two barium fluoride windows and a sample holder. The inside of the stainless steel cube is coated with Teflon in order to avoid HNO$_3$ decomposition on the walls of the infrared cell. For these measurements, the oxide powder (5.7 ± 0.4 mg) was prepared by pressing onto half of a tungsten grid and the other half of the grid was left blank for gas phase measurements. The oxide samples prepared on the tungsten grid are secured inside the infrared cell by Teflon coated sample holder jaws. The sample cell is connected to a chamber through a Teflon tube which contains ports for gas introduction and two absolute pressure transducers (range 0.001- 10.000 torr and 0.1-1000.0 Torr). The total volume of the infrared cell is 1214 ± 4 mL (infrared cube 197 ± 2 mL and mixing chamber 1044 ± 1 mL). The vacuum chamber consists of a two-stage pumping system, a
turbomolecular/mechanical pump for pumping to $10^{-7}$ Torr, and a mechanical pump for rough pumping to $10^{-3}$ Torr. The infrared cell is mounted on a linear translator inside the FT-IR spectrometer. The translator allows both halves of the grid, the blank side for gas phase measurements and the oxide coated side for surface measurements, to be probed by simply moving the infrared cell through the IR beam path. After exposing the aluminum oxide surface with relatively high pressures of nitric acid ($1.78 \pm 0.01$ Torr) for 30 min to saturate the surface with nitrate, the FTIR cell was evacuated overnight to remove all weakly adsorbed products.

Following introduction of water vapor, molecular O$_2$ ($100 \pm 2$ Torr) or both, the valve connecting the FTIR cell to the mixing chamber was closed, letting the gas phase products accumulate inside the cell as the surface was irradiated. In these studies, a 500W broadband Hg arc lamp (Oriel, Model # 66033) followed by a water filter, to remove IR radiation, was used to irradiate the surface. In broadband photolysis, a UV filter ($\lambda < 300$ nm, Oriel filter # 59425) was coupled to the system to remove shorter wavelengths. In narrowband photolysis it was a 310 nm narrowband pass ($\lambda = 310 \pm 2$ nm, Asahi Spectra # XBPA310). The intensity of the broadband light source, reaching to the sample inside the custom made IR cell, was measured using a solar cell (model EI-100, Optical Energy Technologies). Irradiance of the lamp output was measured using a spectro-radiometer (model RPS900-R, International Light Technologies). The lamp output reaching to sample, along with the wavelength selection when passed through above UV filters, is shown in Figure 4.1. According to the results from these experiments, adsorbed nitrate receives broadband light approximately equal to one solar constant. The output spectrum of the light from the Hg-Arc lamp followed by the two filters was similar to the solar
Figure 4.1 The lamp output reaching the sample in the presence of broadband filter (\( \lambda < 300 \text{ nm} \), Oriel filter # 59425) or 310 nm narrowband pass (\( \lambda = 310 \pm 2\ \text{nm} \), Asahi Spectra # XBPA310). The intensity of the light source was measured using a solar cell (model EI-100, Optical Energy Technologies) and Irradiance of the lamp output was measured using a spectro-radiometer (model RPS900-R, International Light Technologies). Sample inside the FTIR cell receives broadband light approximately equal to one solar constant.

spectrum received by the troposphere. After irradiation, infrared spectra were recorded with a single beam Mattson RS-10000 spectrometer equipped with a narrow band MCT detector. Typically, 250 scans were collected with an instrument resolution of 4 cm\(^{-1}\) in the spectral range extending from 900 to 4000 cm\(^{-1}\). Absorbance spectra for gas and adsorbed species were obtained by referencing single beam spectra of the blank grid and
the oxide coated grid to single beam spectra collected prior to the nitric acid exposure. To investigate surface mediated post irradiation processes, the light source was turned off and IR spectra (25 scans, 4 cm\(^{-1}\) resolution) were immediately collected of the gas phase every 3 min for 2 hours.

4.3.3 Ex-situ X-ray Photoelectron Spectroscopy

The irradiated aluminum oxide sample was removed from the tungsten grid and analyzed using a custom-designed Kratos Axis Ultra X-Ray photoelectron spectrometer with a monochromatic Al K\(_\alpha\) X-Ray source. The sample was pressed onto an indium foil, on a copper stub, and introduced into the XPS analysis chamber, which had a pressure that was maintained in the 10\(^{-9}\) Torr range during analysis. Wide energy range survey scans were acquired using the following parameters: energy range from 1200 to -5 eV, pass energy of 160 eV, step size of 1 eV, dwell time 200 ms, X-ray spot size 700 x 300 sq. mm. High resolution spectra were acquired using the following parameters: energy range of 50 – 20 eV depending on the peak examined, pass energy of 20 eV, step size of 0.1 eV, dwell time of 1000 ms. The data collected were analyzed using CasaXPS data processing software.

4.4 Results and Discussion

4.4.1 FTIR Spectroscopy of Adsorbed Nitrate: Effect of Broadband Irradiation and Relative Humidity

The transmission FTIR spectra of \(\gamma\)-Al\(_2\)O\(_3\) exposed to nitric acid vapor followed by evacuation are shown in Figure 4.2(a) at four different relative humidities, <1, 20, 45
and 80%). Under conditions of lowest relative humidity (%RH < 1), adsorbed nitrate binds to the oxide surface in different modes of coordination as monodentate, bidentate and bridging as discussed in detail previously, based on the assignment of the peaks in the nitrate ion $\nu_3$ spectral region between 1200 and 1650 cm$^{-1}$. In the presence of water vapor at different relative humidities (20, 45 and 80%), co-adsorbed water solvates the nitrate ion forming inner and outer sphere complexes which are represented by peaks in the region between 1300 and 1450 cm$^{-1}$ in Figure 4.2(a). Changes in the infrared spectra as a function of relative humidity and the assignment of these peaks have been discussed extensively and the details can be found in Chapter 3.

Following the adsorption of nitric acid and the introduction of water vapor adjusted to the different relative humidities, the sample was irradiated with the broadband light ($\lambda > 300$ nm). Upon irradiation, the FTIR spectra of the nitrated surface at each relative humidity were recorded. It can be seen in Figure 4.2(b) that the spectrum changes after 420 min of irradiation. To further illustrate the surface processes during the broadband photolysis, infrared spectra recorded as a function of irradiation time under dry (at %RH < 1) and wet (%RH 45) conditions are shown in Figure 4.3(a) and (b), respectively. Most notably there is a decrease in the intensity of the spectral bands associated with adsorbed nitrate. An analysis of the changes in the intensities of these bands, including an analysis of the difference spectra, shows there is a loss of intensity at low relative humidity near 1559 cm$^{-1}$, assigned to the monodentate adsorbed nitrate and the bands at 1588 and 1307 cm$^{-1}$ assigned to bridging nitrate. That is to say the monodentate species shows the greatest loss upon irradiation followed by bridged nitrate absorptions. This reveals that there is a greater propensity for certain oxide-coordinated
Figure 4.2  FTIR spectra of surface adsorbed nitrate at different relative humidity conditions (RH < 1, 20, 45 and 80%) and 298K (a). Before broadband irradiation ($t = 0$ min). (b). After 420 min of irradiation ($t = 420$ min) (solid line). The dash line in (b) is the difference spectrum obtained by subtracting the spectrum at $t = 0$ min from the spectrum at $t = 420$ min.

ClONO$_2$ + H$_2$O   \hspace{1cm}    $\text{HOCl} + \text{HNO}_3$  \hspace{1cm} Eq: 6.1
Figure 4.3 FTIR spectra of surface adsorbed nitrate at (a). %RH < 1 (dry) and (b). %RH 45 (wet) conditions at 298 K as a function of broadband irradiation. Each spectrum was referenced to the clean oxide spectrum prior to exposure to nitric acid. Gas phase absorptions were then subtracted from each spectrum.
adsorbed nitrates to undergo photolysis. At higher relative humidity, the solvated nitrate peaks, observed between 1300 and 1450 cm\(^{-1}\), all decrease upon irradiation.

The percent loss of surface nitrate as a function of irradiation time is given in Table 1. The percent loss is determined using normalized integrated absorbance of the entire adsorbed nitrate \(\nu_3\) region extending from ca. 1220 to 1700 cm\(^{-1}\) for \%RH < 1 and from 1200 to 1550 cm\(^{-1}\) for solvated nitrate at higher relative humidity. The effect of molecular oxygen on nitrate photolysis was studied under two different relative humidity conditions, \%RH < 1 and \%RH 45 ± 2. In both the cases, the surface nitrate loss decreased significantly in the presence of molecular oxygen. As shown in Table 1, under dry condition the total nitrate on the surface decreases from 100\% (at time \(t=0\)) to 82 ± 1 \% and 41 ± 8 \%, in the presence and absence of molecular oxygen, respectively, following 420 min of irradiation. Similar changes are observed under humid conditions, 77 ± 2 \% and 40 ± 3\%, upon irradiation in the presence and absence of molecular oxygen, respectively. Control experiments in the presence of molecular nitrogen reveal that changes in the amount of surface nitrate loss is a result of interaction of the surface with molecular oxygen and not just due to the presence of a buffer gas. In a number of experimental and theoretical studies, it has been reported that defect sites including the presence of neutral oxygen vacancies and charged oxygen vacancies are present on aluminum oxide.\(^{166}\) These O(vacancy) sites may play a role, albeit unknown, in the primary photochemical process of adsorbed nitrate or the chemistry of photoproducts. If these sites are primary binding sites for the adsorption of molecular oxygen then oxygen will have a large impact on the photochemistry of adsorbed nitrate as is evident in these studies.
Table 4.1 Percent nitrate on the surface following broadband irradiation (\(\lambda > 300\) nm) under different conditions. \(^{a, b}\)

<table>
<thead>
<tr>
<th>Irradiation Time / min</th>
<th>%RH &lt; 1</th>
<th>20 ± 2</th>
<th>45 ± 2</th>
<th>80 ± 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>With O(_2)</td>
<td>Without O(_2)</td>
<td>With O(_2)</td>
<td>Without O(_2)</td>
</tr>
<tr>
<td>30</td>
<td>95 ± 1</td>
<td>83 ± 3</td>
<td>89 ± 1</td>
<td>72 ± 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(84 ± 1)(^c)</td>
<td></td>
<td>(74 ± 1)(^c)</td>
</tr>
<tr>
<td>120</td>
<td>85 ± 1</td>
<td>61 ± 3</td>
<td>78 ± 3</td>
<td>60 ± 2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(65 ± 2)(^c)</td>
<td></td>
<td>(62 ± 1)(^c)</td>
</tr>
<tr>
<td>420</td>
<td>82 ± 1</td>
<td>41 ± 8</td>
<td>74 ± 1</td>
<td>40 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(44 ± 3)(^c)</td>
<td></td>
<td>(43 ± 2)(^c)</td>
</tr>
</tbody>
</table>

\(^{a}\) At t=0 minutes, there is 100% nitrate on the surface.

\(^{b}\) Reported nitrate loss is the mean of triplicate measurements, and error represents ± 1\(\sigma\).

\(^{c}\) In select experiments, nitrogen (N\(_2\)) was used as a buffer gas at a pressure of 100 Torr and these data are reported in parenthesis. See text for further details.

As seen in Table 4.1, the effect of relative humidity on adsorbed nitrate photolysis is more significant in the presence of molecular oxygen. In the oxidative environment provided by the presence of molecular oxygen, a higher nitrate loss was recorded under humid conditions compared to that of dry (%RH < 1). To further understand the effect of relative humidity on nitrate photolysis, experiments were carried out under additional conditions of relative humidity in the presence of molecular oxygen. The higher loss of surface nitrate under humid conditions can be attributed to the formation of inner and outer sphere complexes of nitrate ion which have less interaction with the surface and less molecular distortion from the planar D\(_{3h}\) symmetry of the free ion compared to the oxide coordinated nitrate structures present under dry conditions.\(^{94}\) Furthermore, in the presence of water vapor, there is a possibility to form hydroxyl radicals as a result of
Figure 4.4 Kinetics of broadband photolysis of adsorbed nitrate (a). Photo-induced surface nitrate loss in the presence of molecular oxygen and (b). Pseudo first order rate analysis for the photolysis of adsorbed nitrate, under different relative humidity conditions (RH < 1, 20, 45 and 80%). $\theta_0$ – adsorbed nitrate concentration on saturated oxide surface at t = 0. $\theta$ – nitrate concentration on oxide surface at irradiation time t. The presented nitrate loss is the mean of triplicate measurements and the error bars represent the standard deviation.
These hydroxyl radicals can initiate new photochemical pathways leading to a higher nitrate loss from the oxide surface. H-bonding between solvated nitrate and co-adsorbed water affects the energetics of the electronic n to π* transition near 300 nm with a red shift resulting in a higher overlap of the absorption profile of nitrate with the broadband irradiation source.

According to Figure 4.4, during several hours of photolysis of adsorbed nitrate, the change in the rate of nitrate disappearance is most significant in the first 90 min. An attempt to fit the time dependence of nitrate photolysis to first order kinetics, in order to gain an estimate of an apparent rate constant is shown in the inset of Figure 4.4(b). According to this analysis, the first order photolysis rate constants are 3.2 ± 0.2 x 10^{-5}, 5.6 ± 0.3 x 10^{-5}, 4.9 ± 0.2 x 10^{-5} and 4.2 ± 0.2 x 10^{-5} s^{-1} for RH < 1, 20, 45 and 80% respectively. Therefore, initial rate of adsorbed nitrate photolysis is approximately 1.5 to 2 times faster in the presence of co-adsorbed water.

Along with the photochemical loss of nitrate, there is the growth of product bands as well. As seen in the spectra shown in Figure 4.2 and 4.3, there is a peak near 1702 cm^{-1} that grows in intensity, under all conditions of relative humidity. The presence of the band at 1702 cm^{-1} on the surface suggests the formation of a new surface product. The assignment of this band is discussed in detail, as well as the assignment of several nitrogen-containing gas phase products, below.

### 4.4.2 Analysis of Gas Phase and Surface Bound Products

As shown in Figure 4.5, gas phase products appear as a function of irradiation of adsorbed nitrate. FTIR spectra of these gas phase products recorded as a function of
Figure 4.5    FTIR spectra of gas phase products formed during photolysis of adsorbed nitrate under dry (%RH < 1) at 298K. (a) In the absence of molecular oxygen. (b) In the presence of molecular oxygen (100 ± 5 Torr). Each spectrum was referenced to the gas phase spectrum prior to exposure to nitric acid.
irradiation time under dry condition (%RH < 1) both in the presence and absence of molecular oxygen are shown. It is relatively easy to identify the major gas phase products as N₂O, NO and NO₂ with characteristic absorptions at 2224, 1872 and 1614 cm⁻¹, respectively. A comparison of the spectra shown in Figure 4.5(a) and (b) reveals a significant change in the gas phase product distribution, in particular the relative N₂O and NO₂ concentrations under these two different environmental conditions. This large difference is noted and will be discussed in detail below. In this work, we also focused on gas product distribution under different relative humidity conditions in an oxidative environment, i.e. in the presence of molecular oxygen, because this is more atmospherically relevant conditions.

Table 4.2 Assignment of major infrared absorption bands and conversion factors used to calculate the gas phase product concentrations.

<table>
<thead>
<tr>
<th>Gas phase products</th>
<th>Vibrational mode⁹</th>
<th>Frequency (cm⁻¹)</th>
<th>Integrated Absorbance spectral range (cm⁻¹)</th>
<th>Conversion (mol·L⁻¹)⁹</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>vₐ</td>
<td>1616</td>
<td>1540–1670</td>
<td>0.31·10⁻⁴</td>
</tr>
<tr>
<td>NO</td>
<td>v</td>
<td>1874</td>
<td>1750–1980</td>
<td>3.08·10⁻⁴</td>
</tr>
<tr>
<td>N₂O</td>
<td>vₐ</td>
<td>2224</td>
<td>2124–2271</td>
<td>0.69·10⁻⁴</td>
</tr>
</tbody>
</table>

⁹ – Refs. 170 - 172

Gas phase concentrations obtained from FTIR analysis followed by broadband (λ > 300 nm) irradiation of adsorbed nitrate in the presence of molecular oxygen under
Figure 4.6  Gas phase concentrations obtained from FTIR spectra following irradiation of adsorbed nitrate in the presence of molecular oxygen at 298K under different relative humidity (%RH) conditions, (a). $< 1$  (b). $20 \pm 2$  (c). $45 \pm 2$  (d). $80 \pm 2$. 
different relative humidity conditions (RH < 1, 20, 45 and 80%) are shown in Figure 4.6. The results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Gas phase concentrations of individual species were determined by converting integrated absorbances to concentrations using calibration factors, given in Table 4.2, for the individual gas phase species. These data show that gas phase NO₂, NO and N₂O are produced at different rates and in different yields.

Before further discussing the photochemistry of adsorbed nitrate and the photoproducts that form, it is first instructive to consider what is known about nitrate photochemistry in solution phase and snow pack. It is well-known that irradiation of the nitrate ion with light at 305 nm under acidic conditions yields nitrogen dioxide and nitrite. Further photolysis of the nitrite ion at 365 nm produces NO, according to the following reactions:

\[ \text{NO}_3^- + \text{H}^+ \overset{305\text{nm}}{\longrightarrow} \text{NO}_2 + \text{OH} \quad \text{Eq: 4.1;} \]

\[ \text{NO}_3^- \overset{305\text{nm}}{\longrightarrow} \text{NO}_2^- + \text{O}(^3\text{P}) \quad \text{Eq: 4.2;} \]

and,

\[ \text{NO}_2^- + \text{H}^+ \overset{365\text{nm}}{\longrightarrow} \text{NO} + \text{OH} \quad \text{Eq: 4.3.} \]

The current results for the surface photochemistry of adsorbed nitrate can begin to be explained in the framework of nitrate ion photochemistry in acidic aqueous media as shown by the reactions Eq: 4.1–4.3. Figure 4.6 shows during the first 30 min of irradiation, adsorbed nitrate yields NO₂ as the major gas phase product in the presence of co-adsorbed water. However, for longer irradiation times, i.e. after 120 min and 420 min,
Figure 4.7 Changes in the gas phase product distribution during irradiation of gas phase NO$_2$ under %RH < 1. (a) FTIR spectra of gas phase products and change of gas phase product (NO and NO$_2$) concentration (b) in the absence of molecular O$_2$, (c) in the presence of 100 Torr of molecular O$_2$. 
the major gas phase product is seen to be NO followed by NO\textsubscript{2} and N\textsubscript{2}O. This change in gas phase product distribution may partially associated with gas phase NO\textsubscript{2} photochemistry to yield NO. In a reaction cell with only gas phase NO\textsubscript{2}, photolysis is measured and determined to be 200-fold faster compared to adsorbed nitrate photolysis. The net production of NO from NO\textsubscript{2} photolysis is cut down approximately by half in the presence of molecular oxygen due to oxidation of NO to NO\textsubscript{2}. Changes in the gas phase product distribution during irradiation of gas phase NO\textsubscript{2} under dry (%RH < 1) condition in the absence and presence of molecular O\textsubscript{2}, is shown in Figure 4.7. Thus, based on these results, in the presence of O\textsubscript{2} a cyclic pathway is operated between NO and NO\textsubscript{2}. Photolysis of adsorbed nitrate contributes to this cycle by producing both gas phase NO and NO\textsubscript{2}. In addition, N\textsubscript{2}O production is higher under the highest relative humidity conditions. These variations in the gas phase product distribution can be seen more clearly in the plots shown in Figure 4.8. These plots, showing the relative gas phase concentrations of NO\textsubscript{2}, N\textsubscript{2}O and NO at short (30 min), medium (120 min) and longer (420 min) irradiation times, were obtained by normalizing the gas phase concentrations to the largest gas phase product species in a given relative humidity, which is NO at longer times in all cases.

As can be seen in the data shown in Figure 4.6 and 4.8, gas phase NO\textsubscript{2} concentration increases up to %RH 20 and slightly decreases after %RH 45. At higher relative humidity conditions, i.e. %RH 45 and 80, there is a possibility to react NO\textsubscript{2} with co-adsorbed water, with a Henry’s law constant of 1.4 x 10\textsuperscript{-2} M-atm\textsuperscript{-1} at 298 K, to yield solvated nitrate on the surface.\textsuperscript{173,174} The re-adsorption of gas phase products is discussed in detail in the discussion of post-photolysis processes. Photolysis of NO\textsuperscript{2}\textsuperscript{-} to NO is not
Figure 4.8  Relative gas phase concentrations obtained from FTIR spectra following irradiation of adsorbed nitrate in the presence of molecular oxygen at 298K under different relative humidity (%RH) conditions, (a) < 1 (b) 20 ± 2 (c) 45 ± 2 (d) 80 ± 2 at short (30 min), medium (120 min) and longer (420 min) irradiation times. The gas phase concentrations have been normalized to the largest gas phase product species after 420 min of irradiation.
predominant under humid conditions during the first 30 min of irradiation. Formation of [NO$_2^-$·H$_2$O] in the presence of co-adsorbed water and lower acidity may be the possible reasons for the above observation. Furthermore, protons (H$^+$) generated from adsorbed water are utilized in a competitive reaction during the formation of N$_2$O under these conditions, as discussed below. In addition, as irradiation proceeds, accumulation of nitrite may favor the production of NO. Although attempts to detect surface adsorbed nitrite were unsuccessful potentially it may be present at low steady-state coverages under these conditions.

As we reported previously, formation of nitrous oxide (N$_2$O) is observed during the photolysis of adsorbed nitrate. The relative N$_2$O concentration is highly significant in the absence of molecular oxygen, and also contributes to a major fraction in the presence of oxygen under humid conditions at the end of seven hours of photolysis. As we have discussed previously surface-catalyzed reactions of NO can lead to the formation of N$_2$O which is easily quenched in the presence of molecular oxygen.$^{175}$ Malecki and Malecka, in their studies on thermal decomposition of metal nitrates, have proposed two other possible reaction mechanisms for the formation of N$_2$O in the presence of NO and NO$_2$. $^{176}$

$$\text{Mechanism 1} \quad \text{NO}_2 + \text{NO}_3^- \rightarrow \text{N}_2\text{O} + 7/4 \text{O}_2 + 1/2 \text{O}_2^- \quad \text{Eq: 4.4}$$

$$\text{Mechanism 2} \quad 2\text{NO} \rightarrow \text{N}_2\text{O}_2 \quad \text{Eq: 4.5}$$

$$\text{N}_2\text{O}_2 + \text{NO} \rightarrow \text{N}_2\text{O} + \text{NO}_2 \quad \text{Eq: 4.6}$$

In the presence of oxygen N$_2$O$_2$ can be oxidized to yield NO$_2$,

$$\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2 \quad \text{Eq: 4.7}$$
In addition, Maric et. al. also has shown a similar mechanism for the formation of N\textsubscript{2}O via a heterogeneous dark conversion of NO\textsubscript{2} and/or N\textsubscript{2}O\textsubscript{5}.\textsuperscript{177} The above two pathways provide possible mechanisms for the production of N\textsubscript{2}O and further elucidates variations observed in relative gas phase concentrations of N\textsubscript{2}O and NO\textsubscript{2}, shown in Figure 4.5, in the presence and absence of molecular oxygen. At higher relative humidities, particularly at %RH 45 and 80, a significant amount of gas phase N\textsubscript{2}O was observed even in an oxidizing environment. In previous studies on heterogeneous hydrolysis of NO\textsubscript{2}, it has been shown that N\textsubscript{2}O is produced under humid conditions and longer reaction times.\textsuperscript{174} Recently, Wiesen et al. and Kleffmann et al. have described a possible reaction mechanism for the formation of N\textsubscript{2}O via HONO in their studies on hydrolysis of NO\textsubscript{2} on an acidic surface.\textsuperscript{178-180} The overall reaction of the proposed mechanism has been described as,

\[
8\text{NO}_2 + 3\text{H}_2\text{O} \xrightarrow{[H^+]_{\text{aq}}} \text{N}_2\text{O} + 6\text{HNO}_3 \quad \text{Eq: 4.8.}
\]

In this reaction pathway, hyponitrous acid (HON=NOH) intermediate is proposed to decompose to N\textsubscript{2}O over a wide pH range, including acidic conditions.\textsuperscript{181-183} These mechanisms and the pathways discussed for NO\textsubscript{2} surface reactions under humid conditions suggest that higher relative gas phase concentration of N\textsubscript{2}O is due to a secondary reaction of NO\textsubscript{2} on the acidic oxide surface. This can also be one of the potential reasons for the observed lower gas phase NO\textsubscript{2} concentrations at extreme relative humidity conditions at which the N\textsubscript{2}O production is highest. Formation of HONO and its photochemical products are further discussed below.
As NO is the major gas phase product, there is a possibility to readsorb NO on the aluminum oxide surface. In previous studies, vibrational modes of adsorb NO have been reported and assigned to bands at ~1700 - 1720 cm$^{-1}$ on different surfaces. The adsorption band near 1702 cm$^{-1}$ in the adsorbed phase spectra that grows during irradiation is most likely due to NO adsorbed on to oxide surfaces. Furthermore, the

![Figure 4.9](image)

*Figure 4.9* A representative XPS of high resolution N 1s of $\gamma$-Al$_2$O$_3$ particles reacted with 1.7 HNO$_3$ and exposed broadband irradiation ($\lambda = 300 – 700$ nm) 420 min in the presence of 100 Torr of O$_2$ pressures. XPS spectra were acquired at 298 K.
X-ray photoelectron spectrum (XPS) in the N(1s) region of the irradiated nitrated aluminum oxide surface revealed a peak at 401 eV which was not observed in the XPS of samples exposed to nitric acid and not irradiated. As seen Figure 4.9, the peak at 401 eV is consistent with the presence of adsorbed NO on the surface. For both samples that were just exposed to nitric acid and those exposed to nitric acid and irradiated, a peak at 407 eV was present in the N(1s) region. This higher energy peak is consistent with adsorbed nitrate on the surface. Higher production of NO₂ in presence of O₂ can lead to NO₂ adsorption on the surface to yield adsorbed nitrates, thus contributing as another source to the overall nitrate on the surface.

In recent studies, evidence is available for photochemical generation of nitrous acid, HONO from the surface reaction of hydroxyl radicals with nitrogen dioxide in the presence of water vapor. Furthermore, it is reported that HONO flux is wavelength dependent and its release is strongest when λ < 320 nm where the absorption of aqueous nitrate is highest. Again gas phase HONO can be photochemically converted back to NO and OH. In these studies HONO was not observed in the gas phase although its photolysis product NO is readily observed.

4.4.3 310 nm Narrowband Photolysis: Conformation of the Proposed Reaction Mechanism

Photochemistry of adsorbed nitrate was further investigated with a specific focus on the gas phase product formation upon narrowband photolysis (310 ± 2 nm), near the wavelength maximum of the n → π* transition, to derive more information of the reaction mechanism and to confirm the reaction scheme proposed. FTIR spectra of gas
Figure 4.10 Gas phase products formed during photolysis of adsorbed nitrate using a 310 nm narrowband pass (a). FTIR spectra of gas-phase products formed under %RH < 1 (dash line) and %RH 45 (solid line) at 298 K. (b). Relative gas phase concentrations in the presence of molecular oxygen at 298K under different relative humidity (%RH) conditions (< 1, 20, 45 and 80) at 420 min irradiation time. Gas phase concentrations have been normalized to the largest gas-phase product species NO₂.
phase products formed during the narrowband photolysis of adsorbed nitrate in the presence of 100 Torr of molecular oxygen are shown in Figure 4.10(a). The solid lines show the gas phase spectra at 45% relative humidity compared to dry conditions (%RH < 1). Under dry conditions, i.e. in the absence of gas phase and adsorbed water, NO₂ is the sole gas phase product observed with a characteristic absorption at 1614 cm⁻¹ whereas under humid conditions of 45% RH, gas phase N₂O is also formed as seen by the absorption band at 2227 cm⁻¹ in addition to NO₂. The relative gas phase concentrations, following 420 min of 310 nm narrowband pass irradiation in the presence of molecular oxygen under different RH conditions (RH < 1, 20, 45 and 80%) are shown Figure 4.10(b). The gas phase concentrations have been normalized to the largest gas phase product species observed after 420 min of irradiation at a given RH, which in all the cases is found to be NO₂. Moreover, N₂O production is increased at the highest RH conditions. Percentage yield of N₂O formation were (2.1 ± 0.1) x 10⁻³, (4.4 ± 0.1) x 10⁻³, (5.4 ± 0.2) x 10⁻³ and (10.1 ± 0.5) x 10⁻³ for %RH<1, 20, 45 and 80 respectively. There is no detectable NO production under all experimental conditions.

As described in the previous section on nitrate photochemistry with the broadband filter, during the 310 nm irradiation, adsorbed nitrate, at ~ 305 nm, yields nitrogen dioxide and nitrite according to reactions given in Eq: 4.1 and Eq: 4.2.²²⁻²⁴, ¹⁶⁴, ¹⁶⁵ Here we can easily detect the NO₂ photoproduct in the gas phase. Further photoreduction of surface adsorbed nitrite, given by Eq: 4.3, does not take place due to the fact that there is no sufficient energy in the radiation reaching the sample. Similar to broadband photolysis, at higher RH, a significant amount of N₂O was observed. In the absence of gas phase nitric oxide, the only possible pathway for the production of N₂O is the
Figure 4.11 Kinetics of narrowband photolysis of adsorbed nitrate (a). Photo-induced surface nitrate loss in the presence of molecular oxygen and (b). Pseudo first order rate analysis for the 310 nm narrowband photolysis of adsorbed nitrate, under different relative humidity conditions. $\theta_0$ – adsorbed nitrate concentration on saturated oxide surface at $t = 0$. $\theta$ – nitrate concentration on oxide surface at irradiation time $t$. The presented nitrate loss is the mean of triplicate measurements and the error bars represent the standard deviation.
heterogeneous hydrolysis of NO$_2$ in the presence of an acidic surface, as given by Eq: 4.8. Relatively lower N$_2$O yields with narrowband photolysis agree with the fact that there is only one reaction pathway in operation and further confirm the proposed reaction mechanism.

The kinetics of the reaction is also seen to change as a function of relative humidity. Photoinduced surface nitrate loss in the presence of molecular oxygen for 310 nm narrowband photolysis of adsorbed nitrate, under different relative humidity conditions are shown in Figure 4.11. The saturated nitrate coverage on alumina surface at $t = 0$ was $7.28 \pm 1.30 \times 10^{14}$ molec/cm$^2$. The rate of nitrate loss upon 310 nm irradiation was monitored more carefully as a function of time for the first 90 minutes using the change in the integrated absorbance of the NO$_3^-$ $\nu_3$ band. Assuming first-order kinetics, the apparent rate constants obtained at different % RH were $(0.5 \pm 0.1) \times 10^{-5}$, $(1.9 \pm 0.2) \times 10^{-5}$, $(1.4 \pm 0.1) \times 10^{-5}$, $(1 \pm 0.1) \times 10^{-5}$ s$^{-1}$ for RH < 1, 20, 45 and 80% respectively. Based on calculated photolysis rate constants for HNO$_3$ and the reported values in the literature, the 310 nm photolysis of adsorbed nitrate on aluminum oxide particle surface is about two orders of magnitude greater than the HNO$_3$ photolysis rate constant of $\sim 7 \times 10^{-7}$ s$^{-1}$ in the gas phase. These facts highlight the significance of involvement of the atmospheric particle surface in renoxification. In a good agreement with the results for broadband photolysis, it is observed that the initial rate of photolysis of adsorbed nitrate at 310 nm is approximately 2 to 4-fold faster under humid conditions.

Consequently, the experimental data observed in this study on photochemistry of adsorbed nitrate on mineral dust proxies can be explained by the above reaction mechanism proposed. Further, the current results under dry and humid conditions can be
Figure 4.12 Schematic of the reaction mechanism of heterogeneous photolysis of adsorbed nitrate. HNO$_3$ (g) (left side of the diagram) adsorbs from the gas phase onto the surface to yield nitrate ion (NO$_3^-$ (a)) and protons (H$^+$) in the presence and absence of co-adsorbed water. Broadband irradiation results in the production of gas phase and surface adsorbed products as shown by the different species. The observed gas phase and surface-bound products, in the transmittance FTIR spectroscopy, are colored green whereas gas phase and surface-bound proposed intermediates not detected by FTIR spectroscopy including gas phase N$_2$O$_2$ and HONO and adsorbed NO$_2^-$ are shown in white.

explained in the framework of nitrate ion photochemistry to yield NO$_2$ and NO followed by a secondary reaction, heterogeneous hydrolysis of gas phase NO$_2$, on acidic surfaces
to yield N\textsubscript{2}O as a product.

The schematic of the proposed reaction mechanism of heterogeneous photolysis of adsorbed nitrate is shown in Figure 4.12. Heterogeneous uptake of nitric acid, HNO\textsubscript{3} (g) on the left side of the diagram, yields nitrate ion (NO\textsubscript{3}\textsuperscript{-} (a)) and protons (H\textsuperscript{+}) on the surface in the presence and absence of co-adsorbed water. Upon broadband irradiation, NO and NO\textsubscript{2} are produced as major gas phase products. Photochemistry of gas phase NO\textsubscript{2} yields NO that makes NO the dominant product. In the absence of O\textsubscript{2}, NO acts as the precursor for N\textsubscript{2}O via a surface-mediated reaction where as the reaction mechanism is poisoned in the presence of molecular oxygen resulting in more NO\textsubscript{2} and less N\textsubscript{2}O. In the presence of co-adsorbed water, NO\textsubscript{2} becomes the precursor for gas phase N\textsubscript{2}O through heterogeneous hydrolysis of NO\textsubscript{2} on the acidic surface. The proposed mechanism involves gas phase species of N\textsubscript{2}O\textsubscript{2} and HONO where as NO\textsubscript{2} (a) is an intermediate of gas phase NO formation via photolysis. In addition, the gas phase species are re-adsorbed onto the surface as nitrate and NO\textsubscript{(a)}.

4.4.4 Dark Reaction: Gas Phase Product Distribution Changes During Post Photolysis: Involvement of a Surface Catalyzed Reaction

Relative gas phase distributions presented in the last section for %RH < 1 and %RH 45 differ from that reported in our previous work\textsuperscript{170}. In the earlier work, following photolysis the lamp was turned off and the FTIR sample compartment was purged for several minutes prior to recording a spectrum so as to remove CO\textsubscript{2} and H\textsubscript{2}O from purge the FTIR compartment with dry air. In the current study, the apparatus was modified so that the lamp was incorporated into the dry air purge box so that extra purge time, post-
Figure 4.13 Changes in the gas phase product distribution during post-irradiation of adsorbed nitrate under %RH < 1. (a). FTIR spectra of gas phase products and (b). Change of gas phase product (NO and NO$_2$) concentrations as a function of time, following irradiation for 420 min.
photolysis, was unnecessary in these current experiments. During the time it took to purge the compartment, there were changes in the gas phase product distribution, unbeknownst in the earlier studies. This change in the gas phase distribution observed here led us to further investigate this post-photolysis dark reaction.

FTIR spectra collected every 3 minutes of the gas phase immediately after the broadband light source was turned off are shown in Figure 4.13(a). As seen in the spectra, the N$_2$O concentration remains constant with time whereas the NO concentration decreases with a concomitant increase in the NO$_2$ concentration. As shown in Figure 4.13(b), at RH < 1%, the NO$_2$ concentration reaches a maximum after around 100 min and NO decays during this period. The same effect was observed under all humidity conditions investigated. However at higher relative humidity NO$_2$ reached a maximum in a shorter time period. The basic chemical reaction most likely responsible for this gas phase conversion is,

$$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \quad \text{Eq: 4.9}.$$  

Catalytic oxidation of NO to NO$_2$ is an important intermediate step involved in NO$_x$ abatement that is being developed for diesel engines.$^{196}$ It is also the first step that occurs in the cyclic NSR (NO$_x$ storage and recycle) process.$^{197}$ Several previous studies can be found in the literature those have been carried out using Pt/Al$_2$O$_3$ monoliths and V$_2$O$_5$-WO$_3$/TiO$_2$ to make the above oxidation process efficient.$^{197, 198}$ In an attempt to fit the NO oxidation reaction to pseudo first order kinetics the calculated apparent rate constants are $5.78 \pm 0.30 \times 10^{-6}$, $6.30 \pm 0.32 \times 10^{-6}$, $6.82 \pm 0.31 \times 10^{-6}$ and $7.20 \pm 0.42 \times 10^{-6}$ s$^{-1}$·cm$^{-2}$ at 298 K for RH < 1, 20, 45 and 80% respectively.
Figure 4.14  Relative gas phase concentrations obtained from FTIR spectra after 120 min of post-irradiation of adsorbed nitrate in the presence of molecular oxygen at 298K under different relative humidity (%RH) conditions, %RH < 1, 20 ± 2, 45 ± 2 and 80 ± 2. The gas phase concentrations have been normalized to the largest gas phase product species in a given relative humidity.

The values reported here are lower than those of catalytic oxidation with noble metal/metal complexes, but higher than gas phase oxidation of NO without a catalyst. This suggests the involvement of the aluminum oxide surface as a heterogeneous
catalyst in the oxidation process. Furthermore, analysis of reaction rates indicated that these rates increase with relative humidity. The percentage increase of adsorbed nitrate during the first 120 min of post photolysis period are 11 ± 1%, 16 ± 1 %, 20 ± 1 % and 24 ± 1 % for RH < 1, 20, 45 and 80%, respectively. Therefore higher oxidation rates under humid conditions are due to removal of NO₂ from the gas phase through re-adsorption. Moreover, higher uptake of NO₂ under humid conditions is another possible reason for the observed decrease in nitrate loss during photolysis.

Relative gas phase distributions after 120 min of post photolysis, under different experimental conditions, are shown in Figure 4.14. In contrast to the distributions given in Figure 4.8, NO₂ is the dominant product in the dark under the most atmospherically relevant conditions, i.e. under humid conditions and in the presence of molecular oxygen. The relative gas phase concentration of N₂O appears to be increasing under humid conditions.

4.5 Conclusions and Environmental Implications

The photochemical conversion of nitric acid to gas phase nitrous oxide, nitric oxide and nitrogen dioxide through an adsorbed nitrate intermediate under different atmospherically relevant conditions has been shown. Under humid conditions, photolysis of solvated nitrate is higher than that of dry conditions. This could be a potentially important, yet previously unknown, surface mediated photochemical pathway in the NOₓ cycle. Here we reported a production of N₂O, an important greenhouse gas, with higher concentrations under humid conditions in the presence of molecular oxygen. We propose that this reaction involves a heterogeneous conversion of gas phase NO and NO₂. Higher
relative gas phase concentrations of N₂O under humid conditions can be attributed to a secondary reaction of NO₂ on acidic oxide surfaces. The present work also focused on chemistry of surface mediated gas phase product distribution changes. In the dark, gas phase NO is oxidized to NO₂ in the presence of O₂ whereas the N₂O concentration remains constant. The rate of this gas phase conversion increases as a function of relative humidity due to increased re-adsorption of NO₂ back to the surface under humid conditions. The higher oxidation rates of NO by molecular oxygen suggest an involvement of the oxide surface in the reaction mechanism. Therefore we propose a surface mediated dark reaction for the above gas phase conversion.

These results have implications for atmospheric processes involving nitric acid, NOₓ and mineral dust aerosol. Furthermore, the results provide some evidence that photochemical reactions of atmospheric significance can take place on the surface of particulate matter. This study also reveals that, in the troposphere, NOₓ level can be affected by these continued reactions of adsorbed nitrate initiated by sunlight. Moreover, the heterogeneous photochemical conversion of nitric acid to NOₓ could contribute to renoxification of the atmosphere. In atmospheric field studies, the interpretation of observed trends in terms of reaction mechanisms is difficult due to involvement of a complex blend of substrates distributed in several phases and the lack of knowledge in composition of particulate matter such as mineral dust and sea-salt and their behavior under different atmospheric conditions. Therefore, detailed studies such as this one of potential reactions involving heterogeneous photochemistry of associated secondary species such as nitrate on aerosols may be useful in better explaining field results of atmospheric chemistry and may be implemented in atmospheric chemistry models that
can be used to explain and predict concentrations of key gas phase constituents under a variety of environmental conditions.

4.6 Acknowledgment

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CHAPTER 5

AN ABIOTIC MECHANISM FOR THE FORMATION OF ATMOSPHERIC NITROUS OXIDE FROM AMMONIUM NITRATE: EFFECT OF CO-ADSORBED AMMONIA AND RELATIVE HUMIDITY ON PHOTOCHEMISTRY OF ADSORBED NITRATE

5.1 Abstract

Nitrous oxide (N\textsubscript{2}O) is an important greenhouse gas and a primary cause of stratospheric ozone destruction. Despite its importance, there remain missing sources in the N\textsubscript{2}O budget. Here we report the formation of atmospheric nitrous oxide from the decomposition of ammonium nitrate (NH\textsubscript{4}NO\textsubscript{3}) via an abiotic mechanism that is favorable in the presence of light, relative humidity and a surface. This source of N\textsubscript{2}O is not currently accounted for in the global N\textsubscript{2}O budget. In this study, pure ammonium nitrate salt is irradiated with broadband (λ > 300 nm) radiation as a function of relative humidity (RH) in the presence of molecular oxygen. Upon irradiation with light, the ammonium nitrate readily undergoes photolysis to yield N\textsubscript{2}O as the sole product, especially at higher relative humidities. Given the importance to heterogeneous photochemistry, nitrate adsorbed on aluminum oxide, a model system for mineral dust aerosol, is exposed to gaseous ammonia to yield a thin layer of adsorbed ammonium nitrate over the particle surface. With adsorbed NH\textsubscript{4}NO\textsubscript{3}, NO\textsubscript{2} is the major gas phase product, upon photolysis under dry conditions (%RH < 1), at 298 K whereas under humid conditions (%RH > 20), N\textsubscript{2}O is the only gas phase product. The estimated N\textsubscript{2}O yields for adsorbed NH\textsubscript{4}NO\textsubscript{3} are at least two orders of magnitude higher than that of the pure salt.
Information from isotopic studies is used to derive a detail reaction mechanism for the abiotic formation of $N_2O$ from $NH_4NO_3$ under ambient environmental conditions. Furthermore, annual production of $N_2O$ from atmospheric aerosols and surface fertilizer application over the continental United States from this abiotic pathway is estimated from results of an annual chemical transport simulation with the Community Multiscale Air Quality model (CMAQ). This pathway is projected to produce $9.3^{+0.7/-5.3}$ Gg $N_2O$ annually over North America. $N_2O$ production by this mechanism is expected globally from both megacities and agricultural areas and may become more important under future projected changes in anthropogenic emissions. In this study the impact that adsorbed and pure ammonium nitrate photochemistry may have on the chemical balance of the atmosphere, especially on the $N_2O$ budget, is discussed.

5.2 Introduction

Nitrous oxide ($N_2O$), presently at 320 parts per billion by volume in the troposphere,\textsuperscript{200,201} is a potent greenhouse gas (GHG) with a long residence time in the atmosphere, $\sim 120$ yrs. $N_2O$ has a global warming potential approximately 300 times larger than $CO_2$ of equal mass,\textsuperscript{202} and is the fourth largest contributor to radiative forcing over the past 250 years.\textsuperscript{203} In addition, $N_2O$ serves as a major source of stratospheric NO$_x$ and thus contributes to catalytic ozone destruction. Ravishankara et al. found that $N_2O$ is currently the single most important ozone depleting substance, and is anticipated to remain the largest throughout the 21$^{st}$ century.\textsuperscript{204} Unlike most other GHGs, the quantification of global nitrous oxide sources is incomplete, with approximately 30% of unknown sources and unidentified mechanisms.\textsuperscript{205}
Figure 5.1  A cartoon representation of two potential photo-induced reaction pathways for an abiotic formation of atmospheric nitrous oxide (N$_2$O), an important greenhouse gas and a dominant ozone depleting agent. This figure shows ammonium nitrate (NH$_4$NO$_3$) found on aerosol dust particles, from atmospheric processing, as well as on soil particles, applied on agricultural lands as fertilizers, become the major sources in this N$_2$O production. Given importance to heterogeneous photochemistry, the significance of these important yet unidentified reaction pathways can be estimated with atmospheric modeling.

Soils are estimated to account for ~50 - 60% of global N$_2$O emissions$^{206}$ with high N$_2$O production rates reported from agricultural soils$^{207}$ linked with soil moisture
Most studies to date have focused on biological processes of nitrification, denitrification and nitrate ammonification as the predominant processes for nitrous oxide production in soil. As 41.8 Tg of solid ammonium nitrate and 13.7 Tg of calcium ammonium nitrate fertilizer are applied to agricultural fields as a N amendment each year (International Fertilizer Association, http://www.fertilizer.org/Home-Page/STATISTICS), it is important to determine if there are other processes leading to 
$\text{N}_2\text{O}$ production from agricultural soils including abiotic processes (vide infra).

Furthermore, ammonium nitrate is also a common component of ambient particles, which can be transported across the globe. It is formed as a secondary species in pure form as a product from gas phase reactions involving nitrogen oxides and ammonia. Nitrate is also formed via reactions of nitrogen oxides on mineral dust and sea salt surfaces, which lead to the formation of adsorbed nitrate, nitrate coatings and deliquesced nitrate layers on the surface of the particles. Gaseous ammonia neutralizes adsorbed nitric acid to yield ammonium nitrate on these particle surfaces. On agricultural soil, the formation of secondary ammonium nitrate coatings can take place via a similar mechanism as on suspended soil particle surfaces. These reservoirs (agricultural soils and atmospheric aerosols) then represent a potential source of nitrous oxide. A cartoon representation of a potential photo-induced reaction pathway for an abiotic formation of atmospheric nitrous oxide is shown in Figure 5.1. This figure shows that ammonium nitrate found on aerosol dust particles, from atmospheric processing, as well as on soil particles, applied on agricultural lands as fertilizers, become the major sources in this $\text{N}_2\text{O}$ production. Besides, given importance to heterogeneous
photochemistry, the significance of these important yet unidentified reaction pathways can be estimated with atmospheric modeling.

Here we present the formation of atmospheric nitrous oxide from the decomposition of ammonium nitrate via an abiotic mechanism that is favorable in the presence of light, relative humidity and a surface. The current study involves broadband ($\lambda > 300$ nm) photolysis of NH$_4$NO$_3$ pure salt, to yield N$_2$O as the major product, especially under humid conditions. So as to understand the effect of particle surface on N$_2$O product yields, nitrate adsorbed on aluminum oxide, a well studied model system for mineral dust aerosol, is exposed to gaseous ammonia, which results a thin layer of adsorbed ammonium nitrate over the particle surface. Upon photolysis of adsorbed NH$_4$NO$_3$, NO$_2$ is observed as the major gas phase product, under dry conditions (%RH < 1), at 298 K whereas under humid conditions (%RH > 20), N$_2$O is the only gas phase product. The estimated N$_2$O yields for adsorbed NH$_4$NO$_3$ are at least two orders of magnitude higher than that of pure salt. Additional isotopic studies are carried out to derive a detail reaction mechanism for the newly identified abiotic formation of N$_2$O from NH$_4$NO$_3$ under ambient environmental conditions. Furthermore, annual production of N$_2$O from atmospheric aerosols and surface fertilizer application over the continental United States from this abiotic pathway is estimated from results of an annual chemical transport simulation with the Community Multiscale Air Quality model (CMAQ). During the simulation studies, the significance of the newly identified abiotic mechanism in the production of N$_2$O from ammonium nitrate is evaluated. The relative humidity dependence of the reaction products, kinetics and the significance of the photo-induced abiotic pathway will be explored in detail in this chapter.
5.3 Experimental Methods

The sources of all the materials, $\gamma$-Al$_2$O$_3$ and clay (Kaolinite), and reagents used in this study are listed in Chapter 2.6.

5.3.1 Laboratory Studies

In laboratory studies, ammonium nitrate coatings on model mineral surfaces were prepared by first reacting particle surfaces with nitric acid to produce a surface layer of adsorbed nitrate. The experimental setup for these experiments is described in detail in Chapter 2.1.1 and 2.1.2. The preparation of saturated surfaces of adsorbed nitrate has been previously described in detail in Chapter 3.

Briefly, alumina ($\gamma$-Al$_2$O$_3$ – Degussa) was used as a model for mineral surfaces and mineral dust aerosol. Approximately 5.5 mg of alumina powder was pressed onto half of a tungsten grid and evacuated for 12 hrs in the FTIR cell to remove adsorbed water from the surface. The alumina surface was then exposed to nitric acid vapor for 30 minutes at a pressure of approximately 1 Torr at 298 K. From previous studies, this process is known to produce a saturated surface coverage of adsorbed nitrate on alumina. The calculated nitrate coverage, when normalized to the BET surface area, is determined to be $\sim 5 \pm 1 \times 10^{14}$ molecules$\cdot$cm$^{-2}$. The alumina surface saturated with nitrate is then exposed to gas phase ammonia for 30 min at a pressure of approximately 1 Torr. This process forms a stable ammonium nitrate coating on the particle surface. Experiments were also done with pure ammonium nitrate and for these experiments powders of the pure substance (Alfa Aesar, ACS, 98.0% NH$_4$NO$_3$) was pressed on to one half of the tungsten grid and evacuated overnight.
The experimental setup that is used in these studies allows for FTIR measurements of the solid and gas phases as well as any changes that occur upon irradiation. These spectroscopic measurements can be done by simply probing each side of the sample grid with the infrared beam. This is done with the use of a linear translator upon which the entire FTIR cell sits inside the spectrometer. Experiments were carried out using different isotopes of ammonia $^{14}\text{NH}_3 (> 99.5 \% {^{14}\text{N}})$ and $^{15}\text{NH}_3 (> 98 \% {^{15}\text{N}})$, to better understand the mechanism of formation of $\text{N}_2\text{O}$. All FTIR spectra were recorded at 298 K. Additional details of the experimental apparatus and protocols followed are provided in Chapter 2.

Ammonium nitrate, either the pure form or coated on alumina, were exposed to light ($300 < \lambda < 700$ nm) using a broadband Hg light source and a broadband filter, as described previously.$^{215, 216}$ Additionally, a water filter was used to minimize heating of the sample ($< 5$K). Studies of the effect of relative humidity at $<1\%$, $20\%$, $45\%$, and $80\%$ were done to assess the importance of ambient moisture on the reaction of ammonium nitrate to yield gas phase nitrous oxide. First order empirical rate constants were estimated upon irradiation of the pure ammonium nitrate and ammonium nitrate coated on alumina particles. Selected experiments were replicated using clay, Kaolinite (Alfa Aesar), as a proxy for soil particles, to understand the differences in heterogamous photochemistry of the two systems, aerosol dust and soil particles.

These data were used in modeling analysis to determine the relative importance of the abiotic decomposition of ammonium nitrate to yield nitrous oxide compared to other pathways (vide infra).
5.3.2 Simulation Studies

Annual photochemical production of $\text{N}_2\text{O}$ from atmospheric aerosols over North America was estimated from hourly ammonium and nitrate concentrations from the 2002 CMAQ atmospheric chemical transport simulation described by Spak and Holloway.\textsuperscript{217} In order to estimate hourly $\text{N}_2\text{O}$ production from fertilizers, monthly ammonium nitrate and calcium ammonium nitrate application rates from Goebes et al.\textsuperscript{218} were allocated to the 36 km x 36 km Lambert conformal conic grid used in CMAQ modeling with agricultural spatial surrogates and diurnal temporal profiles from the 2001 National Emissions Inventory. Relative humidity and insolation were taken from the hourly meteorology used as input to the CMAQ simulation.

Ammonium nitrate concentration was calculated assuming neutralization of sulfate (degree of sulfate neutralization = 1) and the surface catalyzed reaction was calculated only in the presence of mineral aerosol. The reaction is assumed dependent only on RH and incoming solar radiation; independent of temperature, total water vapor mixing ratio, or the composition of the cationic surface mineral. Surface molar ammonium nitrate concentrations were calculated separately for Aitken and accumulation aerosol modes, based on modeled hourly modal surface area.

Experimental rate constants were parameterized as a function of relative humidity from four discrete relative humidity levels (1\%, 20\%, 45\%, and 80\%) using a fifth-order polynomial regression, and the standard deviations of integrated absorbances from the laboratory experiments were propagated to obtain the uncertainties of reaction rate constants. Curves were fit for the average, maximum, and minimum of both mineral surface enhanced and nonenhanced reactions. The photolysis rate assumed a linear
relationship with incoming total solar radiation, as a fraction of the one solar constant used in the laboratory experiments, and was considered independent of wavelength. Error bounds for the surface catalyzed and uncatalyzed reactions were estimated by considering the effects of uncertainty in the experimental rate constants, and uncertainty in fertilizer pellet surface area due to manufacturing specifications for fertilizer pellet radius (0.5-1.2 mm for ammonium nitrate, 1-2.5 mm for calcium ammonium nitrate).

5.4 Results and Discussion

5.4.1 Laboratory Measurements

As discussed here, laboratory measurements using FTIR spectroscopy show that \( \text{N}_2\text{O} \) can be produced via the abiotic decomposition of ammonium nitrate for pure ammonium nitrate samples and for ammonium nitrate coated particles upon broadband irradiation.

5.4.1.1 Photolysis of Pure Ammonium Nitrate Salt

Infrared spectrum of ammonium nitrate at 298 K prior to irradiation is shown in Figure 5.2. Vibrational bands observed are due the presence of ammonium ions (\( \text{NH}_4^+ \)) and nitrate ions (\( \text{NO}_3^- \)) and the IR frequency assignments of the pure crystalline \( \text{NH}_4\text{NO}_3 \) salt are based on the literature studies.\(^{219, 220}\) Peaks observed from Figure 5.2 are therefore assigned as follows: 716, 828, 1046 and 1328 cm\(^{-1}\) are assigned to the \( \nu_4, \nu_2, \nu_1 \) and \( \nu_3 \) modes of \( \text{NO}_3^- \) and the remaining peaks at 1416, 1755, 3056, and 3253 cm\(^{-1}\) are assigned to the \( \nu_4, \nu_2, \nu_1 \) and \( \nu_3 \) vibrational modes of \( \text{NH}_4^+ \) ion. These assignments are summarized in Table 5.1.
Figure 5.2 FTIR spectra of NH$_4$NO$_3$ from a commercially available pure salt.

Infrared spectra recorded of the gas phase under different conditions of relative humidity and light ($300 < \lambda < 700$ nm) are shown in Figure 5.3(a). The absorption band at 2224 cm$^{-1}$ shows that nitrous oxide$^{170-172}$ forms under various conditions but to different extents, with the greatest production in the presence of light and relative humidity of 45%. Figure 5.3(b) shows the data in terms of the relative amounts of N$_2$O formed under these different conditions with the data normalized to the greatest amount of N$_2$O formed during photolysis at 45% RH. Under humid conditions, N$_2$O is the sole gas phase
Table 5.1  Vibrational mode assignments of the NH₄NO₃ from the pure salt.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Vibrational frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Current study</td>
</tr>
<tr>
<td>ν₃ (NH₄⁺)</td>
<td>3253</td>
</tr>
<tr>
<td>ν₁ (NH₄⁺)</td>
<td>3056</td>
</tr>
<tr>
<td>ν₂ (NH₄⁺)</td>
<td>1755</td>
</tr>
<tr>
<td>ν₄ (NH₄⁺)</td>
<td>1416</td>
</tr>
<tr>
<td>ν₃ (NO₃⁻)</td>
<td>1328</td>
</tr>
<tr>
<td>ν₁ (NO₃⁻)</td>
<td>1046</td>
</tr>
<tr>
<td>ν₂ (NO₃⁻)</td>
<td>828b</td>
</tr>
<tr>
<td>ν₄ (NO₃⁻)</td>
<td>716b</td>
</tr>
</tbody>
</table>

a – Ref. 219 and 220

b – Not shown in the spectrum given in Figure 5.2

product, and increases as a function of relative humidity until the deliquescence relative humidity is reached (62% at 298 K),213 after which it decreases. Gas phase concentrations were determined from the integrated absorbances of the nitrous oxide band and experimentally determined conversion factors, given in Table 4.2 in Chapter 4.

An earlier study at low temperatures near 140 K reported N₂O formation from photolysis of thin films of ammonium nitrate.221 Although the amount of N₂O was not quantified or the tropospheric relevance of it discussed, this earlier report provides additional, supportive evidence for the occurrence of this photochemical mechanism over a wide range of conditions.
Figure 5.3  Photolysis of pure NH$_4$NO$_3$ thin film under different experimental conditions at 298K. (a) FTIR spectra of gas phase products formed and (b) relative gas phase concentrations. In (b), the gas phase concentrations have been normalized to the largest gas phase product species, N$_2$O, at %RH 45 and in the presence of molecular oxygen.
Additional control experiments were carried out to compare thermal decomposition of pure NH₄NO₃ to yield N₂O under dry condition. Relative gas phase N₂O concentrations from thermal (298 – 348 K) decomposition of pure ammonium nitrate, in comparison with photo degradation, are shown in Figure 5.4. Based on the results from these experiments, there was no significant N₂O formation from NH₄NO₃ at 298 K in the absence of light. Higher temperatures were needed to yield N₂O but there was much less N₂O production compared to in the presence of light.

Figure 5.4  Relative gas phase N₂O concentrations from photo (at 298K) and thermal (298 – 348 K) decomposition of pure ammonium nitrate.
5.4.1.2 Photochemistry of Adsorbed Ammonium Nitrate on $\gamma$-Alumina: Effect of Particle Surface

We also found that $N_2O$ can be produced from reaction of ammonium nitrate coated particles surfaces. Ammonium nitrate coatings were prepared on alumina surfaces as described in the Experimental section. This coated surface was used as a model for mineral dust in the atmosphere and for an aluminum silicate soil particle to understand the photochemistry of ammonium nitrate coated particles. Additionally, experiments were carried out using different isotopes of ammonia to yield different isotopically labeled adsorbed ammonium nitrate including the mixed labeled coating. The infrared spectra of alumina coated $^{14}NH_4^{14}NO_3$ and $^{15}NH_4^{14}NO_3$ are shown in Figure 5.5 following exposure to first $H^{14}NO_3$ (bottom spectrum) followed by exposure to $^{14}NH_3$ (middle spectrum) or $^{15}NH_3$ (top spectrum) to yield $^{14}NH_4^{14}NO_3$ and $^{15}NH_4^{14}NO_3$, respectively. It is estimated that these are one or two layer coatings on the surface.\textsuperscript{222} The assignments of vibrational frequencies of adsorbed $NO_3^-$ and $NH_4^+$ on $\gamma$-alumina particles, based on the literature,\textsuperscript{223,224} are given in Table 5.2.

Under dry conditions (%RH < 1), adsorbed nitrate binds to the oxide surface in different modes of coordination as monodentate, bidentate and bridging as discussed in detail previously, based on the assignment of the peaks in the nitrate ion $\nu_3$ spectral region between 1200 and 1650 cm$^{-1}$.\textsuperscript{88,225} In the presence of water vapor at different relative humidities (20, 45 and 80%), co-adsorbed water solvates the nitrate ion forming inner and outer sphere complexes which are represented by peaks in the region between 1300 and 1450 cm$^{-1}$ (not shown here).\textsuperscript{225} Changes in the infrared spectra as a function of
relative humidity and the assignment of these peaks have been discussed extensively and the details can be found in Chapter 3.

Figure 5.5 FTIR spectra obtained after exposing γ-Al₂O₃ first to gas phase nitric acid (bottom spectrum) followed by the exposure to gas phase ¹⁴N or ¹⁵N-labeled ammonia, middle and top spectrum, respectively to produce an ammonium nitrate coating on the particle surface. Each spectrum was referenced to the clean oxide prior to exposure to nitric acid and ammonia.
Table 5.2 Vibrational mode assignment of the nitrate and ammonium products following adsorption and reaction of HNO₃ with NH₃ on the surface of γ-Al₂O₃.

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Frequencies for adsorbed $^{14}$NH₄$^{14}$NO₃ ($^{15}$NH₄$^{14}$NO₃) from exposure of nitrated surface to $^{14}$NH₃ ($^{15}$NH₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Current study</td>
</tr>
<tr>
<td><strong>Nitrate (NO₃⁻)</strong></td>
<td></td>
</tr>
<tr>
<td>Monodentate, $v_1$</td>
<td>1044$^b$</td>
</tr>
<tr>
<td>Monodentate, $v_3$</td>
<td>1323$^b$</td>
</tr>
<tr>
<td>δ (OH) of HNO₃</td>
<td>1331$^b$</td>
</tr>
<tr>
<td>Monodentate, $v_3$</td>
<td>1558$^b$</td>
</tr>
<tr>
<td>Bridging $v_3$ (NO₃⁻)</td>
<td>1628$^b$</td>
</tr>
<tr>
<td>$v$ (NO₂) of HNO₃</td>
<td>1679$^b$</td>
</tr>
<tr>
<td><strong>Ammonium (NH₄⁺)</strong></td>
<td></td>
</tr>
<tr>
<td>$v_3$ (NH₄⁺)</td>
<td>3223  (3196)</td>
</tr>
<tr>
<td>$v_1$ (NH₄⁺)</td>
<td>3053  (3025)</td>
</tr>
<tr>
<td>$v_2$ (NH₄⁺)</td>
<td>1701  (1662)</td>
</tr>
<tr>
<td>$v_4$ (NH₄⁺)</td>
<td>1442  (1401)</td>
</tr>
</tbody>
</table>

a – Reference 88 for ($^{14}$NO₃) and reference 170, 223 & 224 for ($^{14}$NH₄)

b – Similar frequencies were observed for adsorbed nitrate with $^{15}$NH₃ isotope

When the surface of nitrated γ-Al₂O₃ was exposed gaseous NH₃, several changes were observed to occur on the surface. The peaks at 1558 and 1628 cm⁻¹ associated with adsorbed nitrate species are observed to disappear while the peaks at 1307 and 1008 cm⁻¹ appear to shift and increase in intensity. New absorption bands at 1442, 1701, 3053 and
3223 cm\(^{-1}\) are seen to grow as the surface is exposed to NH\(_3\)(g). The isotopic studies carried out with labeled ammonia (\(^{15}\)NH\(_3\)) showed an apparent red shift in these new spectral bands suggesting that the new bands may arise due to co-adsorbed ammonia. In the literature, studies on the absorption of ammonia on metal oxides have not been reported, except one study on uptake of ammonia on CaCO\(_3\) particles by Neagle and Rochester to test the presence of exposed Lewis-acidic Ca\(^{2+}\) surface sites.\(^{132}\) They were only able to observe peaks at 3260 and 3380 cm\(^{-1}\) that they attributed to N-H stretching vibrations of molecularly adsorbed ammonia molecules, and other bands of ammonia were not seen because of the broad band of calcite between 1350 and 1650 cm\(^{-1}\).

According to these studies, especially from Raman studies on vibrational modes of the NH\(_4^+\) ion in ammonium salts, four fundamental vibrational modes can be found for NH\(_4^+\) ion.\(^{219,226}\) A summary of these vibrational assignments are given in Table 5.1.

Based on these vibrational assignments and results from isotopic studies, the formation of NH\(_4\)NO\(_3\) on the surface of \(\gamma\)-Al\(_2\)O\(_3\) is proposed to have occurred. Peaks at 1442, 1701, 3053 and 3223 cm\(^{-1}\) are assigned to be associated with \(\nu_4\), \(\nu_2\) \(\nu_1\) and \(\nu_3\) fundamental vibrations of NH\(_4^+\) ion formed by the reaction of ammonia gas with hydroxyl species on the surface of \(\gamma\)-Al\(_2\)O\(_3\). The peaks at 1044 and 1323 cm\(^{-1}\) are assigned to the presence of oxide coordinated \(\nu_3\) and \(\nu_1\) NO\(_3^-\) on the surface and they are shifted from their original Al-(NO\(_3\)) bond because its coordination has changed from being bonded to surface Al\(^{3+}\) species, to being attached to surface NH\(_4^+\) species. Thus, the reaction of ammonia gas with surface adsorbed nitrates can lead to the formation of irreversibly adsorbed ammonium nitrate on the surface of \(\gamma\)-Al\(_2\)O\(_3\).
Figure 5.6  FTIR spectra of gas phase products formed during photolysis of adsorbed ammonium nitrate in the presence of molecular oxygen under (a). dry (%RH < 1) and (b). wet (%RH 45) conditions, at 298K. Each spectrum was referenced to the gas phase spectrum prior to exposure to nitric acid.
Upon broadband irradiation of the ammonium nitrate coated particle surface, nitrous oxide is produced as shown by the absorption band at 2224 cm⁻¹ in Figure 5.6(a) and (b) for dry (%RH < 1) and wet (%RH 45) conditions, respectively, while NO₂ is also a product, with its characteristic peak at 1614 cm⁻¹, at the lower relative humidity. No other gas phase product formation was detected, including nitric oxide (NO), according to the FTIR spectra collected from the gas phase. A comparison of the spectra shown in Figure 5.6(a) and (b) reveals a significant change in the gas phase product distribution under these two different environmental conditions. Gas phase concentrations obtained from FTIR analysis followed by broadband (λ > 300 nm) irradiation of adsorbed ammonium nitrate in the presence of molecular oxygen under different relative humidity conditions (RH < 1, 20, 45 and 80%) are shown in Figure 5.7. The results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Gas phase concentrations of individual species were determined by converting integrated absorbances to concentrations using calibration factors, given in Table 4.2, Chapter 4, for the individual gas phase species. These data show that gas phase NO₂ and N₂O are produced at different rates and in different yields.

These variations in the gas phase product distribution can be seen more clearly in the plots shown in Figure 5.8. These plots, showing the relative gas phase concentrations of NO₂ and N₂O at short (30 min), medium (120 min) and longer (420 min) irradiation times, were obtained by normalizing the gas phase concentrations to the largest gas phase product species in a given relative humidity, which is NO₂ at %RH < 1 and N₂O for all the other relative humidities.
Figure 5.7  Gas phase concentrations obtained from FTIR spectra following irradiation of adsorbed ammonium nitrate in the presence of molecular oxygen at 298K under different relative humidity (%RH) conditions, (a). < 1  (b). 20 ± 2 (c). 45 ± 2  (d). 80 ± 2.
Figure 5.8  Relative gas phase concentrations obtained from FTIR spectra following irradiation of adsorbed ammonium nitrate in the presence of molecular oxygen at 298K under different relative humidity (%RH) conditions, (a). %RH < 1  (b). 20 ± 2  (c). 45 ± 2   (d). 80 ± 2 at short (30 min), medium (120 min) and longer (420 min) irradiation times. The gas phase concentrations have been normalized to the largest gas phase product species in a given relative humidity.
Gas phase products formed during from irradiation of $^{15}$NH$_4^{14}$NO$_3$, shown in red, compared to $^{14}$NH$_4^{14}$NO$_3$ in the presence of molecular oxygen under dry (%RH < 1) and wet (%RH 45) conditions, at 298K, are shown in Figure 5.8(a) and (b), respectively. It is notable that upon irradiation of the mixed labeled $^{15}$NH$_4^{14}$NO$_3$, under dry condition (%RH < 1), there is the formation of only the mixed nitrogen isotope product for nitrous oxide, with an isotopic shift of the asymmetric stretch to lower frequency. The connectivity of the atoms can be determined from the nitrous oxide absorption frequencies for this $\nu_3$ vibrational mode. A shift of 24 cm$^{-1}$ conclusively demonstrates that the $^{15}$N$^{14}$NO product is formed and $^{14}$N$^{15}$NO, which has a larger isotope shift of 40 cm$^{-1}$ for this stretching mode, is not formed.$^{227}$

The difference between isotopic ratio in the central nitrogen and the terminal nitrogen atoms is defined as the $^{15}$N site preference in N$_2$O.$^{202}$ This information derived from the distribution of $^{15}$N within the gas phase N$_2$O molecule reflects the possible sources and reaction mechanisms of N$_2$O formation.$^{228}$ The site preference of N$_2$O from adsorbed $^{15}$NH$_4^{14}$NO$_3$ using the $\nu_3$ mode shows that under dry conditions N$_2$O has a very narrow range of isotopic signature and almost one hundred percent of the gas phase N$_2$O is in the form of $^{15}$N$^{14}$NO. These results reveal that the nitrogen-nitrogen bond in gas phase nitrous oxide forms from one nitrogen atom in each of the ions in ammonium nitrate. Focusing on this light initiated reaction pathway, the production of N$_2$O and its isotope signature can be explained in terms of the photoreduction of nitrate coupled to the oxidation of NH$_4^+$.$^{83,221}$ according to the following reaction sequence:

$$^{14}\text{NO}_3^- \overset{305\text{ nm}}{\longrightarrow} ^{14}\text{NO}_2 + \text{O}^- \quad \text{Eq: 5.1}$$
Figure 5.9 FTIR spectra of gas phase products formed after 420 min irradiation of $^{15}$NH$_4$$^{14}$NO$_3$ (red) compared to $^{14}$NH$_4$$^{14}$NO$_3$ (blue) in the presence of molecular oxygen under (a) dry (%RH < 1) and (b) wet (%RH 45) conditions, at 298K. Each spectrum was referenced to the gas phase spectrum prior to exposure to nitric acid.
Figure 5.10  Analysis of FTIR spectra of gas phase products formed during photolysis of adsorbed $^{15}$NH$_4$$^{14}$NO$_3$ in the presence of molecular oxygen under wet (%RH 45) condition, at 298K. (a). Peak fitting for the different nitrous oxide isotopes formed ($^{15}$N$^{14}$NO and $^{14}$N$^{14}$NO). (b) Relative gas phase contributions of $^{15}$N$^{14}$NO (orange) and $^{14}$N$^{14}$NO (green) as a function of irradiation time following photolysis of $^{15}$NH$_4$$^{14}$NO$_3$ coated alumina surface.
Furthermore, it can be seen in Figure 5.9(b) that under humid conditions, the N₂O isotope signature becomes more complex as a result of the formation of several different isotope products. As seen in Figure 5.10, after analyzing the gas phase FTIR spectra with peak fitting software, the infrared band for the v₃ mode of N₂O is seen to be composed of two different absorption bands, as a result of the formation of both $^{15}$N$^{14}$NO and $^{14}$N$^{14}$NO. This suggests another reaction pathway becomes available at higher relative humidity. It is well-known that the heterogeneous formation of N₂O occurs from the hydrolysis of gas phase NO₂ via HONO on acidic and oxide surfaces. $^{174,179,229}$ Reactions of HONO and its protonated forms (H$_2$ONO$^+$ or possibly NO$^+$) have shown to generate hyponitrous acid, HON=NOH. The self reaction of (HON)$_2$ is known to decompose to N₂O over a wide range of pH values, including under highly acidic conditions. The net reaction yields N₂O and HNO₃ according to:

$$^{15}$NH$_4^+$ + O$^-$ $\rightarrow$ $^{15}$NH$_2$ + H$_2$O \quad \text{Eq}: \ 5.2$$

and,

$$^{15}$NH$_2$ + $^{14}$NO$_2$ $\rightarrow$ $^{15}$N$^{14}$NO + H$_2$O \quad \text{Eq}: \ 5.3$$

The surface mediated secondary reaction of the primary gas phase photoproduct, NO₂, a product that can be easily seen in the infrared spectra (Figure 5.9), may be responsible for the higher N₂O concentrations observed, and, in particular, accounts for the production of $^{14}$N$^{14}$NO following photolysis of $^{15}$NH$_4^{14}$NO$_3$, especially at longer photolysis times (Figure 5.10(b)).

$$8 \ ^{14}$NO$_2$ + 3H$_2$O $\rightarrow$ $^{14}$N$^{14}$NO + 6 H$^{14}$NO$_3$ \quad \text{Eq}: \ 5.4$$
As seen in Figure 5.3, the relative gas phase concentration of N\textsubscript{2}O from pure NH\textsubscript{4}NO\textsubscript{3} decomposition for under the conditions of light, presence of molecular oxygen and a relative humidity < 1% is ~0.8 and reaches a maximum (1.0) under similar conditions but at a relative humidity of 45%. Even if we assume that this increase of ~0.2 from %RH < 1 to %RH 45 is due to heterogeneous hydrolysis of NO\textsubscript{2} then it represents a 20% increase of the total N\textsubscript{2}O. Therefore, for pure NH\textsubscript{4}NO\textsubscript{3}, the mechanism shown in reactions Eq: 5.1 – 5.3 is appear to be the most important. In the case of adsorbed ammonium nitrate on mineral surfaces, relatively higher amounts of NO\textsubscript{2} are produced from photolysis of nitrate on the surface and this leads to the secondary mechanism, i.e. heterogeneous hydrolysis of NO\textsubscript{2}, enhancing the production of N\textsubscript{2}O. Higher N\textsubscript{2}O concentrations and N\textsubscript{2}O fluxes have been observed from the rewetting of agricultural lands, and have been attributed entirely to the biological formation of nitrous oxide.\textsuperscript{208, 230} Based on our results, a significant fraction of N\textsubscript{2}O formation under those conditions may also come from abiotic processes as discussed above.

Quantification of N\textsubscript{2}O formation shows that the extent of reaction is at least two orders of magnitude greater for the ammonium nitrate coated particle surface than for solid ammonium nitrate. Percent yield of N\textsubscript{2}O formation following broadband irradiation of thin NH\textsubscript{4}NO\textsubscript{3} surface coatings and pure NH\textsubscript{4}NO\textsubscript{3} for ninety minutes determined from the loss of ammonium nitrate are given in Table 5.3. The percentage yields of N\textsubscript{2}O are calculated from the amount of gas phase N\textsubscript{2}O produced after 420 min of irradiation with respect to decrease in absorptions associated with ammonium nitrate as a function of irradiation time.
Differences in N₂O formation efficiency between the pure ammonium nitrate and the ammonium nitrate coated particle can be attributed to the strength and mode of coordination and the ability of the two species, nitrate and ammonium, to be reduced or oxidized. Because nitrate is a polyatomic oxyanion, it is capable of binding to the alumina surface in different adsorption modes, including bidentate and bridging coordination modes, which is not the case in ammonium nitrate salt. Therefore, the observed enhancement in the abiotic N₂O formation in the presence of a surface may be due to the ability of these reactants to form surface complexes with preferred orientation for an effective reaction coordinate to yield N₂O.

The additional experiments carried out using Kaolinte, known to be a non-swelling clay, as the reactive surface highlight the surface specificity of the photolytic reaction (not shown). The percentage yields of the N₂O formation following broadband irradiation of adsorbed ammonium nitrate on Kaolinite are 0.18 (± 0.04) and
1.16 (± 0.18) under dry (%RH < 1) and wet (%RH 45) conditions, respectively. The reported lower yields for the clay surface may be due to the fact that HNO3 is found absorbed onto the Kaolinite surface differently depending on the surface exposed, so as the formation of adsorbed ammonium nitrate layer. Kaolinite consists of hydrophobic tetrahedral silicon oxide surface and a hydrophilic octahedral aluminum oxide surface that produced either mostly molecularly adsorbed HNO3 or irreversibly adsorbed nitrate, respectively. Thus, the type of the surface and the specific crystal planes that are exposed in the reaction evidently determine the rate and the yield of the abiotic N2O formation from adsorbed NH4NO3.

Additionally, the secondary reaction of nitrogen dioxide, given by Eq: 5.4, occurs on particle surfaces to yield more nitrous oxide. It should be noted that nitrous oxide is a well-known undesirable product in the selective catalytic reduction (SCR) reaction of NOx with ammonia on solid catalytic surfaces including metal oxide surfaces. SCR reactions are typically done at much higher temperatures on the order of two hundred degrees Kelvin higher than conditions discussed here.

Surface enhanced rate constants were determined by quantifying decrease in absorptions associated with ammonium nitrate as a function of irradiation time and fitting these data to a first order rate expression. In the calculation of pseudo first order rate constants for the overall reaction of ammonium nitrate decomposition, given by Eq: 5.5, to yield gas phase N2O, the integrated absorbance of \( \nu_3 \) region of nitrate (ca. 1220 to 1700 cm\(^{-1}\)) and \( \nu_4 \) band of adsorbed ammonium (1442 cm\(^{-1}\)) in the IR spectra was measured.

\[
\text{NH}_4\text{NO}_3 \xrightarrow{k} \text{N}_2\text{O} + 2\text{H}_2\text{O}
\]

Eq: 5.5
Figure 5.11 Kinetics of adsorbed nitrate photolysis (a). Photo-induced surface NH$_4$NO$_3$ loss in the presence of molecular oxygen and (b). Pseudo first order rate analysis for the photolysis of adsorbed NH$_4$NO$_3$, under different relative humidity conditions (RH < 1, 20, 45 and 80%). $\theta_0$ – adsorbed NH$_4$NO$_3$ concentration on saturated oxide surface at t = 0. $\theta$ – NH$_4$NO$_3$ concentration on oxide surface at irradiation time t. The presented NH$_4$NO$_3$ loss is the mean of triplicate measurements and the error bars represent the standard deviation.
The surface area normalized integrated absorbance ($\theta$) was then calculated using the sample weight (w; g) and BET surface area (SA; m$^2$/g), according to,

$$\theta = \frac{\text{Integrated absorbance}}{w \text{ (g)} \times \text{SA (m}^2\text{/g)}}$$

Eq: 5.6

According to Figure 5.11, during several hours of photolysis of adsorbed nitrate, the change in the rate of adsorbed ammonium nitrate disappearance is most significant in the first 90 min. Therefore, these data was fitted to a first order rate equation, Eq: 5.7, and rate constants were calculated.

$$\ln \theta = \ln \theta_0 - kt$$

Eq: 5.7

where, $\theta_0$ – adsorbed ammonium nitrate concentration on saturated oxide surface at t = 0 ($\sim 5 \times 10^{14}$ molecules·cm$^{-2}$). $\theta$ – ammonium nitrate concentration on oxide surface at irradiation time t. An attempt to fit the time dependence of nitrate photolysis to first order kinetics, in order to gain an estimate of an apparent rate constant is shown in the inset of Figure 5.11(b). Uncertainties from triplicate measurements were propagated to obtain average ($k$), maximum ($k_{\text{max}}$) and minimum ($k_{\text{min}}$) rate constants. First order rate constants determined in this rate analysis are given in Table 5.4. These rate constants at specific relative humidity levels were fit to continuous curves, as shown in Figure 5.12, using fifth-order polynomial regression assuming no reaction at 100% relative humidity.
Table 5.4  First order rate constants for N$_2$O formation following broadband irradiation of thin NH$_4$NO$_3$ surface coatings and pure NH$_4$NO$_3$ under different relative humidity conditions.

<table>
<thead>
<tr>
<th>%Relative Humidity</th>
<th>First order rate constants x $10^5$ s$^{-1}$</th>
<th>surface adsorbed NH$_4$NO$_3$</th>
<th>pure NH$_4$NO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k$</td>
<td>$k_{\text{min}}$</td>
<td>$k_{\text{max}}$</td>
</tr>
<tr>
<td>1</td>
<td>0.5</td>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>20</td>
<td>2.1</td>
<td>1.8</td>
<td>2.4</td>
</tr>
<tr>
<td>45</td>
<td>1.5</td>
<td>1.3</td>
<td>1.7</td>
</tr>
<tr>
<td>80</td>
<td>0.8</td>
<td>0.7</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Figure 5.12  Fifth order polynomials fit to first order rate constants for N$_2$O formation following broadband irradiation of thin NH$_4$NO$_3$ surface coatings and pure NH$_4$NO$_3$ as a function of relative humidity, assuming no reaction at 100% relative humidity.
The laboratory experiments provide evidence for the formation of nitrous oxide from ammonium nitrate under ambient conditions that is enhanced in the presence of light, relative humidity and a surface. This source is currently not accounted for in the global N2O budget. Modeling analysis discussed below can provide an estimate of the relative contributions from the mechanism discussed here compared to other known processes.

5.4.2 Model Analysis

Annual production of N2O from atmospheric aerosols and surface fertilizer application over the continental United States from these abiotic photochemical pathways can be estimated from results of an annual chemical transport simulation with the Community Multiscale Air Quality model. Input data for the simulations are provided in Experimental section and hourly N2O production from ammonium nitrate in each 3D model gridcell was calculated as,

\[ N_2O = (AN_{SFC}) \cdot (1 - e^{-v \cdot f(RH) \cdot 3600}) \]  

Eq: 5.8

where \( v \) is the modeled hourly broadband solar radiation (W/m²) as a fraction of one solar constant (1366 W/m²) as used in the experiments; \( f(RH) \) is the rate constant \( k \) (s⁻¹) as a fifth-order polynomial fitted to the experimental rate constants for N2O photolysis, expressed for the hourly modeled RH; and \( AN_{SFC} \) is the gridcell surface mass of ammonium nitrate, calculated for the Aitken and accumulation modes from their modeled surface areas. In aerosol ammonium nitrate, we conservatively assume ammonium nitrate surface area is proportional to its percentage of total aerosol mass. The CMAQ model...
Figure 5.13 Annual N₂O production over the continental United States from ammonium nitrate (metric tons); (a). Vertical profile over study domain from atmospheric aerosols. (b). Integrated vertical column. (c). Surface-level production from atmospheric aerosols. (d). From solid ammonium nitrate and calcium ammonium nitrate fertilizers.
does not account for the aging of individual particles, and we recognize that ammonium nitrate coatings on fractal surfaces of mineral and carbonaceous aerosols may lead to higher surface concentrations of ammonium nitrate.

Estimated annual N\textsubscript{2}O production over the continental United States from ammonium nitrate from CMAQ is shown in Figure 5.13. Surface-enhanced photolysis of aerosol ammonium nitrate is estimated to yield $3,964^{+239/-241}$ metric tons N\textsubscript{2}O/year, with most production occurring in the free troposphere (Figure 5.13(a)), above cloud level. In the absence of a surface, photolysis would yield $2,014^{+3/-10}$ tons/year. Annual tropospheric column yields are highest over California—including southern California, the central valley, and offshore plumes—due to elevated ammonium nitrate concentrations and sunny conditions throughout the year (Figure 5.13(b)), peaking in summer. Near the surface, urban areas throughout the country produce local hotspots, and the Midwest is a widespread regional source (Figure 5.13(c)). The seasonality of N\textsubscript{2}O production over the interior of the continent from this mechanism is consistent with nitrate seasonality, with a maximum in the winter and a summertime minimum.

Estimating photolysis yields from solid pellet ammonium nitrate fertilizers is difficult due to incomplete documentation on their contemporary application in practice. In particular, the percentage of these fertilizers applied to the surface of fields or “side dressed” below the topsoil varies by season and crop in best practices, but actual surface application rates are not reported. We assume that 50\% of solid ammonium nitrate fertilizers are applied to the surface, and fertilizer surface area facing the sun is not in contact with a surface. Thus, production from photolysis of “top dressed” solid ammonium nitrate and calcium ammonium nitrate fertilizers applied to the surface of
agricultural soils is estimated at $5,322^{+488/1328}$ tons N$_2$O/year, with less than 10% due to calcium ammonium nitrate. The spatial distribution of N$_2$O from this source (Figure 5.13(d)) is similar to production from atmospheric aerosols, reflecting the common source of ammonia emissions from agriculture. However, the seasonality over the continental interior was reversed, matching the application of nitrogenous fertilizers during the growing season. Uncertainties due to variability in the size distribution of manufactured pellet radius (62.2%) are larger than uncertainties in experimental photolysis rates (19.5%) and modeled ammonium nitrate concentrations (32.9%) combined. The potential for impurities in solid fertilizer pellets and loose soil particles to provide an effective surface that can enhance these rates and the undocumented rate of actual fertilizer application introduce large additional uncertainties. The amount of ammonium nitrate fertilizer used in the U.S. is so large that only one layer of pellets applied to fertilized croplands and photolyzed by catalytic reaction would produce more N$_2$O than the contemporary national emissions inventory for all sources.

Initial N$_2$O production estimates of $9,286^{+726/-5,288}$ tons/year place this mechanism as the 9th-ranked total source and 7th-ranked abiotic source of N$_2$O in the United States, comparable to adipic acid production, and representing 0.90% of the current estimated national total from all natural and anthropogenic sources. However, much of the estimated production from photolysis of synthetic fertilizers may already be accounted for in field measurements contributing to the highly uncertain estimate for emissions due to nitrogen mineralization from synthetic fertilizers, to which it would contribute 4.04%.
Model estimates suggest that the influence of ammonium nitrate photolysis on ambient N₂O concentrations may be observable in situ. Maximum local surface-level yields from atmospheric aerosols peak at 1.5 µg/hour/m² over New York City, leading to potential concentration changes of up to 37.1 ppt, as compared to the 890 ppt daily variability in surface level concentrations over a managed agriculture area at the West Branch, Iowa tall tower monitoring site in 2007 and 2008. Emissions from surface fertilizer application during the spring planting season reach a maximum of 930 µg/hour/m² leading to instantaneous concentration changes of up to 22.0 ppb, but in the presence of other N₂O emissions from managed agricultural soils.

Based on results over North America, N₂O production by this mechanism is expected globally from both megacities and agricultural areas. Projected changes in anthropogenic emissions suggest that this mechanism may become more important in the future. As NOₓ emissions increase and sulfur dioxide emissions decline, aerosol ammonium nitrate concentrations will rise. However, the continued transition from solid fertilizers to liquid mixes and urea concentrates for many crops suggests that N₂O production from photolysis of fertilizers may decline as the atmospheric aerosol source increases.

5.5 Conclusions and Environmental Implications

These findings add to the body of evidence that abiotic mechanisms for N₂O production from nitrate ion (in this particular case ammonium nitrate) are important and estimated to produce approximately 5% of total U.S. anthropogenic N₂O emissions. A recent study by Samarkin et al. has also shown that nitrate in soil pore spaces is reduced
by minerals containing Fe(II). Based on the mechanism discussed here, we predict that the amount of N₂O would be seasonal and follow an isotope signature similar to the biotic mechanism, making it difficult to distinguish between the two. However, since for the predominant production observed here, the abiotic mechanism is sunlight initiated its correlation with diurnal and seasonal patterns of solar irradiance allows it to be distinguished from N₂O produced from biota. This would require routine measurements of atmospheric N₂O at a higher temporal resolution than the current daily and monthly monitoring regimes.

5.6 Acknowledgements

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6.1 Abstract

Accuracy of predictions of future changes in the global climate as well as the chemical balance of the atmosphere greatly depends on the level of understanding of ozone concentrations in the lower stratosphere and upper troposphere. It has been well-established that the observed large-scale ozone depletion during the Antarctic springtime is in part a result of the reaction between gaseous hydrogen chloride and nitric acid via heterogeneous reactions on polar stratospheric cloud (PSC) particles to yield molecular chlorine, an active reservoir species for chlorine atoms. Furthermore, chlorine active species, in the troposphere, can result from reactions between nitrogen oxides and hydrogen chloride on aerosol dust particles. In the current study, we present a new reaction pathway in which gaseous HCl in the presence of chemisorbed nitric acid, NO$_3^-$, on aerosol particles yielding active chlorine and nitrogen species. We combine transmission Fourier transform infrared spectroscopy with X-ray photoelectron spectroscopy to investigate changes in the composition of both gas phase and surface bound species during the reaction between adsorbed nitrate and gaseous HCl under different conditions of relative humidity. Given that aluminum oxides and aluminum
silicates contribute to a major fraction of atmospheric dust aerosol, aluminum oxides are used as model systems to begin to understand various aspects of nitrogen oxide and hydrogen chloride reactions on mineral dust aerosol. Exposure of nitrated aluminum oxide particle, from reaction with nitric acid, to gaseous HCl yields several gas phase products, including NOCl, NO₂, HNO₃ under dry (%RH < 1) condition. Under humid conditions (%RH > 20), NO and N₂O are the only gas products observed. The experimental data suggest that, in the presence of adsorbed water, NOCl is hydrolyzed on the surface of the particles to yield NO and NO₂ via HONO, and NO₂ undergoes further hydrolysis result in N₂O via a surface mediated reaction. Upon broadband irradiation (λ > 300 nm) of secondary gas phase products, NOCl photodissociates to NO and active Cl (Cl\(^•\)). The gas phase product distribution highly depends on presence of a particle surface, relative humidity and the presence of co-adsorbed gases such as NH₃. The newly identified reaction pathways discussed here involve continuous production of active ozone depleting Cl and N species from sources such as gas phase HCl and HNO₃ as a result of heterogeneous reactions on mineral dust particle surfaces.

6.2 Introduction

In the 20\(^{th}\) century, a combination of laboratory studies, computer models, and atmospheric observations provided basic information to better understand the stratospheric ozone depletion. Understanding ozone trends in the lower stratosphere and upper troposphere is vital for accurate predictions of future changes in the global climate and the chemical balance of the atmosphere. In laboratory studies, a wide variety of chemical reactions that takes place in the stratosphere, important to ozone concentrations,
have been discovered. The importance of heterogeneous chemistry of halogen species and nitrogen oxide on polar stratospheric cloud (PSC) particles has been well established and accounts for the observed large-scale ozone depletion during the Antarctic springtime. During the polar sunrise, “low ozone events”, i.e. levels of 40 ppb ozone are depleted over a period of 5 days to < 5 ppb, have been observed. The sources of such decreases have been attributed to elevated levels of chlorine (Cl$_2$) and bromine (Br$_2$) that directly or indirectly destroy ozone in the stratosphere. Although bromine was thought to be mostly responsible for the ozone loss, the presence of chlorine atoms has been inferred from the distribution of hydrocarbons and $^{13}$C/$^{12}$C ratio of CO.

The proposed mechanism begins with enhancements to atmospheric HCl and ClONO$_2$, by breakdown of chlorine sources, i.e. CFC, in the presence of sunlight. Numerous field studies have shown that heterogeneous reactions occurring on PSCs play an important role in the conversion of these inactive chlorine compounds into labile forms, defined as ClO$_x$ ($\sim$ ClO + ClO$_2$). It has been shown that, in PSCs, both solid and liquid particles can promote heterogeneous reactions such as the followings.

$$\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HNO}_3 \quad \text{Eq: 6.1}$$

$$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O} \quad \text{Eq: 6.2}$$

$$\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3 \quad \text{Eq: 6.3}$$

In low ozone events ClO$_x$ act as highly reactive gases that is involved in catalytic ozone destruction cycles throughout the stratosphere. Laboratory studies on
reaction kinetics have further enabled a parameterization of these fundamental reactions to be included into atmospheric chemistry models.\textsuperscript{235, 236, 253-258}

Although the atmospheric conditions necessary for efficient heterogeneous chlorine activation on PSCs have been well established, little is known about a detail chemical mechanism for the activation of gaseous HCl on aerosol dust particles. Exploring new reaction pathways involved in the production of active Cl and N species from sources such as gas phase HCl and HNO\textsubscript{3} may provide additional information on ozone concentrations not only in the stratosphere but the troposphere as well. Atmospheric HCl is reported at higher concentrations, few parts per billion (ppbv), in polluted areas and in some indoor settings.\textsuperscript{259-263} The major anthropogenic sources of gas phase HCl includes coal burning, waste incineration, chlorinated hydrocarbons, automobile exhaust, burning of garbage, biomass and agricultural products.\textsuperscript{264-266} Industrial activities, i.e. petroleum and semiconductor manufacturing, also contribute to a significant fraction of atmospheric HCl.\textsuperscript{267} The existence of gas phase HCl in marine air is well established. Sea salt arising from wave action, containing large amount of Cl\textsuperscript{-}, potentially becomes a major source of gaseous HCl. Due to the fact that a larger fraction of these HCl is originated from combustion sources and found in polluted regions, nitrogen oxides, including NO\textsubscript{2} and HNO\textsubscript{3}, are typically present simultaneously.

In addition to reactive chlorine species, these nitrogen oxides, in particular NO, NO\textsubscript{2} and N\textsubscript{2}O, are important in determining atmospheric ozone concentrations in the lower atmosphere. These nitrogen oxides participate in a complex series of chemical and photochemical reactions to produce tropospheric ozone in a non-linear relationship with respect to the ozone concentrations. Therefore, peak ozone levels are affected by the
Figure 6.1 A cartoon representation of nitrogen and chlorine activation from heterogeneous reactions of nitrogen oxides and hydrogen chloride. The dust particles emitted from the Earth crust react with atmospheric HNO₃ (or NO₂) result in an adsorbed nitrate layer over the particle surface. These “nitrated” particle surfaces further react with HCl, when mixed with either polluted air or with sea salt containing Cl⁻, possibly to yield active N and Cl species, i.e. NO, NO₂, N₂O and Cl (or ClO) or combination of these gas phase products. It should be noted the sun shown in the Figure, given that during the daytime photactive N and Cl species, i.e. NO₂ and Cl₂, NOCl, can photodissociate altering the gas phase distribution.

amount of nitrogen oxides present in the gas phase which depends on the ground base emissions and subsequent reactions in the lower atmosphere.⁴⁵, ⁸⁸, ¹¹⁴ N₂O serves as a major source of stratospheric NOₓ and thus contributes to catalytic ozone destruction. Ravishankara et al. found that N₂O is currently the single most important ozone depleting substance, and is anticipated to remain the largest throughout the 21st century.²⁰⁴
Nitrogen oxide species are released into the atmosphere mainly in the form of NO, which is then readily oxidized to NO₂, and those are collectively known as NOₓ. The principal sources of NOₓ are biomass burning and fossil fuel combustion from vehicles, which results in approximately half of the global concentration. In the atmosphere, nitrogen oxides readily react with particulate matter (e.g. mineral dust and sea salt aerosol) to yield adsorbed nitrate. Valuable information regarding the chemical speciation, as the coordination of products adsorbed on the surface, has been obtained using FTIR spectroscopy. Several surface species have been proposed following the adsorption of nitrogen oxides on mineral oxide surfaces which include nitrate (NO₃⁻), nitrite (NO₂⁻) and nitrosyl (NO⁺). Under humid conditions, it has been shown that co-adsorbed water molecules readily solvate adsorbed nitrate ions on the aluminum oxide surface forming inner and outer sphere complexes. The cartoon shown in Figure 1 summarizes some of the important aspects of nitrogen and chlorine activation from the reactions of nitrogen oxides and hydrogen chloride. The dust particles emitted from the Earth crust react with atmospheric HNO₃ (or NO₂ and H₂O) result in an adsorbed nitrate layer over the particle surface. When these particles interact with either atmospheric HCl or mixed with sea salt containing Cl⁻, it is expected to yield active N and Cl species, including NO, NO₂, N₂O and Cl (or ClO) or combination of these gas phase species.

In a recent study by Raff et al., a surface-mediated coupling of nitrogen oxides and halogen activation cycles has been shown in which uptake of gaseous NO₂ and N₂O₅ on solid silica substrate generates adsorbed intermediates, NO⁺NO₃⁻ and NO₂⁺NO₅⁻, that reacts with HCl to yield NOCl and ClNO₂.
chemistry and photochemistry in which gaseous HCl is activated in the presence of adsorbed nitrate, from the reaction of nitric acid, on aerosol particles yielding active chlorine and nitrogen species. Here we combine transmittance Fourier transform infrared (FTIR) spectroscopy with X-ray photoelectron spectroscopy (XPS) to investigate both gas phase and surface changes during the reaction between adsorbed nitrate and gaseous HCl under different relative humidity conditions. Given that aluminum oxides and aluminum silicates contribute \( \approx 8\% \) by mass to the total dust burden in the atmosphere,\(^{107, 225}\) aluminum oxides are used as model systems to begin to understand various aspects of nitrogen oxide and hydrogen chloride reactions on mineral dust aerosol. Exposure of “nitrated” alumina surfaces to gaseous HCl yield several gas phase products NOCl, NO\(_2\) and HNO\(_3\) under dry (%RH < 1) conditions. Under humid conditions, NO and N\(_2\)O were the only gas products observed. Upon irradiation (\( \lambda > 300 \) nm) of secondary gas phase products, NOCl photodissociated to NO generating active Cl (Cl\(^{\bullet}\)). The gas phase product distribution highly depends on presence and absence of particle surface, relative humidity and presence of co-adsorbed gases such as NH\(_3\). The new reaction pathways explored in this chapter will lead to explain and predict concentrations of active N and Cl species under a various environmentally relevant conditions.

6.3 Experimental Methods

6.3.1 Source Materials

Commercially available \( \gamma \)-Al\(_2\)O\(_3\) (Degussa, Aluminum oxide C) and CaCO\(_3\) (OMYA) with surface areas of 101 (\( \pm 4 \)) and 10 (\( \pm 0.4 \)) m\(^2\) - g\(^{-1}\), respectively, were used in these experiments. Dry gaseous nitric acid was taken from the vapor of a 1:3 mixture of
concentrated HNO₃ (70.6% HNO₃, Mallinckrodt) and 95.9% H₂SO₄, (Mallinckrodt). Dry gas phase hydrogen chloride was generated from the vapor of concentrated HCl (37% HCl, Fisher). Distilled H₂O (Fisher, Optima grade) was degassed prior to use.

6.3.2 Transmission FTIR Spectroscopy Studies

Nitrate coatings on model mineral surfaces were prepared by reacting particle surfaces with nitric acid to produce a surface layer of adsorbed nitrate. The experimental setup for these experiments is described in detail in Chapter 2.1.1. The preparation of saturated surfaces of adsorbed nitrate has been previously described in detail in Chapter 3.

In brief, approximately 5.5 mg of alumina (γ-Al₂O₃ – Degussa) powder, a model for mineral surfaces and mineral dust aerosol, was pressed onto half of a tungsten grid and evacuated for 12 hrs in the FTIR cell to remove adsorbed water from the surface. The alumina surface was then exposed to nitric acid vapor for 30 minutes at a pressure of approximately 1.70 Torr at 298 K followed by a 4 hour evacuation of the FTIR cell to remove all weakly adsorbed products. From previous studies, this process is known to produce a saturated surface coverage of adsorbed nitrate on alumina. The calculated nitrate coverage, when normalized to the BET surface area, is determined to be ~ 5 ± 1 x 10¹⁴ molecules·cm⁻². Following introduction of gas phase HCl and water vapor (adjusted to different RHs), the valve connecting the FTIR cell to the mixing chamber was closed, letting the gas phase products accumulate inside the cell as the nitrated surface was reacting with HCl. During the experiment, infrared spectra were recorded with a single beam Mattson RS-10000 spectrometer equipped with a narrow band MCT
detector. Typically, 250 scans were collected with an instrument resolution of 4 cm\(^{-1}\) in the spectral range extending from 900 to 4000 cm\(^{-1}\). Absorbance spectra for gas and adsorbed species were obtained by referencing single beam spectra of the blank grid and the oxide coated grid to single beam spectra collected prior to the nitric acid exposure.

After 2 hours of the reaction, the secondary gas phase products were exposed to light (300 < \(\lambda\) < 700 nm) using a broadband Hg light source and a broadband filter, as described previously.\(^{215,216}\) The experimental setup for these experiments is described in detail in Chapter 2.1.2. Selected experiments were replicated using CaCO\(_3\) (OMYA, 98% CaCO\(_3\)), as a proxy for aerosol particles, to understand the effect of additional water associated with secondary structures on the particle surface.

6.3.3 Ex-situ X-ray Photoelectron Studies

The reacted aluminum oxide sample was removed from the tungsten grid and analyzed using a custom-designed Kratos Axis Ultra X-Ray photoelectron spectrometer with a monochromatic Al K\(_{\alpha}\) X-Ray source. The sample was pressed onto an indium foil, on a copper stub, and introduced into the XPS analysis chamber, which had a pressure that was maintained in the 10\(^{-9}\) Torr range during analysis. Wide energy range survey scans were acquired using the following parameters: energy range from 1200 to -5 eV, pass energy of 160 eV, step size of 1 eV, dwell time 200 ms, X-ray spot size 700 x 300 sq. mm. High resolution spectra were acquired using the following parameters: energy range of 50 – 20 eV depending on the peak examined, pass energy of 20 eV, step size of 0.1 eV, dwell time of 1000 ms. The data collected were analyzed using CasaXPS data processing software.
6.4 Results and Discussion

As discussed here, laboratory measurements using FTIR spectroscopy and XPS data show that active N and Cl species, including NOCl, NO, NO₂, and N₂O can be produced via surface mediated reactions between nitrogen oxide, in this particular case HNO₃, and HCl.

6.4.1 Analysis of Gas Phase Products from the Reaction Between Adsorbed Nitrate and Gas Phase HCl

Heterogeneous uptake of nitric acid on aluminum oxide yields a chemisorbed nitrate layer on the particle surface as discussed in detail in Chapter 3 and 4 (not shown here). Vibrational frequencies of adsorbed nitrate have been assigned and interpreted using quantum chemical calculations of binuclear alumina cluster models. Under dry condition (%RH < 1), adsorbed nitrate binds to the oxide surface in different modes of coordination as monodentate, bidentate and bridging, based on the assignment of the peaks in the nitrate ion ν₃ spectral region between 1200 and 1650 cm⁻¹. In the presence of water vapor at higher relative humidities, co-adsorbed water solvates the nitrate ion forming inner and outer sphere complexes which are represented by peaks in the region between 1300 and 1450 cm⁻¹ in the FTIR spectrum. Changes in the infrared spectra as a function of relative humidity and the assignment of these peaks have been discussed extensively and the details can be found in Chapter 3.

Gas phase product formation upon exposure of nitrated surface to gaseous HCl is shown in Figure 6.2. FTIR spectra of gas phase products were recorded as a function of reaction time under dry condition (%RH < 1) at 298 K. The data show that several
several gas phase products appear and grow in intensity as the reaction proceeds. Based on the vibrational frequency, it is relatively easy to identify the major gas phase products as NOCl, HNO3 and NO2 (see Tale 6.1). The spectra shown in Figure 6.2 reveal a significant change in the gas phase product distribution during the course of the reaction, especially gas phase species NOCl and NO2 grow in concentration whereas HNO3 shows a decay with the reaction time indicating its participation in a secondary reaction. An enlarged region of FTIR spectra between 1200 and 2000 cm⁻¹ is shown in

Figure 6.2  FTIR spectra of gas phase products formation during the reaction of gas phase HCl and adsorbed nitrate on γ-Al₂O₃ under dry (%RH < 1) condition at 298K.
Figure 6.3  Gas phase product formation from the reaction between gas phase HCl and adsorbed nitrate on $\gamma$-Al$_2$O$_3$ under dry (%RH < 1) at 298K. (a). Enlarged region of FTIR spectra between 1200 and 2000 cm$^{-1}$ (b). Variation of gas phase products as function of reaction time.
Figure 6.3(a) to be evidence for the above described gas phase product variations. Gas phase concentrations obtained from FTIR analysis followed by the reaction between gaseous HCl and adsorbed nitrate under dry condition is shown in Figure 6.3(b). The results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Gas phase concentrations of individual species were determined by converting integrated absorbances to concentrations using calibration factors, given in Table 6.2, for the individual gas phase species.

<table>
<thead>
<tr>
<th>Gas phase products</th>
<th>Vibrational mode</th>
<th>Frequency ($\text{cm}^{-1}$)</th>
<th>Integrated absorbance spectral range ($\text{cm}^{-1}$)</th>
<th>Conversion factor (mol·L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_3$</td>
<td>$\nu_2$</td>
<td>1709</td>
<td>1654-1754</td>
<td>$(0.87 \cdot 10^{-4})^b$</td>
</tr>
<tr>
<td>HCl</td>
<td>$\nu_1$</td>
<td>2886</td>
<td>2614-3090</td>
<td>$(5.58 \cdot 10^{-4})^b$</td>
</tr>
<tr>
<td>NOCl</td>
<td>$\nu_1$</td>
<td>1800</td>
<td>1760-1854</td>
<td>$(0.92 \cdot 10^{-4})^c$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>$\nu_3$</td>
<td>1616</td>
<td>1540–1670</td>
<td>$(0.31 \cdot 10^{-4})^d$</td>
</tr>
<tr>
<td>NO</td>
<td>$\nu_1$</td>
<td>1874</td>
<td>1750–1980</td>
<td>$(3.08 \cdot 10^{-4})^d$</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>$\nu_1$</td>
<td>2224</td>
<td>2124–2271</td>
<td>$(0.69 \cdot 10^{-4})^d$</td>
</tr>
</tbody>
</table>

a – Refs. 170 – 172, 269
b – Experimentally determined values
c – Ref. 269
d – Ref. 170 - 172
Figure 6.4  Gas phase product formation from the reaction between gaseous HCl and adsorbed nitrate on γ-Al₂O₃ under wet (%RH 45 ± 2) at 298K. (a). Enlarged region of FTIR spectra between 1500 and 2250 cm⁻¹ (b). Variation of gas phase products as a function of reaction time.
Interestingly, under humid conditions (%RH 45) gas phase product distribution showed significant differences, with no NOCl, NO₂ or HNO₃ formation in the gas phase, but, instead there is the growth of NO and N₂O as a function of reaction time.¹⁷⁰-¹⁷² FTIR spectra of gas phase product formation upon exposure of nitrated alumina surface to gas phase HCl under wet condition (%RH 45) at 298 k is shown in Figure 6.4(a). The variation of gas phase concentration under these conditions can be seen in Figure 6.4(b). A comparison of the gas phase concentrations shown in Figure 6.3(b) and 6.4(b) reveals a significant change in the gas phase product distribution and total gas phase production between dry and wet conditions. This large difference was noted and the laboratory experiments were focused more on gas product formation under different relative humidities ranging from %RH ~3 to 80.

6.4.2 Effect of Relative Humidity on Gas Phase Product Distribution

Water is a relatively abundant species in the atmosphere and plays an important role in almost all the chemical and photochemical processes. The tri-component system, HCl-HNO₃-H₂O, has being the subject in numerous atmospheric investigations, theoretical²⁷⁰-²⁷² and experimental,²⁷³-²⁷⁵ and has clearly proven that in the presence of water along with HNO₃ result in the formation of stable complexes. It is well established that in PSCs hydrogen chloride binds to the particle surface, in the presence of HNO₃ and H₂O, leading to the transformation of HCl into more photolabile Cl₂.²⁷⁶-²⁷⁸ A recent study by Weiser et al. on Arctic stratosphere under synoptic conditions showed that HCl dissolved in liquid particles along with HNO₃-H₂O, following an unexpected ratio.²⁷⁹

Here the experiments were carried out under different humid conditions,
Figure 6.5 Relative gas phase concentrations obtained from FTIR spectra following the reaction between gas phase HCl and adsorbed nitrate on γ-Al2O3 298K under different relative humidities, ranging from %RH < 1 to 80. The gas phase concentrations have been normalized to the largest gas phase product species under all the conditions, NOCl at %RH < 1.

including %RH 3, 8, 12, 20, 45, and 80.

The relative gas phase product distributions under relative humidity conditions are shown in Figure 6.5. The plot, showing the relative gas phase concentrations of NOCl, NO2, HNO3, HCl, N2O and NO under %RH < 1, %RH 3, 8, 12, 20, 45 and 80 after 120 min of the reaction time, were obtained by normalizing the gas phase concentrations to the largest gas phase product under all the studied conditions,
Figure 6.6  Gas phase product formation from the reaction between gas phase HCl and adsorbed nitrate on γ-Al₂O₃ under wet (%RH 12 ± 2) at 298K. (a). FTIR spectra (b). Variation of gas phase products as a function of reaction time. Inset in Figure (a) shows the FTIR spectrum of the gas phase products after 120 min of reaction.
which is NOCl at %RH < 1. Based on the results observed under different relative humidities, RH greater than 8% appears to yield a different gas phase product distribution. Thus, these data will be used in the following discussion to understand the variation of gas phase product formation as a function of relative humidity. The gas phase product formation at %RH 12 is shown in Figure 6.6. As seen in Figure 6.6(a), the FTIR spectra indicate early formation of NOCl and NO2 in higher concentrations followed by decay as the reaction progress. These trends can be clearly seen in Figure 6.6(b) showing variation of gas phase product concentrations as a function of

Table 6.2 Surface area normalized initial rate of gas phase product formation, determined from linear regression, during the reaction between gas phase HCl and adsorbed nitrate on $\gamma$-Al2O3 under different relative humidity conditions.

<table>
<thead>
<tr>
<th>%Relative humidity</th>
<th>NOCl (g)</th>
<th>NO2 (g)</th>
<th>NO (g)</th>
<th>N2O (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1</td>
<td>41 (± 3)</td>
<td>3.4 (± 0.14)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>12</td>
<td>38 (± 2)</td>
<td>2.6 (± 0.12)</td>
<td>8.0 (± 0.4)</td>
<td>0.35 (± 0.021)</td>
</tr>
<tr>
<td>20</td>
<td>1.1 (± 0.12)</td>
<td>-</td>
<td>18 (± 1)</td>
<td>1.1 (± 0.010)</td>
</tr>
<tr>
<td>45</td>
<td>-</td>
<td>-</td>
<td>31 (± 2)</td>
<td>4.8 (± 0.23)</td>
</tr>
<tr>
<td>80</td>
<td>-</td>
<td>-</td>
<td>56 (± 1)</td>
<td>4.8 (± 0.38)</td>
</tr>
</tbody>
</table>

a – Results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Gas phase product formation data from the first 30 min were used in the rate determination.

b – Rates are normalized to the corresponding BET surface area.
reaction time. Loss of NOCl and NO₂ at longer time scale suggests initiation of secondary reactions yielding more gas phase or surface products. In addition to NOCl and NO₂, here we observe formation of NO and N₂O, the major gas phase products at higher relative humidities, %RH < 20.

The rate of secondary gas phase production is greatest initially (t < 30 min), followed by a slower rate of change over time. Initial rates of gas phase product formation under different relative humidities at 298 K, determined from linear regression analysis, are given in Table 6.2. The rates are normalized to the BET surface area of γ-alumina. It can be clearly seen from these data that production of NOCl and NO₂ is highest in %RH < 12 and addition of more water vapor triggers formation of NO and N₂O at higher rates. The information from these experiments can begin to understand the mechanism involve with the reaction between adsorbed nitrate and gas phase HCl on mineral dust particle surfaces.

6.4.3 Mechanism for the Production of Secondary Gas Phase Products

Before further discussing the heterogeneous interactions of gaseous HCl with adsorbed nitrate and the secondary gas phase products that form, it is first instructive to consider what is known about uptake of HNO₃ and HCl on metal oxide surface, in particular on alumina. It is well-known that heterogeneous uptake of HNO₃ by the metal oxide surface yields adsorbed nitrate via, \[ \text{HNO}_3(g) + \text{OH}^-(a) \rightarrow \text{NO}_3^-(a) + \text{H}_2\text{O} \] Eq: 6.4.
Figure 6.7  A representative XPS of high resolution (a). N 1s region and (b). Cl 2p region of γ-Al₂O₃ particles before and after the reaction between gas phase HCl and adsorbed nitrate under dry (%RH < 1) condition at 298 K.
In addition to FTIR data, presence of chemisorbed nitrate on alumina surface was further confirmed in ex-situ XPS analysis, as seen in Figure 6.7(a). High resolution XPS data, after exposure to HNO$_3$ acid, showed one additional surface species with a binding energy of 407 eV. This can be assigned to nitrate (N1s) on the surface.$^{215}$

According to Figure 6.7(b), the spectral band with the binding energy of 200 eV for Cl 2p indicates a significant uptake of HCl by the alumina surface.$^{280}$ Adsorption of HCl, on metal oxide surfaces such as alumina is thought to occur via two distinct reaction mechanisms. The first involves the dissociation of HCl onto aluminum oxygen pairs forming new OH groups and Al-Cl species.$^{281,282}$ Several theoretical and laboratory studies have confirmed the formation of new OH groups and, thus, existence of this mechanism. In the second pathway, the reaction likely occurs via analogous mechanism,

![Chemical Reaction Diagram](image)

**Figure 6.8** A schematic representation of the adsorption of HCl at a medium-strong Lewis acid site and the effect of subsequent H$_2$O loss. This transformation leads to the regeneration of a more acidic Lewis acid site on the alumina surface. The asterisks indicate coordinative unsaturation. Adapted from Ref 284.
dissociative adsorption of HCl, whereupon chlorine replaces a surface OH group via an exchange mechanism.\textsuperscript{283} In a recent study, McInroy et al.\textsuperscript{284} highlighted the importance of replacing surface OH groups by chlorine, followed by a loss of water molecule, to regenerate a more acidic Lewis acid site for further reaction. The proposed schematic representation of HCl adsorption on alumina is shown in Figure 6.8. Thus, HCl is actively taken up by the alumina surface via,

\[
\text{HCl (g)} \rightarrow \text{H}^+ (a) + \text{Cl}^- (a) \quad \text{Eq: 6.5.}
\]

It is well established that nitrate ion is a strong oxidizing agent in highly acidic solutions that is capable of changing the oxidation state of halogen species.\textsuperscript{285-287} Therefore, here we propose that interaction between adsorbed nitrate and chloride, on acidic alumina surface, yields NO\textsuperscript{+}NO\textsubscript{3}\textsuperscript{−} via acid catalysis, as given in Eq: 6.6.

\[
2\text{NO}_3^−(a) + 2\text{H}^+(a) + 2\text{Cl}^−(a) \rightarrow \text{NO}^+\text{NO}_3^−(a) + 2\text{OH}^−(a) + \text{Cl}_2(g) \quad \text{Eq: 6.6}
\]

This surface complex has been proposed to readily react with further HCl forming gas phase NOCl and HNO\textsubscript{3}, as major products.\textsuperscript{268} The overall reaction mechanism is given in Eq: 6.7.

\[
\text{NO}^+\text{NO}_3^−(a) + \text{HCl}(g) \rightarrow \text{NOCl}(g) + \text{HNO}_3(g) \quad \text{Eq: 6.7}
\]

The secondary gas phase product, HNO\textsubscript{3}, is readsorbed on the alumina surface result in more adsorbed nitrate. This agrees with FTIR data shown in Figure 6.2 and 6.3 that
indicated an early production of gas phase HNO$_3$ followed by a decay as a function of reaction time.

Gas phase NO$_2$ is formed via desorption of NO$^+$NO$_3^-$ in a self reaction of adsorbed nitrogen species in analogues to the reaction mechanism between gas phase NO and NO$_3$, according to Eq: 6.8.$^{288, 289}$

\[
\text{NO}^+\text{NO}_3^-(a) \rightarrow 2\text{NO}_2(g) \quad \text{Eq: 6.8}
\]

Based on the observations under dry conditions, it appears that gas phase NO$_2$ is in an equilibrium with NO$^+$NO$_3^-$ due to the fact that it is not the major gas phase product. It also must be mentioned that this mechanism solely based on the observed NOCl and NO$_2$ products species, and must therefore be viewed as one of the many possible reaction schemes, such as follows.

\[
\begin{align*}
\text{NO}_3^-(a) + \text{Cl}^-(a) + 2\text{H}^+(a) & \rightarrow \text{HOCl} (g) + \text{HONO}(g) \quad \text{Eq: 6.9} \\
\text{HONO}(g) + \text{Cl}^-(a) + \text{H}^+(a) & \rightarrow \text{NOCl} (g) + \text{H}_2\text{O}(a) \quad \text{Eq: 6.10} \\
\text{HOCl}(g) + \text{Cl}^-(a) + \text{H}^+(a) & \rightarrow \text{Cl}_2 (g) + \text{H}_2\text{O}(a) \quad \text{Eq: 6.11}
\end{align*}
\]

As seen in Figure 6.4 and 6.6, under humid conditions, NO and N$_2$O are formed as major gas phase products with a concomitant loss of NOCl and NO$_2$. Previous studies have shown that hydrolysis on aqueous solutions may be a loss process for NOCl in the atmosphere.$^{290, 291}$ In contrast to these observations, Raff et al.$^{268}$ discuss of an enhancement of NOCl production on SiO$_2$ surface in the presence of thin films of adsorbed water (%RH 9 – 13), competing with the hydrolysis reaction. This study further
claim the observed enhancement occurs via a barrierless channel where water acts as a conduit to transfer a proton from HCl to nitrate, facilitating the formation of NOCl. In our studies with active alumina surface, we observed higher production of NOCl at lower relative humidities (%RH < 12), yet no significant enhancement. In alumina, atmospheric water vapor readily adsorbs on particle surface and dissociates resulting in a hydroxyl terminated surface. Adsorbed water can hydrogen bond to these hydroxyl groups in equilibrium with water vapor. It has been shown that co-adsorbed water molecules readily solvate adsorbed nitrate ions on the aluminum oxide surface forming inner and outer sphere complexes. For alumina, it has been shown that the first surface adsorbed water layer is formed around %RH 17 and this takes place at even lower relative humidities in the presence of adsorbed nitrate. Water uptake on alumina has been discussed in detail in Chapter 3. On the basis of these information and observations, at higher relative humidities, (%RH > 12), formation of 2 to 4 layers of water on the particle surface may trigger heterogeneous hydrolysis of NOCl to yield NO and NO₂ via,

\[
\text{NOCl(g) + H}_2\text{O(a) } \longrightarrow \text{HONO(g) + HCl(g) \quad Eq: 6.12}
\]

\[
2\text{HONO(g) } \longrightarrow \text{NO(g) + NO}_2\text{(g) + H}_2\text{O(a) \quad Eq: 6.13}
\]

Furthermore, \(\text{NO}^+\text{NO}_3^-(a)\) reacts with water to produce more HONO via,

\[
\text{NO}^+\text{NO}_3^-(a) + \text{H}_2\text{O(g) } \longrightarrow \text{HONO(g) + HNO}_3\text{(g) \quad Eq: 6.14}
\]

It is well-known that N₂O is formed during the heterogeneous hydrolysis of gas phase NO₂ via HONO on acidic oxide surfaces. Reactions of HONO and its
protonated forms ($H_2ONO^+$ or possibly $NO^+$) have shown to generate hyponitrous acid, $HON=NOH$. The self reaction of $(HON)_2$ is known to decompose to $N_2O$ over a wide range of pH values, including under highly acidic conditions. The net reaction yields $N_2O$ and $HNO_3$ according to:

$$8^{14}NO_2 + 3H_2O \rightarrow ^{14}N^{14}NO + 6H^{14}NO_3$$

Eq: 6.15.

Thus, a surface mediated secondary reaction of a primary gas phase product, $NO_2$, a product that can be easily seen in the infrared spectra at lower RHs, may be responsible for the higher $N_2O$ concentrations observed, especially at longer reaction times.

6.4.4 Role of Particle Surface in the Reaction Mechanism

The proposed mechanism above for the formation of secondary gas phase products from the reaction between $HNO_3$ and $HCl$, given by Eq: 6.4 to 6.7, occurs via surface adsorbed intermediates. To better understand and further confirm the involvement of the particle surface, selected control experiments were carried out in the absence of the alumina surface. The gas phase product formation from homogeneous reaction of gaseous $HCl$ and $HNO_3$ is shown in Figure 6.9. According to Figure 6.9(a) showing FTIR spectra of the gas phase, significantly lower production of NOCl and $NO_2$ can be seen compared to that of in the presence of alumina surface. This is further highlighted in Figure 6.9(b) that shows a comparison of NOCl and $NO_2$ production in the presence (dash line) and absence (solid line) of the surface. Initial rates of gas phase product formation under different relative humidities at 298 K, determined from linear regression analysis, are given in Table 6.3. Here the rates are normalized to the BET surface area of $\gamma$-alumina of
Figure 6.9  Gas phase product (NOCl and NO₂) formation from the reaction between gas phase HCl and HNO₃ under dry (%RH < 1) condition at 298K. (a). FTIR spectra (b). Variation of gas phase products. In Figure (b) the two dash lines represent corresponding gas phase product variations in the presence of γ-Al₂O₃ surface.
Table 6.3  Surface area normalized initial rate of gas phase product formation, determined from linear regression, during the reaction between gas phase HCl and HNO₃ under dry and wet conditions.

<table>
<thead>
<tr>
<th>%Relative humidity</th>
<th>Surface area normalized initial rate of gas production x 10⁻¹⁵ (molecules·m⁻³·s⁻¹·cm⁻²)b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NOCl(g)</td>
</tr>
<tr>
<td>&lt;1</td>
<td>1.1 (± 0.05)</td>
</tr>
<tr>
<td>45</td>
<td>n.o.</td>
</tr>
</tbody>
</table>

a – Results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Gas phase product formation data from the first 30 min were used in the rate determination.

b – Rates are normalized to the corresponding BET surface area.

n.o. – No gas phase products were detected due to formation of HCl-HNO₃-H₂O aggregates.

equivalent mass used in heterogeneous experiments. In a comparison of initial rates of NOCl and NO₂ production under dry (%RH < 1) condition in the presence and absence of a surface (Table 6.2 and 6.3), we can clearly see approximately a 40 fold enhancement for the production of NOCl during the first 30 min and it is ~ 4 fold for NO₂. At longer time scale the enhancement is only ~ 8 fold for NOCl.

Homogeneous reaction between HNO₃ and HCl, in the presence and absence of water is well documented.²⁴⁹, ²⁵⁸, ²⁹², ²⁹³ On the basis of reactants and identified gas phase products in several studies, the proposed overall reaction is similar to the one observed with aqua regia.²⁴⁹, ²⁹⁴ In this reaction pathway, gas phase nitric dissociates to yield NO₂⁺ and NO₃⁻ which react with Cl⁻ from gaseous HCl to form ClNO₂ that readily dissociates to Cl₂ and HONO. HONO reacts with more Cl⁻ to yield NOCl as given in Eq: 6.16 to 6.24.
Thus, NOCl is formed even in the absence of a surface, yet the product yields are much smaller compared to the heterogeneous process. Interestingly, the overall reaction for the heterogeneous process, the net reaction of Eq: 6.4 to 6.7, is similar to the overall reaction obtained for the homogeneous NOCl formation, Eq: 6.24. Based on the mechanism discussed here, we predict that the production of NOCl from the surface mediated process is similar to the homogeneous pathway, making it difficult to distinguish between the two.

6.4.5 Influence of Additional Water Associated with Secondary Surface Structures

The reaction pathways proposed in this study for the formation of NOCl and NO₂ is expected to inhibit in the presence of co-adsorbed water. Further investigation of
Figure 6.10  Gas phase product formation from the reaction between gas phase HCl and adsorbed nitrate on CaCO₃ at 298K. (a). FTIR spectra of the gas phase under dry (%RH < 1) condition. Variation of gas phase product formation under (b). dry (%RH < 1) and (c). wet (%RH 45) conditions. The insert in Figure (a) is an enlarged region of FTIR spectra between 900 and 2000 cm⁻¹.
Figure 6.11  Gas phase product formation upon exposure of nitrated CaCO₃ surface to
gas phase HCl under dry (%RH < 1) condition at 298K. Adsorbed nitrate is
generated by reacting CaCO₃ surface and with a mixture of HNO₃ and H₂O
(%RH 80) followed by 4 hour evacuation. (a). FTIR spectra of gas phase
(b). Variation of gas phase products as a function of reaction time.
Table 6.4  Surface area normalized initial rate of gas phase product formation, determined from linear regression, during the reaction between gas phase HCl and adsorbed nitrate on CaCO₃ under dry and wet conditions.

<table>
<thead>
<tr>
<th>Relative humidity</th>
<th>Surface area normalized initial rate of gas production x 10⁻¹⁵ (molecules·m⁻³·s⁻¹·cm⁻²)³</th>
<th>NOCl(g)</th>
<th>NO₂(g)</th>
<th>NO(g)</th>
<th>N₂O(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;1</td>
<td></td>
<td>6.2 (± 0.3)</td>
<td>6.4 (± 0.3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>45</td>
<td></td>
<td>-</td>
<td>-</td>
<td>1.7 (± 0.07)</td>
<td>-</td>
</tr>
</tbody>
</table>

a – Results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Gas phase product formation data from the first 30 min were used in the rate determination.

b – Rates are normalized to the corresponding BET surface area.

influence of additional water, adsorbed on particle surface, was done using CaCO₃ as the model system. In our earlier work, it has been shown that water plays a major role during the uptake of HNO₃ on calcium carbonate due to the fact that co-adsorbed water increases the ionic mobility of adsorbed ions on the surface, leading to the formation of micropuddles of calcium nitrate. These secondary structures on the surfaces, micropuddle, are associated with additional water even after evacuation forming Ca(NO₃)₂·xH₂O. These micropuddles are formed during successive cycles of HNO₃ exposures followed by H₂O vapor exposures. (Discussed in detail in Chapter 3.4.4.). Secondary gas phase product formation, under dry (%RH < 1) condition, from the reaction between gaseous HCl and adsorbed nitrate on CaCO₃, in the presence of additional associated water, is shown in Figure 6.10(a) and (b). As evidence by these data, the gas phase production, in particular NOCl, is less compared to that of alumina surface. This difference is further confirmed by the calculated initial rates of gas phase
product formation given in Table 6.4. Surprisingly, initial rate of NO₂ formation with CaCO₃ is higher compared to alumina surface under the same conditions. As shown in Figure 6.10(c), there was no N₂O formation even at higher relative humidities when CaCO₃ was used as the reactive surface. Therefore, it can be proposed that heterogeneous hydrolysis of NO₂ to yield N₂O dose not occur on CaCO₃ surface due to lower acidity of the carbonate surface leading to a higher gas phase concentration of NO₂. Additional experiments were carried out using CaCO₃ in which adsorbed nitrate associated with even more water, Ca(NO₃)₂(aq), was obtained by exposing the carbonate surface to a gaseous mixture of HNO₃ and H₂O (at %RH 80) followed by a four hour evacuation. The gas phase products formation from this surface upon exposure to HCl, under dry (%RH < 1) condition, is shown in Figure 6.11. The data highlight poor gas phase production and formation of NO. Production of NO can be attributed to heterogeneous hydrolysis of NOCl, in the presence of extra water on the surface even under dry conditions.

Therefore, additional water associated with secondary structures on particle surface greatly influence gas phase product distribution and the data from these experiments further confirm the reaction mechanism proposed for the heterogeneous of HCl and adsorbed nitrate.

6.4.6 NOCl Production in the Presence of Co-Adsorbed Ammonia

Exposure of adsorbed nitrate to gas phase ammonia (NH₃) yields a thin layer of ammonium nitrate, one or two monolayers of adsorbed NH₄NO₃, over the particle surface. A thorough discussion on formation of NH₄NO₃ on alumina surface is given in Chapter 5. Gas phase NH₃ is also known to titrate surface acidity upon adsorption.
Figure 6.12  Gas phase product formation following exposure of adsorbed ammonium nitrate on $\gamma$-Al$_2$O$_3$ at 298K under dry ($\%$RH < 1) condition. (a). FTIR spectra of gas phase (b). Variation of gas phase products as a function of reaction time.
Surface mediated acid catalysis is one of the key steps in the proposed reaction mechanism, especially during the formation of NO$_2$NO$_3$-(a) intermediate. In this set of experiments, effect of co-adsorbed ammonia was investigated by exposing adsorbed ammonium nitrate on alumina surface to gas phase HCl. Gas phase formation from the reaction between HCl and adsorbed NH$_4$NO$_3$, under dry (%RH < 1) condition, is shown in Figure 6.12. Lower gas phase production can be clearly noted. Presence of unreacted HCl, even after 120 min of reaction time, further verifies less reactivity of the surface. The initial rate of NOCl and NO$_2$ production were determined to be 1.4 (± 0.05) and 0.11 (± 0.01) molecules·m$^{-3}$·s$^{-1}$·cm$^{-2}$, respectively. The lower reactivity, in the presence of co-adsorbed NH$_3$, can be partially assigned to the less availability of surface protons for the acid catalysis. Less accessibility to the reaction sites during the HCl uptake can possibly be another explanation for the poor NOCl production.

6.4.7 Photochemistry of Secondary Gas Phase Products

Given that photochemistry dominates the daytime gas phase chemistry of the atmosphere, and new light induced pathways continue to be discovered,$^{162}$ there is quite a lot of information available in the literature to realize that the surface and near surface regions of particles catalyze photochemical reactions that perturb the composition of the atmosphere. The photochemistry of secondary gas phase species, in particular NOCl, has long been a subject of active interest. NOCl absorbs radiation throughout the visible and near ultraviolet region, as shown in Figure 6.13.$^{296,297}$ Based on numerous studies, it is well-known that NOCl photodissociates to yield gas phase NO and chlorine atoms via,$^{174}$

$$\text{NOCl(g)} \xrightarrow{hv} \text{NO (g)} + \text{Cl}^*$$

Eq: 6.25.
Figure 6.13  The overlap between the UV-vis absorption spectra of NOCl and CINO₂ and emission spectra from the Sun and fluorescent lamps typical of indoor settings. Adapted from Ref. 44.

From the analysis of the NOCl spectrum and theoretical calculations, quantum yield of this photochemical reaction is determined to be roughly equal to one in the wavelength region from 365 to 635 nm.²⁹⁸, ²⁹⁹ As seen in Figure 6.13, strong overlap between NOCl absorption cross section and solar actinic flux point out greater NO and Cl yields from the photodissociation under atmospheric conditions potentially leading to an accelerated ozone depletion. In this study, photolysis of secondary gas phase species was monitored by irradiation of the FTIR cell with broadband (λ > 300) light, after
Figure 6.14 Gas phase product formation upon irradiation of secondary gas phase products yielded from the reaction between gas phase HCl and adsorbed nitrate on γ-Al₂O₃ at 298K under dry (%RH < 1) condition. (a). FTIR spectra of gas phase (b). Variation of gas phase products.
Figure 6.15  Gas phase product formation upon irradiation of secondary gas phase products yielded from the reaction between gas phase HCl and adsorbed nitrate on $\gamma$-Al$_2$O$_3$ at 298K under wet (%RH 45 ± 2) condition. (a). FTIR spectra of gas phase (b). Variation of gas phase products.
completion of the reaction (120 min) between HCl and adsorbed nitrate on alumina. Gas phase product formation upon irradiation at 298K, under dry (%RH < 1) and wet (%RH 45 ± 2) conditions, are shown in Figure 6.14 and 6.15 respectively. As seen in Figure 6.14, we observed formation of NO with a simultaneous decay of the major gas phase product, NOCl, upon photolysis under dry condition. In addition, HNO₃ and NO₂ showed a similar loss from the gas phase with broadband irradiation. Under humid conditions (Figure 6.15), no additional gas phase species were observed, but a continuance production of NO and N₂O.

In good agreement with previous studies, here active Cl and NO species are generated from photodissociation of NOCl under dry condition. Produced Cl can initiate chain reactions inside the FTIR cell, starting with the reaction with NOCl result in more NO and Cl₂. ²⁹⁷

\[
\text{Cl}^* + \text{NOCl(g)} \rightarrow \text{NO(g)} + \text{Cl}_2(g) \quad \text{Eq: 6.26}
\]

Similarly active Cl can potentially react with gas phase HNO₃ and HCl yielding more products to the reaction mixture. Moreover, the reaction mixture becomes even more complex due to photoreduced products of adsorbed nitrate, NO, NO₂⁻ and NO₂. ⁸²-⁸⁴, ¹⁶⁴, ¹⁶⁵, ¹⁷⁰, ²¹⁵.

Thus, daytime chemistry of HCl and adsorbed nitrate is even more complicated to understand compared to nighttime chemistry and influence the chemical balance of the atmosphere to a greater extent. These laboratory experiments further provide evidence for the formation of highly reactive chlorine atoms on aerosol dust particles that is currently not included in atmospheric chemistry models.
6.5 Conclusions and Environmental Implications

The chemistry and photochemistry discussed in this work may be of particular importance in the upper troposphere and lower stratosphere those are in contact with highly polluted coastal urban areas. Conversion of atmospheric nitric acid and hydrogen chloride to active N and Cl species, including NOCl, NO, NO₂, Cl and Cl₂, through an adsorbed nitrate intermediate under different atmospherically relevant conditions has been shown. Extrapolation of laboratory results to real environmental conditions needs to begin with similar surfaces with adsorbed nitrate. Nemours filed studies have shown, via heterogeneous interactions, HNO₃ react with mineral dust and other atmospheric aerosols to yield adsorbed nitrate, nitrate coatings, and concentrated nitrate solutions. Atmospheric mixing of dust particles, having nitrated surfaces, with sea salt in marine environments is one potential way of initiating the formation of NOCl and other active gas phase species. Besides, atmospheric HCl originated from various natural and anthropogenic sources can react with adsorbed nitrate on mineral dust particles result in similar gas phase products. Analysis of gas phase and surface products with transmittance FTIR and XPS provided sufficient information to propose a detail reaction mechanism for the formation of active N and Cl species. The reaction pathway involves a surface bound NO⁻NO₃⁻ intermediate that is produced in an acid catalysis reaction between adsorbed nitrate and chlorine. Co-adsorption of gas phase NH₃ on nitrated alumina surface weaken the surface acidity result in a significant drop in NOCl production confirming the importance of acid catalysis to the reaction mechanism.

The results reported in this work emphasize significant dependence of the gas phase distribution on relative humidity. At higher relative humidities, high enough to
form multiple layers of water on particle surface, NOCl hydrolyses yielding HONO that dissociates to NO and NO₂. NO₂ is further hydrolyzed on acidic surfaces forming N₂O. The involvement of additional water associated with the particle surface was confirmed in the experiments with CaCO₃. The studies with CaCO₃ also underlined the importance of Lewis acidity of the reactive surface on gas phase product formation. Based on the mechanism discussed here, we predict that heterogeneous formation of NOCl from gas phase HNO₃ and HCl is similar to the overall reaction of homogeneous process, making it difficult to distinguish between the two. However, since for the predominant production observed here, the heterogeneous mechanism correlates with the mineral dust loading and allows it to be distinguished from NOCl produced from the gas phase reaction.

The chemistry involved with N and Cl activation on dust particle surface becomes even more complex in the presence of sunlight. During the daytime, NOCl photodissociates to NO and active Cl initiating a chain of secondary reactions with other gas phase species in the atmosphere. These active N and Cl species are also capable of further participating in nitrogen and chlorine cycles. Thus, heterogeneous conversion of HNO₃ and HCl to labile nitrogen and chlorine species in the atmosphere could potentially alter the peak concentration and geographical distribution of ozone.

6.6 Acknowledgements

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CHAPTER 7
NANOROD DISSOLUTION QUENCHED IN THE AGGREGATED STATE: EFFECT OF PARTICLE SIZE AND pH ON IRON DISSOLUTION IN LOW pH ENVIRONMENT

7.1 Abstract

Metal-containing nanorods are of great interest from a number of technological perspectives and they are also present in the natural environment. In the current study, we investigate whether nanoscale size-effects are observed for the dissolution of iron oxyhydroxide under different environmentally relevant conditions. The synthesized goethite particles are first characterized using a variety of techniques, including surface area measurements, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), X-Ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The solubility of two particle sizes of goethite, $\alpha$-FeOOH in nano and microscale, in aqueous suspensions at pH 1 and 2 is studied to mimic a deliquescent layer and the low pH environment of an aerosol due to the uptake of acidic gases in the atmosphere. Here we show that dissolution, both rate and extent is greater for rod-shaped $\alpha$-FeOOH particles on the nanoscale at pH 2 relative to microrods. However when nanorods aggregate, either at lower pH and/or high ionic strength, dissolution is either completely quenched or severely quenched, by orders of magnitude. To support this argument, additional experiments were carried out combining several techniques including dynamic light scattering (DLS), transmission electron microscopy (TEM) imaging of suspended
particles, and sedimentation rates determined by monitoring changes in the visible light transmitted through each suspension as a function of time. The data further reveal that nanorod suspensions are less stable compared to microrod suspensions resulting in nanorod aggregation under conditions where microrods stay fairly well dispersed. Although recent evidence suggests that particle size is a controlling factor in the solubility of iron oxides, a fundamental understanding of the influence of particle size is just beginning to emerge. The results presented here not only address some of the complexities of size-dependent dissolution of metal-containing nanorods in solution they also contribute to our understanding of the factors that can influence Fe-mobilization in the global environment.

7.2 Introduction

Iron (Fe) oxides and oxyhydroxides are two common constituents of the Earth’s crust. Ferrous and ferric ions, the soluble forms of iron, is one of the most well-known redox couples, playing vital roles in various environmental systems including, air, water and soil. In natural environments, these iron minerals are often display a wide distribution of particle sizes that ranges from ultra-fine aerosols to precipitates in soils and sediments. The occurrence of these particles in nanoscale has been previously established in numerous field and laboratory measurements. Iron oxide and oxyhydroxide nanoparticles are of interest because, they are produced in the environment and may display unique properties and higher reaction rates that differ from larger-sized iron particles. Among many different forms of iron, hematite (α-Fe₂O₃) was thought to be the only important iron oxide in atmospheric processing and found in atmospheric
models. However, evidence from recent field studies has suggested a predominance of nanoscale goethite (α-FeOOH) in some natural aquatic systems.\textsuperscript{305} Nanoparticles of iron oxides could yield from co-precipitation or surface complexation that inhibits further growth into larger crystallites.\textsuperscript{305} Besides, it is also possible that the surface energies of some oxides are low enough to allow nanoparticles to represent metastable phases, such as oxyhydroxides that can be found in both spherical and rod-like shapes.\textsuperscript{306}

Other than in natural systems, nanoparticles are of interest from a number of different perspectives. Synthetic metal and metal oxide nanoparticles and nanorods (nanoparticles with high aspect ratios) exhibit interesting optical\textsuperscript{307} and energy transfer\textsuperscript{308} properties and can be used as sensors\textsuperscript{309} and catalysts.\textsuperscript{310, 311} Due to their high prominence in natural environments as well as in industry,\textsuperscript{312} the size-dependent properties and reactivity of iron oxides have long been the focus of laboratory investigations.\textsuperscript{313} In general, nanoparticles are assumed to be more reactive than larger particles, and this higher reactivity is sometimes attributed to very high specific surface areas of the nanoparticles.\textsuperscript{314, 315} However, a number of size-dependent trends observed in recent dissolution rates of iron oxide nanoparticles could not be explained by differences in specific surface areas alone. Rather, these trends could be explained by having either a greater density of reactive sites per unit surface area on nanoparticle surfaces or an increase in the inherent reactivity of smaller-sized particles.\textsuperscript{106, 316, 317} These studies have focused on common iron oxides such as goethite, ferrihydrite and hematite, and have reported enhanced nanoparticle reactivity with respect to interfacial processes such as cation adsorption, electron transfer and, in particular, oxide dissolution.\textsuperscript{106, 317, 318} Although it is well known that variables such as solution pH, light, and organic ligands,
can influence the rate and extent of iron oxide dissolution, particle size is another important variable. Factors potentially responsible for dissolution rates of iron oxide nanoparticles were recently detailed in a review by Waychunas et al., and these include surface restructuring, surface curvature, and quantum confinement effects, all of which could emerge as a function of decreasing particle size.

Furthermore, nanoparticle aggregation has been increasingly discussed as an important consideration in iron oxide nanoparticle reactivity, yet, it is often difficult to decouple the role of aggregation in size-dependent studies of particle reactivity. In field and laboratory studies, particle aggregation makes it difficult to determine whether the observed reactivity of nanoparticle suspensions reflects the behavior of larger particle aggregates or the inherent particle size effect. In previous studies, nanoparticle aggregation has shown significant effects on particle transport, thermal conductivity, and toxicity and potentially may have a significant influence on dissolution.

In the current study, we investigate whether nanoscale size-effects are observed for the dissolution of iron oxyhydroxide under different environmentally relevant conditions. In our experimental approach, the synthesized goethite particles are first characterized using a variety of techniques, including surface area measurements, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), X-Ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The solubility of two particle sizes of goethite, $\alpha$-FeOOH, in nano and microscale, in aqueous suspensions at pH 1.0 and 2.0 is studied to mimic a deliquescent layer and the low pH environment of an aerosol due to the uptake of acidic gases in the atmosphere. Here, we clearly
demonstrate that in the absence of aggregation, the proton-promoted dissolution of goethite, \( \alpha \)-FeOOH, is higher for nanoparticles compared to particles in microscale on both a per mass and per surface area basis and that in the aggregated state dissolution is quenched. The size and nature of aggregates in suspensions under different experimental conditions are estimated using a combination of techniques including dynamic light scattering (DLS), transmission electron microscopy (TEM) imaging of suspended particles, and sedimentation rates determined by monitoring changes in the visible light transmitted through each suspension as a function of time. Comparison of the size-dependent reactivity trend identified from batch studies to the results of dry particle and wet suspension characterization provided an opportunity to explore the effect of pH and particle size on iron dissolution. Not only do the results of these studies address the complexities of size-dependent dissolution of nanorods, they also contribute to our understanding of Fe-mobilization in the environment.\(^{326}\)

7.3 Experimental Methods

The sources of all the materials and reagents used in this study are listed in Chapter 2.6.

7.3.1 Synthesis of Goethite Particles

Ferric nitrate nonahydrate (Fe(NO\(_3\))\(_3\)·9H\(_2\)O), Sigma Aldrich, 98%), sodium bicarbonate (NaHCO\(_3\), Sigma Aldrich, 99.5%), and potassium hydroxide (KOH, Sigma Aldrich; ACS reagent) were used for \( \alpha \)-FeOOH synthesis. Nanoparticles were synthesized according to the method of Anschutz and Penn\(^{106}\) as previously described in
an earlier publication.\textsuperscript{327} Briefly, Drop wise addition of NaHCO\textsubscript{3} to a solution of Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O results formation of ferrihydrite nanoparticles subsequently these are allowed to age at pH 12 for 24 h at 90 °C to yield the nanoscale goethite. Microrods were synthesized using the method of Schwertmann and Cornell reported in the literature.\textsuperscript{312} Experimental protocols are described in detail in Chapter 2.

7.3.2 Characterization of Goethite Particles

Goethite samples were characterized using a variety of techniques, including surface area measurements, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM), X-Ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). A detailed description of the experimental setups and techniques used in this chapter are discussed in Chapter 2.

Surface areas of goethite particles were also approximated from the average rod dimensions measured with TEM using the approach of Anschutz and Penn, who modeled goethite rods as rhomboidal prisms bonded by (011) faces. Note that widths correspond to the 011-type faces; absolute widths of goethite particles measured with TEM were corrected to account for the preferred orientation of the particles on the grid according to the procedure outlined by Anschutz and Penn. Geometric surface areas were calculated assuming a goethite density of 4.26 g·cm\textsuperscript{−3}.\textsuperscript{328} Nitrogen adsorption isotherms were collected using a Quantachrome Nova 4200e multipoint BET apparatus. Prior to surface area analysis, samples (~ 0.5 g) were heated at 80 °C and degassed overnight. BET Surface areas were compared with the calculated geometric surface areas.
7.3.3 Iron Dissolution Experiments

The experiments were carried out in a custom-made glass reactor using synthesized nano and micro-sized goethite particles. Reactor design and the details of the experimental procedure used for total Fe and Fe(II) measurements have been described in detail in Chapter 2.3. All the experiments were carried out in the dark, wrapped in aluminum foil. The temperature was kept constant through use of a water jacket integrated to the reaction vessel. The experiments were performed under deoxygenated conditions, suspensions were purged with N$_2$ for ~15 min prior to stirring, and during the experiment the headspace of the reaction vessel was purged to maintain positive N$_2$ pressure. Solutions consisted of 0.1 N (pH 1.0) and 0.01 N HNO$_3$ (pH 2.0). The sample loading in all the systems was maintained around 0.2 g L$^{-1}$ of $\alpha$-FeOOH. The stirring rate was kept constant for all experiments. At each sampling event, enough sample volume was taken to allow for analysis of total dissolved iron colorimetrically with 1, 10-phenanthroline. This colorimetric measurement has been described in detail previously.$^{329}$ All dissolution experiments were conducted in triplicate.

7.3.4 Dynamic Light Scattering and Sedimentation

All DLS measurements were made with a Zeta Sizer S series from Malvern instruments operated at a laser wavelength of 532 nm. Suspensions for DLS analysis were consisted of goethite concentration of 0.2 g L$^{-1}$. The experiments were carried out using HNO$_3$ acid solutions of pH 1, pH 2 and pH 2 at higher ionic strength (added 0.09 M NaNO$_3$). All suspensions were prepared 8 h prior to DLS analysis and were not sonicated prior to light scattering measurements. For a typical analysis, 1 mL of a well-mixed
suspension was delivered to a 1-cm pathlength cuvette, and the suspension was allowed to sit for approximately 30 s prior to analysis to allow any extremely large aggregates to settle out of solution.

Furthermore, time course light scattering measurements to follow particle sedimentation were obtained to provide additional insights into the nanorod suspensions. Goethite suspensions were added to a 1-cm pathlength cuvette and the change in light transmittance at $\lambda = 510$ nm was monitored as a function of time. Suspensions were prepared as discussed above for DLS measurements.

7.3.5 Transmission Electron Microscopy Analysis of Reacted Particles

To examine how proton-promoted dissolution reactions influenced the morphology of goethite particles, samples were taken from each of these experimental systems at the conclusion of experiments for TEM analysis. Approximately 200 $\mu$L of sample was removed from each reactor and diluted in 1 mL of deionized water. A drop of this suspension was then added to a Cu TEM grid. This procedure allowed us to differentiate between suspensions that contained fairly dispersed versus highly aggregated particles. Images of goethite particles were collected on a JEOL JEM-1230 transmission electron microscope operated at a 100 keV accelerating voltage. For particle size distributions, digital images were acquired using a Gatan UltraScan CCD camera with Gatan imaging software. The size of goethite particles was then determined by analyzing TEM images in the software package Image J. Particle size distributions were determined from the analysis of approximately 500 particles.
7.3.6 Zeta Potential Measurements

Zeta potential measurements were conducted using the Zeta sizer Nano ZS (Malvern, Southborough, MA). The goethite particles were suspended in aqueous nitric acid solutions at each pH studied at a concentration of 0.2 g·L⁻¹. The zeta potential determinations were based on electrophoretic mobility of the particles in the aqueous medium, which were performed.

7.4 Results and Discussion

During the rest of the chapter, a nomenclature for goethite particles introduced by Anschutz and Penn,¹⁰⁶ is used to refer the different particle sizes as nanorods, goethite particle in nanoscale, and microrods, for those in microscale.

7.4.1 Physical and Chemical Characterization of Goethite Particle

Physical properties determined from the characterization of powders of nanorods and microrods of synthetic goethite are summarized in Table 7.1, whereas SEM and TEM images showing the acicular, or rod-like, morphology of each primary particle size are shown in Figure 7.1(a) and (b) for microrods and nanorods, respectively. Figure 7.1(c), shows the dominant crystal planes of goethite particles. Based on these results, goethite rods are elongated along the crystallographic c-axis [001] and can be modeled as rhomboidal prisms bounded by (110) with ends capped by (021) surfaces. This model yields rods with a diamond-like cross section,¹⁰⁶ and does not account for minor faces such as the (100) and (010), which only develop to a limited extent, if at all, during synthesis.³³⁰⁻³³² Nanorods have dimensions of 75 (± 20) nm by 6 (± 2) nm
Figure 7.1 Representative SEM images of individual particles of (a) microrods and (b) nanorods, and (c) illustrates the dominant crystal faces of goethite particles. The goethite particles are rod like in shape and elongated along the crystallographic c-axis [001] and modeled as rhomboidal prisms bounded by (110) with ends capped by (021) surfaces. This model yields rods with a diamond-like cross section, and does not account for minor faces such as the (100) and (010), which only develop to a limited extent.

and N₂-adsorption measured surface areas of 119 (± 3) m²·g⁻¹. Microrods have larger dimensions of 1006 (± 55) nm by 25 (± 6) nm and lower surfaces areas of 39 (± 2) m²·g⁻¹.
Table 7.1. Nanorod and microrod dimensions along with calculated and measured surface areas.

<table>
<thead>
<tr>
<th></th>
<th>(^a\text{Length (TEM)}) (nm)</th>
<th>(^a\text{Width (TEM)}) (nm)</th>
<th>(^b\text{W(110)}) (nm)</th>
<th>(^c\text{Surface Area (Geometric)}) (m(^2)/g)</th>
<th>(^d\text{Surface Area (BET)}) (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanorods</td>
<td>75 ± 20</td>
<td>10 ± 3</td>
<td>6 ± 2</td>
<td>224</td>
<td>119 ± 3</td>
</tr>
<tr>
<td>Microrods</td>
<td>1006 ± 55</td>
<td>43 ± 7</td>
<td>25 ± 6</td>
<td>51</td>
<td>39 ± 2</td>
</tr>
</tbody>
</table>

a – Length and width of the particle observed on the TEM grid.

b – Corresponds to the width of the (110) face according to the convention of Anschutz and Penn.\(^{106}\)

c – Geometric surface area calculations assume a rod geometry of a rhomboidal prism as in Anschutz and Penn.\(^{106}\)

d – Surface areas determined from seven-point N\(_2\)-BET measurements.

(uncertainties represent one standard deviation). Note that widths correspond to the 110-type faces; absolute widths of nanorods and microrods measured with TEM were corrected to account for the particles’ preferred orientation on the grid according to the procedure outlined by Anschutz and Penn.\(^{106}\) The values are somewhat lower than estimates of geometric surface area for nanorods (~ 200 m\(^2\)/g) and microrods (~ 50 m\(^2\)/g) determined using the aforementioned particle dimensions and structural model of goethite.

More pronounced differences between nanorods and microrods were identified in the characterization with ATR-FTIR spectroscopy. A comparison of ATR-FTIR spectra collected for dry powders of nanorods and microrods are shown in Figure 7.2. An enlarged region of spectra between 3400 and 3800 cm\(^{-1}\), illustrating differences in surface
Figure 7.2  Comparison of ATR-FTIR spectra collected for dry powders of nanorods and microrods, (a). spectral regions between 700 to 4000 cm$^{-1}$ and (b). enlarged region of spectra between 3400 and 3800 cm$^{-1}$, in which features indicative of surface hydroxyl groups are shown to be more prominent for nanorods.
hydroxyl groups, is given in Figure 7.2(b). Most clearly observed are distinct absorption bands at 3490 and 3660 cm\(^{-1}\) in the spectra for nanorods, which are much stronger than the corresponding bands in the spectra of microrods. These bands arise from hydroxyl groups on the surface of the goethite nanorods.\(^{126}\) The distinct absorption bands at 3490 and 3660 cm\(^{-1}\) have been assigned to surface O-H groups of higher coordination (doubly and triply coordinated) and singly coordinated surface hydroxyl groups, respectively.\(^{333}\) In a recent study by Boily and Felmy,\(^{126}\) however, assigned both bands to singly coordinated O-H groups arising from the protonation of -O groups on the (110) and (021) faces of the goethite surface. These additional hydroxyl groups on the mineral surface are suspected to play an important, if not dominant, role in adsorption reactions.

Slight differences were observed for nanorods and microrods in the spectral region below 1000 cm\(^{-1}\). According to previous studies,\(^{129,334}\) the bands around \(\sim 890\) and \(\sim 790\) cm\(^{-1}\) can be assigned to the bending modes of the bulk hydroxyl groups in (\(\delta\)OH) and out (\(\gamma\)OH) of the (001) plane. For nanorods these were observed at 897 and 796 cm\(^{-1}\) whereas in microrods the bands are slightly shifted to lower wavenumbers, and observed at 892 and 794 cm\(^{-1}\). According to Cambier et al. and others,\(^{106,129,334}\) the location of the O-H bending bands can be used to diagnose the relative crystallinity of goethite particles. The peak-to-peak separation between the bending bands narrows with decreasing particle size and crystallinity. In contrast to these observations, the results from this study showed opposite trends with respect to particle size; the O-H bending modes for nanorods are located at higher frequencies and display greater peak-to-peak separation relative to microrods. Accordingly, these diagnostics seem to suggest that nanorods exhibit a higher degree of crystallinity than the microrods.\(^{102}\)
Figure 7.3 Powder X-ray diffraction for microrods (top) and nanorods (middle) of $\alpha$-FeOOH with XRD pattern for the reference goethite compound (bottom). The spectral bands corresponding to specific crystal planes are labeled within parenthesis.

Powder X-ray diffraction patterns for microrods and nanorods, shown in Figure 7.3, were consistent with that expected for goethite, with the pattern for nanorods
revealed considerable line broadening, as is typically observed with decreasing particle size. As discussed in Chapter 3.4, XPS spectra were similar for both particle sizes, with the survey spectra and spectra of the Fe 2p and O 1s regions essentially being independent of particle size.

7.4.2 Enhanced Iron Dissolution Beyond Surface Area Effects

In these studies, dissolution is monitored for nanorods and compared to larger microrods. The dissolution of rod-shaped $\alpha$-FeOOH particles (0.2 g·L$^{-1}$ suspensions) is monitored at pH 2.0 at T=298 K. Since these experiments are done in the absence of light, only Fe(III) is observed. Thus the total iron dissolution is equivalent to the Fe(III) concentration.

The data presented in Figure 7.4 show a comparison of the dissolution data of nanorods versus microrods at pH 2.0. These data are plotted on both per mass, Figure 7.4(a), and per BET-surface area, Figure 7.4(b), basis. The rate of iron dissolution and the production of dissolved ions are greatest initially ($t < 10$ hrs), followed by a slower rate of change over time. It can be clearly seen from these data that nanorod dissolution, as evidence by the amount of Fe(III) in solution, is larger than microrod dissolution on both a per mass and a per surface area basis. The production rate of dissolved Fe(III) in proton-promoted iron dissolution, which is equal to the rate of goethite dissolution, is described by a second-order rate law, in which the rate is proportional to the surface concentration of adsorption complex of inorganic anion, [-O-Fe-A], and the concentration of H$^+$, given by equation Eq: 7.1.$^{328, 329}$

$$\frac{d[\text{Fe(III)}]}{dt} = k[\text{Adsorption complex}][\text{H}^+]$$  \hspace{1cm} \text{Eq: 7.1}
Figure 7.4  Proton-promoted dissolution of rod-shaped $\alpha$-FeOOH particles is monitored by the formation of soluble Fe(III) at pH 2.0. These plots compare the dissolution of nanorods (circles) to microrods (squares); (a). per mass and (b). per surface area basis. The solutions were acidified with HNO$_3$.

Since the concentration of the adsorption complex is unknown, we have compared here the rate of dissolution between nanorods and microrods. Initial rates of total iron dissolution for nanorods and microrods at pH 2.0, in 298 K, determined from linear regression analysis, are given in Table 7.2. The rate of dissolved iron production in nanorods at pH 2.0 is 56 ($\pm$ 5) μmol·g$^{-1}$·h$^{-1}$. For microrods, this rate is only 6.1 ($\pm$ 0.4) μmol·g$^{-1}$·h$^{-1}$ indicating an enhancement factor of $\sim$3 after normalizing for differences in BET surface area and $\sim$1.5 after normalizing using geometric area.
Table 7.2 Initial rates of total iron dissolution at pH 2, determined from linear regression, for nanorods and microrods of $\alpha$-FeOOH. 

<table>
<thead>
<tr>
<th>Particle type</th>
<th>Mass normalized Dissolution rate ($\mu$M·g$^{-1}$·h$^{-1}$)</th>
<th>Surface area normalized Dissolution rate ($\mu$M·cm$^{-2}$·h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanorods</td>
<td>56 (± 5)</td>
<td>0.48 (± 0.02)</td>
</tr>
<tr>
<td>Microrods</td>
<td>6.1 (± 0.4)</td>
<td>0.17 (± 0.03)</td>
</tr>
</tbody>
</table>

a – Results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Dissolution data from the first 10 hrs were used in the rate determination.

b – Dissolution rates are normalized to the corresponding BET surface area measured.

7.4.3 Quenching of Iron Dissolution from Nanorods at Lower pH (pH 1)

At lower pH, it is expected that the rate of proton-promoted dissolution for both microrods and nanorods will increase. Figure 7.4 shows a comparison of dissolution data taken at lower pH, pH 1.0, for nanorods and microrods. These data are again plotted on both a per mass, Figure 7.5(a), and per surface area, Figure 7.5(b), basis. Initial rates of total iron dissolution for nanorods and microrods at pH 1, in 298 K, determined from linear regression analysis, are given in Table 7.3. In contrast to the plots shown in Figure 7.4 and dissolution rates data given in Table 7.2, these data clearly show that nanorod dissolution, as evidenced by the amount of Fe(III) in solution, is much less compared to microrod dissolution. These results are unexpected based on thermodynamic and kinetic considerations for proton-promoted,
Table 7.3 Initial rate of total iron dissolution at pH 1, determined from linear regression, for nanorods and microrods of $\alpha$-FeOOH. a

<table>
<thead>
<tr>
<th>Particle type</th>
<th>Mass normalized Dissolution rate ($\mu$M·g$^{-1}$·h$^{-1}$)</th>
<th>Surface area normalized$^b$ Dissolution rate ($\mu$M·cm$^{-2}$·h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nanorods</td>
<td>38 (± 3)</td>
<td>0.41 (± 0.02)</td>
</tr>
<tr>
<td>Microrods</td>
<td>502 (± 13)</td>
<td>13 (± 1)</td>
</tr>
</tbody>
</table>

a – Results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Dissolution data from the first 10 hrs were used in the rate determination.

b – Dissolution rates are normalized to the corresponding BET surface area measured.

Figure 7.5 Proton-promoted dissolution of rod-shaped $\alpha$-FeOOH particles is monitored by the formation of soluble Fe(III) at pH 1.0. These plots compare the dissolution of nanorods (circles) to microrods (squares); (a). per mass and (b). per surface area basis. The solutions were acidified with HNO$_3$. 
dissolution which involves,

\[
\begin{align*}
\equiv O - Fe - OH + A^- + OH^- & \rightleftharpoons \equiv O - Fe - A + H^+ \\
\rightarrow Fe(OH)A^+ & \quad \text{Eq: 7.2,}
\end{align*}
\]

where \( A^- \) is the inorganic anion. In comparison to pH 2.0, the dissolution rate is for nanorods is between 10-100 times less than microrods when normalized to BET-surface area. Furthermore, when both surface area and a nanoscale “enhancement factor” are taken into account, the decrease in dissolution rate for nanorods is even greater. These results in general show that the nanorods have a greater propensity to undergo dissolution compared to microrods at pH 2.0 but this is not the case at pH 1.0.

Earlier studies of Cornell et al.\textsuperscript{328, 329} showed that surface-area-normalized rates for the proton-promoted dissolution of goethite increased with decreasing particle size, similar to what is observed here at pH 2.0. Furthermore, they proposed that rates of dissolution were greatest on smaller particles in part because they possessed the largest fraction of highly reactive faces. In particular, it was proposed that (021) faces were more reactive as a result of coordination and concentration of surface O-H groups. Consistent with this hypothesis, Barón and Torrent calculated that the highest density of surface O-H groups occurs on the (021) surface plane (8.2 groups/nm\(^2\)) whereas lower density (\( \sim 3 \) groups/nm\(^2\)) was determined for the (110) planes.\textsuperscript{335} As discussed in the previous section, in the IR spectrum, relatively higher intense bands at 3490 and 3660 cm\(^{-1}\) for nanorods arise from these additional singly coordinated O-H groups from the two different surface planes.

Although these earlier studies can begin to explain the data at pH 2.0, they do not explain the results obtained at pH 1.0. To better understand these differences, TEM
Figure 7.6 TEM images of α-FeOOH (microrods and nanorods) suspensions dried onto a TEM grid. These images show that microrods are fairly dispersed at both pH 1.0 and 2.0 whereas nanorods are similar to microrods at pH 2.0 but highly aggregated at pH 1.0. A higher magnification at pH 1.0 (right panel) shows the aggregate is made up of tightly bundled nanorods and according to the graphical representation of the nanorods in the aggregated state, nanorods are bound to each other via (110) plane diminishing access to the reactive (021) plane.
images of nanorod and microrod suspensions at pH 2.0 and pH 1.0 deposited and dried onto TEM grids were examined. These data are shown in Figure 7.6. The images provide in Figure 7.6(a)-(d) evidence for fairly well-dispersed nanorods at pH 2.0 and microrods at both pH 1.0 and pH 2.0. However, in contrast, the nanorods imaged from suspension at pH 1.0 show large aggregates. As seen in Figure 7.6(e), a higher magnification of the aggregate at pH 1.0, the aggregate is made up of tightly bundled nanorods. The graphical representation of the nanorods in the aggregated state, shown in Figure 7.6(f), illustrates that these nanorods are bound to each other via (110) plane diminishing access to the reactive (021) plane. These data suggest that nanorod aggregation is quenching the dissolution expected for the smaller-sized rods at the lower pH. In addition, these data show that there are large differences in the stability of α-FeOOH nanorods versus microrod suspensions that clearly impact dissolution behavior.

7.4.4 Effect of Ionic Strength on Iron Dissolution

Since aggregation is a function of ionic strength, the dissolution of nanorods at pH 2.0 but at higher ionic strength using NaNO₃, equivalent to the ionic strength of the pH 1.0 solution was conducted to further test the hypothesis that aggregation caused a decrease in dissolution. These dissolution data at pH 2.0 and higher ionic strength for microrods and nanorods are shown in Figure 7.7(a) and (b), plotted on both a per mass and per surface area basis, respectively. As seen in Figure 7.7, there is no detectable iron dissolution over a 48 hr period at pH 2.0 with the higher ionic strength. Thus at pH 2.0, nanorod dissolution at higher ionic strength is shown to be
Figure 7.7  Proton-promoted dissolution of rod-shaped $\alpha$-FeOOH particles is monitored by the formation of soluble Fe(III) at pH 2.0 with added 0.09 M NaNO$_3$ to increase the ionic strength of the solution. These plots compare the dissolution of nanorods (squares) to microrods (circles); (a). per mass and (b). per surface area basis. The solutions were acidified with HNO$_3$.

completely quenched. Evidence to corroborate the conclusion that aggregation is occurring at pH 2.0 with added NaNO$_3$ and that impacts proton-promoted dissolution of $\alpha$-FeOOH nanorods is provided by dynamic light scattering (DLS) measurements. DLS shows larger sized particles in solution and a multimode distribution of sizes at pH 2.0 upon the addition of NaNO$_3$ to increase the ionic strength whereas there is no evidence for aggregate formation at pH 2.0 without the added NaNO$_3$. DLS data are further supported by higher rates of sedimentation for nanorods at pH 2 at the different ionic strengths used. On the other hand, the microrods remain stable under all conditions. The DLS and sedimentation measurements are shown in Figure 7.8(a) and (b),
Figure 7.8 Dynamic light scattering and sedimentation measurements at pH 2.0, with and without 0.09 M NaNO₃. (a). Intensity-weighted size distributions for nanorod suspensions determined from DLS and (b). Sedimentation plots for nanorods shown as a function of time at pH 2.0 with and without 0.09 M NaNO₃.

It can be asked, why do nanorods aggregate to a greater extent at pH 1.0 compared to pH 2.0? and why are nanorod suspensions less stable compared to microrods? Derjaguin, Landau, Verwey and Overbeek (DLVO) theory assumes the stability of a colloidal suspension is the sum of attractive van der Waals forces and repulsive electrostatic forces between particles as they undergo Brownian motion.

Therefore, lower surface charge density yields dominant attractive forces with sufficient energy to overcome repulsion leading to aggregation. Zeta potential measurements provide a good estimate of the particle surface charge. Zeta potentials values measured for nanorods and microrods of α-FeOOH, under different experimental
Table 7.4  Zeta potential measurements for nanorods and microrods of α-FeOOH under different pH and ionic strength.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Suspension</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nanorods</td>
</tr>
<tr>
<td>pH 1</td>
<td>34.59 ± 3.74</td>
</tr>
<tr>
<td>pH 2</td>
<td>74.66 ± 4.66</td>
</tr>
<tr>
<td>pH 2 (HIS)\textsuperscript{b}</td>
<td>34.23 ± 1.74</td>
</tr>
</tbody>
</table>

\textsuperscript{a} – Results presented here are the average value of triplicate measurements and the reported error represents one standard deviation.

\textsuperscript{b} – Ionic strength is equivalent to the solution at pH 1 (0.01).

conditions, are given in Table 7.4. Based on these results at pH 2.0 the nanorods are stable with a zeta potential of 75 ± 5 mV. The stability of the nanorods decreases at pH 1.0 and at pH 2.0 solutions prepared at higher ionic strength as in these cases the zeta potential decreases to 35 ± 4 mV\textsuperscript{4} and 34 ± 2 mV, respectively. For the microrods, the zeta potentials are greater indicating increased stability under all conditions compared to nanorods. In addition, molecular dynamic simulations suggest that the charging behavior of (021) faces is influenced by goethite particle size,\textsuperscript{338} behavior that would potentially affect both the interfacial reactivity of nanorods compared to microrods and the stability of nanorod suspensions, i.e. the ability of nanorods to aggregate. These simulations can begin to explain the data presented herein. There is increasing evidence that aggregation of nanorods as well as nanoparticles is important in the microscopic and macroscopic behavior of these materials and that aggregation plays a role in cellular interactions.
Furthermore, once in the aggregated state, the nanorod surface free energy and reactivity can no longer be expected to be the same as the dispersed nanorods.

Interestingly, a very recent study of the environmentally and industrially important mineral galena, PbS, also showed the impact of aggregation on nanoparticle dissolution. In particular, in the study by Liu et al.\textsuperscript{339} it was determined that the dissolution rate of PbS varied as a function of particle size and by aggregation. For PbS, dissolution rates normalized for surface area were found to be a factor of ca. five times higher for 14 nm nanocrystals compared to 3.1 μm microcrystals when dispersed. This size-difference in dissolution rates was attributed to differences in nanotopography and the crystallographic faces present on the different sized particles. Furthermore, it was shown that when PbS nanocrystals aggregated the rate of dissolution was nearly an order of magnitude slower compared to well-dispersed nanocrystals. Liu et al. proposed that dissolution rates decreased in the aggregated state due to transport inhibition in the highly confined spaces between densely packed, aggregated nanocrystals, where self-diffusion coefficients of water and ions decrease dramatically. These effects may also be important for the quenched dissociation of the aggregated nanorods.

7.5 Conclusions and Environmental Implications

An important factor that has not been clearly delineated in aqueous phase dissolution studies of nanorods is nanorod aggregation. Here we clearly show that aggregation impacts dissolution. Proton-promoted dissolution of nanorods is nearly or completely quenched in the aggregated state. Given the role of iron mobilization in the biogeochemical cycling of iron in the global environment and the proposal that
atmospheric reactions can lead to low pH environments in Fe-containing atmospheric aerosols and the high ionic strength found in seawater, it is important to understand factors such as pH and aggregation that can influence iron mobilization. Additionally, there is growing interest in the potential environmental and health impacts of nanomaterials. The dissolution of metal and metal oxide nanomaterials has been linked to potential harmful and deleterious effects. Thus, better understanding the conditions in which dissolution can occur will be important in understanding the environmental, health and safety of metal-containing nanomaterials. The results reported herein on α-FeOOH and the recent results on PbS reported by Liu et al. suggest that these may be important general phenomena for nanomaterial dissolution, i.e. 

(i) enhanced dissolution for well dispersed nanomaterials compared to larger –micron sized materials; 
(ii) quenched dissolution by an order of magnitude or more for nanomaterials in the aggregated state relative to the well-dispersed state and; 
(iii) aggregation occurs more readily for nanomaterials compared to larger-sized, micrometer-sized materials.

7.6 Acknowledgements

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8.1 Abstract

Primary production of phytoplankton and related uptake of atmospheric CO\textsubscript{2} and algal blooms in fresh and sea waters are limited by the amount bioavailable iron in the associated water body. Among many different sources of Fe to the ocean, windblown dust is the largest source to the open ocean. A number of recent studies have shown that iron dissolution in Fe-containing dust aerosol can be linked to source material (mineral or anthropogenic), mineralogy and iron speciation. All of these factors need to be incorporated into atmospheric chemistry models if these models are to accurately predict the impact of Fe-containing dusts into open ocean waters. In this report, we combine dissolution measurements along with spectroscopy and microscopy to focus on nanoscale size-effects in the dissolution of Fe-containing minerals in low pH environments and the importance of acid type, including HNO\textsubscript{3}, H\textsubscript{2}SO\textsubscript{4} and HCl, on dissolution. All of these acids are present in the atmosphere and dust particles have been shown to be associated with nitrate, sulfate and/or chloride. These measurements are done under light and dark conditions so as to simulate and distinguish between daytime and nighttime atmospheric chemical processing. Both size (nano- versus micron-sized particles) and anion (nitrate, sulfate and chloride) are found to play significant roles in the dissolution of α-FeOOH under both light and dark conditions. Furthermore, effect of two other important
oxyanions, carbonate ($CO_3^{2-}$) and phosphate ($PO_4^{3-}$), on iron dissolution was investigated. The data revealed complete opposite effects, result in a 3 to 5 fold enhancement for microrods whereas for nanorods quenching the dissolution reaction by at least one order of magnitude, in the presence of above oxyanions. The current study highlights these important, yet unconsidered, factors in the atmospheric processing of iron-containing mineral dust aerosol.

8.2 Introduction

Iron is an essential element for all biological organisms including those in marine environments. It has been suggested that 30% of the oceans are comprised with high nutrient low chlorophyll regions where phytoplankton primary productivity is limited by the amount of bioavailable iron. Iron is the fourth most abundant element on the Earth’s crust and is mostly found in its thermodynamic stable oxidation state, Fe(III). Fe(III) is relatively insoluble in oxic pH 8 seawater, thus limits the inorganic concentration to 0.1 nM and any inorganic iron above this concentration will form an iron oxide solid phase. Despite this limitation, ocean total iron concentrations range from 0.1 – 2 nM. Therefore, iron addition to surface waters from dissolved iron in Fe-containing dust deposition are thought to elevate the total amount of dissolved, and bioavailable, iron.

Mineral dust aerosol, mainly desert dust and dust from volcanic eruptions, is a source of iron and has been previously thought to account for ~ 95% of the globally averaged atmospheric iron budget. Approximately 450 Tg of mineral dust is annually deposited into ocean waters. Among many different iron-containing solid
phases found in mineral dust, hematite ($\alpha$-Fe$_2$O$_3$) has been thought to be the most important form for soluble iron and biological utilization$^{348}$ and it is currently the only form of iron minerals incorporated into atmospheric chemistry models. However, a number of very recent studies indicate that this approach is far too simplistic and does not accurately reflect both the complexities of atmospheric sources of iron and/or the most important iron-mineral phases involved in dissolution. For example, Journet et al. showed that Fe-containing clays accounted for more than 90% of soluble iron.$^{349}$ Cwiertny et al. proposed that iron in the form of Fe$^{2+}$ in clay minerals is a highly labile source of iron.$^{350}$ Other studies highlight the contribution from anthropogenic sources of soluble iron, mainly from combustion sources.$^{343, 351, 352}$ These combustion sources are concentrated in both industrialized and biomass burning regions and can represent up to 5% - 30% of the total iron deposited into ocean regions.$^{343}$

Since heterogeneous chemistry and atmospheric processing can impact the amount of soluble iron in Fe-containing dusts, the atmospheric lifetime of iron dust particles is another important factor. Atmospheric lifetimes of dust particles can vary depending on particle size from days for particles greater than 2 $\mu$m to weeks for the smaller particles$^{353}$ and, as a result, the size distribution of the aerosol changes as it is transported through the atmosphere.$^{354}$ In addition, it has been recently suggested that cloud processing can cause the formation of nanosize Fe particles.$^{355}$ Thus size-effects and small particles below 100 nm can play an important role in the atmospheric chemistry of iron-containing dust particles. A cartoon representation of atmospheric processing of iron oxide and oxyhydroxide minerals at low pH is shown in Figure 8.1. This figure highlights several important aspects of iron dissolution, i.e. uptake of acidic
Figure 8.1  A cartoon representation of atmospheric processing of iron oxide and oxyhydroxide minerals at low pH. During the atmospheric transport, these iron containing minerals, emitted from the ground, act as scavenges of acidic gases and water vapor, forming an acidic deliquescence layer over the particle surface. Protons, H^+, dissociated from the acidic gases can potentially react on the particle surface and release Fe(III) to the aqueous medium. During the daytime, this Fe(III) is photoreduced to Fe(II), making it more soluble and, thus, bioavailable. Once these particles are deposited into the ocean the dissolve iron become nutrients to the ocean life.

In this chapter, we investigate the dissolution of Fe-containing minerals under simulated atmospheric conditions. Given that iron oxyhydroxides are a major fraction of Fe-containing solid phases in mineral dust, goethite, \( \alpha \)-FeOOH, can be used as a model to
begin to understand various aspects of size effects in iron dissolution. The current study investigates the size-dependent solubility of $\alpha$-FeOOH in aqueous suspensions at pH 2 to mimic a deliquescent layer and the low pH environment of an aerosol due to the uptake of acidic gases in the atmosphere. The effect of acid type (HCl, HNO$_3$ and H$_2$SO$_4$) and associated inorganic anion (Cl$^-$, NO$_3^-$ and SO$_4^{2-}$) on iron dissolution are investigated as dust particles have been found to be associated with sulfate, nitrate and chloride in the atmosphere. Experiments are done under both light and dark so as to simulate and differentiate between daytime and nighttime atmospheric processing. Dissolution measurements of well-characterized samples are combined with spectroscopy and microscopy to reveal some important, yet unconsidered, processes that can occur in the atmosphere for iron-containing dusts and, as such, some of the complexities of iron-mobilization in the global environment.

8.3 Experimental Methods

A detailed description of the experimental setups and techniques used in this chapter are discussed in Chapter 2. The important and specific experimental protocols are highlighted below.

8.3.1 Source Materials

Ferric nitrate nonahydrate (Fe(NO$_3$)$_3$·9H$_2$O; Sigma Aldrich; 98%), sodium bicarbonate (NaHCO$_3$, Sigma Aldrich, 99.5%), and potassium hydroxide (KOH, Sigma Aldrich; ACS reagent) were used for $\alpha$-FeOOH synthesis. In iron dissolution experiments, solutions of 0.1 N (pH 1) and 0.01 N (pH 2) were prepared from
concentrated HNO$_3$ (70.6% HNO$_3$, Mallinckrodt), H$_2$SO$_4$ (95.9% H$_2$SO$_4$, Mallinckrodt) and HCl (37.6% HCl, Fisher). Measurements of dissolved Fe(II) and total dissolved iron were performed with 1,10-phenanthroline ($\geq$ 99%, Sigma-Aldrich), hydroxylamine hydrochloride (98%, Sigma Aldrich), a buffer from ammonium acetate (98.5%, Fisher) and glacial acetic acid (99.7%, EMD).

8.3.2 Synthesis of Goethite

$\alpha$-FeOOH nanoparticles were synthesized according to the method of Anschutz and Penn$^{106}$ as previously described.$^{350}$ Dropwise addition of NaHCO$_3$ to a solution of Fe(NO$_3$)$_2$·9H$_2$O results formation of ferrihydrite nanoparticles subsequently these are allowed to age at pH 12 for 24 h at 90 °C to yield the nanoscale goethite. Microrods were synthesized using the method of Schwertmann and Cornell reported in the literature.$^{312}$

8.3.3 Goethite Characterization

Synthesized goethite particles were characterized using powder X-ray diffraction (XRD) performed on a Bruker D-5000 diffractometer with a Cu K$_\alpha$ source. Surface areas were determined from a seven-point N$_2$ adsorption isotherm using a Quantachrome Nova 1200 surface area analyzer. Samples for surface area analysis were evacuated overnight (~12 h) at a temperature of 80 °C. Particle dimensions were obtained from single particle analysis with TEM. Suspensions (~0.2 g/L) of goethite particles were prepared in deionized water, and a single drop was applied to a TEM grid. Particle size was determined from the analysis of approximately 500 particles. In addition, to examine how dissolution reactions change the morphology of goethite particles, samples were taken.
from each of these experimental systems at the conclusion of experiments for TEM analysis.

8.3.4 Dissolution Experiments

The experiments were carried out in a custom made glass reactor using synthesized nano and microscale particles of \( \alpha \)-FeOOH. Reactor design has been described previously in Chapter 2.3. These experiments were conducted in the absence and presence of a solar simulator (150 W xenon lamp, Oriel Corp). The temperature was kept constant through use of a water jacket. The experiments were performed under deoxygenated conditions, suspensions were purged with \( N_2 \) for \( \sim 15 \) min prior to irradiation, and during irradiation the headspace of the reaction vessel was purged to maintain positive \( N_2 \) pressure. The sample loading was maintained 0.2 g/L of \( \alpha \)-FeOOH in solutions of HNO\(_3\), H\(_2\)SO\(_4\) and HCl at pH 2. Under these conditions, goethite suspensions were stable and the particles were fairly well dispersed. All dark and light experiments were conducted in triplicate with average measurements reported. Reported errors represent one standard deviation.

8.3.5 Analytical Methods

Ferrous iron was measured colorimetrically with 1,10-phenanthroline, which forms a complex with Fe(II) that absorbs light at 510 nm.\(^{356}\) For Fe(II) analysis, 200 \( \mu \)L of a 5 mM 1,10-phenanthroline solution and 200 \( \mu \)L of an ammonium acetate buffer were added to 1 mL of sample. Total dissolved iron was determined via a similar protocol, except that 40 \( \mu \)L of 1.5 M hydroxylamine hydrochloride, which reduces Fe(III) to Fe(II),
was added to the sample. Fe(III) concentrations were then determined by difference (Total Fe - and Fe(II)).

8.3.6 ATR-FTIR Spectroscopy

A detailed description of the experimental setup is given in Chapter 2.1.4. ATR-FTIR spectroscopy was done using a modified horizontal AMTIR ATR cell (Pike Technologies, Inc.) and a Thermo Nicolet FTIR spectrometer equipped with a mercury cadmium telluride (MCTA) detector. The crystal was coated with a hydrosol of goethite rods (approximately 1.5 mL of a 2 g/L goethite suspension) and allowed to air-dry for 24 h. This process left behind a thin layer of goethite that uniformly coats the crystal. Solution-phase experiments using pH 2 acid solution was also conducted on the bare crystal.

8.4 Results and Discussion

During the rest of the chapter, a nomenclature for goethite particles introduced by Anschutz and Penn,\textsuperscript{106} is used to refer the different particle sizes as nanorods, goethite particle in nanoscale, and microrods, for those in microscale.

8.4.1 Dissolution of Iron Oxyhydroxide at pH 2: Role of Particle Size and Simulated Sun Light

In natural systems, nanoscale-sized iron oxide and iron oxyhydroxides particles are of great interest because they are produced in the environment and may exhibit dissolution properties that differ from larger-sized particles.\textsuperscript{102} Here the dissolution of
α-FeOOH was investigated in terms of total iron dissolution and speciation (i.e. Fe(II) (aq) and Fe(III) (aq)) in low pH environments at pH 2. Goethite forms rod-shaped particles and, to investigate size effects, different sized rods were synthesized. Synthesized nanorods were 75 (± 20) nm by 6 (± 2) nm with N₂-adsorption measured surface areas of 119 (± 3) m²·g⁻¹ whereas larger microrods were 1006 (± 55) nm by 25 (± 6) nm and with a lower surface area of 39 (± 2) m²·g⁻¹. Dissolution of these different sized rods was investigated in low pH environments to examine size-dependent behavior in under simulated nighttime and daytime conditions. For nighttime conditions, experiments were done in the dark whereas simulation of daytime mineral dust chemistry was accomplished through the use of a solar simulator to investigate the effect of light on iron dissolution of nanorods as compared to larger microrods.

The data presented in Figure 8.2 show a comparison of total iron dissolution of nanorods versus microrods at pH 2 under dark and light conditions. These data have been normalized to both the total mass and surface area of the initial α-FeOOH in solution. The rate of iron dissolution and the production of dissolved ions are greatest initially (t < 10 hrs), followed by a slower rate of change over time. In both mass normalized and surface area normalized data, and under both dark and light conditions, it can be clearly seen that nanorods dissolve faster and to a greater extent relative to microrods. Initial rates of total iron dissolution under both dark and light conditions for nanorods and microrods at pH 2.0 in 298 K, determined from linear regression analysis, are given in Table 8.1. Under dark conditions, the initial rate of total iron dissolution for nanorods is 55.4 (± 4) μmol·g⁻¹·h⁻¹ whereas for microrods, this is 6.1 (± 0.4) μmol·g⁻¹·h⁻¹. No Fe(II) is detected in these dark experiments so the total iron is in the form of Fe(III).
Figure 8.2  Proton-promoted dissolution of rod-shaped \( \alpha \)-FeOOH particles is monitored by the formation of total soluble Fe in solution at pH 2. The solutions were acidified with HNO\(_3\). These plots compare the dissolution of nanorods to microrods under dark and light conditions on a per mass (a and c) and per surface area (b and d) basis.
After normalizing to surface area differences (Figure 8.1(b)), there is still an enhancement in the dissolution of nanorods compared to microrods by nearly a factor of three. Figure 8.2(c) and (d) compare results for total iron dissolution of nanorods versus microrods at pH 2 in irradiated suspensions on a per mass basis and per surface area basis, respectively. The initial rate of total iron dissolution under light conditions for nanorods is $119 \pm 4$ μmol·g⁻¹·h⁻¹ whereas for microrods, this is $15.4 \pm 2.7$ μmol·g⁻¹·h⁻¹.

In addition to the two-fold enhancement for the total iron production, a change in the soluble iron speciation was also observed in the irradiated system with the formation of Fe(II). The production of dissolved Fe(II) is shown in Figure 8.3(a) and (b) on a per mass and per surface area basis, respectively, under the same conditions. As seen in Figure 8.3(a) and (b), the Fe(II) production is greater in irradiated nanorod suspensions compared to that of microrods. Additionally, there are differences in the ratio of Fe(II) to

<table>
<thead>
<tr>
<th>Particle type</th>
<th>Mass normalized dissolution rate ($\mu$M·g⁻¹·h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In the absence of light</td>
</tr>
<tr>
<td>Nanorods</td>
<td>56 (± 5)</td>
</tr>
<tr>
<td>Microrods</td>
<td>6.1 (± 0.4)</td>
</tr>
</tbody>
</table>

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Table 8.1  Initial rate of total iron dissolution at pH 2, determined from linear regression, in the presence and absence of light for nanorods and microrods.¹

¹ – Results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Dissolution data from the first 10 hrs were used in the rate determination.
total Fe dissolution between nanorods and microrods. The initial (t < 10 hrs) Fe(II) fraction with respect to total dissolved Fe is ~ 0.50 for nanorods, but for microrods the Fe(II) fraction is only ~ 0.25. Over time, the rate changes and levels off with an Fe(II) fraction of ~ 0.7 for nanorods and ~ 0.5 for microrods.

8.4.2 Mechanism for Enhanced Dissolution of Nanoscale α-FeOOH at pH 2

In earlier studies, it has been shown that surface area normalized rates for low pH, proton-promoted dissolution of α-FeOOH increased with decreasing particle size $^{328,329}$ and that higher rates of iron dissolution in smaller particles partially come from their
largest fraction of reactive surface planes. According to Cornell et al., the non-reductive iron dissolution involves,

\[
\begin{align*}
\equiv \text{O} &- \text{Fe} - \text{OH} \xrightarrow{\text{H}^+ + \text{A}^-} \equiv \text{O} - \text{Fe} - \text{A} &\rightarrow &\text{Fe(OH)A}^+ \\
\text{Eq: 8.1},
\end{align*}
\]

where A\(^-\) is the inorganic anion. In this proposed mechanism, acid anion primarily reacts with the surface O-H groups followed by a proton attack yielding surface protonation. This polarizes and weakens the Fe-O bond followed by bond dissociation enabling the detachment of the Fe cation that enters into the solution\(^{349, 357}\). In goethite rod shaped particles, the end of the rods that expose (021) surface planes are more reactive as a result of coordination sites with higher concentration of surface O-H groups. Thus the presence of more reactive sites in crystal faces, i.e. (021), with highly concentrated surface O-H groups results in enhanced reactivity. Nanorods have a greater number of exposed (021) surface planes on a per mass and per surface area basis.

Similarly, in light experiments, the observed trends in the production of Fe(II) lend insights into the enhancement in the photochemical dissolution of nanoscale \(\alpha\)-FeOOH. For these semiconductor iron oxyhydroxide particles, photoexcitation leads to the formation of electron-hole \((e^-/h^+)\) pairs. In the absence of surface complexing organic ligands, the photoredox reaction proceeds through surface hydroxyl groups donating an electron to a photoexcited Fe(III) surface atom resulting in surface bound Fe(II) and subsequent detachment of Fe(II) into solution\(^{358}\). Therefore, in irradiated systems, the enhanced Fe(II) production in nanorods can also be a result of the (021) surface planes
Figure 8.4   TEM images of nanorods (a). prior to reaction with HNO₃ and (b). after the reaction with 0.01 M HNO₃ (pH 2) in the light. The arrows highlight the changes that occur on the ends, (021) faces, of the nanorods as a result of iron dissolution. Analysis of many particles (N = 500) was used to construct distributions for the length and width of nanorods before and after reaction with 0.01 M HNO₃ (pH 2) in the light. Only the length distributions showed any change. These are plotted in (c). for unreacted nanorods (blue) and red reacted nanorods (red).
with higher density of surface O-H groups. Recent field and laboratory studies have shown that, in marine surface waters and in acidic surface waters, light-induced reduction of Fe(III) to Fe(II) is a key process and serves to increase the solubility of marine aerosol Fe.\textsuperscript{359,360} As such, any processes that enhance production of soluble Fe(II) are important and increase total iron dissolution. Furthermore, at longer time scales, the Fe(II) production in nanorods is considerably greater than that of observed for microrods. For example, after 40 hrs of light exposure, the concentration of Fe(II) for nanorods is nearly seven times larger than that of microrods. This difference is again reflected in the total iron dissolution for nanorods compared to microrods. Thus, the results of these studies clearly address size-dependent reactivity under both dark and light conditions, and dissolution of iron containing minerals on the nanoscale. These results point specifically to the presence of a greater abundance of specific reactive surface planes that can lead to enhancements in reactivity not only on a per mass basis but on a per surface area basis showing that these nanoscale-sized particles are inherently more reactive under both light and dark conditions.

Interestingly, changes in nanorod morphology were observed upon exposure to low pH environment. The transmission electron microscope (TEM) images of nanorods before and after the reaction with 0.01 N HNO\textsubscript{3} (pH 2.0) in light are shown in Figure 8.4(a) and (b) respectively. Nanorods prior to exposure show sharp, well-defined ends characteristic of their (021) surface planes. In contrast, after completion of 46 hrs in the acidic environment, particles show changes in morphology; over time, nanorods became cigar-shaped, developing narrow, rounded ends. Furthermore, analysis of the particle size distribution shows an anisotropic change in the distribution. In particular, a frequency
Table 8.2 Analysis of particle width and length of nanorods during the dissolution process at pH 2 in the presence of light.\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>Particle length (nm)</th>
<th>Particle width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t = 0 )</td>
<td>75 (± 6)</td>
<td>6 (± 2)</td>
</tr>
<tr>
<td>( t = 46 \text{ hrs} )</td>
<td>69 (± 4)</td>
<td>6 (± 1)</td>
</tr>
<tr>
<td>( %\Delta )</td>
<td>~ 9 %</td>
<td>-</td>
</tr>
</tbody>
</table>

\( \text{a} \) – Results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Distributions were determined by analyzing ~500 particles before and after reaction with 0.01 M HNO\textsubscript{3}.

Analysis of the length and width of many particles (N ~ 500) before and at the end of 46 hr of irradiation in acidic solution from additional TEM images besides those presented in Figure 8.5 show that the length of nanorods has significantly decreased (approximately 9% on average), whereas the distribution change observed in the width of the nanorods remains the same. The change in the length distribution for nanorods is shown in Figure 8.5(c) and the length and width of nanorods, before and after the reaction, are given in Table 8.2. Given, higher fraction of particles with smaller lengths, relative to nanorods before the reaction, clearly indicates that the proton-promoted dissolution takes place on exposed surface planes at the ends of the nanorods. The observed morphological changes support the argument that rates of dissolution are greatest on the (021) faces of \( \alpha \)-FeOOH. Thus, the anisotropic dissolution of \( \alpha \)-FeOOH is observed.
8.4.3 Role of Acid Type on Iron Dissolution

Another potentially important factor that has not been previously considered in the dissolution of pure iron oxide phases in the atmosphere is the impact of acid type. Under acidic conditions, the deliquescence layer on particle surfaces often contain high concentration of anions, i.e. sulfate, nitrate and chloride. Therefore, not all dissolved Fe(III) is expected to be present as free ions but in fact complexed and coordinated to anions in the deliquescent layer. Some of these complexes, as well as the inorganic anions themselves, can be photoactive which may play a role in the overall dissolution process for Fe mobilization in sunlight. Furthermore, these anions can coordinate to the surface in different adsorption modes and with different bond strengths to the surface, this too will impact iron dissolution. Here the role of different atmospherically relevant acids on the generation of soluble iron and iron speciation in nanorod suspensions were investigated with three acids, HNO$_3$, H$_2$SO$_4$ and HCl, at pH 2 under simulated nighttime and daytime atmospheric processing.

Data for total iron dissolution from the three acids studied in dark condition are shown in Figure 8.5(a). It can be clearly seen that NO$_3^-$ yields the highest total dissolved Fe whereas the lowest is in the presence of Cl$^-$ and in the case of SO$_4^{2-}$, the total Fe dissolution is just slightly less than that of NO$_3^-$. In the dark, there is no detectable Fe(II) production. Comparison of the total iron dissolution for the three different acids in the presence of light is shown in Figure 8.5(b). As shown for HNO$_3$ in Figure 8.2, iron dissolution is enhanced in the presence of light for both H$_2$SO$_4$ and HCl. According to Figure 8.5(b), this behavior is most pronounced for HCl, for which had initial rates of total dissolved Fe that are nearly four times greater in the presence of light compared to
Figure 8.5 Dissolution of α-FeOOH nanorod particles is monitored by the formation of total soluble Fe and Fe(II) in solution at pH 2.0. These plots compare the dissolution of nanorods in three different acids, HNO₃, H₂SO₄ and HCl under dark and light conditions. (a). Total iron (Fe(III) only) in the dark. (b). Total iron dissolution (Fe(III) and Fe(II)) in light. (c). Fe(II) production in the presence of light. (d). Fraction of total dissolved Fe present as Fe(II) as a function of time.
suspensions acidified with HNO₃ and H₂SO₄ where light induced a two-fold enhancement. Figure 8.5(c), compares the photochemical production of dissolved Fe(II) with NO₃⁻, SO₄²⁻ and Cl⁻. As seen in Figure 8.5(c), dissolved Fe(II) concentrations with HNO₃ and HCl are found to be similar and significantly higher than that of H₂SO₄. The fraction of total dissolved Fe present as Fe(II) as a function of time is shown in Figure 8.5(d). For suspensions that were acidified with HCl, the Fe(II) to total iron ratio is one indicating that all of the dissolved iron present in the suspension is present as Fe(II). For the other two acids, Fe(II) fraction (Fe(II)/Total Fe) is much less, SO₄²⁻ it is ~ 0.3 and for NO₃⁻ this fraction is ~ 0.6. These data show that the production of Fe(II) is strongly dependent on anion type and that sulfate yields the lowest amount of Fe(II).

8.4.4 Mechanism for Dissolution of α-FeOOH with Different Acids

In the absence of light, total iron dissolution for the different anions can be related to the strength and mode of anion adsorption, and the ability of the complex to be further protonated, as shown in Eq: 8.1. Sulfate and nitrate ions are polyatomic oxyanions that can bond to the surface in different adsorption modes, including a bidentate and bridging coordination mode which chloride is unable to form. Bridging and bidentate coordination can potentially enhance iron dissolution. As such it is the ability of anions to form certain surface complexes that can explain the differences in total iron dissolution in the dark.

The effect of inorganic anion on dissolved Fe(II) concentrations in the presence of light can be explained in part by considering the photochemistry of aqueous iron complexes at low pH. In the absence of other anions, [Fe(OH)₆]³⁺ is the dominant species at pH less than 2.5 whereas the concentration of [Fe(OH)₂₃(OH)]²⁺ is the most
important chromophore at visible wavelength with a maximum concentration at \( \sim \text{pH 3.5} \).\(^{348}\) The photoreduction of \([\text{Fe(OH}_2\text{)}_5\text{(OH)}]^2+\) is given by,

\[
[\text{Fe(OH}_2\text{)}_5\text{(OH)}]^2+ + \text{H}_2\text{O} + \text{hv} \rightarrow [\text{Fe(OH}_2\text{)}_6]^2+ + \text{OH}^* \text{ Eq: 8.2.}
\]

In Cl\(^-\)-containing suspensions, \([\text{Fe(OH}_2\text{)}_5\text{Cl}]^2+\) and \([\text{Fe(OH}_2\text{)}_4\text{Cl}_2]^+\) coexist at low pHs where the former is the dominant species at \( \sim \text{pH 1} \) whilst the \([\text{Fe(OH}_2\text{)}_5\text{(OH)}]^2+\) is only present at a very low level.\(^{363-365}\) Both chloride containing iron species are photoactive in UV and visible regions of the solar spectrum. As reported by Hsu et al., \([\text{Fe(OH}_2\text{)}_5\text{Cl}]^2+\) is photoreduced to \([\text{Fe(OH}_2\text{)}_6]^2+\) according to,

\[
[\text{Fe(OH}_2\text{)}_5\text{(Cl)}]^2+ + \text{H}_2\text{O} + \text{hv} \rightarrow [\text{Fe(OH}_2\text{)}_6]^2+ + \text{Cl}^* \text{ Eq: 8.3}
\]

The quantum yield of the photodissociation of \([\text{Fe(OH}_2\text{)}_5\text{(Cl)}]^2+\) is approximately twice the value of \([\text{Fe(OH}_2\text{)}_5\text{(OH)}]^2+\) and photoreduction of \([\text{Fe(OH}_2\text{)}_6]^3+\) is not a principal source of \(\text{OH}^*\) because its absorption spectrum does not significantly overlap the solar spectrum.\(^{364,365}\) Based on above facts and the data presented, it can be suggested that the formation of Fe(III)-Cl complexes would result in higher rate of Fe(II) production in suspensions with the chloride ion. Furthermore, formation of Fe-Cl complexes can result a decrease in the redox potential of Fe(III)/Fe(II) couple and thus enhance the production of Fe(II) in these systems.
In the case of HNO$_3$, NO$_3^-$ is a weak ligand and does not readily form solution phase iron complexes leaving [Fe(OH$_2$)$_6$]$^{3+}$ and [Fe(OH$_2$)$_5$(OH)]$^{2+}$ as dominant species. Photolysis of [Fe(OH$_2$)$_5$(OH)]$^{2+}$ efficiently yields OH$^-$ radicals, a strong oxidizer, that reoxidizes Fe(II) back to Fe(III). In addition, NO$_3^-$ in acidic waters is a well-known chromophore which absorbs light ~ 305 nm to yield NO$_2$ and NO$_2^-$ and OH$^-$ via, $^{83}$

\[
\text{NO}_3^- + H^+ \xrightarrow{305\text{nm}} \text{NO}_2 + \text{OH}^- \quad \text{Eq: 8.4}
\]

\[
\text{NO}_3^- \xrightarrow{305\text{nm}} \text{NO}_2^- + \text{O}^{(3P)} \quad \text{Eq: 8.5.}
\]

On the basis of the above information, it can be suggested that the higher OH$^-$ concentration originated from the photolysis of both NO$_3^-$ and [Fe(OH$_2$)$_5$(OH)]$^{2+}$ results in a faster transformation of [Fe(OH$_2$)$_6$]$^{2+}$ back to [Fe(OH$_2$)$_6$]$^{3+}$; thus, a lower Fe(II) fraction compared to Cl$^-$ suspensions.

The effect of sulfate, SO$_4^{2-}$, on proton-promoted iron dissolution of $\alpha$-FeOOH is different from the other anions. According to Figure 8.5(b) and (c), the total iron dissolution in H$_2$SO$_4$ suspensions is enhanced by a factor of ~2, equivalent to HNO$_3$ suspensions, whereas the fraction of Fe(II) is only ~0.3, half of that observed with HNO$_3$. Therefore, ~70% of the dissolved iron acidified with H$_2$SO$_4$ exists in the form of soluble Fe(III). As Fe(III) is less soluble compared to Fe(II), it can be proposed that the dissolve Fe(III) fraction is coordinate with sulfate forming solution phase Fe(III)-sulfato complexes with different photochemical behavior leading to less Fe(II) formation.
8.4.5 Anion Adsorption on $\alpha$-FeOOH Nanorod and Microrod Surfaces

To gain additional molecular level insights into the behavior of $\alpha$-FeOOH nanorods and microrods in pH 2 solutions, Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectroscopy was used to investigate surface adsorption of nanorods and microrods in the presence of the different acids used in this study. Adsorption of both HCl and HNO$_3$ from solution phase on to the nanorods, gave little spectral information in the 1000 to 4000 cm$^{-1}$ spectral range as expected based on the frequencies of the surface complexes, for chloride frequencies below 1000 cm$^{-1}$ and the strength of the interaction with the surface, nitrate forms surface complexes with weak absorption band intensities and frequencies similar to that of nitrates in solution. However for sulfate, ATR-FTIR spectroscopy revealed distinct absorption bands with clear differences observed between sulfate adsorbed on nanorod compared to microrod surfaces.

Figure 8.6 shows several ATR-FTIR spectra for sulfate adsorption on both nanorods and microrods at pH 2. For comparison, a solution-phase spectrum of sulfate anion in the absence of goethite is also shown. As a free anion, sulfate has tetrahedral symmetry and belongs to the $T_d$ point group. The relationship between the molecular symmetry of sulfate complexes and the observed infrared spectrum they produce is shown in Figure 8.7. For this symmetry, only one peak at $\sim$1100 cm$^{-1}$ is expected for the triply degenerate $\nu_3$ asymmetric stretch.$^{366}$ However in aqueous solutions, several species can exist and the symmetry is reduced leading to additional absorption bands in this spectral region. For sulfate adsorbed on the $\alpha$-FeOOH surface, it can be seen that there is an even greater number of absorption bands present in the spectra due to a further
Figure 8.6 ATR-FTIR spectra of sulfate adsorption at pH 2. Spectra are shown for six successive additions of 0.01 N H₂SO₄ in 15 min intervals. The solution phase spectra, collected in the absence of α-FeOOH, are shown in (a). The spectra for adsorbed sulfate are shown for nanorods and microrods, (b) and (c), respectively. Solution phase absorptions have been subtracted from the spectra shown in (b) and (c).
Figure 8.7 The relationship between the molecular symmetry of sulfate complexes and the observed infrared spectrum they produce. Adapted from Peak et al. (336).

reduction in symmetry upon surface adsorption and the presence of different surface complexes. Further inspection of these spectra shown in Figure 8.6 shows distinct differences between the ATR-FTIR spectra for sulfate adsorbed on nanorods compared to
microrods. For example, the absorption band at 1240 cm\(^{-1}\) clearly observed for nanorods is barely present in microrod spectra.

When sulfate adsorbs on the surface as an inner-sphere surface complex, the symmetry is lowered. In the case of a monodentate inner-sphere complex with C\(_{3v}\) symmetry, the \(v_3\) band of free sulfate anion splits into two and the symmetric stretch, \(v_1\), becomes infrared active with a band at \(\sim 975\) cm\(^{-1}\).\(^{367}\) Therefore the observed spectral

![Graphical representation of major forms of adsorbed sulfate complexes on microrods and nanorods of goethite.](image)

**Figure 8.8** Graphical representation of major forms of adsorbed sulfate complexes on microrods and nanorods of goethite. (a). Free sulfate in solution with \(T_d\) symmetry (b). Monodentate complex of sulfate on microrods with \(C_{3v}\) symmetry. (c). Bidentate-binuclear complex of sulfate on nanorods with \(C_{2v}\) symmetry.
bands at ~1140, 1042 and 975 cm$^{-1}$, shown in Figure 8.6(b), suggest formation of inner-sphere monodentate complexes of sulfate, as the major adsorbed species, with surfaces of goethite microrods. As seen in Figure 8.6(c), four distinct peaks can be found in the spectra collected for nanorods. Based on previous studies, sulfate can also form a bidentate binuclear (bridging) surface complex, the symmetry is further lowered to C$_{2v}$, splitting the v$_3$ band into three bands between 1050 and 1250 cm$^{-1}$ in addition to the v$_1$ band at lower wavenumbers. Therefore the splitting indicates the presence of an inner-sphere bidentate binuclear sulfate complex on the surface of goethite nanorods. A graphical representation of major forms of adsorbed sulfate complexes on microrods and nanorods of goethite is given in Figure 8.8.

Additional experiments were carried out to investigate the solution phase contribution, especially from [Fe(III)-SO$_4^{2-}$]$^+$, by equilibrating nanorods (10 mg) in 0.01N H$_2$SO$_4$ (10 ml) solution followed by filtration and collecting IR spectra of the reacted H$_2$SO$_4$ solutions. ATR-FTIR data from these additional experiments are shown in Figure 8.9. The IR spectral band frequencies collected from reacted H$_2$SO$_4$ solutions were similar to that of unreacted H$_2$SO$_4$ indicating that there is no contribution from [Fe(III)-SO$_4^{2-}$]$^+$ in the spectra shown in Figure 8.6. Higher absorption intensities and formation of binuclear complexes point out the presence of additional, and potentially more reactive, sites for nanorod surface which can lead to higher dissolution rates, as observed from nanorod suspensions at pH 2. Thus, these spectroscopic results provide evidence that differentiate between the surface chemistry of nanorods compared to microrods. In addition, these results further our understanding of the role of acid anion in forming surface complexes with $\alpha$-FeOOH.
8.4.6 Effect of Carbonate and Phosphate Ions on Iron Dissolution

Mineral-oxyanion interactions play a vital role in the natural environment. From a microscopic point of view, adsorption of multivalent oxyanions, i.e. carbonate (CO$_3^{2-}$) and phosphate (PO$_4^{3-}$), on goethite surface could follow typical trends expected for anion adsorption, with adsorption favored at low pH, and alter surface chemistry and, thus, the dissolution. Dissolved inorganic carbon species such as carbonic acid (H$_2$CO$_3$), bicarbonate (HCO$_3^-$) and CO$_3^{2-}$ are ubiquitous in natural waters. At low pH, it is H$_2$CO$_3$,
and at very high pH, it is CO$_3^{2-}$. The natural concentration range in ground water is about 10$^{-4}$ – 10$^{-2}$ M, whereas in marine environments, higher concentrations (~ 0.05 -0.2 M) of carbonate can be found. Dissolved phosphate is of major concern in environmental chemistry. Although, it is a well-known plant nutrient and essential for the growth of plants including phytoplankton in the ocean, excess PO$_4^{3-}$ has been recognized as a nonpoint-source agricultural pollutant throughout the world due to over application of both synthetic and animal based fertilizers. Here the role of carbonate and phosphate on the generation of soluble iron and iron speciation in microrods and nanorod suspensions were investigated at pH 2.

The experiments were carried out using the custom made reaction set up described in the previous section and under similar conditions, except 2 mM CO$_3^{2-}$ or PO$_4^{3-}$ were added to the reaction medium, along with 5mM NaClO$_4$ to keep the ionic

<table>
<thead>
<tr>
<th>Suspension</th>
<th>Proton (H$^+$) source</th>
<th>Ionic strength buffer</th>
<th>Oxyanion</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 2</td>
<td>0.01 N HNO$_3$</td>
<td>5 mM NaClO$_4$</td>
<td>-</td>
</tr>
<tr>
<td>pH 2 with NO$_3^-$</td>
<td>0.01 N HNO$_3$</td>
<td>5 mM NaClO$_4$</td>
<td>2 mM NaNO$_3$</td>
</tr>
<tr>
<td>pH 2 with CO$_3^{2-}$</td>
<td>0.01 N HNO$_3$</td>
<td>5 mM NaClO$_4$</td>
<td>2 mM Na$_2$CO$_3$</td>
</tr>
<tr>
<td>pH 2 with PO$_4^{3-}$</td>
<td>0.01 N HNO$_3$</td>
<td>5 mM NaClO$_4$</td>
<td>2 mM Na$_3$PO$_4$</td>
</tr>
</tbody>
</table>
Figure 8.10  Proton-promoted dissolution of rod-shaped $\alpha$-FeOOH particles is monitored by the formation of total Fe in solution at pH 2 in the presence of 2mM NO$_3^-$, CO$_3^{2-}$ and PO$_4^{3-}$. Mass normalized dissolution from (a). microrods and (b). nanorods at 298 K.

strength constant. In addition to CO$_3^{2-}$ and PO$_4^{3-}$, effect of 2 mM NO$_3^-$ is shown for comparison purpose. The compositions of reaction media used in the study are given in Table 8.3.

The data presented in Figure 8.10 show a comparison of total iron dissolution of nanorods versus microrods at pH 2 in the presence of 2mM NO$_3^-$, CO$_3^{2-}$ and PO$_4^{3-}$ under dark conditions. These data have been normalized to the total mass of the initial $\alpha$-FeOOH in solution. Based on these data, under dark conditions, it can be clearly seen that microrods dissolve faster and to a greater extent in the presence of oxyanions, especially with CO$_3^{2-}$ and PO$_4^{3-}$, whereas in nanorods the reaction seem to be quenching in the
Table 8.4 Initial rate of total iron dissolution at pH 2, determined from linear regression, in the presence of 2 mM CO$_3^{2-}$ and PO$_4^{3-}$ for nanorods and microrods.$^a$

<table>
<thead>
<tr>
<th>Suspension</th>
<th>Mass normalized dissolution rate ($\mu$M·g$^{-1}$·h$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microrods</td>
</tr>
<tr>
<td>pH 2</td>
<td>6.1 (± 0.4)</td>
</tr>
<tr>
<td>pH 2 with NO$_3^-$</td>
<td>6.6 (± 0.8)</td>
</tr>
<tr>
<td>pH 2 with CO$_3^{2-}$</td>
<td>23 (± 1)</td>
</tr>
<tr>
<td>pH 2 with PO$_4^{3-}$</td>
<td>32 (± 2)</td>
</tr>
</tbody>
</table>

$^a$ – Results presented here are the average value of triplicate measurements and the reported error represents one standard deviation. Dissolution data from the first 10 hrs were used in the rate determination.

presence of these oxyanions. Initial rates of total iron dissolution for nanorods and microrods at pH 2.0 in 298 K, determined from linear regression analysis, are given in Table 8.4. The initial rate of total iron dissolution for microrods in the absence of oxyanions, is 6.1 (± 0.4) $\mu$mol·g$^{-1}$·h$^{-1}$ whereas in the presence of PO$_4^{3-}$, this is 32 (± 2) $\mu$mol·g$^{-1}$·h$^{-1}$ with a 5 fold enhancement. In the case of nanorods, without oxyanions the initial rate of dissolution is 55 (± 4) and the dissolution rate is cut down by at least one order of magnitude in the presence of phosphate. These data reveal that the same oxyanion shows completely different behavior on the two different particle sizes. The data normalized to surface area differences are shown in Figure 8.11. According to Figure 8.11(a), the enhancement previously observed for nanorods at pH 2, due to the inherent reactivity of nanoscale particles, is now been masked in the presence of 2 mM NO$_3^{-}$. 
Figure 8.11  Proton-promoted dissolution of microrods and nanorods of $\alpha$-FeOOH is monitored by the formation of total Fe in solution at pH 2. Surface area normalized dissolution in the presence of (a). 2mM NO$_3^-$, (b). 2mM CO$_3^{2-}$ and (c). 2mM PO$_4^{3-}$ at 298 K.
Figure 8.12 TEM images of nanorods and microrods from the reaction with HNO₃ at pH 2.0 in the presence of 2mM NO₃⁻, CO₃²⁻ and PO₄³⁻.
Figure 8.11(b) and (c) highlight even further enhanced dissolution from suspensions containing microrods in the presence of CO$_3^{2-}$ and PO$_4^{3-}$.

To understand these differences, TEM images of nanorod and microrod suspensions at pH 2.0, containing 2mM NO$_3^-$, CO$_3^{2-}$ and PO$_4^{3-}$, deposited and dried onto TEM grids were examined. These data are shown in Figure 8.12. The images provide in Figure 8.12(a) and (b) evidence for well-dispersed nanorods and microrods in the presence of 2mM NO$_3^-$ and microrods in the presence of both CO$_3^{2-}$ and PO$_4^{3-}$, with a slight tendency to form agglomerates. However, in contrast, the nanorods imaged from the suspensions in the presence of 2 mM CO$_3^{2-}$ and PO$_4^{3-}$ show large aggregates, especially in the presence of PO$_4^{3-}$ very tightly packed aggregates were observed. These data suggest that nanorod aggregation is quenching the dissolution expected for the smaller-sized rods at pH 2.0, result in lower dissolution rates. In addition, these data show that there are large differences in the stability of $\alpha$-FeOOH nanorods versus microrod suspensions that clearly impact dissolution behavior.

Although these TEM studies can begin to explain the data for nanorods, they do not explain the results obtained for microrods. To gain additional molecular level insights into the behavior of $\alpha$-FeOOH nanorods and microrods in the presence of CO$_3^{2-}$ and PO$_4^{3-}$, ATR-FTIR spectroscopy was used to investigate surface adsorption of nanorods and microrods in the presence of oxyanions used in this study. Figure 8.13(a) and (b) show several ATR-FTIR spectra for carbonate and phosphate adsorption on both nanorods and microrods. For comparison, a solution-phase spectrum of carbonate and phosphate in the absence of goethite is also shown. The free carbonate ion has a plane structure with D$_{3h}$ symmetry. In Figure 8.13(a), the solution spectrum shows strong
Figure 8.13  ATR-FTIR spectra of (a). carbonate and (b). phosphate adsorption on nanorods and microrods at pH 2. Spectra are shown for exposure of goethite surface to either 2mM CO$_3^{2-}$ or PO$_4^{3-}$ for 15 min. The solution phase spectra, collected in the absence of α-FeOOH, are shown at the bottom of each plot. Solution phase absorptions have been subtracted from the surface spectra shown in top and middle.
Figure 8.14 Proposed surface complexes for adsorbed carbonate and phosphate on nanorods and microrods of goethite.
vibrations at 1630 and 1363 cm\(^{-1}\) for the \(\nu_2\) and \(\nu_3\) modes of HCO\(_3^+\) and the peak at 1386 cm\(^{-1}\) can be assigned to the asymmetric stretching of CO\(_3^{2-}\).\(^{374,375}\) Based on its geometry, CO\(_3^{2-}\) can form both mono- and bidentate complexes with metal irons and metal ion containing surfaces, where symmetry is lowered from D\(_{3h}\) to C\(_{2v}\) with corresponding loss of degeneration and activation of vibrations in the IR spectrum.\(^{376}\) Upon exposure of microrods to carbonate (Figure 8.12(a) – middle spectrum), the peak at 1549 cm\(^{-1}\) can be assigned to the asymmetric O–C–O stretching of adsorbed carbonate and peak at 1393 cm\(^{-1}\) to the symmetric stretch.\(^{377,378}\) This splitting of 156 cm\(^{-1}\) is close to the observed differences for monodentate configurations of aqueous Co(III)-carbonato complexes.\(^{375,379,380}\) When carbonate is absorbed on nanorods, (Figure 8.13(a) – top) the splitting of \(\nu_3\) mode is even greater, \(~390\) cm\(^{-1}\), indicating further distortion of D\(_{3h}\) symmetry of the carbonate molecule. According to the literature, similar splitting has been observed for Co(III) bidentate complexes with carbonate, [(NH\(_3\))\(_4\)CoCO\(_3\)]\(^+\) (\(\Delta\nu_3\sim 300\) cm\(^{-1}\)) \(^{379,380}\) and bidentate binuclear complexes (\(\Delta\nu_3\sim 700\) cm\(^{-1}\)).\(^{381}\) However, in several studies on adsorption of carbonate on goethite, the observed \(\Delta\nu_3\) is much smaller than earlier values and still had assigned for a bidentate binuclear complex.\(^{374}\) Here, by taking all these facts into consideration, we propose that carbonate forms a monodentate complex with microrods and a bidentate binuclear complex with nanorods as major products. Further, we suggest that there is a possibility to form “molecular bridges” between nanorod particles via carbonate molecules to result such a higher splitting in the \(\nu_3\) mode. The proposed surface complexes for adsorbed carbonate and phosphate on microrods and nanorods of goethite are given in Figure 8.14(a) and (b), respectively.
The changes in the IR spectrum observed for phosphate are fairly similar to those observed with sulfate. At lower pH, the symmetry of the dominant phosphoric acid (H₃PO₄) is C₃ᵥ and the spectrum (Figure 8.13(b) – bottom) shows doublets of ν₃ vibrations at 1181 and 1005 cm⁻¹. The broad envelop resulted in the exposure of microrods to phosphate solution (Figure 8.13(b) – middle) is an assembly of three ν₃ vibrations positioned at 1101, 1028 and 970 cm⁻¹, indicating formation of monodentate complex as the major product with C₂ᵥ or lower symmetry. Several molecular geometries are possible for this monodentate complex (Figure 8.14 (e) to (i)). For nanorods, additional splitting of the ν₃ mode can be observed indicating formation of inner-sphere complexes (Figure 8.13(b) – top). According to Tejedor-Tejedor and Anderson, the peaks at 1100, 1024, 930 and 890 cm⁻¹ can be assigned to deprotonated bidentate complex of phosphate, (FeO)₂PO₂, with the goethite surface (Figure 8.14(a)). Similar spectral feature have been observed and assigned to (FeO)₂PO₂ in several laboratory and computational studies on phosphate adsorption on goethite. It is also important to note the two shoulders at ~ 1006 and 1124 cm⁻¹, which goes away at longer reaction times (not shown). This suggests that at least initial one extra surface complex is formed, initially, and under the influence of the surface it transforms to deprotonated phosphate. According to the literature, these spectral bands indicate the formation of monoprotonated bidentate complex of phosphate, (FeO)₂(OH)PO (Figure 8.14(b)). Thus, the data reveal that binding to the surface result in deprotonation of surface-bound phosphate complexes, yielding more protons to the reaction medium.

Similar to sulfate adsorption, higher absorption intensities and formation of binuclear complexes indicate the presence of additional and potentially more reactive,
surface sites for nanorod which can lead to higher uptake of oxyanions result in a lower surface charge and, thus, forming tight aggregates. Although these results reveal the formation of monodentate complexes as the major adsorbed product with microrods, the data do not explain the enhanced dissolution from microrods in the presence of carbonate and phosphate. Additional experiments were carried out at neutral pH in the presence of above oxyanions to investigate the iron dissolution from microrods due to oxyanions along. No dissolve iron was detected from these experiments highlighting the importance of protons (H\(^+\)) in the dissolution mechanism. Therefore, it can be postulated that polarization of Fe-O bond upon binding of oxyanions and formation of more soluble [Fe(III)-oxyanion](aq) coordination complexes could be the reason for the observed enhancement in the iron dissolution from microrods.

8.5 Conclusions and Environmental Implication

Using \(\alpha\)-FeOOH as a proxy for a source of iron from mineral dust aerosol, several factors that effect iron dissolution in low pH environments have been investigate. Some of the key points addressed here include the role of particle size and the mechanisms involved in the enhanced chemical activity of nanoscale iron oxides. In particular, the importance of reactive surface planes that yield enhanced concentrations of dissolved iron during simulated daytime and nighttime atmospheric processing that go beyond surface area considerations. For \(\alpha\)-FeOOH, an important aspect is the higher density of surface O-H groups on the (021) plane that lead to both enhanced proton-promoted and photoreductive dissolution and thus greater amounts of soluble iron. To best understand the implications of size-dependent dissolution and an increase the amount of soluble and
bioavailable forms of iron, the dissolution at longer time scales is most important. Since atmospheric transport of mineral dust is associated with these longer time scales, dissolved iron from nanorods may be a more important long-term source of bioavailable Fe compared to larger microrods. The dominant contribution to total dissolved iron in the presence of light is dissolved Fe(II) which is produced in greater quantities for nanorods relative to microrods. Given the potential importance to heterogeneous photochemical processes on particle surfaces, redox reactions that enhance the solubility of iron oxides are particularly indispensable in controlling the extent of iron dissolution and speciation in atmospheric waters.387

Furthermore, these results clearly indicate that iron dissolution for nanorods in low pH environments is greatly influenced by the nature of the acid. Once mineral dust aerosol undergoes atmospheric transport and aging in polluted environments, they contain relatively high concentrations of inorganic species. In general, nitrate and sulfate tend to enhance iron dissolution in the dark relative to chloride. These results reveal that iron-containing mineral particles that become mixed with sea salt or become associated with chloride ion in some other way (e.g. heterogeneous uptake of HCl) will yield less total soluble iron in daytime and nighttime atmospheric processing, yet there will be a higher fraction of dissolved Fe(II) during daytime processing relative to the other inorganic anions. Sulfate in comparison shows a larger fraction of Fe(III) in irradiated systems. Moreover, multivalent oxyanions such as carbonate and phosphate show a significant effect on iron dissolution process. The data from the current study evident for a complete opposite effects on nanorods and microrods, showing a 3 to 5 fold enhancement for microrods whereas for nanorods quenching the dissolution reaction by
at least one order of magnitude, in the presence of above oxyanions. These differences can be attributed to the differences in the inherent reactivity of the two particle sizes and the solubility of the coordination complexes formed by the oxyanions. It is also worth noting that changing global emissions of sulfur and nitrogen oxides will influence HNO₃ and H₂SO₄ concentrations. According to recent field studies and model predictions, it is anticipated that global SO₂ emissions are to be reduced over the next century while the global NOₓ emission is expected to increase. This will result in more nitrate adsorbed on to mineral dust particle surfaces that will influence iron mobilization from dust. Finally, in order to accurately predict bioavailable iron in acidified mineral dust aerosol plumes and marine environments, these factors that influence iron solubility will need to be included in future atmospheric chemistry models. The current study presents important information that can be further used in atmospheric chemistry models.

8.6 Acknowledgments

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CHAPTER 9
CONCLUSIONS AND FUTURE DIRECTIONS

Mineral dust aerosols emitted from the Earth crust during various natural and anthropogenic processes continuously alter the chemical balance of the atmosphere via heterogeneous processes and thus, impact on the global climate. Today, understanding of heterogeneous chemistry and photochemistry on mineral dust has become vital in order to accurately predict the effect of mineral dust loading on the Earth’s atmosphere. Laboratory studies, focused on the behavior of the physiochemical properties of model systems representing atmospheric aerosols, and atmospheric chemistry model analysis, intended to predict important global climate impacts based on laboratory results and field observations, are two scientific approaches extensively used in atmospheric chemistry studies. Here, laboratory measurements were coupled with model studies to understand heterogeneous chemistry and photochemistry in the atmosphere with the specific focus on reactions on mineral oxide surfaces.

Investigation of the reactions of trace atmospheric gases with selected mineral dust components, including alumina, iron oxides and carbonates, were done using multiple experimental techniques. These experimental methods include FTIR spectroscopy, both transmission and attenuated total reflection (ATR)-FTIR spectroscopy, as well as the use of a quartz crystal microbalance, X-ray diffraction, and scanning electron microscopy. In addition to these techniques, several other complementary collaborative techniques were used to help with characterization of samples. In some instances, the coupling of these techniques allowed for both qualitative
and quantitative measurements. Development of new reaction systems, i.e. (i) transmission FTIR spectroscopy combined with XPS analysis and, (ii) ATR-FTIR spectroscopy coupled with a quartz crystal microbalance, enhanced the analytical power of experimental methods making it possible to look into the surface processes even closer. Atmospheric model studies projected these laboratory scale measurements to a global scale to highlight the significance of new reaction pathways identified in the current study.

A large area of uncertainty in atmospheric models is in heterogeneous reaction rates involving nitrogen oxide species, including HNO₃, NO₂, NO plus these trace gases act as key elements in numerous catalytic cycles altering the chemical balance of the atmosphere. In the current study, custom made reaction systems were brought into play to explore heterogeneous uptake of gas phase nitric on well characterized metal oxides, oxyhydroxides and carbonates. Data from these studies emphasized binding of nitric acid to the mineral oxide surfaces in different modes including monodentate, bidentate and bridging under dry conditions.

It is becoming increasingly clear that the heterogeneous chemistry is a function of relative humidity (RH) as water on the surface of these particles can enhance or inhibit its reactivity depending on the reaction. In this thesis, the uptake of water on metal oxides, oxyhydroxides and carbonates, as well as change in bonding of adsorbed species in the presence of co-adsorbed water were investigated. All the studied model systems showed a significant uptake of water with the highest uptake by CaCO₃. Quantitative analysis of water uptake indicated formation of multilayers of water over these reactive surfaces which can change the reactivity of the particle surface. The large amounts of water
adsorbed, especially for CaCO₃ and γ-Fe₂O₃, provides additional evidence for the importance of water uptake on these mineral components of dust and the role it may play in the atmosphere. Water alone was found to reversibly adsorb on the surface of calcium carbonate, resulting in a thin water film, which exhibit a two-dimensional layer growth mode prior to three-dimensional growth.

Under humid conditions, on metal oxide and oxyhydroxide surfaces, co-adsorbed water was found to have an effect on local bonding of the nitrate ion, as well as geometry and vibrational frequencies. Both experimental and calculation work showed there can be two water solvated nitrate coordination modes that is inner-sphere and outer-sphere, which differ by nitrate proximity to the surface. Water was found to play a role in the uptake of HNO₃ on calcium carbonate due to the fact that co-adsorbed water increases the ionic mobility of adsorbed ions on the surface, leading to the formation of micropuddles of calcium nitrate. The formation of these new structures exposed additional sites on the calcium carbonate surface that allows for an increase in the uptake of HNO₃ onto the surface. Thus, adsorbed water significantly influences the uptake of most trace gases, including nitrogen oxides, onto aerosol dust components in the atmosphere. Quantum chemical calculations, done in collaboration with Dr. Jonas Baltrusaitis, using binuclear aluminum cluster models helped to aid in the assignment of the complex vibrational spectrum of adsorbed nitrate species on the surface following reaction of nitric acid vapor with alumina in the absence and presence of co-adsorbed water.

HNO₃ uptake by mineral dust can be considered as a removal mechanism for the nitrogen species in the atmosphere which would be only half of the story. In this work, we showed photochemical conversion of nitric acid to gas phase nitrous oxide, nitric
oxide and nitrogen dioxide through an adsorbed nitrate intermediate under different atmospherically relevant conditions. This could be a potentially important, yet previously unknown, surface mediated photochemical pathway in the NO\textsubscript{y} cycle. The relative ratio and product yields of these gas phase products change with relative humidity, with NO being the highest under all the studied conditions and relatively higher N\textsubscript{2}O production at the higher relative humidities. Here we also reported an efficient dark reaction readily converts the major NO product into NO\textsubscript{2} during post-irradiation. Findings of this work have implications for atmospheric processes involving nitric acid, NO\textsubscript{x} and mineral dust aerosol where NO\textsubscript{x} level is affected by these continued reactions of adsorbed nitrate initiated by sunlight result in renoxification of the atmosphere. The study further provides evidence that photochemical reactions of atmospheric significance can take place on the surface of particulate matter.

In atmospheric studies, the interpretation of chemical and photochemical processes in terms of reaction mechanisms is difficult due to involvement of a complex blend of trace gases mixing with particulate matter in various compositions. Photochemistry of adsorbed nitrate on mineral aerosol dust may be influenced by the presence of different other gases in the atmosphere making it complicated to understand. This thesis converses formation of active nitrogen, N\textsubscript{2}O, NO, and NO\textsubscript{2}, and chlorine, Cl\textsubscript{2}, Cl, ClO, species that could potentially regulate the peak concentration and geographical distribution of ozone. Understanding ozone trends in the lower stratosphere and upper troposphere is crucial for accurate predictions of future changes in global climate and chemical balance of the atmosphere. Here we reported formation of atmospheric N\textsubscript{2}O, from the photodecomposition of adsorbed nitrate in the presence of co-adsorbed NH\textsubscript{3},
thin coating of NH$_4$NO$_3$ over the particle surface, via an abiotic mechanism that is favorable in the presence of light, relative humidity and a surface. This source of N$_2$O is not currently accounted for in the global N$_2$O budget. Due to the fact that ammonium nitrate is also a common component of ambient particles transported across the globe, the contribution from this mechanism alone is expected to be significant. Estimated annual production of N$_2$O over the continental United States from this abiotic pathway, from Community Multiscale Air Quality model (CMAQ), is $9.3^{+0.7/-5.3}$ Gg N$_2$O, approximately 5% of total U.S. anthropogenic N$_2$O emissions. According to Ravishankara et al., N$_2$O is currently the single most important ozone depleting substance, and is anticipated to remain the largest throughout the 21st century. Therefore, detailed studies such as this one leading to an abiotic production of N$_2$O via heterogeneous photochemistry of ammonium nitrate on aerosols may be useful in better explaining field and model results of atmospheric chemistry.

Here we claim that not only co-adsorbed ammonia but also reactions between gaseous HCl and adsorbed nitrate are capable of activating N and Cl “inert” reservoir species. Conversion of atmospheric nitric acid and hydrogen chloride to active N and Cl species, including NOCl, NO, NO$_2$, Cl and Cl$_2$, through adsorbed nitrate under different atmospherically relevant conditions was shown using transmittance FTIR and XPS analysis. The reaction pathway involves a surface bound NO$^+$NO$_3^-$ intermediate that is produced in an acid catalysis reaction between adsorbed nitrate and chlorine. The results reported further emphasize significant dependence of the gas phase distribution on relative humidity. The chemistry and photochemistry discussed here may be of particular importance in the upper troposphere and lower stratosphere those are in contact with.
highly polluted coastal urban areas. Atmospheric mixing of mineral dust particles, having nitrated surfaces, with either sea salt in marine environments or polluted air over urban areas, can possibly initiate the formation of NOCl and other active gas phase species. These findings need to be implemented in atmospheric chemistry models that can be used to explain and predict concentrations of ozone under a variety of environmental conditions.

Mineral dust aerosol is a major source of bioavailable iron to the ocean with an annual deposition of ~ 450 Tg of dust into the open ocean waters. Iron dissolution in Fe-containing dust aerosol can be linked to source material, mineralogy, and iron speciation. All of these factors need to be incorporated into atmospheric chemistry models if these models are to accurately predict the impact of Fe-containing dusts into open ocean waters. In this study, we combined dissolution measurements along with spectroscopy and microscopy, using $\alpha$-FeOOH as a proxy for a source of iron from mineral dust aerosol, to focus on nanoscale size effects in the dissolution in low-pH environments. The role of acid type, including HNO$_3$, H$_2$SO$_4$, and HCl, oxyanions (CO$_3^{2-}$ and PO$_4^{3-}$) in iron dissolution were the other key topics discussed in the related work. An important aspect for chemical activity of nanoscale iron oxides is the higher density of surface O-H groups on the (021) plane that lead to both enhanced proton-promoted and photoreductive dissolution and thus greater amounts of soluble iron. To best understand the implications of size-dependent dissolution and an increase in the amount of soluble and bioavailable forms of iron, the dissolution at longer time scales is most important. Since atmospheric transport of mineral dust is associated with these longer time scales, dissolved iron from nanorods may be a more important long-term source of bioavailable Fe compared to
larger microrods. The dominant contribution to total dissolved iron in the presence of light is dissolved Fe(II) which is produced in greater quantities for nanorods relative to microrods. Thus, redox reactions that enhance the solubility of iron oxides are particularly indispensable in controlling the extent of iron dissolution and speciation in atmospheric waters.

Here we further report with clear evidence that aggregation impacts dissolution. Proton-promoted dissolution of nanorods is nearly or completely quenched in the aggregated state. Given the role of iron mobilization in the biogeochemical cycling of iron in the global environment and the proposal that atmospheric reactions can lead to low pH environments in Fe-containing atmospheric aerosols and the high ionic strength found in seawater, it is important to understand factors such as pH and aggregation that can influence iron mobilization. In addition, iron dissolution for nanorods in low pH environments is greatly influenced by the nature of the acid. Once mineral dust aerosol undergoes atmospheric transport and aging in polluted environments, they contain relatively high concentration of inorganic species, i.e. nitrate, sulfate and chloride. The results from these experiments revealed that iron-containing mineral particles that become mixed with sea salt or become associated with chloride ion in some other way will yield less total soluble iron in daytime and nighttime atmospheric processing, yet there will be a higher fraction of dissolved Fe(II) during daytime processing relative to the other inorganic anions.

Polyatomic oxyanions, such as carbonate and phosphate, also showed a significant effect on iron dissolution process. The data from the current study evident for a complete opposite effects on nanorods and microrods, result in a 3 to 5 fold
enhancement for microrods whereas for nanorods, quenching the dissolution reaction by at least one order of magnitude, in the presence of above oxyanions. These differences were attributed to the differences in the inherent reactivity of the two particle sizes and the solubility of the coordination complexes formed by the oxyanions. These dissolution studies highlighted important, yet unconsidered, factors in the atmospheric processing of iron-containing mineral dust aerosol. Finally, in order to accurately predict bioavailable iron in acidified mineral dust aerosol plumes and marine environments, these factors that influence iron solubility will need to be included in future atmospheric chemistry models.

In conclusion, the work reported in this thesis provides insight into the heterogeneous chemistry and photochemistry of mineral dust aerosols under different atmospherically relevant conditions. Mineral dust can be further regarded as one of the key elements that links the lithosphere to atmosphere to hydrosphere. The knowledge gained on dynamic properties and processes of aerosol dust particles can be combined to understand variations of the chemical balance of these different environments and accurately predict global climatic changes.
APPENDIX

INSTRUMENTAL PARAMETERS AND MACRO PROGRAMS FOR FTIR MEASUREMENTS

Instrumental parameters for FTIR measurements on the Mattson Infinity Gold and Mattson Research Series I infrared spectrometers were specified and saved in the Method Setup of the Control Panel window in the WinFirst program. Macro programs were written and modified using the macro toolbox in the WinFirst program.

A1. Instrumental Setup for Transmission FTIR Measurements

This scan method was used to collect single beam spectra (.sbm) by averaging 250 scans per sample. The file names were assigned in a prompt window or automatically by choosing that option in the Method Setup window.

************************************************************************
Sample Scans: 250   Resolution: 4 cm⁻¹
Background Scans: 1   Gain: 1
________________________________________________________________________
Forward Velocity
Reverse Velocity
Frequency Start: Varied from 600 to 1000 cm⁻¹ (window dependent)
Frequency End: 4000 cm⁻¹
Spectral Range: Mid-IR
Zero Fill: 1X
FFT Symmetry: Double
Apodization: Triangle
Phase Correction: Mertz
Phase Apodization: Triangle
Phase Type: Real
************************************************************************
A2. Instrumental Setup for ATR-FTIR Measurements

Sample Scans: 500   Resolution: 4 cm⁻¹
Background Scans: 1   Gain: 1

Forward Velocity
Reverse Velocity
Frequency Start: Varied from 600 to 800 cm⁻¹ (IRE dependent)
Frequency End: 4000 cm⁻¹
Spectral Range: Mid-IR
Zero Fill: 1X
FFT Symmetry: Double
Apodization: Triangle
Phase Correction: Mertz
Phase Apodization: Triangle
Phase Type: Real

A3. Macro Program for Collecting FTIR Spectra

Macro programs were used to instruct the spectrometer to continuously collect spectra at varying scan rates depending on the speed of collection needed. An example of a macro used is 8 scans per sample every 10 seconds. The collected single beam spectra files were converted into absorbance spectra (.abs) and saved in a specific directory. In addition, absorbances could also be integrated over different regions depending on the adsorbed species present. The integrated absorbances were then saved in a WinFirst report (.txt) and exported to Microsoft Excel in order to be processed.

Sample Macro:

For \( x = 1 \) to 500 step 1
begin

sleep 10
Bench:Scan
ratio c:\gayan\jan08\jan20
A4. Macro Program for Ratioing Single Beam Files to Absorbance Spectra

Sample Macro:

```plaintext
cd c:\gayan\aug09\04aug
S = findFirstFile "0804a*.sbm"
A = stringLength S
if (A > 0)
{
    while (A > 0)
    {
        B = load S
        ratio "c:\gayan\aug09\04aug\0804al01.sbm"
        ras2abs
        save
        S = findNextFile
        A = stringLength S
    }
}
```

A5. Macro Program for Subtracting Spectra

Absorbance spectra were acquired of a surface and the corresponding gas-phase for a given experiment. The gas-phase spectra were subtracted from the surface spectra in order to produce the adsorbed species using this macro.
Sample Macro:

************************************************************************
cd c:\gayan\ aug09\04aug
S = findFirstFile "0804al*.abs"
A = stringLength S
if (A > 0)
{
    while (A > 0)
    {
        B = load S
        loadRef " c:\gayan\aug09\04aug\0804al01.abs"
        subtract 1.0
        show
        save
        S = findNextFile
        A = stringLength S
    }
}
************************************************************************

A6. Macro Program for Integrating Specific Bands in Existing Spectra

In order to integrate specific bands in existing spectra, the macro program is used
to load a series of absorbance spectra files and integrate specific bands.

Sample Macro:

************************************************************************
cd c:\gayan\ aug09\04aug
S = findFirstFile "0804a*.abs"
A = stringLength S
if (A > 0)
{
    while (A > 0)
    {
        B = load S
        A = integrate 1720 1560
        save
        S = findNextFile
    }
}
************************************************************************
A7. Macro Program for Integrating Specific Bands in Gas-Phase Spectra

In order to integrate specific bands in existing spectra, the macro program is used to load a series of absorbance spectra files and integrate specific bands.

Sample Macro:

```plaintext
cd c:\gayan\aug09\04aug
S = findFirstFile "0804a*.abs"
A = stringLength S
if (A > 0)
{
  while (A > 0)
  {
    B = load S
    A = integrate 2400 2285
    A = integrate 2275 2150
    A = integrate 1950 1795
    A = integrate 1675 1550
    save
    S = findNextFile
    A = stringLength S
  }
}
```

************************************************************************
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