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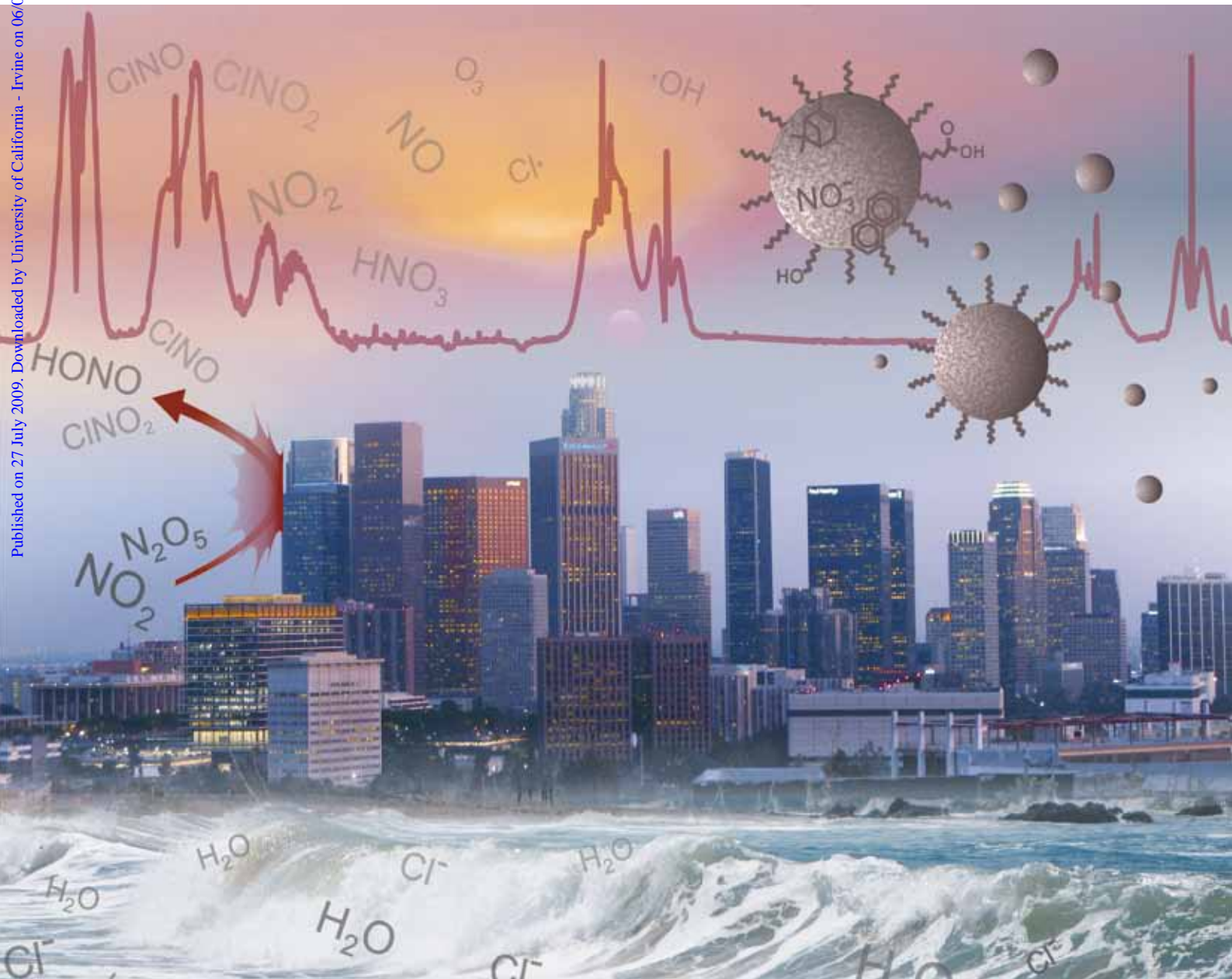
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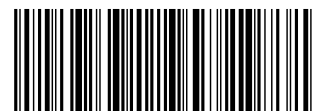


Themed Issue: Physical chemistry of aerosols

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COVER ARTICLE

Finlayson-Pitts

Reactions at surfaces in the atmosphere:
integration of experiments and theory**HOT ARTICLE**Herrmann *et al.*Laboratory chamber studies on the
formation of organosulfates from reactive
uptake of monoterpene oxides

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Reactions at surfaces in the atmosphere: integration of experiments and theory as necessary (but not necessarily sufficient) for predicting the physical chemistry of aerosols

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While particles have significant deleterious impacts on human health, visibility and climate, quantitative understanding of their formation, composition and fates remains problematic. Indeed, in many cases, even qualitative understanding is lacking. One area of particular uncertainty is the nature of particle surfaces and how this determines interactions with gases in the atmosphere, including water, which is important for cloud formation and properties. The focus in this Perspective article is on some chemistry relevant to airborne particles and especially to reactions occurring on their surfaces. The intent is not to provide a comprehensive review, but rather to highlight a few selected examples of interface chemistry involving inorganic and organic species that may be important in the lower atmosphere. This includes sea salt chemistry, nitrate and nitrite ion photochemistry, organics on surfaces and heterogeneous reactions of oxides of nitrogen on proxies for airborne mineral dust and boundary layer surfaces. Emphasis is on the molecular level understanding that can only be gained by fully integrating experiment and theory to elucidate these complex systems.

Introduction

The term “aerosol” is formally defined as a mixture of particles suspended in a gas.¹ While “aerosol” is more commonly used in the atmospheric chemistry literature to refer to only the particles, the strict definition is really more

appropriate because of the important and complex interactions that occur between gases and particles in air. Some of this interplay between the gaseous and condensed phase will be highlighted in this “perspectives” article, with an emphasis on processes occurring at the interface between the two.

Particles play a central role in the health effects of air pollution.^{2–5} They have been linked to increased mortality since at least the 1930s,^{6,7} and more recently associations with cardiovascular disease, lung cancer and asthma have been identified.^{3–5,8} In addition, they scatter light and reduce visibility which results in negative radiative forcing, *i.e.*, cooling, while absorption of light by soot and other components gives a positive radiative forcing, *i.e.*, warming.^{9,10} Particles also have an indirect effect on climate *via* changing cloud properties such as the number, concentration and size distribution of cloud droplets, which changes their light scattering (albedo), their lifetimes and precipitation rates.^{11–21} For example, changes in the number and size of cloud droplets downwind of ship plumes has been well documented.^{22–27} As seen in Fig. 1, particles have been identified by the Intergovernmental Panel on Climate Change⁹ as responsible for the greatest uncertainty in quantifying the impact of particles on radiative forcing and climate. Finally, particles play a central role in atmospheric chemistry of both the troposphere and stratosphere. A dramatic example is the “ozone hole” formation in the Antarctic due to the generation of chlorine and bromine atom precursors through heterogeneous reactions of gases such as ClONO₂ and N₂O₅ with HCl on the surfaces of polar stratospheric clouds.^{28–31}

Studying atmospheric processes associated with particles presents unique challenges compared to reactions in the bulk gas or condensed phases. First, not only the chemical but also

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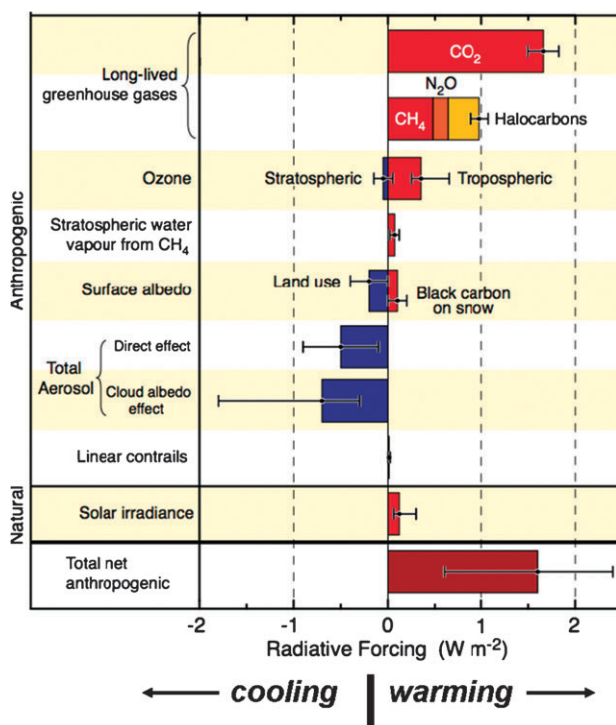


Fig. 1 Estimates of radiative forcing by atmospheric gases and particles, with estimated uncertainties, and the net anthropogenic contribution. Note that most of the uncertainty in the net forcing comes from that associated with aerosols. From ref. 9.

the physical properties of particles play an important role in their impact and in their interactions with gases. For example, particles with diameters in the 0.1–1 μm size range are most efficient per unit volume at scattering visible light.¹ The efficiency of deposition of particles in the lung is also strongly dependent on the particle diameter, with the smallest particles reaching the pulmonary region.³² The increased particle number concentration in and downwind of polluted areas provides an increased number of nucleation sites, leading to a larger number of smaller cloud droplets which are not large enough to rain out.¹³ Smaller particles also tend to interact with gases differently than do bulk solids; for example, at 298 K bulk NaCl deliquesces at 75% relative humidity (RH), but for particles smaller than ~ 40 nm, the deliquescence RH increases, as does the efflorescence RH.^{33–43}

Second, the chemical composition of individual particles can vary significantly, even within one air mass. Before the advent of techniques for single particle analysis, it was uncertain if airborne particles were “externally” or “internally” mixed, *i.e.*, whether an ensemble of particles in air consisted of individual particles with single components or whether each particle contained a mixture. With the application of techniques such as transmission and scanning electron microscopy (TEM/SEM)^{44–46} and single particle mass spectrometry,^{47–53} it appears that in most cases, airborne particles are composed of complex internal mixtures of inorganics and organics, including high molecular weight material and oligomers.^{54–56} A further complicating factor is that even within one particle, there may be structural and chemical inhomogeneities, and these may determine their

chemistry. In any case, the complexity of the composition makes developing good model systems for laboratory studies challenging.

Third, a number of species undergo reversible exchange between the gas and particle phases as transport occurs in the atmosphere. For example, NH_4NO_3 in the condensed phase is in equilibrium with the gas phase $\text{HNO}_3 + \text{NH}_3$, and the partitioning is sensitive to both water vapor and temperature.¹⁰ Partitioning also occurs for semi-volatile organics, and this is believed to play a significant role in the formation of secondary organic aerosols (SOA).^{57–62} Indeed, there may be a reservoir of such semi-volatile organics that are not currently measured in air but contribute to SOA formation.^{63–65} This would help to reconcile the difference between predicted SOA concentrations in air and the measured values, which can be as much as an order of magnitude greater than predicted.^{66,67}

Finally, it had been thought for many years that the uptake of gases into particles and their subsequent reactions in the condensed phase in the atmosphere could be treated in terms of well-known physical (*e.g.*, diffusion in the gas and liquid phases, mass accommodation at the surface) and chemical processes. Even this relatively simple picture is complicated by the dramatic differences in gas uptake that have been seen for surfactant-coated liquids where the coating can either enhance or inhibit gas uptake, or have no effect, depending on the specific gas/surfactant combination.⁶⁸ In addition, there is increasing evidence that the interface between the gas and condensed phases does not simply represent an inert “barrier”, but rather presents an opportunity for unique chemistry to occur.

Reactions at interfaces become increasingly important as the size of the particle decreases. For example, Table 1 summarizes for particles of different diameters the percentage of molecules in the particle that are on the surface for a typical particle density of 1.2 g cm^{-3} , a chemical composition with average molecular mass of 300 g mol^{-1} , and assuming for one monolayer an area per molecule of $2 \times 10^{-15} \text{ cm}^2$. Only 1% of the molecules in the particle are on the surface for a $1 \mu\text{m}$ diameter particle but 25% for a 50 nm particle. At 3 nm, the smallest size measurable by commercially available systems at present, 100% of the molecules in the particle are on the surface! Indeed, in the latter case, the particle might best be thought of as a molecular cluster. Interface chemistry thus becomes increasingly important for nanoparticles.

This area of chemistry and photochemistry at interfaces in the atmosphere is the focus of this article. Reactions at interfaces, particularly solid–gas interfaces, historically have been the purview of surface science which has provided detailed molecular level insights into processes at interfaces. Such studies have typically been carried out under high vacuum conditions in the absence of water vapor and oxygen/air, and with only one or a few gases present to interact with the surface. However, atmospheric interfaces are typically present in relatively high pressures of air containing water vapor and a complex mixture of organic and inorganic gases which compete for the surface sites and potentially alter the chemistry. Finally, there are trade-offs between studying simple model systems that provide molecular level insights but

Table 1 Percentage of molecules on the surface of particles as a function of size^a

Particle diameter (μm)	Volume per particle (cm ⁻³)	Total number of molecules	Surface area per particle (cm ²)	Number of molecules on surface	Percentage of molecules on surface
1.0	5.2×10^{-13}	1.3×10^9	3.1×10^{-8}	1.6×10^7	1.2
0.5	6.6×10^{-14}	1.6×10^8	7.9×10^{-9}	3.9×10^6	2.5
0.1	5.2×10^{-16}	1.3×10^6	3.1×10^{-10}	1.6×10^5	12
0.05	6.6×10^{-17}	1.6×10^5	7.9×10^{-11}	3.9×10^4	25
0.003	1.4×10^{-20}	34	2.8×10^{-13}	34	100

^a Assuming a spherical liquid particle with a bulk density of 1.2 g cm^{-3} and that this applies even at the smallest sizes, an average molecular mass of 300 and a surface concentration of $5.0 \times 10^{14} \text{ molecules cm}^{-2}$.

may not capture synergistic interactions that occur in the complex atmospheric milieu *versus* studying complex systems more representative of the atmosphere, but which are sufficiently complicated that extracting molecular level insights is difficult.

Given these complexities, combining theory and experiments becomes essential for obtaining detailed understanding of processes associated with atmospheric aerosols. Ultimately, the insights obtained through laboratory studies must be integrated into computer models of the atmosphere. Such models are sufficiently large and complex that the chemistry of aerosols must be parameterized. However, in order to develop accurate parameterization of aerosol processes in atmospheric models, it is critical to first understand the fundamental physical chemistry that occurs in and on particles.

One would ideally like to carry out experiments using concentrations that are relevant to the atmosphere, *e.g.* for gases, in the part-per-billion (ppb, parts per 10^9 v:v) and parts per trillion (ppt, parts per 10^{12} v:v) range. Reliably generating and measuring such concentrations and their reaction products is a challenge. In addition, the possibility of interference by unrecognized contaminants becomes more problematic as the reactant concentrations are lowered. For example, complete conversion of only 1 ppb of a gas with molecular mass 300 g mol^{-1} to the condensed phase would give a mass concentration of particles of 12 μg m^{-3} !

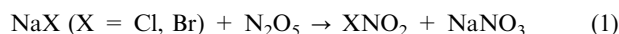
However, if the fundamental physical chemistry can be elucidated at higher concentrations in laboratory studies, extrapolation to atmospheric conditions can be made with confidence. For example, rate constants and mechanisms for reactions of the OH free radical, which drives atmospheric chemistry, have been determined in numerous studies over decades using concentrations of both OH and the second reactant that are orders of magnitude greater than found in the atmosphere. However, once the fundamental chemistry is understood, the kinetics and mechanisms derived from such studies can be incorporated into atmospheric models with confidence.

This “perspectives” article is not intended to be a comprehensive review of the area, but rather a personal outlook on some chemistry occurring at the interface between air and condensed phases that is of potential importance in the atmosphere. For recent collections of papers on the subject of reactions at interfaces, the reader is referred to selected issues of *Chemical Reviews*⁶⁹ and the *Journal of Physical Chemistry C*.³⁵¹ Four areas of current interest in the author’s

laboratory are considered here, with examples drawn primarily from our work: (1) reactions of sea salt particles; (2) photochemistry of nitrate and nitrite ions at interfaces; (3) oxidation of surface organics; and (4) heterogeneous reactions of oxides of nitrogen on surfaces that are models for mineral dust particles and boundary layer surfaces. The critical need to integrate experiments and theory in order to obtain molecular level insights into atmospheric reactions is emphasized. Apologies are offered in advance for the omission of many other important areas relevant to aerosols in the atmosphere and much outstanding work that is not within the scope of this article.

Chemistry at the interface of sea salt particles

The key role of halogen atoms from chlorofluorocarbons in ozone destruction in the stratosphere was recognized about 30 years ago.^{70,71} In the troposphere, the oceans provide a large source of halogens, particularly chlorine and bromine, but they are in the form of dissolved ionic salts rather than highly reactive gas phase atoms. Sea salt becomes airborne in the form of particles formed by wave action,^{72–74} and they can travel significant distances inland,⁷⁵ interacting with other atmospheric constituents as they are transported. This has the potential to convert halide ions into photochemically active products that photolyze to generate halogen atoms, and indeed a number of such reactions have been identified (*e.g.*, Fig. 2 for $X = \text{Cl}^-$):



The halogen products in each case absorb light in the actinic region above 290 nm, yielding highly reactive halogen atoms.

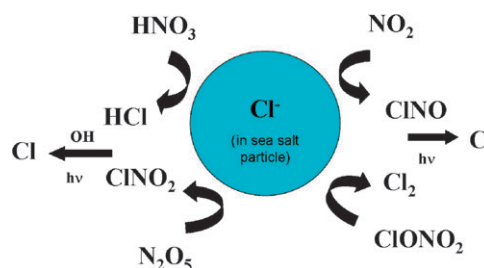
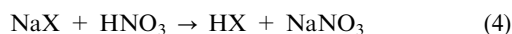
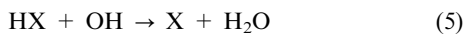


Fig. 2 Summary of reactions of chloride ions in sea salt particles with trace gases to generate chlorine atoms in air.

Nitric (and sulfuric) acid also reacts with sea salt to generate the hydrogen halide acids,

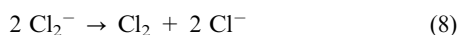
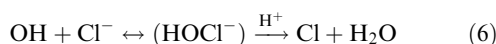


which can be converted to halogen atoms *via* reaction with OH:

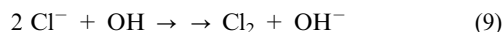


For the case of deliquesced sea salt particles, uptake of the reactant gases into the salt solution followed by reaction with the halide ions can be treated conventionally by including the separate steps: (1) diffusion to the particle surface; (2) mass accommodation; (3) reaction in the liquid with kinetics and mechanisms taken from studies using bulk liquid phases; and (4) diffusion of the volatile products back into the gas phase.

However, it is now clear that a number of reactions do not require mass accommodation, but rather, occur at the interface itself in parallel with uptake and reaction in the bulk. For example, oxidation of dissolved Cl^- by the OH free radical can occur at the air–water interface, with kinetics and mechanisms that are quite different from the reaction in the bulk aqueous phase. In the latter case, an acid is required.⁷⁶



In the case of the interface reaction, not only is acid *not* required, but TOF-SIMS measurements^{77,78} show that the overall reaction generates hydroxide ions:



The interface reaction is very fast, with a lower limit of $\gamma = 0.1$ for the reaction probability.⁷⁹ This is faster by about two orders of magnitude than the reaction of OH with solid NaCl.^{80–83} Experimental evidence for this interface reaction was based primarily on much greater (by a factor of $\sim 10^3$) gas phase Cl_2 production than could be quantitatively predicted by treating uptake and reaction of OH by the conventional mechanism. However, the exact mechanism remains to be elucidated. Based on theoretical calculations,⁸⁴ a likely mechanism involves formation of a $(\text{OH} \cdots \text{Cl})^-$ hydrogen-bonded complex, followed by its reaction with a second chloride ion to generate $\text{Cl}_2^- + \text{OH}^-$; electron transfer from Cl_2^- to an incoming OH then generates Cl_2 .

This is a prime case where theory has provided new insights and support for interface chemistry. Clearly, such a mechanism is not feasible unless chloride ions are available for reaction at the interface. While chloride ions had been proposed to reside on the surface of small water clusters if their polarizability was taken into account,^{85–88} the presence of halide ions at the surface of bulk solutions was not generally recognized, although there was some indirect evidence. For example, Hu *et al.*⁸⁹ had proposed that the unusually fast uptake measured for Cl_2 and Br_2 on solutions containing I^- and Cl^- was caused by a contribution of a reaction at the interface. However, molecular dynamics (MD) simulations^{90–97}

of solutions of NaX where $\text{X} = \text{F}^-$, Cl^- , Br^- and I^- (Fig. 3) showed that while F^- prefers to be fully solvated in the bulk, the other ions are increasingly present at the interface as one proceeds down the series, which has also been predicted in theoretical studies using a partitioning model.⁹⁸ Oxidants such as OH and O_3 are also predicted to be stable at the interface,^{99–101} increasing the interface reactivity.

The MD predictions have since been confirmed experimentally using high pressure X-ray photoelectron spectroscopy (XPS), in which enhancement of bromide and iodide ions was seen on deliquesced salt surfaces, but fluoride was not.^{102–105} Second harmonic generation spectroscopy experiments¹⁰⁶ support enhancement of I^- at the interface, and electrospray ionization mass spectrometry of salt solutions also suggests enhancement of Cl^- , Br^- and I^- ions in the surface layer.¹⁰⁷ Vibrational sum frequency spectroscopy of aqueous salt solutions show changes in the interfacial water by the addition of alkali halide salts, although the interpretation in terms of enhancement of interfacial ion concentrations is not as direct.^{108–110}

In light of the MD simulations, surface reactions of Br^- and I^- would be expected to be even more important than in the

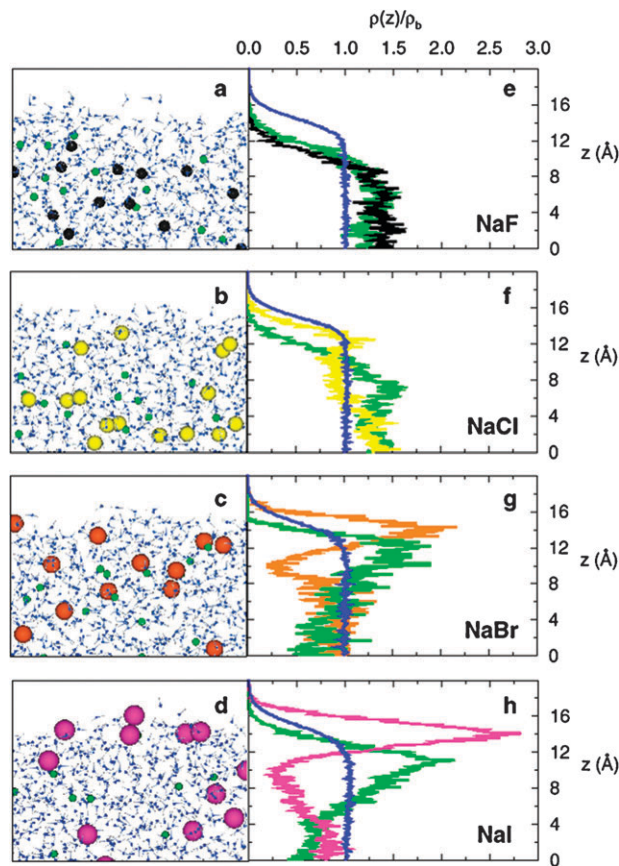


Fig. 3 Results of molecular dynamics simulations of the sodium halides (18 ion pairs of each) in a slab containing 864 water molecules. This is equivalent to 1.2 M solutions of the salts. The left panels are a side view of the slab showing typical snapshots of the dissolved salts. The right panels show the number density profiles for O atoms in water, and the F^- , Cl^- , Br^- and I^- ions (scaled for clarity), respectively. The zero point corresponds to the center of the slab and the interface region can be seen by the drop-off in the water O-atom density. From ref. 90.

case of Cl^- . A significant complication in probing these reactions is that the increased reactivity of bromide and iodide ions in bulk solution in many cases overshadows the interface chemistry. Thus, while OH is likely to react with these halide ions at the interface, the uptake into the bulk followed by oxidation sets off a rapid series of chain reactions that generates gas phase Br_2 and a so-called “bromine explosion”^{111,112} that quickly overwhelms the interface chemistry.^{113,114} In contrast, the interface oxidation of Br^- by O_3 does make a significant contribution to the formation of Br_2 in the dark.^{115–117}

Despite the progress on understanding the structure of salt solutions and the impacts on reactivity, much remains speculative. For example, the $(\text{OH} \cdots \text{Cl})^-$ complex proposed at the interface has not been observed, and the mechanism by which such a complex forms gaseous Cl_2 is not confirmed. In addition, most of the studies demonstrating the importance of interface reactions have been carried out on simple model systems in which NaCl is used to represent the major chloride salt in seawater. However, sea salt is a complex mixture (Table 2) that contains hygroscopic salts such as $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.^{118,119} As a result, even at low relative humidity, the surface of sea salt particles has a liquid layer that is concentrated in the least soluble salts such as those associated with magnesium.^{119,120} Surface reactions of such liquid layers can be quite different both in terms of kinetics and the mechanisms.¹²¹ For example, Park *et al.*^{83,122} observed that as the RH increased, the reaction probability for OH radicals on MgCl_2 and sea salt particles below their deliquescence points also increased. They attributed this to acidification of the surface *via* the reaction of Mg^{2+} with water to form $\text{MgOH}^+ + \text{H}^+$, followed by an acid-catalyzed $\text{OH} \cdots \text{Cl}^-$ reaction similar to that in bulk liquid solutions. Clearly, probing the acidity of such surfaces is also important.

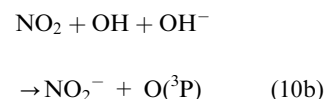
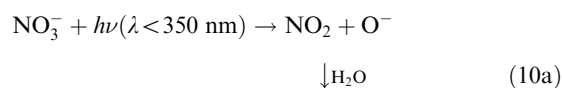
Finally, the effects of other species such as organics on the halide ion distribution and reactivity are not known. Frinak and Abbatt¹²³ studied the production of Br_2 from the reaction of OH with aqueous solutions containing chloride and bromide and showed that the Br_2 produced was decreased by about an order of magnitude when the surfactant sodium dodecyl sulfate was present. Krisch *et al.*¹²⁴ showed that the presence of an alcohol surfactant on the surface of an iodide salt diminished the surface propensity of the I^- ion compared

to the situation without the organic, although anions were still present in the interface region. A counterbalancing effect of lowered anion concentrations may be trapping of oxidants such as ozone in the organic chains of the surfactants, which theory predicts leads to increased residence times and likelihood of reaction on the surface.¹²⁵ Clearly, there is a great deal more to be learned about both the physical and chemical properties of such complex systems.

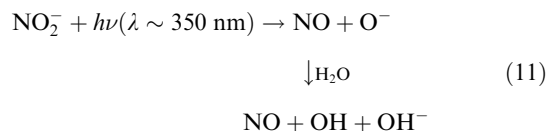
Nitrate and nitrite ion photochemistry

Nitrate ions are ubiquitous components of airborne particles because of the conversion through a number of reactions of NO_x ($\text{NO}_x = \text{NO} + \text{NO}_2$) emitted from fossil fuel combustion to HNO_3 .¹⁰ Nitric acid reacts with NH_3 to form particulate NH_4NO_3 .¹⁰ In addition, HNO_3 can be taken up into particles as the acid and react to form particulate nitrate. For example, it is well known that HNO_3 is taken up into sea salt particles, degassing chloride as HCl when the particles become sufficiently acidic, leaving behind NO_3^- .^{126–136} For many years, nitrate was regarded as the end-product of NO_x oxidation, with removal *via* wet and dry deposition. However, with the discovery of very active photochemistry in the polar snowpacks^{137,138} and the finding that reactive oxides of nitrogen such as HONO, NO and NO_2 were being generated in the process, came the realization that nitrate ion photolysis may be an important initiator of this chemistry.^{139–154}

Nitrate ions have a well-known and rich photochemistry^{139,155,156} in solution that is recognized to generate NO_2 and nitrite ions:



Nitrite ions formed in reaction (10b) also photolyze to generate $\text{NO} + \text{O}^-$ and hence OH radicals:^{155,156}



An intriguing issue is whether this photochemistry is different at the air–water interface compared to the bulk. Photolysis of ions such as nitrate and nitrite in bulk solution tends to be inefficient because of the effect of the solvent cage which holds the fragments formed in close contact, increasing their recombination rate. For example, the overall quantum yields for reaction (10a) and (10b) at room temperature are only ~ 0.01 and 0.006, respectively in the actinic region above 290 nm. In contrast, photolysis of neutral species tends to be much more efficient; for example photolysis of HONO in solution has a quantum yield of 0.35 at 295 K¹⁵⁷ and 0.18 at 274 K,¹⁵⁸ compared to 1.0 in the gas phase.¹⁰

There is increasing evidence, both theoretical and experimental, that the quantum yields for photolysis at interfaces are indeed significantly greater than in the bulk.^{159–168}

Table 2 Composition of seawater^a

Constituent	Mass in grams per kg of seawater	Moles per kg of seawater
Chloride	19.35	0.546
Sodium	10.76	0.468
Sulfate	2.71	0.0282
Magnesium	1.29	0.0532
Calcium	0.413	0.0103
Potassium	0.387	9.9×10^{-3}
Bicarbonate	0.142	2.3×10^{-3}
Bromide	0.067	8.4×10^{-4}
Strontium	0.008	9.1×10^{-5}
Boric acid	0.026	4.2×10^{-4}
Fluoride	0.001	5.3×10^{-5}

^a From ref. 118.

The simplistic view is that species at the interface are surrounded by half a solvent cage; ejection of one of the fragments into the gas phase prevents recombination that would normally occur. Yabushita *et al.*¹⁶⁷ reported the production of gas phase O(³P) with three different translational energies from photolysis of NO₃⁻ on ice at 193 nm; the fastest component was attributed to direct production from excited NO₃⁻ on the ice surface *via* reaction (10b). This was not detected for photolysis at 305 nm, however, which they suggested could be due to the smaller absorption cross sections as well as lower quantum yields for O(³P) formation at this longer wavelength. In a similar study,¹⁶⁶ they detected gas phase OH from nitrate ion photolysis, but the wavelength dependence suggested it was being produced by photolysis of surface H₂O₂ formed by recombination of the OH generated in reaction (10a) above.

Evidence for the production of gas phase OH by irradiation of aqueous NO₃⁻ also comes from the decay of the individual alkanes in a gaseous mixture of *n*-butane, *i*-butane and propane exposed to either pure NaNO₃ particles or to mixtures of NaNO₃ and NaCl on the walls of a TeflonTM chamber during irradiation at 306 nm.¹⁶⁹ Fig. 4 shows the measured ratio of *i*-butane to *n*-butane as a function of the ratio of *i*-butane to propane for the pure NaNO₃ case. As discussed by Jobson *et al.*,¹⁷⁰ the two butane isomers should decay at approximately the same rate if they are being removed by reaction with OH (solid line in Fig. 4). On the other hand, *i*-butane and propane should decay at the same rate if they are being removed by chlorine atoms which as discussed below, are formed during photolysis of chloride–nitrate mixtures (dotted line in Fig. 4). It is clear that the decay for pure NaNO₃ matches that expected for OH. In addition, the decay rates were quantitatively matched by assuming that OH was injected into the gas phase from nitrate ion photolysis.

The enhancement of quantum yields at interfaces has a number of potential atmospheric implications. For example, if oxidants such as OH and O(³P) are formed in the interface region where there is a potential well,^{100,101,171} they could initiate the oxidation of adsorbed organic compounds. There is, indeed, evidence for such a process. Irradiation of sodium nitrate particles on the walls of a TeflonTM chamber in the

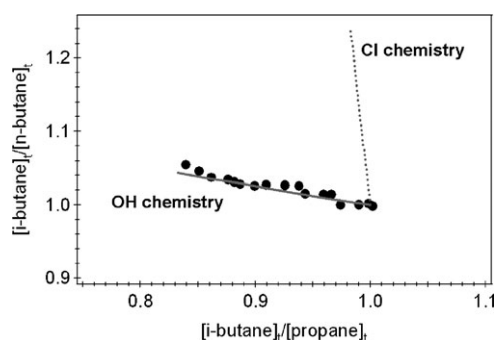


Fig. 4 Ratio of *i*-butane to *n*-butane versus the ratio of *i*-butane to propane in a TeflonTM chamber coated with NaNO₃ deliquesced particles and irradiated using broadband lamps centered at 306 nm. The solid line is a model prediction assuming oxidation of the alkanes by OH. Oxidation by chlorine atoms in NaCl:NaNO₃ mixtures would follow the dotted line. From ref. 169.

presence of α -pinene in air at sufficiently high relative humidities to deliquesce the particles resulted in generation of gas phase NO₂ as expected.¹⁷² NO₂ also photolyzes in this system, generating O₃ and probably OH and NO₃ as well. The α -pinene was oxidized and a variety of gas and particle products were formed. However, the loss of the pinene was significantly larger than measured in comparable experiments with NO₂ alone,¹⁷³ while the yields of gas phase products were significantly smaller. In addition, organic products such as pinonic and pinic acids and *trans*-sobrerol were observed in the wall washings only when NaNO₃ was present. Support for this being an interface process was provided by molecular dynamics simulations which showed that α -pinene has a significant residence time, at least a nanosecond, on the surface of a concentrated NaNO₃ solution.¹⁷² The generation of *trans*-sobrerol is particularly interesting in that it is a product of the oxidation of α -pinene by O(³P), which is one of the products of NO₃⁻ photochemistry, reaction (10b) above. It is also formed in small (\sim 3%) yield in the ozone reaction.^{174–176}

Nitrate ions in air exist in complex mixtures rather than a simple concentrated solution of NaNO₃, and there is increasing evidence that the photochemistry is dependent on the other species in solution. For example, as discussed above, nitrate ions are often present in sea salt particles due to their reaction with HNO₃, giving mixtures that have varying amounts of Cl⁻ and Br⁻ present as well. There is experimental evidence that NO₃⁻ photolysis is enhanced by the presence of Cl⁻ and Br⁻ ions. Thus, the production of gas phase NO₂ by photolysis of deliquesced NaNO₃ particles on the walls of a TeflonTM chamber was followed as the NaNO₃ was replaced to varying extents by NaCl. Surprisingly, as seen in Fig. 5a, the NO₂ generated per NO₃⁻ ion in the particles *increased* as the fraction of chloride ions increased!¹⁷⁷ Again, MD simulations provide key molecular insights into why this is the case. Fig. 5b and c show the results of MD simulations that predict that the surface chloride ions pull nitrate ions closer to the interface *via* formation of a double layer with Na⁺ which attracts NO₃⁻.¹⁷⁷ Since the quantum yield for NO₂ production in pure nitrate solutions at wavelengths above 300 nm is only \sim 0.01,^{139,155,156} even a relatively small shift in nitrate towards the surface could cause a significant increase in the efficiency, as is observed. Thus, theory again provided molecular level insight into what was initially a surprising experimental result.

Predicting the surface propensity of nitrate ions has been challenging. Initial MD simulations¹⁷⁸ suggested that NO₃⁻ in aqueous solutions would prefer the air–water interface while subsequent studies^{179–181} indicated it prefers bulk solvation, for which there is recent experimental evidence.^{182,183} A partitioning model predicted that nitrate ions would be equally distributed between the surface and the bulk,⁹⁸ while electrospray ionization mass spectrometry studies of salt solutions that nitrate ions have a propensity for the interface.¹⁰⁷ More recent theoretical studies¹⁸⁴ show that the surface *versus* bulk propensity actually depends on the amount of water; in clusters up to \sim 300 water molecules, nitrate prefers the interface but in larger quantities approximating bulk liquid, it is predominantly solvated in the bulk. This suggests that nitrate ion photochemistry at interfaces will become more

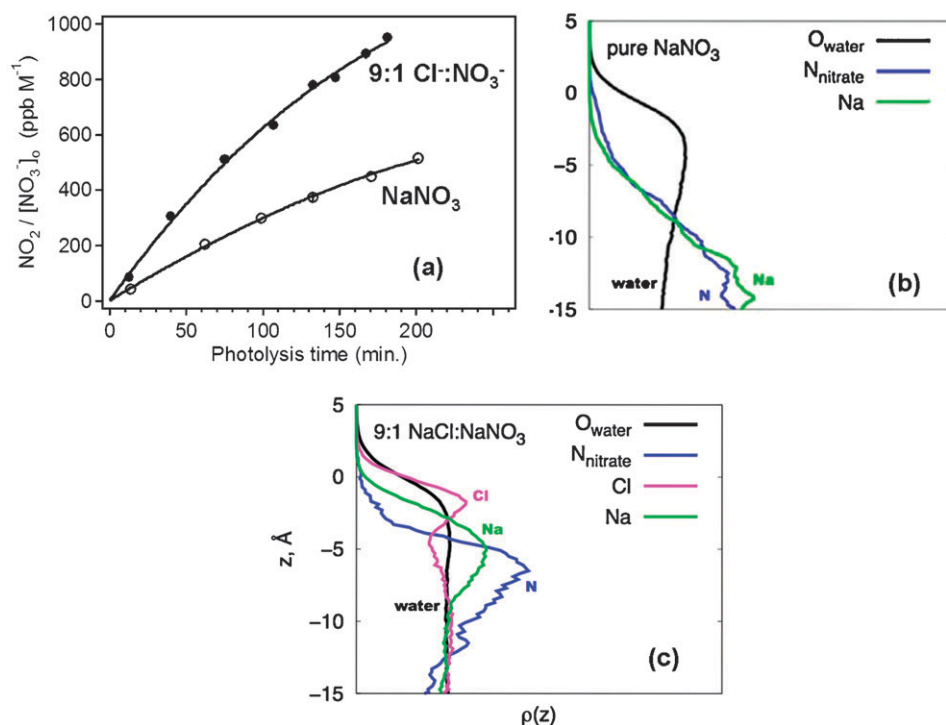


Fig. 5 (a) Gas phase NO_2 generated per nitrate ion in the photolysis of deliquesced NaNO_3 particles using broadband lamps centered at 306 nm. The closed circles are data from a 9:1 $\text{NaCl}:\text{NaNO}_3$ mixture and the open circles from pure NaNO_3 ; (b) molecular dynamics predicted density profiles for the water oxygen and nitrate ion nitrogen as a function of distance in a slab with 864 water molecules and 86 NaNO_3 molecules; (c) same as (b) but with 65 Cl^- , 7 NO_3^- and 72 Na^+ atoms to give a 9:1 ratio of Cl^- to NO_3^- . From ref. 177.

important as the particle size decreases as expected from the data in Table 1, and may contribute to the observation of nitrogen along with organics in the smallest particles whose chemical composition can currently be measured.¹⁸⁵

An additional factor in the photochemistry of nitrate, and likely other ions that absorb in the actinic region, is that the absorption spectra may depend on the concentration. For example, Grassian and coworkers observed a shift in the absorption spectra of NaNO_3 and $\text{Ca}(\text{NO}_3)_2$ as a function of concentration, and the quantum yield for photolysis of $\text{Ca}(\text{NO}_3)_2$ was also shown to decrease with increasing salt concentration.^{186,187}

Because photolysis of nitrite ions generates OH radicals, reaction (11) above, similar oxidation of adsorbed organics would be expected during irradiation of particles containing NO_2^- , and this has indeed been observed.^{188,189} In this case, a phospholipid, 1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine (OPPC), was adsorbed on a dilute (0.4 wt%) $\text{NaNO}_2/\text{NaCl}$ salt solid mixture and the loss of nitrite and OPPC and the formation of organic products followed with time using diffuse reflection infrared Fourier transform spectrometry (DRIFTS).¹⁹⁰

In the absence of added water vapor (but some strongly adsorbed water remains on the salt and zwitterionic end of OPPC), products due to O^- attack on the OPPC were observed, particularly carboxylates, $\text{RC}(\text{O})\text{O}^-$, to which the 1580 cm^{-1} peak was assigned (Fig. 6). This is expected from reaction (11) above since water is not readily available to convert all of the O^- to OH radicals. However, as seen in Fig. 6, on addition of water vapor, the product distributions shifted to those characteristic of OH attack on OPPC, such as a hydroxy

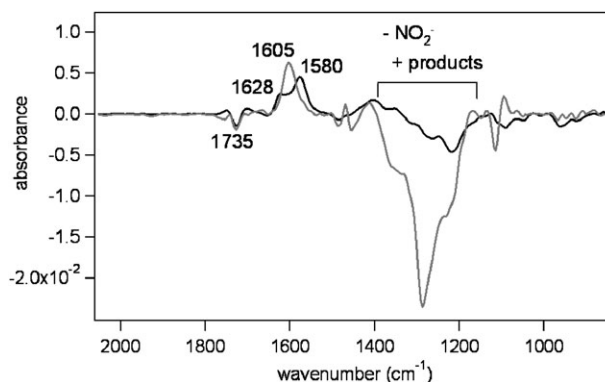


Fig. 6 Diffuse reflection infrared Fourier transform (DRIFTS) spectra of a mixture of $\text{NaNO}_2/\text{NaCl}$ coated with 1-oleoyl-2-palmitoyl-*sn*-glycero-3-phosphocholine (OPPC) after 90 min of UV photolysis in air at $\sim 15\%$ RH (gray line) and at $\sim 0\%$ RH (black line). The y axis is $\log_{10}(S_1/S_2)$ where S_1 and S_2 are the single beam spectra of OPPC/ $\text{NaNO}_2/\text{NaCl}$ before and after photolysis, respectively. From ref. 189.

organic nitrate (1605 cm^{-1}). This identification was confirmed using matrix assisted laser desorption ionization mass spectrometry (MALDI-MS).

In this system, water vapor not only converts the chemistry from reactions of O^- to OH, but also plays a role in enhancing product yields due to increased ion mobility on the surface of the salts. It is well documented that passivation of such salt surfaces occurs during reactions with gases, which effectively terminates chemistry of the parent surface ions.^{191–196} For

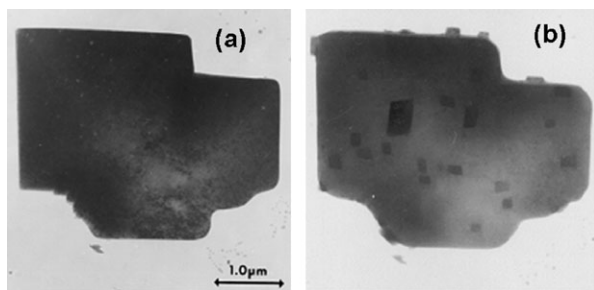


Fig. 7 TEM images of NaCl (a) before exposure to gaseous HNO_3 and (b) after exposure to $1.2 \times 10^{15} \text{HNO}_3 \text{ cm}^{-3}$ for 15 min followed by exposure to water vapor (<15 Torr). From ref. 192.

example, Fig. 7a shows the TEM image of an unreacted single crystal of NaCl. Reaction with gaseous HNO_3 generates a surface that looks similar in morphology to the unreacted crystal.¹⁹² In reality, the NaCl has a thin coating of sodium nitrate. Upon exposure to water vapor, the surface ions are mobilized and microcrystallites of NaNO_3 form on the NaCl (Fig. 7b). In the case of NaNO_2 , photolysis generates O^- which in the presence of water, forms OH and OH^- . The surface is thus converted from NaNO_2 to NaOH during the reaction. Water mobilizes the surface ions, bringing fresh NO_2^- to the surface for further reaction. This increases the extent of reaction, which is clearly seen in Fig. 6 where the loss of the band around 1300 cm^{-1} due in part to NO_2^- (with overlapping product peaks) is much larger in the presence of water vapor.

The effect of water vapor in this system is a good illustration of the importance of studying atmospherically relevant reactions in the presence of water vapor and air, which can alter not only the reaction mechanisms but also the extent of reaction and product yields.

Oxidation of surface organics

The formation and fate of secondary organic aerosols (SOA) is an area of intense research interest at present, with a very large number of papers appearing in the literature reflecting this activity. For example, there are hundreds of papers on formation of SOA from α -pinene alone. While a comprehensive treatment of SOA is outside the scope of the present article, understanding reactions at interfaces and interactions of the surfaces with water vapor are important challenges for understanding the formation, fate and role of SOA.

As one example, it has been generally accepted that oxidation of the surface of hydrophobic organic particles would lead to the formation of polar functionalities, increasing the hydrophilicity of the surface. This is certainly consistent with chemical intuition. However, there is increasing evidence that oxidation does not necessarily generate a more hydrophilic surface. Developing a molecular level understanding of the oxidation processes, the nature of the surface functional groups and their interaction with water and trace gases, is therefore a critical part of being able to predict the ability of such particles to act as ice and cloud condensation nuclei (IN, CCN) and hence affect climate through the indirect effect. Even in the event they do not act as IN or CCN, water uptake can change the particle size and hence their light scattering

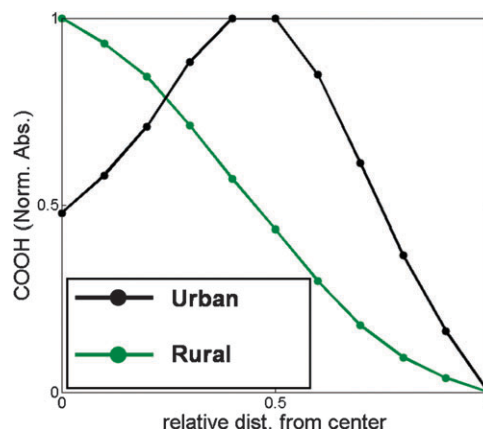


Fig. 8 Carboxylic acid groups measured by STXM in particles collected in urban Mexico City and in a rural area as a function of distance from the center of the particles. These polar groups are seen to be concentrated at or towards the center of the particles, rather than on the surface. Figure graciously provided by Ryan Moffet and Mary Gilles from ref. 198.

properties.¹ Finally, it is the surface of particles that first interacts with biological systems such as the lung, and their uptake and toxicology may therefore depend at least in part on the nature of the particle surface as well as its overall composition.

A significant challenge in probing surface properties of SOA is the lack of appropriate analytical techniques to identify and measure a broad range of individual organic components of single particles in real time.^{47,52} Ideally, one would like to peel the particle apart like an onion, probing the specific organic components and functional groups, particularly those on the surface, and do so in real time. Promising advances for 3-D analysis of collected samples have been made using techniques such as scanning transmission X-ray microscopy (STXM).¹⁹⁷ Fig. 8, for example, shows a plot of the relative amounts of carboxylic acid groups as a function of distance from the center of the particles collected in Mexico City.¹⁹⁸ The $-\text{COOH}$ groups are seen to be concentrated in the center of the particle for the rural sample, and midway between the center and surface for the urban sample, indicating differences in the processes leading to their formation. However, the fact that the carboxylic acid groups are not found on the surface of the particles indicates that they may be hydrophobic, despite the presence of polar, oxygenated groups. Similar results have been observed for aggregates formed on surfaces when alkene SAMs are ozonized (see below).¹⁹⁹

While sophisticated particle mass spectrometry techniques are undergoing continuing development, achieving this level of detail in real time will require much more research. However, such a capability will provide enormous molecular level insights into the formation and fate of SOA, as well as their impacts on visibility, health and climate.

In the absence of such techniques, model systems for organics on surfaces have been studied.^{200,201} Some involve relatively thick (several μm) organic films on solid substrates, while others use monolayers on liquid solutions or on solid substrates.^{200–230} Self-assembled monolayers (SAMs) are particularly appealing as a model system because there are

well-established techniques for forming and characterizing them,^{231–237} and in principle, their chemistry should be less complex and therefore more amenable to obtaining detailed molecular level insights.

SAMs formed by reaction of trichloroalkylsilanes on SiO_x surfaces, for example on the thin oxide layer on silicon, may be particularly relevant to reactions of organic compounds on dust and on building materials for which silicates can be major components.^{208,238–244} Another advantage is that silicon crystals are readily available which can be used to make real-time measurements of the oxidation of SAMs attached to their surface using attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. In one study,²²¹ ozonolysis of terminal alkene SAMs with 3- and 8-carbon atoms was observed to give C=O groups as products as expected, at least a portion of which were in the form of carboxylic acids that could be converted to carboxylates by reaction with gaseous NH_3 . The measured kinetics of formation of the C=O groups suggested a Langmuir–Hinshelwood (L–H) mechanism in which ozone first adsorbed to the SAM surface and subsequently reacted with the double bond in competition with desorption back to the gas phase. This results in calculated decreasing overall reaction probabilities with increasing ozone concentrations. MD simulations predicted that O_3 has a significant residence time on the surface, effectively having multiple encounters with the surface during one “collision”. However, the experimentally derived lifetime for O_3 on the surface assuming L–H kinetics was $\sim 10^{12}$ orders of magnitude larger than the theoretical calculation, ~ 7 s vs. 17 ps!

Interestingly, the reactions of ozone with a number of other surface-bound organics which are chemically dissimilar have also been observed to have kinetics consistent with a L–H mechanism. This includes reactions with soot,^{245,246} benzo[*a*]pyrene on soot,²⁴⁷ polycyclic aromatic hydrocarbons at the air–water interface^{207,211,213,214} chlorophyll at the air–water interface²⁴⁸ and aqueous salt aerosols containing oleate.²⁴⁹

More recently, the ozonolysis of the 8-carbon alkene SAM has been revisited using ZnSe and SiO_x -coated ZnSe ATR crystals.²⁵⁰ SAMs on ZnSe are not nearly as well characterized as those on silicon,^{251–253} but have the advantage that ZnSe transmits down to $\sim 650\text{ cm}^{-1}$, well beyond the $\sim 1500\text{ cm}^{-1}$ cut-off for the silicon ATR crystal. This allows one to probe for additional products that absorb below 1500 cm^{-1} . Fig. 9 shows a typical difference spectrum after O_3 oxidation of the C8 alkene SAM. This spectrum is obtained by ratioing the single beam spectrum after reaction to that just before the addition of O_3 , so that product peaks are positive and reactant peaks negative. In addition to the expected product peak due to C=O in the $1700\text{--}1750\text{ cm}^{-1}$ region, strong peaks at 1110 cm^{-1} and 1385 cm^{-1} are observed, which are attributed to the secondary ozonide (1,2,4-trioxolane, SOZ). The derivative shape in the C–H stretching region (Fig. 9, inset) is due to overlap of negative bands from the parent SAM as reaction occurs and the formation of positive bands from products that are slightly shifted. Correction for the loss of the parent SAM peaks in the $2800\text{--}3000\text{ cm}^{-1}$ region reveals new product peaks at 2860 and 2929 cm^{-1} (not shown), and these are also assigned to the SOZ. The magnitudes of the

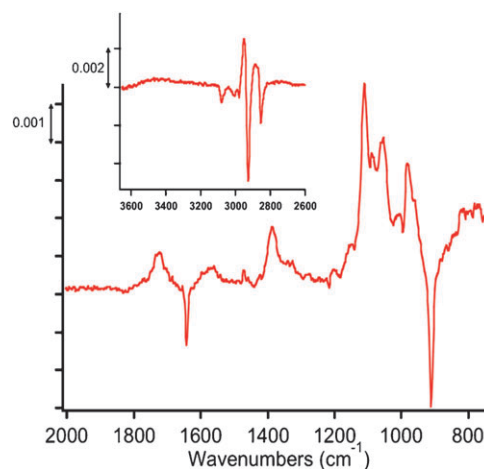


Fig. 9 Ratio of infrared spectrum after to before reaction of a C8 alkene SAM on a ZnSe crystal with $2.9 \times 10^{13}\text{ O}_3$ per cm^3 for 118 min. From ref. 250.

product peaks suggest that SOZ may indeed be the major reaction product, but its characteristic peaks could not be observed in earlier studies due to the cut-off of the silicon ATR crystal.

On ZnSe, the initial rate of SOZ formation increased linearly with the O_3 concentration to a concentration of $\sim 1 \times 10^{14}\text{ cm}^{-3}$, the highest concentration for which meaningful kinetics data could be obtained. This is inconsistent with a L–H mechanism. There are several possible explanations for this. First, there was evidence for some multilayer formation on the ZnSe ATR crystal, which may be partly responsible for significantly more scatter in the kinetics data than is the case using a silicon ATR crystal where monolayer formation is well characterized.^{231–237} Second, it may be that the mechanism of formation of C=O is not, indeed, L–H but rather a more complex one that leads to a similar parameterization of the rate data. Given the lack of a convincing mechanism that would lead to L–H kinetics for the disparate surfaces for which it has been suggested, it is clear that much more remains to be understood at a molecular level about the interaction of O_3 , and likely of other oxidants as well, with organics at interfaces.

An intriguing observation was made of the formation of irregular, porous aggregates when unsaturated SAMs on a silicon substrate were oxidized by O_3 .²²² Fig. 10a shows an atomic force microscope (AFM) image of one such aggregate. Clearly, cross-linking of the original SAM chains on the surface must have occurred *via* an as yet unknown mechanism. Fig. 10b shows the line scan across an aggregate made using Auger spectroscopy; the aggregate is clearly composed of carbon and oxygen. Fig. 10c shows the O/C ratio for one of the aggregates measured using secondary ion mass spectrometry (nanoSIMS) as a function of depth into the particle.¹⁹⁹ This ratio increases with depth into the particle, showing that oxygen-containing groups are on the interior, similar in concept to what was observed for particles collected in Mexico City (Fig. 8).

Thus, both airborne particles and the aggregates from ozonolysis of alkene SAMs may have hydrophobic surfaces,

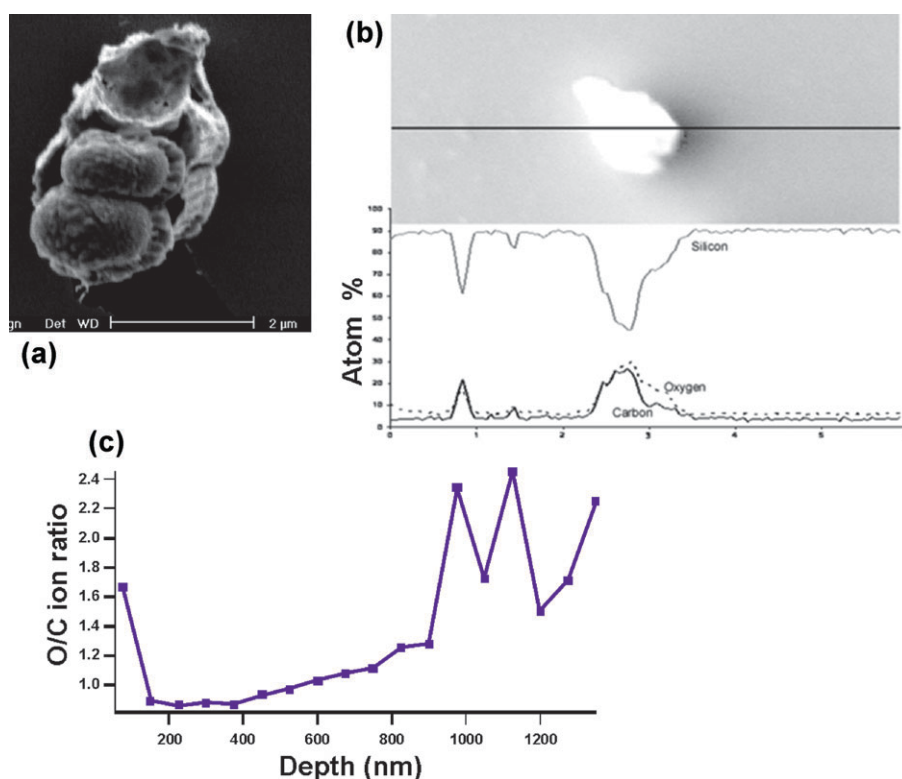


Fig. 10 (a) AFM of a typical organic aggregate formed by reaction of a C8 alkene SAM on a silicon substrate with $\sim 10^{13}$ O_3 per cm^3 for 40 min; (b) semi-quantitative measurements of elemental composition using Auger spectroscopy along a line scan for the particle shown in the top portion; (c) O/C ratio as a function of distance from the surface of the particle measured using nanoSIMS. Parts (a) and (b) are from ref. 222 and part (c) from ref. 199.

with the polar groups buried in the interior of the particles. This is very important from the point of view of interaction of particles with water vapor and their possible role as CCN. While bulk chemical analysis of such particles would suggest they were at least partially oxidized and hence might be expected to be hydrophilic, this is clearly not the case if the polar groups are not available at the surface. This again highlights the need for 3-D mapping of the chemical composition and structure of airborne particles.

There are an increasing number of observations that oxidation does not necessarily lead to more water uptake. For example, Voss *et al.*²⁵⁴ reported that oxidation of oleic acid formed volatile and/or water soluble species but the remaining coating was still hydrophobic. Similarly, a surprise in the SAM ozonolysis studies was that there was no significant change in water uptake on the SAM surface after oxidation compared to before oxidation.^{222,224} The same was true of the SAM surface after oxidation by KMnO_4 , which is known to form terminal carboxyl groups.²²⁴ The reasons for this are not clear, but could involve hydrogen-bonding between $-\text{C}(\text{O})\text{OH}$ groups on the surface so that they are not as available to hydrogen bond with water.^{255,256}

Finally, while there is yet much to be learned about the sources and composition of SOA in air, even less is known about the fates of SOA. Physical processes such as coagulation and deposition will certainly be important, but there is increasing evidence that chemical reactions^{257–261} and photochemistry^{229,230,262,263} also contribute.

Heterogeneous reactions of oxides of nitrogen on airborne dust particles and on boundary layer surfaces

Long-range transport of airborne dust particles has been documented for decades.^{127,264} While there are obvious impacts on visibility and climate, including their role as IN and CCN,^{265–267} it has been increasingly recognized that some interesting and important chemistry also takes place on their surfaces during transport.²⁶⁸ We shall focus here on the chemistry of oxides of nitrogen as a source of HONO, recognizing that other interactions such as those with O_3 and organics are also important in air.^{269–271} Additionally, there is evidence that dust and sea salt discussed earlier have some interesting interactions in air, including effects on particle size^{272,273} and uptake of chlorine gases from sea salt on dust particles.^{274,275}

It is important to note that similar chemistry is expected to occur on boundary layer surfaces, and indeed, such chemistry may be more important close to the earth's surface than that on airborne particles. For example, in the first 38 m closest to the Earth's surface (corresponding to a typical boundary layer bin in airshed models),^{276–278} the surface area of particles in a $1 \text{ cm} \times 1 \text{ cm} \times 38 \text{ m}$ volume is 0.3 cm^2 for $0.5 \mu\text{m}$ diameter particles at a concentration of 10^4 particles cm^{-3} . This is less than the 1 cm^2 area provided by the box at the earth's surface, and indeed the latter is a lower limit since it does not take into account soil porosity, building surfaces and molecular scale/BET surface areas. There are field measurements of HONO

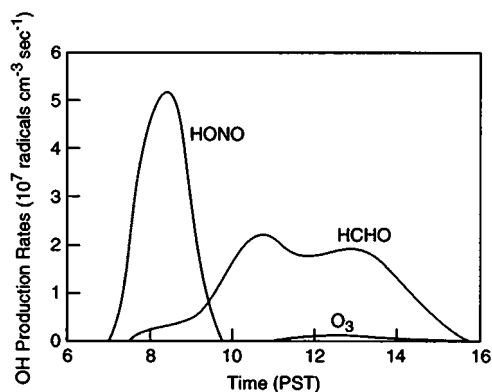
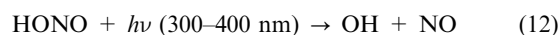


Fig. 11 Calculated rates of OH radical production as a function of time in Long Beach, CA on December 10, 1987, based on measured concentrations of the precursors HONO, HCHO and O₃. From ref. 284.

and its precursors that also suggest that reactions at the Earth's surface may dominate over that on particles under some conditions.^{279,280} For example, Yu *et al.*²⁸⁰ estimate that ground surfaces contributed similar amounts to HONO formation as did particle surfaces in a field study in Kathmandu, Nepal.

During long range transport at higher altitudes, boundary layer surfaces cannot contribute to this chemistry. However, there is clear evidence that reactions on windblown dust can be responsible for HONO formation within the boundary layer. For example, Wang *et al.*²⁸¹ measured a dramatic increase in the HONO/NO₂ ratio in Phoenix during a major dust storm. An interesting potential complication of such dust storms is the possibility that the particles become electrically charged,²⁸² which could potentially affect their chemistry.

A major reason for interest in the reactions of oxides of nitrogen on airborne dust particles is that nitrous acid is typically a product of this heterogeneous chemistry, and HONO is a major source of the OH radical in continental areas:



Nitrous acid absorbs strongly in the visible region and has a quantum yield of one, within experimental error.²⁸³ Fig. 11 shows the calculated rates of OH production from HONO, HCHO and O₃ photolysis at a location in Southern California.²⁸⁴ These rates were obtained by measuring the precursor concentrations using differential optical absorption spectrometry (DOAS) and applying the known absorption cross sections and quantum yields to calculate rates of OH generation from each compound. Nitrous acid is seen to be essentially the sole source of OH at dawn, and a major source even when averaged over 24 h. In a number of studies at many different continental sites, HONO has been found to be responsible for as much as half of the OH production over the course of a day.^{284–292}

Thermal hydrolysis of NO₂ as a source of HONO in the dark.

The heterogeneous hydrolysis of NO₂ on surfaces is well known to produce HONO in the dark:²⁹³

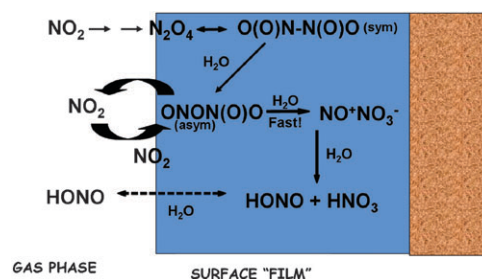


Fig. 12 Some proposed steps in surface heterogeneous hydrolysis of NO₂ to form gas phase HONO.

The reaction has been written this way for decades to indicate that the reaction proceeds in the presence of a surface but is too slow in the gas phase to be significant. While a great deal of the focus has been on this reaction, other sources have also been studied, including, for example, the reaction of NO₂ with organics.^{294–296}

Although reaction (13) represents the overall stoichiometry, it clearly does not capture the mechanism. Fig. 12 shows a simplified schematic of some steps that may be important in the reaction on surfaces. The rate of HONO formation has consistently been shown in many laboratory studies to be first order in NO₂ and first order in water vapor.²⁹³ This would seem to rule out gaseous N₂O₄ in equilibrium with gas phase NO₂ as a key intermediate. In addition, measured rates of HONO formation can exceed the calculated upper limit for uptake of equilibrium concentrations of N₂O₄ at low NO₂ concentrations.

However, the situation is more complicated than is apparent from the overall kinetics, and N₂O₄ on the surface may still be a key intermediate. For example, an intriguing possibility suggested by theoretical studies²⁹⁷ is that the asymmetric dimer can be formed by the direct reaction of two NO₂. Calculations by Pimentel and coworkers²⁹⁷ suggest that this reaction in the gas phase is barrierless and has a potential well of ~20 kcal mol⁻¹. In the case of heterogeneous reactions, one molecule could be adsorbed on the surface, and the limiting step is the interaction of this surface species with a second NO₂ to give the asymmetric dimer directly. As discussed shortly, the desorption of HONO from surfaces post-reaction is enhanced by water vapor; if such desorption occurred during reaction of small concentrations of NO₂, a higher rate of HONO formation might result than expected from the direct chemistry.

Once the asymmetric dimer is formed, autoionization to NO⁺NO₃⁻ is expected to occur. Recent theoretical studies²⁹⁸ shed light on this process. Molecular dynamics simulations using “on the fly” MP2 potentials show that in the absence of water, ONONO₂ only decomposes to NO₂. In the presence of one water molecule, formation of NO⁺NO₃⁻ occurs in a few ps, but in the presence of eight water molecules (Fig. 13), it occurs in a few fs! This is so fast that it is debatable whether the asymmetric dimer can even be considered to be a *bona fide* intermediate in the reaction.

Chou *et al.*²⁹⁹ predicted, based on density function studies of the interaction of NO₂ and N₂O₄ with water, that NO₂ interacting with three water molecules forms a cyclic structure

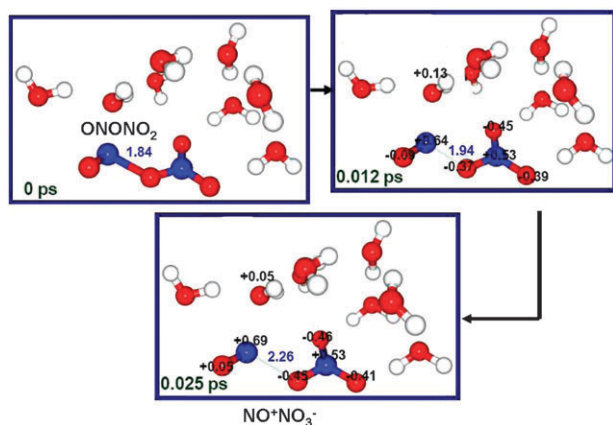


Fig. 13 Theoretically predicted snapshot of the ionization of *cis*-ONONO₂ with eight water molecules at 200 K. Oxygen–nitrogen bond distances are shown in blue. The partial charges on the atoms are also shown as the reaction proceeds to completion in 25 fs. From ref. 298.

in which water transfers a proton to NO₂ and additional proton transfers occur between the water molecules to generate HONO·HO·(H₂O)₂ as an intermediate which then reacts with an additional NO₂ molecule to form the products. The activation energy was calculated to be 20 kcal mol⁻¹ for the reaction with 3 water molecules, below the 27 kcal mol⁻¹ for the reaction involving only two water molecules. These are gas phase calculations that will not apply quantitatively to reaction with condensed phase water, but they do suggest decreasing activation energies with increasing numbers of water molecules.

Gustafsson *et al.*³⁰⁰ proposed that HONO is generated on mineral dust surfaces by the dissociation of water to H + OH on surface defects, followed by reaction of H with NO₂ to form HONO. However, these temperature programmed desorption (TPD) experiments were carried out using an ultra high vacuum system by dosing water on the mineral dust at 170 K followed by an equivalent dose of NO₂. While the pressure of NO₂ was sufficiently small that negligible amounts of N₂O₄ were impinging directly on the surface, the use of low pressures and temperatures does not mimic atmospheric conditions, nor does it rule out the formation of species such as N₂O₄ on the ice *via* sequential reactions. For example, Wang and Koel³⁰¹ observed infrared bands due to N₂O₄ and N₂O₃ when 1 monolayer (ML) NO₂ was dosed onto 1 ML H₂O that had been predosed on Au(111) at 86 K; the N₂O₃ was attributed to the reaction of chemisorbed NO₂ with “background” NO generated from NO₂ decomposition on the chamber walls and the N₂O₄ to sequential reactions of NO₂. The TPD data reported by Wang and Koel³⁰² are quite similar to those of Gustafsson *et al.*³⁰⁰

Another issue is that the surface of mineral dust in the atmosphere will have adsorbed species such as O₂ and organic compounds, as well as water and NO₂; whether the reaction of H atoms with NO₂ will be competitive under these conditions is not clear. In addition, the surface and reactivity of the water/ice film or islands may be quite different at room temperature (see below) than at 170 K. Finally, the formation of HONO from heterogeneous hydrolysis of NO₂ has been

observed on a variety of surfaces such as quartz and borosilicate glass,²⁹³ as well as Teflon™ and vegetation,²⁸⁹ on which thermal dissociation of water has not been observed, and indeed, seems unlikely.

In short, while the proposed mechanism involving dissociation of water on defects may be operative under some laboratory conditions, it is unlikely to be responsible for the majority of HONO production under atmospheric conditions.

The overall first order kinetic dependence of HONO formation on water vapor concentration likely masks even more complex relationships. Equilibrium concentrations of adsorbed water on solid surfaces typically follows BET or similar adsorption isotherms,^{303–306} which are approximately linear in intermediate ranges of relative humidity (RH) but highly non-linear at low and high RH. In addition, there is evidence from both laboratory³⁰⁷ and field studies³⁰⁸ that HONO or a precursor to HONO remains adsorbed to the surface and is displaced into the gas phase by water, presumably in a competitive adsorption type of process. Thus, the dependence of the measured rates of HONO formation on the gaseous water concentration will reflect not only the relationship between the gas phase and adsorbed water concentrations which determines the reaction kinetics, but also the competition between HONO and H₂O for surface sites. As discussed in detail by Stutz *et al.*,³⁰⁸ this introduces considerable uncertainty into the overall kinetics that must be taken into account in parameterizing this chemistry for inclusion in models of HONO formation in the tropospheric boundary layer.

An important, unresolved issue for both heterogeneous NO_x reactions on airborne dust particles and on other surfaces in the boundary layer is the nature of water on those surfaces. It is likely not well represented by bulk liquid water, and may consist of small islands³⁰⁹ or clusters. For example, Moussa *et al.*²²⁴ have carried out FTIR studies of water adsorption on organic self-assembled monolayers (SAMs) on borosilicate glass surfaces and on the glass substrate itself. The SAM-coated glass is a model for organics adsorbed on airborne dust particles and on boundary layer surfaces. Fig. 14a shows the spectra measured at equilibrium with 20, 40 and 80% RH on a saturated C18 SAM. Even at 80% RH, the spectrum is not well matched by that of bulk liquid water which peaks at ~3400 cm⁻¹; an additional component peaking around 3200 cm⁻¹ must be included to fit the data adequately. Such a red-shifted component of the spectrum for water has been observed in many studies on different surfaces^{109,310–317} and has been described as “ice-like”. We prefer the term “structured” since surface water at room temperature is unlikely to have the ice structure, particularly on a hydrophobic surface.

Fig. 14b also shows the results of MD simulations of 99 water molecules on a –CH₃ terminated SAM that is representative of the C18 SAM used in the experiments. As expected,³¹⁸ water is predicted to form a cluster on the surface. However, an analysis of the hydrogen bonding in the cluster raises intriguing questions. Fig. 14c shows for the water in the cluster the probability of forming 1 or 2 hydrogen bonds, compared to 3 or 4 hydrogen bonds as a function of the number of water molecules, *i.e.*, size of the cluster. For small

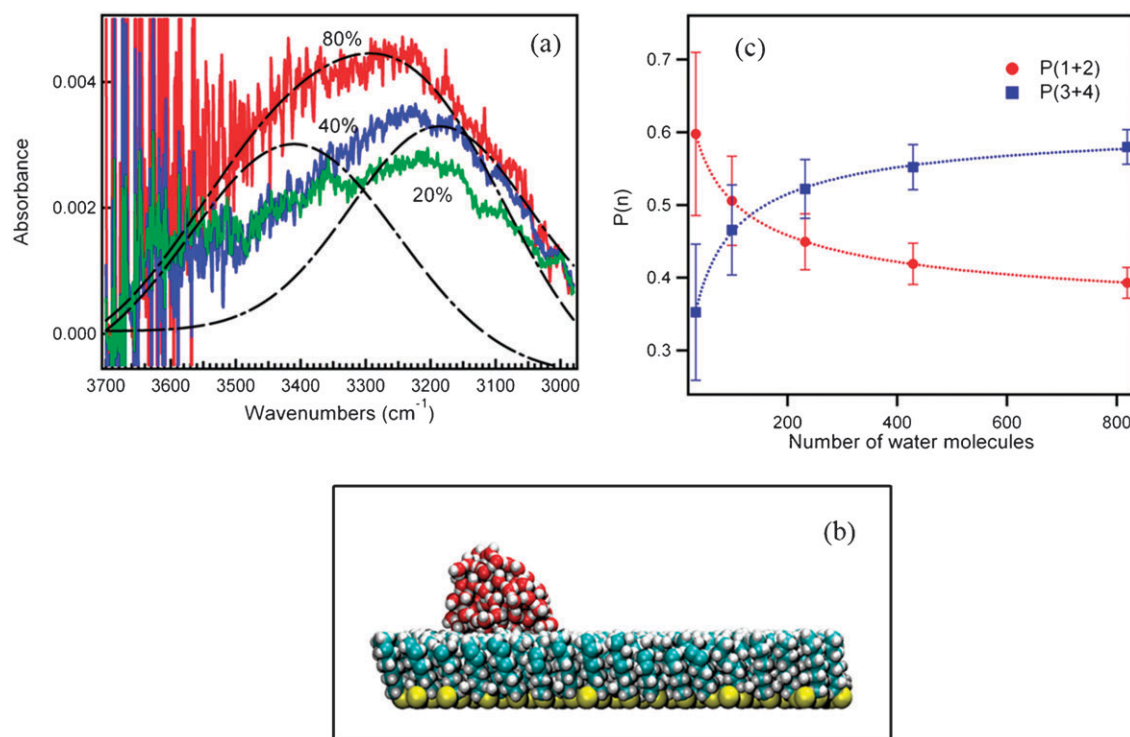


Fig. 14 (a) Infrared transmission spectrum of water adsorbed on a C18 saturated SAM on borosilicate glass at 20, 40 and 80% RH and 292 K. The dashed lines show the two components used to fit the experimental data, with the one peaking at $\sim 3400\text{ cm}^{-1}$ being that of bulk liquid water; (b) results of molecular dynamics simulations for 99 H_2O on a $-\text{CH}_3$ terminated saturated SAM; (c) probability of forming one or two H-bonds compared to forming three or four H-bonds as a function of the number of water molecules, *i.e.* size of the cluster. From ref. 224.

clusters, the majority of water molecules form 1 or 2 hydrogen bonds and closer inspection shows these to be largely on the surface of the cluster. Those with 3 or 4 hydrogen bonds are found predominantly in the center of the cluster. The experimental and theoretical data would be consistent if the 1–2 hydrogen bonded species on the cluster surface were responsible for the 3200 cm^{-1} peak and those with 3–4 hydrogen bonds, typical of bulk liquid water, for the 3400 cm^{-1} peak. However, this needs to be explored through more detailed calculations, which are currently underway.³¹⁹

Given the different degrees of hydrogen bonding predicted for water on the surface of clusters compared to bulk liquid water, it is reasonable that gases will interact with these clusters in a different manner than with bulk liquid water. However, this is an area that remains to be explored.

An additional aspect of surface water on dust particles or boundary layer surfaces is that some of it becomes tied up as complexes with HNO_3 as reaction (13) described above occurs. Fig. 15 for example, shows the infrared spectrum of the surface species formed in the NO_2 heterogeneous hydrolysis, obtained using ATR-FTIR. As discussed in detail elsewhere,³²⁰ theoretical studies indicate that this broad feature is due to molecular HNO_3 complexed to one, two or three water molecules, and to itself (*i.e.*, the nitric acid dimer). This is very surprising, given that the surface was in equilibrium with water vapor at 50% RH where dissociation of HNO_3 to H_3O^+ and NO_3^- might be expected. Theoretical estimates suggest that close to half of the surface nitric acid is in the form of these molecular complexes at 50% RH! Thus, as the reaction

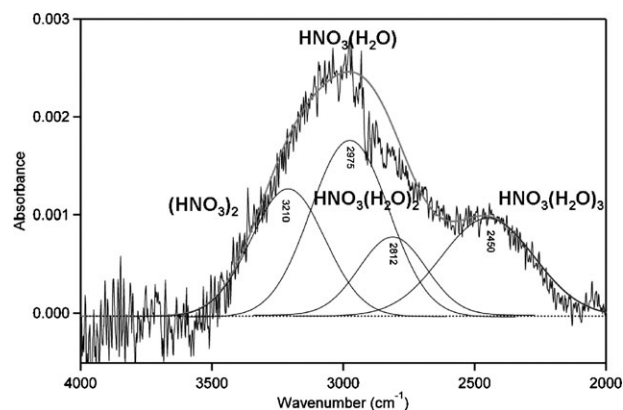


Fig. 15 Infrared spectrum of surface film after hydrolysis of 184 ppm NO_2 at 51% RH. The smooth lines are the contributions from the mono-, di- and trihydrates of HNO_3 and the dimer predicted from first principles electronic structure calculations. From ref. 320.

proceeds the nature of the surface species changes. How this affects reactions on the surface is also not known. However, theoretical calculations³²¹ and Raman studies³²² suggest that complexes between HNO_3 or NO_3^- and $\text{NO}_2/\text{N}_2\text{O}_4$ may be formed on the surface and potentially play a role in the chemistry or photochemistry (see below).

Finally, there is new evidence that heterogeneous reactions of oxides of nitrogen and halogen chemistry may be closely intertwined in interesting ways. Raff *et al.*³²³ have shown that intermediates in the heterogeneous hydrolysis of NO_2 on a

silica surface react with gas phase HCl to generate ClNO. What is very intriguing about this chemistry is that it is *catalyzed* by water, rather than water competing to form HONO *via* reaction (13). This catalysis by water was seen in experiments as well as predicted theoretically. Equally as intriguing is that surfaces exposed to N₂O₅ undergo similar chemistry with HCl to form ClNO₂, which is again catalyzed by water. This chemistry may be important in a number of situations where both HCl and oxides of nitrogen are present, including urban coastal areas, downwind of incineration and biomass burning and of some industrial processes such as semiconductor manufacturing, as well as indoors.^{324–327}

Surface photochemistry of oxides of nitrogen to form HONO.

There is a variety of evidence from both field and laboratory studies that HONO is generated from photochemistry of some as yet unidentified surface nitrogen oxide species.^{292,296,328–330} For example, Zhou *et al.*³³⁰ reported that HONO was formed when a glass sampling manifold at the PROPHET site in Michigan was irradiated in sunlight; however, when the manifold was shielded from light or when the surface was cleaned, HONO formation was not observed. They attributed this to photolysis of HNO₃ taken up on the surface to form NO₂, which then hydrolyzed on the surface *via* the chemistry described above to form HONO. This was supported by laboratory experiments³³¹ in which a borosilicate glass surface was treated with HNO₃ and water vapor. Upon irradiation, HONO, NO₂ and small amounts of NO were formed. However, the heterogeneous hydrolysis reaction (13) is sufficiently slow that it is unlikely to be responsible for the production of these species, and the mechanism remains unclear.

An intriguing set of experiments was carried out using the SAPHIR environmental chamber in Jülich, Germany. This is a large (270 m³) chamber made of double-walled thin (125 μm and 250 μm film thickness) Teflon™ film.³³² The space between the walls is flushed with clean air to reduce diffusion of outside gases into the chamber. Despite flushing the chamber with clean air overnight so that all measurable trace gas concentrations were below their detection limits, photolytic production of HONO as well as NO₂ and NO was still observed upon exposure to sunlight. The rate of HONO production was measured to be proportional to the rate of NO₂ photolysis, and to increase with RH and temperature. An optical filter that cut out wavelengths below 370 nm decreased the rate of HONO production by less than a factor of two. This showed that photolysis of precursors such as HNO₃ and NO₃⁻ in the region below 370 nm, where the filter reduced the light intensity by two orders of magnitude, could not be responsible for the HONO production.

The filter decreased the light transmission by only 15% above 420 nm, but the rate of HONO formation decreased by 40%, suggesting that photochemistry at these higher wavelengths was also not a major contributor. A source for the observed HONO has been suggested in the gas phase³³³ where electronically excited NO₂* at wavelengths below the photodissociation limit has been observed to form HONO in the presence of water vapor. In the SAPHIR experiments, addition of some NO₂ initially also did not increase the rate of

HONO formation as might be expected if the latter mechanism was operative. In addition, earlier experiments suggested that the NO₂* reaction with water was not fast enough to be a significant source of HONO.³³⁴

Photocatalytic reduction of NO₂ to HONO on TiO₂ and on mineral dust has also been observed.^{335–338} There is potential for such chemistry to occur on self-cleaning windows, for example, that contain TiO₂, and on surfaces where segregation of trace constituents into photochemically active material can occur on exposure to atmospheric gases such as HNO₃.³³⁹ Photochemically driven reactions with organics are another possible source of HONO,^{296,340–342} but will not be discussed further here.

It should be noted that many of the studies of HONO formation at low (ppt) levels utilized non-spectroscopic methods that involve uptake into solution and measurement of the nitrite formed. At present, available spectroscopic methods do not have sufficient detection limits to detect low ppt levels of HONO. There has been extensive testing of the chemical techniques for interferences, which have been shown to become particularly important at low NO_x concentrations.^{343,344} Specific spectroscopic identification is clearly preferred, and development of such methods with ppt sensitivity is a high priority for both laboratory and field studies.

The possibility that NO₂ or N₂O₄ complexed to HNO₃ or NO₃⁻ on the surface could be the photochemical precursor(s) to HONO has been examined as well.³²¹ The largest binding energies were for N₂O₄ complexed to HNO₃ (–8 kcal mol⁻¹) or NO₃⁻ (–14 kcal mol⁻¹), and infrared³²¹ and Raman spectra³²² provided experimental evidence for these complexes under laboratory conditions. Under atmospheric conditions, these complexes need not be formed directly by uptake of N₂O₄, but as discussed earlier, possibly by sequential uptake first to form the NO₂ complex and subsequently the N₂O₄ complex.²⁹⁷ However, the role of such complexes in the photochemical production of HONO remains to be fully explored.

Finally, there is an active and growing body of literature on the chemistry and photochemistry occurring in snowpacks.¹⁵⁴ Much of this appears to be driven by photochemistry of oxides of nitrogen, particularly nitrate ions.^{140,141,144,145,345–348} While there are likely some commonalities between the chemistry of heterogeneous nitrogen oxide reactions on tropospheric surfaces at room temperature and that in and on ice, the linkage needs further work to elucidate the relationships between the two.

In short, there is much yet to be learned about the detailed mechanisms and kinetics of both the thermal and photochemical production of HONO from heterogeneous reactions of oxides of nitrogen on tropospheric surfaces.

Indeed, this is another example where choosing model systems to represent complex atmospheric mixtures must be approached with caution. For example, both the physical and chemical interactions of oxides of nitrogen with an organic-coated mineral dust particle, vegetation or boundary layer surfaces^{239,241} may be quite different than with an uncoated particle, and different from the chemistry on relatively inert surfaces such as Teflon™. Certainly, there may be different

mechanisms of formation of HONO on different substrates and under different conditions. This is an area that remains to be explored.

Future needs and directions

As highlighted throughout this article, there are many atmospheric chemistry problems that remain to be resolved in order to confidently and quantitatively predict the impacts of control strategies on air quality, visibility, health, and climate change. The following is not intended to be a comprehensive list of future needs and directions, but rather illustrative of the areas in which new and transformative research is urgently needed:

- Development and application for techniques to probe the structure of liquids and particles, molecular layer by molecular layer, to provide a 3-D molecular level characterization of both organics and inorganics. This must include speciation of individual organics and species such as H^+ and OH^- , whose presence at the interface is controversial;

- Development and application of techniques to detect and measure reactive intermediates at surfaces, such as the $(OH-Cl)^-$ species proposed for the interface OH-chloride reaction, free radicals such as OH and $O(^3P)$ generated during photochemical and possibly thermal, reactions at interfaces;

- Elucidation on a molecular level of the chemistry of more complex systems relevant to the atmosphere, *e.g.* those containing organics and inorganics, and perhaps having heterogeneity in their 3-D structure as well;

- Elucidation of the mechanisms and quantum yields of photochemical reactions at interfaces relevant to the atmosphere;

- Elucidation of the interaction of O_3 with a variety of surfaces and in particular, why Langmuir-Hinshelwood kinetics seems to apply to a wide variety of substrates whose interactions with ozone would not be expected to be so similar;

- Elucidation of the structure of water on boundary layer surfaces and on airborne particles, and how its surface properties determine its reactivity towards gases or co-adsorbed species;

- Identification and measurement of the missing low-volatility organics in air, their sources, and their role not only in SOA formation but in other atmospheric processes;

- Determination of the interactions between biogenic/geogenic and anthropogenic emissions, and the implications for air quality and climate. For example, is this related to the puzzling observation that formation of SOA is typically associated with regions of high fossil fuel combustion, yet more than half of the carbon in such SOA is often contemporary (*i.e.* non-fossil fuel) carbon?^{349,350}

- Determination of the molecular form of nitrogen oxides on surfaces and their chemical and photochemical reactions, and lifetimes, particularly those involved in the formation of HONO.

It is clear that obtaining the molecular level insights needed to answer these and other important questions for air quality and climate change will require the full arsenal of experimental and theoretical techniques available today, as well as development of new approaches in the future. In addition, these molecular level insights must be scaled from the

angstrom size range to km used in atmospheric models, and from ps and shorter time scales to hours and years relevant to processes in the atmosphere. Developing this new knowledge and integrating it in a form that is useful in a predictive sense presents a major challenge for understanding particles and surfaces and their interactions with, and impacts on, the atmosphere. At the same time, it presents major challenges and exciting new opportunities for physical chemistry.

Acknowledgements

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