

Computational Studies of Atmospherically-Relevant Chemical Reactions in Water Clusters and on Liquid Water and Ice Surfaces

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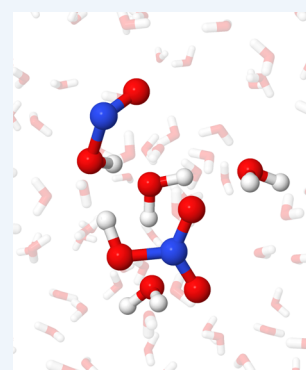
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CONSPECTUS: Reactions on water and ice surfaces and in other aqueous media are ubiquitous in the atmosphere, but the microscopic mechanisms of most of these processes are as yet unknown. This Account examines recent progress in atomistic simulations of such reactions and the insights provided into mechanisms and interpretation of experiments. Illustrative examples are discussed. The main computational approaches employed are classical trajectory simulations using interaction potentials derived from quantum chemical methods. This comprises both *ab initio* molecular dynamics (AIMD) and semiempirical molecular dynamics (SEMD), the latter referring to semiempirical quantum chemical methods.

Presented examples are as follows: (i) Reaction of the $(\text{NO}^+)(\text{NO}_3^-)$ ion pair with a water cluster to produce the atmospherically important HONO and HNO_3 . The simulations show that a cluster with four water molecules describes the reaction. This provides a hydrogen-bonding network supporting the transition state. The reaction is triggered by thermal structural fluctuations, and ultrafast changes in atomic partial charges play a key role. This is an example where a reaction in a small cluster can provide a model for a corresponding bulk process. The results support the proposed mechanism for production of HONO by hydrolysis of NO_2 (N_2O_4). (ii) The reactions of gaseous HCl with N_2O_4 and N_2O_5 on liquid water surfaces. Ionization of HCl at the water/air interface is followed by nucleophilic attack of Cl^- on N_2O_4 or N_2O_5 . Both reactions proceed by an $\text{S}_{\text{N}}2$ mechanism. The products are ClNO and ClNO₂, precursors of atmospheric atomic chlorine. Because this mechanism cannot result from a cluster too small for HCl ionization, an extended water film model was simulated. The results explain ClNO formation experiments. Predicted ClNO₂ formation is less efficient. (iii) Ionization of acids at ice surfaces. No ionization is found on ideal crystalline surfaces, but the process is efficient on isolated defects where it involves formation of H_3O^+ -acid anion contact ion pairs. This behavior is found in simulations of a model of the ice quasi-liquid layer corresponding to large defect concentrations in crystalline ice. The results are in accord with experiments. (iv) Ionization of acids on wet quartz. A monolayer of water on hydroxylated silica is ordered even at room temperature, but the surface lattice constant differs significantly from that of crystalline ice. The ionization processes of HCl and H_2SO_4 are of high yield and occur in a few picoseconds. The results are in accord with experimental spectroscopy. (v) Photochemical reactions on water and ice. These simulations require excited state quantum chemical methods. The electronic absorption spectrum of methyl hydroperoxide adsorbed on a large ice cluster is strongly blue-shifted relative to the isolated molecule. The measured and calculated adsorption band low-frequency tails are in agreement. A simple model of photodynamics assumes prompt electronic relaxation of the excited peroxide due to the ice surface. SEMD simulations support this, with the important finding that the photochemistry takes place mainly on the ground state.

In conclusion, dynamics simulations using quantum chemical potentials are a useful tool in atmospheric chemistry of water media, capable of comparison with experiment.



1. INTRODUCTION

Water in different states is the medium for a vast number of atmospheric chemical reactions.^{1,2} Processes of atmospheric importance take place in seas and in lakes, in cirrus clouds, in fogs and aqueous aerosols, on ice and snow surfaces, in water layers adsorbed on minerals, and in many other water environments. These media are highly complex, and it is therefore extremely difficult to develop a microscopic understanding of the systems and the processes. It is a great challenge

for computational theory in this area to pursue atomistic level insights by simulations, in close interaction with experiments. The rapid development of powerful simulation tools makes this research direction timely and promising. Two of the approaches that have played a key role in this field are *ab initio* molecular dynamics (AIMD)^{3,4} and to a lesser extent semiempirical

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molecular dynamics (SEMD).⁵ These approaches use quantum-chemical methods to generate the interaction potentials that govern the systems and to directly propagate the trajectories that describe the dynamics. The potentials are evaluated along the trajectories at each point in time. Suitable quantum-chemical methods can adequately describe bond breaking and bond making, unlike standard force fields. The challenge is to find quantum-chemical methods that correctly describe the reaction and are computationally feasible.

This Account overviews progress in computational studies of atmospherically relevant chemical reactions in water media, with focus on the microscopic insights that the calculations provide and on their usefulness for the interpretation of experiments. Several examples are presented from the work of the authors, covering different types of reactions in water media. Differences as well as similarities for the molecular-level mechanisms of the different reactions are highlighted. Our work builds on important contributions by several other groups, especially on applications of AIMD to aqueous systems, for example, refs 2 and 6–8. The types of reactions examined here are as follows. Section 2 analyzes the reaction of the $(\text{NO}^+)(\text{NO}_3^-)$ ion pair with water, a process that can be described by a small water cluster. Section 3, in contrast, presents examples (reactions of HCl with NO_x species on water) where a realistic, extended model of the air–water interface is essential. Sections 4 and 5 treat the ionization of acids on ice and on wet silica surfaces, where the hydrogen-bonded network is more rigid than in liquid water. Section 6 analyzes photochemical reactions in water media, highlighting the influence of the latter on excited electronic states.

2. CLUSTERS AS MODELS FOR REACTIONS ON WATER SURFACES

To demonstrate the utility of clusters in examining the effect of solvation on atmospheric reactions (e.g., see Vaida²), we will focus on the final step in hydrolysis of NO_2 . Several processes in a proposed mechanism⁹ based on experimental studies of NO_2 hydrolysis were studied using cluster models^{10–14} and the QM/MM¹⁵ approach to incorporate explicit solvent. These processes include dimerization of NO_2 to form N_2O_4 , isomerization of *sym*- N_2O_4 to *asym*- N_2O_4 , ionization to $(\text{NO}^+)(\text{NO}_3^-)$, and finally reaction with H_2O to form HONO and HNO_2 . Additionally, alternate mechanisms have arisen from AIMD simulations of the reaction with one to seven water molecules.¹²

For the reaction of $(\text{NO}^+)(\text{NO}_3^-)$ with water, a cluster size of $(\text{H}_2\text{O})_4$ was used based on previous work that established the role of the hydrogen-bonding network in promoting reaction of NO^+ with water.¹⁶ A similar water configuration was identified solvating the *cis*-ONONO₂ and *trans*-ONONO₂ isomers of *asym*- N_2O_4 [Figure 1a,b].¹⁴ A transition state [Figure 1c] for reaction to form HONO and HNO_3 [Figure 1d] was identified, and the process was explored through AIMD. The barrier to HONO formation was found to be less than 5 kcal/mol for the *trans* isomer. (The barrier is several kcal/mol higher for the *cis* isomer.) At the transition state, a reacting water molecule inserts between the NO^+ and NO_3^- fragments. Prior to insertion, the charge separation increases as the (NO^+) and (NO_3^-) fragments separate.

In cluster simulations, the charge separation, $\delta(\text{NO})-\delta(\text{NO}_3)$, was used to monitor progress of the reaction and determine the nature of the reacting species. It is useful to compare the charge separation in a small cluster to that found

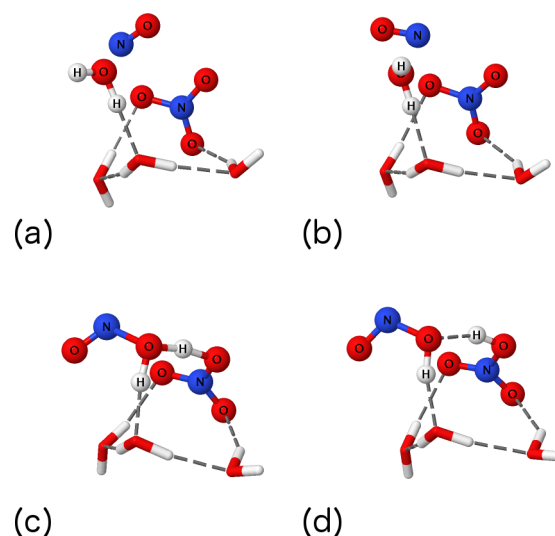
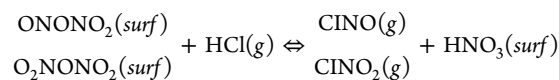


Figure 1. Structures for (a) *cis*-ONONO₂·(H₂O)₄, (b) *trans*-ONONO₂·(H₂O)₄, (c) a transition state, and (d) HONO and HNO₃.

in systems with additional solvation. The average charge separation of *cis*-ONONO₂ on a water slab was extracted¹⁷ from AIMD simulations carried out as discussed in section 3. To compare the charge separation supported by the various configurations of solvating water in a small cluster to the charge separation at a water surface, the Mulliken partial charges were determined using BLYP-D/TZVPP. For *cis*-ONONO₂·(H₂O)₄, $\delta(\text{NO})-\delta(\text{NO}_3)$ is 0.88 compared with an average $\delta(\text{NO})-\delta(\text{NO}_3)$ of 0.86 for *cis*-ONONO₂ on a water slab. In contact with the square water tetramer, with limited hydrogen-bonding, or in a *cis*-ONONO₂·(H₂O)₂ cluster, with fewer solvating waters, $\delta(\text{NO})-\delta(\text{NO}_3) \leq 0.75$. For the small cluster model, a specific configuration promotes charge separation and reaction, while many configurations of bulk water can support a similar charge separation and reaction. In summary, a cluster of small but sufficient size can serve as a model system for the reaction of $(\text{NO}^+)(\text{NO}_3^-)$ with water. The reaction is triggered by a structural fluctuation away from equilibrium, which induces a significant change in the charge distribution. AIMD nicely supports¹⁴ an experimentally based mechanism.⁹

3. HETEROGENEOUS REACTIONS OF GAS PHASE MOLECULES AND ADSORBATES IN AN AQUEOUS ENVIRONMENT: FORMATION OF NITROGEN OXYCHLORIDES

We consider atmospherically relevant reactions that involve formation of ClNO and ClNO₂ when gaseous hydrogen chloride strikes a surface that has been exposed to $\text{NO}_2/\text{N}_2\text{O}_4$ or to N_2O_5 , respectively. The stoichiometric equations are



ONONO₂ (*asym*- N_2O_4) is considered the reactive form of the NO_2 dimer. ClNO and ClNO₂ photolyze to generate highly reactive chlorine free radicals, which initiate oxidation of organics in air, conversion of NO to NO_2 , and ultimately ozone formation.¹ Laboratory studies demonstrate production of these gaseous products, and theoretical studies elucidate a mechanism consistent with it.^{18,19} ONONO₂ and N_2O_5 are postulated to disproportionate on an aqueous surface, and

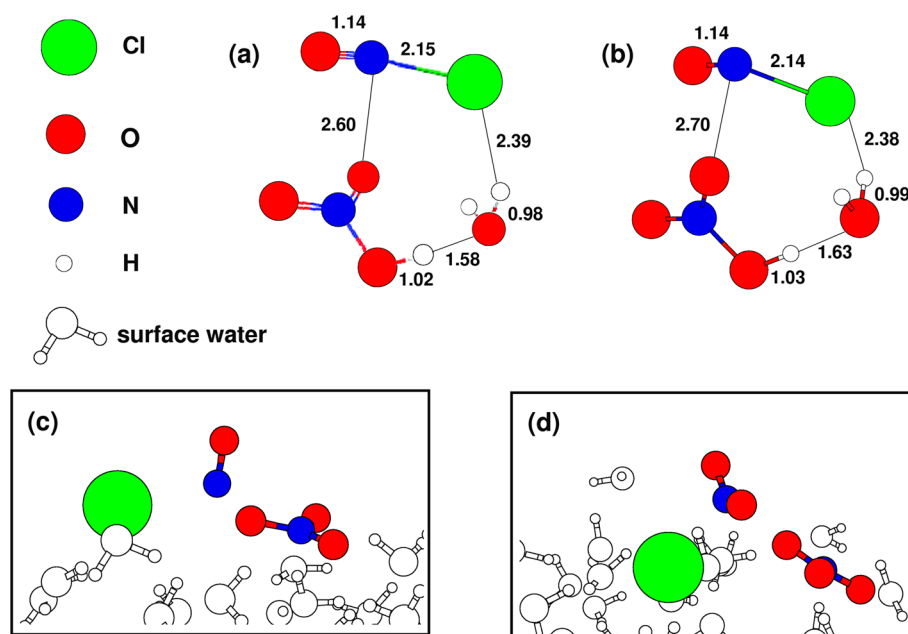


Figure 2. Water cluster model for reaction of *asym*-N₂O₄ with HCl: (a) product from MP2/cc-pVDZ calculation on *asym*-N₂O₄/HCl/H₂O; (b) same cluster geometry optimized at BLYP-D3/TZV2P level of theory. BLYP-D3/TZV2P AIMD simulations of the reaction with nitrogen oxides adsorbed on a thin water slab: (c) *asym*-N₂O₄; (d) N₂O₅.

theory supports incipient ionization.^{11,13,18,19} Due to the level of quantum theory involved, these theoretical approaches model the aqueous layer by small water clusters.^{18,19}

More recent AIMD simulations of this system in a water slab geometry were performed, which employ a more realistic model of an extended aqueous surface.¹⁷ Both cluster and bulk studies indicate that water has a profound influence on the oxide's geometry and promotes charge separation between fragments: (NO^{δ+}, NO₃^{δ-}) for ONONO₂ and (NO₂^{δ+}, NO₃^{δ-}) for N₂O₅, forming a species more amenable to reaction. With sequential addition of water molecules, the bridge O–N distance between fragments increases along with the fragment charge separation, where three H₂O are needed to form an ion pair.^{11,18} Less charge separation is observed in AIMD trajectories of N₂O₅ compared with ONONO₂. Isomerization to *asym*-N₂O₄ on a (H₂O)₂₀ ice model also provides evidence of the ion pair.¹³

However, a major difference between models arises for reaction in a thin film aqueous environment. The small cluster model excludes the possibility of gaseous HCl ionizing after impacting the film. The model simply does not contain a sufficient number of water molecules to support ionization.^{18,19} This is shown in Figure 2 for the product of an *asym*-N₂O₄/HCl/H₂O cluster from an MP2 electronic structure calculation, Figure 2a, and a BLYP-D3 geometry optimization, Figure 2b. In both cases, the chlorine atom attaches to the nitroso N while the proton participates in a proton wire, leading to nitric acid and nitrosyl chloride. As discussed in section 5, HCl ionization is thwarted until three H₂O molecules provide H-bonds for acid solvation.²⁰ Similar behavior is noted in sections 4 and 5 for HNO₃ and H₂SO₄.^{21,22} A cluster with one water cannot ionize, and the reduced dimensionality treatment forces the proton wire pathway.

The AIMD simulations offer a plausible alternative to the proton wire mechanism for oxychloride formation (details in ref 17). They provide an alternative, more realistic atomistic interpretation for the experiments of Raff et al.¹⁸ Water

preconditions the nitrogen oxide for reaction by relaxing the geometry until the bridge O–N bond lengthens considerably. Bonding electron density concurrently migrates to increase fragment charge separation over its gas phase value. For N₂O₄, electron density even transfers from surrounding waters. H-bonding to the aqueous surface tethers the rather floppy nitrogen oxide adsorbate so that it is more positioned for reaction. Localized, with bonds lengthened and a N atom with enhanced electrophilicity, the oxide is primed for nucleophilic attack. When gaseous HCl strikes the aqueous surface, it ionizes within 2–10 ps upon acquisition of the necessary solvation structure. The liberated chloride ion traverses the surface and subsurface layers of the film. Upon encountering the nitrogen oxide, it can attack. The reaction occurs by a concerted S_N2 mechanism where, as the chloride enters, the nitrate group leaves, stabilized by H-bonding to water. Figure 2c,d exhibits a dynamic transition state for this process where it is clearly seen that the nitrate is not protonated, that is, HNO₃ has not formed.

4. IONIZATION MECHANISMS ON ICE SURFACES

Acid ionization in aqueous media is governed by the Grotthuss²³ mechanism: fortuitous oscillations in the hydrogen-bonded network of water molecules expose a “target” molecule having a certain number of donated and accepted H-bonds, which accepts the incoming proton from the acid [Figure 3a and subsequent panels]. The acid's soon-to-be conjugate base also requires sufficient solvation (omitted in Figure 3). Figure 3 demonstrates formation of a contact ion pair (CIP) for an acid with a base “M”. In panel b, an oscillation creates an instantaneous “target” molecule, denoted DD (double-donor, zero-acceptor). In panel c, the acid H-bonds to this species, converting it to ADD (single-acceptor, double-donor). After proton transfer, panel d, the target water molecule becomes a DDD species (triple donor, zero acceptor), a hydronium ion, producing a stable CIP.

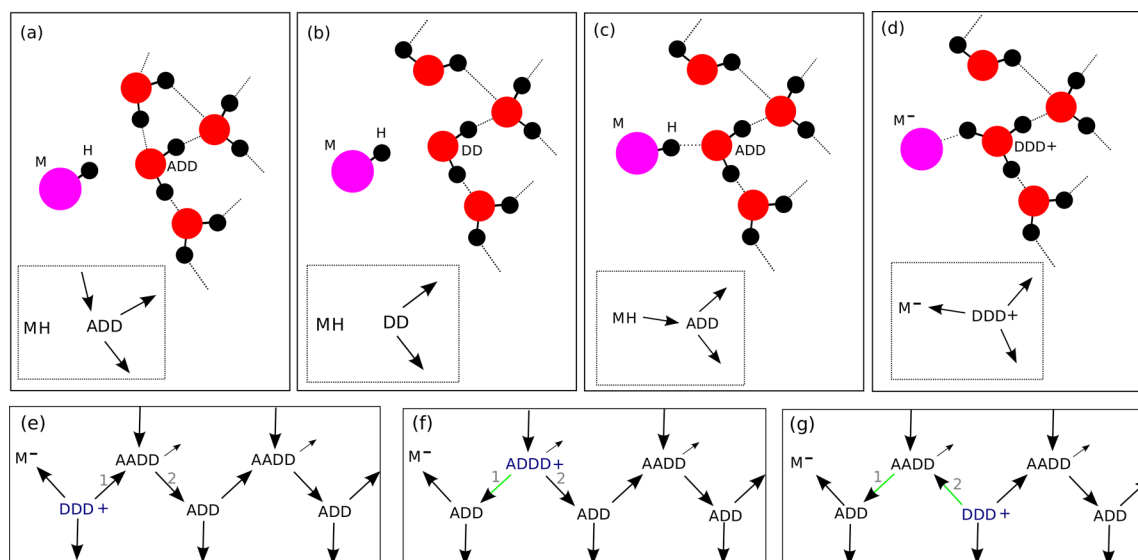


Figure 3. Mechanism of acid ionization on an aqueous surface, viewed from above. Insets of panels a–d give a schematic view of H-bonding near the contact ion pair, where arrows denote direction of H-bond donation. The + depicts the hydronium ion site. Panels e–g demonstrate hydronium migration on the ice basal plane. Two H-bonds are denoted by 1 and 2. H-bonds with their directions reversed during migration are highlighted in green.

A significant concentration of weakly hydrogen-bonded ADD species exists on a water film surface.²⁴ Acid–ADD complexes also form readily on hydroxylated silica surfaces, where H-bonds of the water overlayer are strained and therefore weak.²⁰ For ice surfaces, the water ice basal plane has a large amount of ADD water molecules, but their H-bonds are strong and not susceptible to breakage. However, crystalline point defects disrupt the H-bonded network and create weakly H-bonded ADD and DD species.²⁵ Kink and edge sites, where two facets with different crystalline orientations meet, are expected to enhance acid ionization.²⁶ We observed rapid (picosecond time scale) ionization of nitric acid at cryogenic temperatures ($T = 40, 200$ K).²⁵ In these AIMD simulations, density functional theory (DFT) with dispersion corrections²⁷ was used, with deuterium masses for hydrogens. The results for HNO_3 are in accord with the experiments of Ayotte.²⁸

Proton migration on the ice basal plane was also examined.²⁵ Panels e–g of Figure 3 show a schematic view of the plane. Panel g demonstrates a stable surface site for the Eigen ion. The proton hops between these sites via the Grotthuss mechanism,²³ while protons along two H-bonds [marked 1 and 2 in Figure 3], jump simultaneously. Such collective proton movement is known for ice,²⁹ where the ADDD+ species is a shallow energy minimum. Possible large quantum effects of proton motion are an open issue that merits attention.

A further study²¹ used a more realistic ice surface, the ice quasi-liquid layer (QLL) that forms at temperatures above 200 K.³⁰ Nanosecond-time scale simulations, performed with force fields, established the QLL molecular structure, while ionization calculations were done using AIMD. The equilibrated systems revealed that the QLL structure is the ice basal plane with a large concentration of crystalline point defects and admolecules in the topmost ice bilayer.²¹ The point defects provide weakly H-bonded ADD molecules, making the QLL reactive. We observed rapid picosecond time scale ionization for HI and HNO_3 .²¹ For the latter, ionization required complete solvation of the nitrate ion with the proton delocalized over three water

molecules. For HI, a stable solvent-separated ion pair (SSIP) always formed.²¹

On water films, weakly bonded ADD waters result from rapid making and breaking of H-bonds, while on the QLL, they derive from long-lived, stable structural motifs. Once an acid ionizes on the QLL, its conjugate base is “anchored” at the defect site.²¹ Penetration of atmospheric species beyond the QLL layer is blocked by the crystalline ice layers, exposing the ionized acid to further reaction with adsorbed species.²¹

An environment that exhibits large surface area of QLL is the upper troposphere. It is inhabited by cirrus clouds consisting of micrometer-sized ice particles.³¹ Since cirrus clouds regularly cover up to 20% of the globe, our theoretical studies suggest an enhanced chemical reactivity in this region.

5. ACID IONIZATION ON WET QUARTZ

Silica forms 60% of dust particles,³² and its heterogeneous chemistry is atmospherically interesting.^{9,18,32} Its thermodynamics and structure have been well-studied, but its atmospheric acidification processes have not. α -Quartz is the most common SiO_2 allotrope. Its surface can chemisorb water, becoming hydroxylated with silanol groups ($-\text{SiOH}$) and hydrophilic. At 296 K and $\sim 20\%$ relative humidity, a water monolayer physisorbs on hydroxylated silica particles,³³ causing half of the inter-silanol H-bonds to transfer to water.^{34,35} Subsequent water layers may adsorb and begin to resemble liquid water,³⁴ while the water layers closest to the silica surface remain highly ordered and form a tessellation ice, even at ambient temperature. In our AIMD (BLYP-D2 DFT) wet quartz studies^{20,22} of acid ionization of the common tropospheric acids¹ HCl and H_2SO_4 , the chemistry of the water monolayer was studied because it is atmospherically relevant³³ and the mineral surface’s effects are most pronounced.

On the surface, prior to interaction with the acid [see Figure 4, panel a and left portion of panel b], there exist two populations of silanols and water molecules (H-down and in-plane), having H-bonds of varying strengths, leading to distinct features in the vibrational spectrum.^{20,22,34,35} Each water

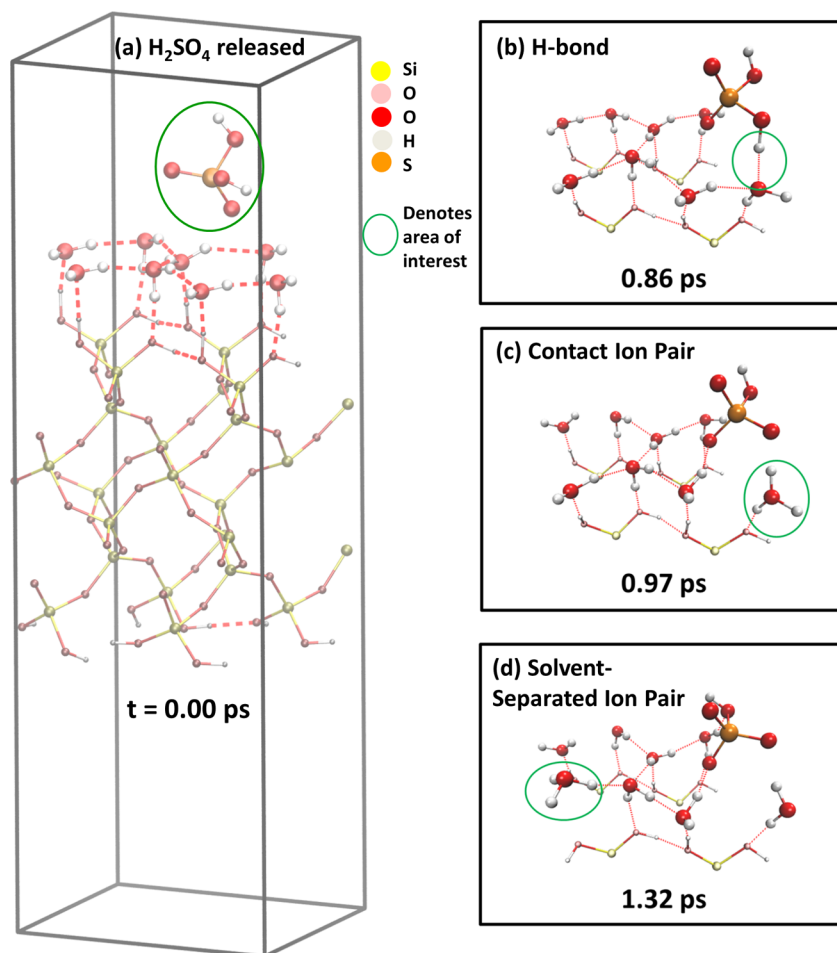


Figure 4. Snapshots from 250 K trajectory displaying steps in H₂SO₄ ionization on hydroxylated (0001) α -quartz with water monolayer: (a) model system, (b–d) uppermost portion. Adapted with permission from ref 22. Copyright 2014 by Royal Society of Chemistry.

molecule is of H-bonding type DDAA (fully saturated H-bonds), and thus the water layer may be expected to be virtually unreactive to incoming adsorbates. However, due to a lattice mismatch with the underlying quartz surface, the $O_{\text{water}}-O_{\text{water}}$ separation is about 0.1–0.2 Å longer than that in the basal plane of ice I_h, making the water bilayer nearly flat and the H-bond angles often far from tetrahedral.^{20,22,35} The lattice mismatch weakens the inter-water H-bonds, and increases the water molecules' H-bonding ability with potential adsorbates as well as the surface reactivity.

Figure 4, panel a, also shows a *trans* conformer H₂SO₄ molecule (HCl results were similar) in its initial position above the surface. H₂SO₄ is attracted to the surface, and in panel b, it has donated one of its H-bonds to a water molecule, followed by (c) initial ionization (forming CIP) and (d) proton migration (forming SSIP). Proton migration disorders the water layer. The detailed mechanisms of ionization (e.g., breaking and establishment of H-bonds, stable H-bond state of the resulting H₃O⁺ being DDD, and necessity of solvation of HSO₄[−]) are similar to those described in section 4. Our simulated spectra^{20,22} are in agreement with experimental spectra of acidified aqueous surfaces,^{36,37} where the main signal of decrease in pH is loss of features and appearance of a proton continuum.

Sixty-five percent of trajectories were ionized (2 ps average ionization time). The remaining trajectories did not ionize (in our 5–10 ps simulations), due to H₂SO₄ landing on the surface

as *cis* conformer (both its H-bonds donated to waters) or to its insufficient solvation. The second deprotonation, producing SO₄^{2−}, occurred only if the system was further solvated. This was observed in studies of H₂SO₄ in liquid water and clusters (see ref 38).

In summary, at 250–330 K, a monolayer of water on hydroxylated quartz allows spontaneous (few picosecond) ionization of HCl and H₂SO₄. The increased ion concentration and acidity on mineral surfaces may increase uptake and reactions of adsorbates.

6. PHOTOCHEMICAL REACTIONS ON ICE AND WATER

Peroxides are a major class of reagents in photochemical atmospheric reactions, as shown by field measurements.³⁹ The absorption spectrum of gaseous methyl hydroperoxide (MHP) is dominated by the dissociative $n \rightarrow \pi^*$ transition centered below 200 nm, its red shoulder extending into the atmospherically relevant region. The absorption spectrum of MHP on water and ice has been experimentally and theoretically investigated.⁴⁰ The emphasis of the study was to understand the effect of water or ice on the absorption spectrum. Theoretically, a cluster of CH₃COOH immersed in 20 water molecules was chosen to describe the system, see Figure 5.

Excitation spectra were calculated using molecular dynamics on a semiempirical potential energy surface,⁴¹ calibrated with a high level quantum chemical method, ADC(2).⁴² The simulations were done at several different temperatures. Figure

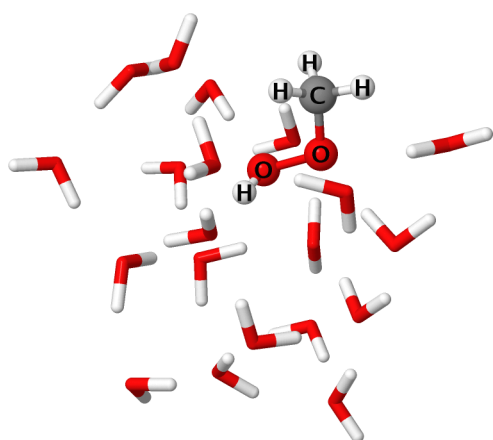


Figure 5. Structure of MHP adsorbed with 20 water molecules.

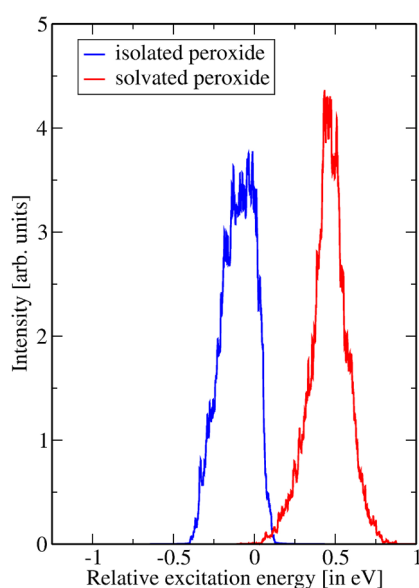


Figure 6. Computed excitation spectra of bare and solvated methyl hydroperoxide at 50 K.

6 shows the absorption spectra of bare MHP compared with MHP on ice. The excitation energy was found to correlate strongly with the COOH angle of MHP. The line shape of the spectrum of adsorbed MHP is very similar to that of the gas phase. Both spectra are very narrow due to confinement of the COOH dihedral angle to a small range. At 50 K, hydration of CH_3COOH shifts the spectrum by 0.5 eV to higher energy compared with the bare molecule, representing a strong blue shift. At 200 K, there is a large overlap of the spectrum of the hydrated MHP with the spectrum of the bare MHP. Analysis of the structural changes reveals that all molecules are very loose so that a wider range of dihedral angles can be accessed, resulting in a broader spectrum. For frozen water (0 °C), the red tails of the absorption spectrum were measured and the computed spectrum is in good accord.⁴¹ Thus, SEMD provides an interpretation of the absorption tails.

Another study⁴³ explored the deactivation dynamics due to ice of the excited MHP. The study combined a nonadiabatic surface hopping method with a semiempirical method. We find that ice has a large effect on the deactivation dynamics. Ice enhances the depopulation dynamics of the excited state by shortening the time scale for reaching the conical intersection

for deactivation to the ground state. Second, ice prohibits transfer back to the S_1 state and, by this, makes the deactivation far more efficient. The O–O cleavage for the peroxide adsorbed on ice occurs much faster compared with the bare peroxide. Ice permits recombination events between the fragments.

Several works included a detailed comparison of semiempirical methods with a high level *ab initio* method [ADC(2)].^{40,43} It was found that semiempirical methods are qualitatively comparable to *ab initio* potentials for organic systems, with the great advantage of significantly faster computation time. It is therefore suggested to use this method for larger systems. Our impression is that advances in semiempirical methods for excited states opens up possibilities for major progress on this topic.

The AIMD applications described in Sections 2–5 have an important limitation: The number of trajectories that can be practically sampled is modest, due to the computational demands. This is a challenge for future developments. The use of semiempirical potentials for the dynamics, as in this section, seems promising in this respect since many long trajectories can be computed. This hinges on establishing the validity of semiempirical potentials for an increased variety of reactions.

7. ATMOSPHERIC IMPLICATIONS AND CONCLUDING REMARKS

Water is ubiquitous in air, and so it is not surprising that it plays a significant role in the chemistry of the atmosphere. For example, even at 10% relative humidity at 25 °C at the Earth's surface, the concentration of water vapor is ~3000 ppm (parts per million by volume), compared with ppb (parts per billion) or ppt (parts per trillion) for most trace gases. The polar nature of water and its ability to form strong hydrogen bonds result in uptake onto essentially all surfaces in the boundary layer, in addition to uptake onto or into airborne particles. There is a variety of evidence from field and laboratory studies that reactions on such surfaces play a key role in atmospheric reactions.^{44–48} However, these reactions often display kinetics and mechanisms that cannot be predicted from the corresponding gas phase or bulk aqueous phase reactions, suggesting there are unique characteristics of water on surfaces and of the interface of aqueous particles that become evident in the interactions with gases. One example that has been problematic for many decades is the formation of nitrous acid, HONO, from the interaction of NO_2 with water on surfaces.⁹ Nitrous acid absorbs light quite strongly in the 300–400 nm region and generates OH + NO with a quantum yield of one.⁴⁹ The OH radical, which drives atmospheric chemistry, has a variety of sources; however, measurements of HONO in air consistently indicate that it is a major source in continental regions where oxides of nitrogen are available.^{50–53} Despite this, atmospheric models generally do not include HONO generation from such heterogeneous chemistry due to the lack of molecular level understanding of the process. What has been missing is an understanding of the nature of water on surfaces as well as its interaction with likely surface-bound intermediates. These have proven difficult to study experimentally, and computational studies such as those described above have provided key insights into these processes.

Computational approaches have also been highly synergistic with experiments where initially surprising experimental data have been supported by theory. For example, in the reactions of surface bound oxides of nitrogen with gas phase HCl described

in section 3, a surprising experimental observation was that the addition of water vapor enhanced the production of ClNO and ClNO₂, rather than competing with the HCl reaction and forming HONO. As described above, computation provided a solid foundation to understand this. A related example is the chemistry that occurs at low temperatures on polar stratospheric clouds, which generates species such as Cl₂ that photolyze at polar sunrise to initiate ozone destruction in the upper atmosphere.¹ Elucidating the nature of water and ice surfaces and ionization processes has been key to quantitatively modeling and predicting the observed dramatic ozone loss.

In short, computational studies of water on surfaces and at interfaces have proven to be central to developing a molecular-level understanding of a variety of heterogeneous reactions that are very important in understanding the chemistry of our atmosphere. A necessary component of the studies described here has been the smooth integration of theory, experiment, and atmospheric modeling facilitated by the environment of a collaborative project, AirUCI. Such integrated studies will undoubtedly become even more important in the future as the capability of addressing larger systems computationally increases. These significant advances facilitate the inclusion of previously omitted processes into atmospheric models and increase their application to the development of reliable control strategies for air quality and climate change.

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The authors declare no competing financial interest.

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Audrey Dell Hammerich received her B.S. in mathematics from Rutgers University in New Jersey. She obtained her Ph.D. in physical chemistry from the University of California at Los Angeles. After postdoctoral work at Hebrew University in Jerusalem, she joined the faculty of the Chemistry Department at the University of Illinois at Chicago where she is a clinical assistant professor. Her interests lie in instilling the joy of chemistry, especially physical chemistry, into her students and using *ab initio* molecular dynamics to elucidate reaction mechanisms.

Sampsa Riikonen obtained his M.Sc. in engineering mathematics and physics from Helsinki University of Technology (presently Aalto University) and his Ph.D. in computational material physics from the University of the Basque Country, Spain. His interests include proton ordering in ice and ice-like systems and acid ionization reactions.

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Gerber, where he uses AIMD to study chemical reactions in aqueous media.

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