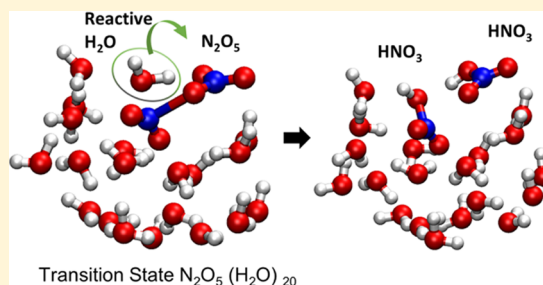


Microscopic Mechanisms of N₂O₅ Hydrolysis on the Surface of Water Droplets

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Supporting Information

ABSTRACT: Reactions of N₂O₅, in particular heterogeneous hydrolysis, play a vital role in determining the chemistry of the atmosphere. The N₂O₅ heterogeneous hydrolysis reaction has been the subject of extensive research for decades, yet the physicochemical details of the mechanism have not been established. In this study, we show that this reaction can occur on the surface of a pure water droplet. We compute a relevant transition state for a nano-size model system and follow its evolution in time by means of ab initio molecular dynamics. This transition state, where N₂O₅ has a strong ion-pair character, leads directly to HNO₃. Both electrophilic and nucleophilic mechanisms take place. It is suggested that corresponding simulations for hydrolysis in the bulk are desirable.



INTRODUCTION

It is well established that the nitrogen oxides (NO_x ≡ NO + NO₂) play a key role in controlling the oxidative capacity of the atmosphere.^{1–6} The hydrolysis of N₂O₅ in the gas phase is considered to be too slow to account for the atmospheric lifetime of N₂O₅.^{7,8} In fact, the heterogeneous reaction (RRR1) is believed to be the main cause for N₂O₅ removal.^{1,9–11}



Some models^{12–14} assume that RRR1 is a bulk reaction. Other studies^{8,15,16} proposed hydrolysis happening at the surface. For none of the two cases, bulk or surface, was a molecular-level description of the mechanism established so far.

Hydrolysis is considered as a rare event, and only a fraction of all of the N₂O₅ molecules in the gas phase that reach the water surface reacts. This fraction is referred to as reactive uptake (γ) and in pure water is estimated to be ~ 0.03 .^{7,13}

Among the key species affecting N₂O₅ hydrolysis in tropospheric aerosol particles are chloride and nitrate ions and organic molecules. The variability in these species potentially causes changes in γ that can alter the range of global ozone concentrations by up to 12%.³

The issue of hydrolysis in the presence of anions in water, and the competition with other processes, is of much interest, and it is discussed in a number of publications.^{17,18}

We focus on the hydrolysis of N₂O₅ in pure water, which remains poorly understood. We give a novel microscopic mechanistic description of the process, one that occurs at the surface of an aqueous particle, and we provide computational evidence that such a mechanism is valid.

METHODS

We computed several equilibrium amorphous N₂O₅·(H₂O)₂₀ cluster structures, as well as a crystalline one, using the B3LYP hybrid density functional theory (DFT),¹⁹ with the 6-31G+ basis set, adding D3 Grimme correction for dispersion.²⁰ Experience from related applications²¹ indicates that this level of potential function adequately describes the system of interest. These structures were considered as possible initial states for the ab initio molecular dynamics (AIMD)²² using the same level of theory. Following the entire process from these equilibrium configurations to products by computing picosecond trajectories was not feasible; thus, we pursued instead AIMD simulations from a relevant transition state (TS). Trajectories from the TS, referred to as the exit TS, lead directly to products. More details on the methodology can be found in the supplied Supporting Information (SI).

RESULTS AND DISCUSSION

We find and describe a relevant TS, with a strong ion-pair character: The NO₃^{δ−} part of the N₂O₅ in the TS has a substantial negative charge, while the NO₂^{δ+} carries instead a significantly smaller positive charge. Not all of the water molecules in the system are exactly neutral, and in particular, the reactive water molecule has a mild positive charge. Our results show that this TS leads directly to HNO₃ in femtoseconds and at room temperature via either a nucleophilic or an electrophilic process. We finally show that

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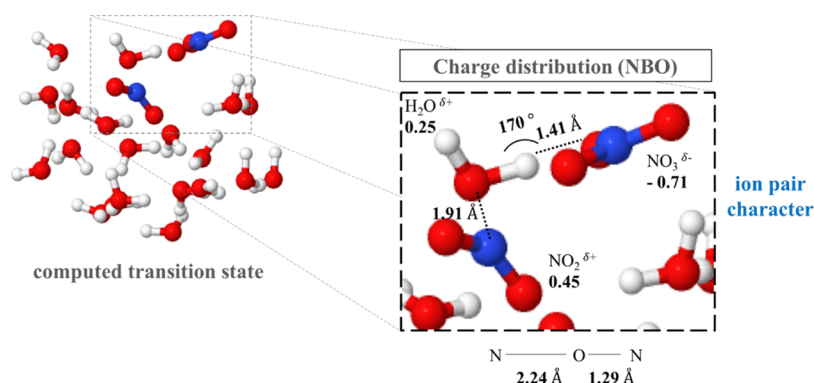


Figure 1. Computed exit channel TS for $\text{N}_2\text{O}_5 \cdot (\text{H}_2\text{O})_{20}$.

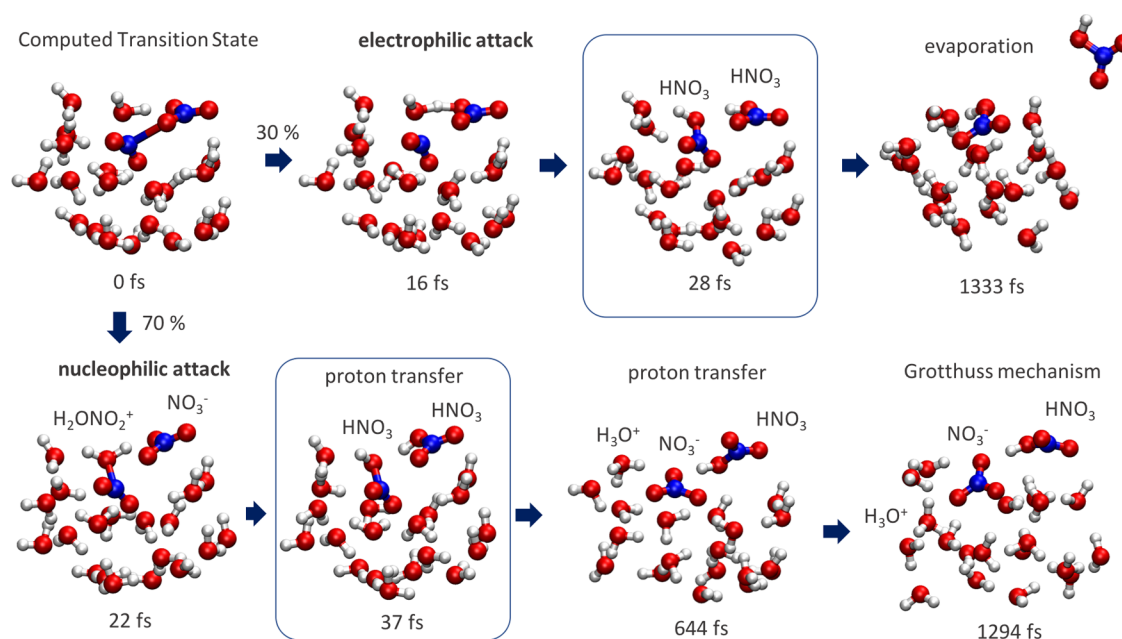


Figure 2. Surface mechanisms for N_2O_5 in pure water.

the nascent products of hydrolysis can be molecular or ionic. The mechanism found for this cluster model can be extended to larger systems. In a recent study,²³ we computed equilibrium structures of $\text{N}_2\text{O}_5 \cdot (\text{H}_2\text{O})_n$ clusters with $n = 1$ –20 and observed that N_2O_5 had a prominent ion-pair character for $n = 20$. $\text{NO}_3^{\delta-}$ carries a significant partial negative charge, and $\text{NO}_2^{\delta+}$ carries a smaller partial positive charge along with a water molecule that is also positively charged. In that state, N_2O_5 is expected to be more prone to hydrolyze.^{15,24} Previous studies on water clusters have successfully modeled reactions on the surface of water, ice, and aerosols.^{25–30} However, no hydrolysis was observed when starting from the equilibrium structure for $\text{N}_2\text{O}_5 \cdot (\text{H}_2\text{O})_{20}$; large partial charges on N_2O_5 develop rarely in time. A TS 12 kcal mol^{−1} higher in energy than the amorphous minimum was located as explained in the methodology section in the Supporting Information (SI), and it is presented in Figure 1. In this structure, we observe that (1) one of the N_2O_5 central N–O bonds is 2.24 Å long, very elongated (compared with the 1.72 Å length for the same bond in the equilibrium structure); (2) the $\text{NO}_3^{\delta-}$ and $\text{NO}_2^{\delta+}$ charges are -0.71 and $+0.45$, respectively, and the ion-pair character in this structure is stronger than in the equilibrium structure; (3) the oxygen of H_2O carries a negative charge of

-0.81 , being able to act as a nucleophile with $\text{NO}_2^{\delta+}$; and (4) the positively charged H_2O stabilizes the negative charge on $\text{NO}_3^{\delta-}$ by forming a strong hydrogen bond: angle O–H...O is almost linear, 170°, and the distance H...O is 1.41 Å.

Starting from that TS, we run over a hundred trajectories at 300 K, for ~4 ps. The analysis of the 75 reactive ones shows that two general mechanisms are possible. These mechanisms are presented in Figure 2. Both mechanisms show ultrafast hydrolysis, once the system has reached the exit TS. Nonreactive trajectories (Movie supplied in SI) confirm that the system explores multiple structures before reaching the TS.

Mechanism 1 (30%) starts by an ultrafast proton transfer from a surface water molecule to $\text{NO}_3^{\delta-}$, forming the first HNO_3 molecule. Twelve femtoseconds later, the remaining $\text{OH}^{\delta-}$ from the same water molecule bond to $\text{NO}_2^{\delta+}$ forming the second HNO_3 molecule. The hydrolysis reaction at the transition state is completed in ~30 fs—this time is obtained as an average over the trajectories following the mechanism. In 25% of the trajectories, one of the two HNO_3 product molecules evaporates. The evaporation rate is system-size-dependent, and in a bigger system, evaporation can be slightly lower. Mechanism 2 (70%) starts by the nucleophilic attack of a surface water molecule on $\text{NO}_2^{\delta+}$, producing one HNO_3

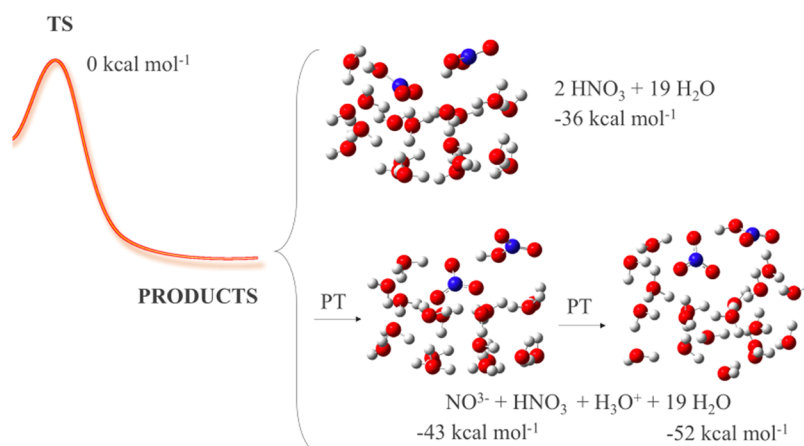


Figure 3. Energetic comparison of charged and neutral optimized products from two possible hydrolysis mechanisms.

molecule. It is worth noting that $\text{NO}_2^{\delta+}$ is not a proper nitronium atom but strongly coupled to $\text{NO}_3^{\delta-}$ and a water molecule. Prior literature has invoked solvent-separated species $\text{NO}_2^{\delta+}$ in reactions of N_2O_5 .^{16,31,32} Computational studies had shown that $\text{NO}_2^{\delta+}$ clustered with one or two water molecules can exist but in larger clusters, and this species is unstable.³³ This observation is consistent with our interpretation. The formation of the second HNO_3 molecule by a subsequent proton transfer step is also fast, and the hydrolysis reaction is completed at ~ 35 fs. The reaction continues further, and one of the HNO_3 molecules transfers a proton to a nearby H_2O molecule. We observe how the hydrolysis reaction may lead to either 2 HNO_3 or $\text{HNO}_3/\text{NO}_3^-/\text{H}_3\text{O}^+$.

Figure 3 shows that the products are stabilized by proton transfer. Once the hydrolysis is completed, in 32% of the trajectories, one of the HNO_3 molecules transfers a proton to a nearby water molecule, within 1–1.5 ps. One-third of these trajectories show further proton transfers by the Grotthuss mechanism.³⁴

In Figure 4, we show schematically two different equilibrium structures that come from optimization of points along a

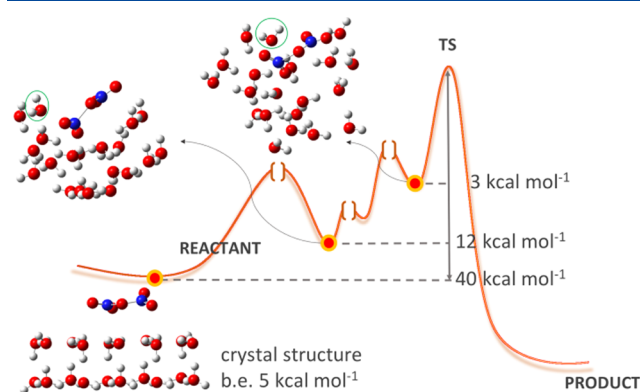


Figure 4. Schematic PES for the hydrolysis reaction for a post-TS nonreactive trajectory.

trajectory going from the TS, set as 0 kcal mol^{−1}, in the direction of the reactants (nonreactive trajectory). One of the equilibrium structures resembles more the structure of the computed TS and is 3 kcal mol^{−1} lower in energy. Another equilibrium structure is much lower in energy (by 12 kcal mol^{−1}), where the reactive water is further from the reactive

zone. The energy of the crystal structure, presented in the SI, is 40 kcal mol^{−1} lower than that of the TS. Not all equilibrium structures along the intrinsic reaction coordinate could be determined, since their number is very large. Neither was it feasible to compute the full reaction path. Hence, a quantitative reaction rate is not computed. Note that the points on the curve of the PES are solely for illustrative purposes.

The atomic-level description of the mechanism for hydrolysis presented here using our nano-size model system can be extended to the understanding of the hydrolysis on the surface of bigger systems. It can also describe the hydrolysis on thin layers, where no proper bulk is defined, and also for ice particles as well as the hydrolysis of molecules other than N_2O_5 .

Further studies of N_2O_5 in bulk water will certainly aid our understanding of the competition between surface and bulk hydrolysis reactions. Studies of the process in bulk require a larger model system, one that can properly accommodate a bulk site. We estimate that about 100 water molecules may be necessary. Locating a TS for the bulk system and using the level of theory used here become impractical to simulate picosecond trajectories. An alternative approach should be considered. We plan to pursue such simulations in the future.

CONCLUSIONS

The main result of this paper is the demonstration of the feasibility of a surface mechanism for the hydrolysis of N_2O_5 in a reaction with a pure water droplet. Microscopic details of the mechanism were established, including the structure of the exit channel TS, the role of partial charges on different atoms in the process, the distribution of adsorbed versus evaporated HNO_3 formed, and the nascent formation of deprotonated versus molecular HNO_3 . Interestingly, two variants of the microscopic hydrolysis mechanism were found: one involves nucleophilic attack by the O end of H_2O on the $\text{NO}_2^{\delta+}$ part of N_2O_5 , as the very first step of the reaction, and the second describes the initial step as H^+ transfer from the relevant H_2O molecule to the $\text{NO}_3^{\delta-}$ part of N_2O_5 . The relative contribution of the two mechanism variants is 0.7 (nucleophilic) to 0.3 (electrophilic).

It is certainly desirable to pursue the bulk reaction also on a microscopic level and to compare with the surface mechanism proposed here.

In summary, this study unraveled the first atomistic-level description of mechanisms of hydrolysis of N_2O_5 on a water surface. The mechanism may be relevant to other related processes, e.g., hydrolysis of N_2O_5 on thin water films upon solids and on ice surfaces. Furthermore, some elements of the mechanism may be applied also to the hydrolysis of molecules other than N_2O_5 on liquid water and on ices.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.9b08900>.

Detailed methodology, movie describing the dynamical evolution of the system before the TS, and structure of the TS (MPG)

Molecular dynamics simulations of $\text{N}_2\text{O}_5 \cdot (\text{H}_2\text{O})_{20}$ at thermal equilibrium; equilibrium structures for the $\text{N}_2\text{O}_5 \cdot (\text{H}_2\text{O})_{20}$ system; calculation of the exit TS; post-TS dynamics simulations (PDF)

Cartesian matrix corresponding to the exit channel transition state (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Dentener, F. J.; Crutzen, P. J. Reaction of N_2O_5 on Tropospheric Aerosols: Impact on the Global Distributions of NO_x , O_3 , and OH. *J. Geophys. Res.* **1993**, *98*, 7149–7163.
- (2) Thornton, J. A.; Abbatt, J. P. D. N_2O_5 reaction on Submicron Sea Salt Aerosol: Kinetics, Products, and the Effect of Surface Active Organics. *J. Phys. Chem. A* **2005**, *109*, 10004–10012.
- (3) Macintyre, H. L.; Evans, M. J. Sensitivity of a Global Model to the Uptake of N_2O_5 by Tropospheric Aerosol. *Atmos. Chem. Phys.* **2010**, *10*, 7409–7414.
- (4) Chang, W. L.; Bhawe, P. V.; Brown, S. S.; Riemer, N.; Stutz, J.; Dabdub, D. Heterogeneous Atmospheric Chemistry, Ambient Measurements, and Model Calculations of N_2O_5 : A Review. *Aerosol Sci. Technol.* **2011**, *45*, 665–695.
- (5) Abbatt, J. P. D.; Lee, A. K. Y.; Thornton, J. A. Quantifying Trace Gas Uptake to Tropospheric Aerosol: Recent Advances and Remaining Challenges. *Chem. Soc. Rev.* **2012**, *41*, 6555–6581.
- (6) Martins-Costa, M. T. C.; Anglada, J. M.; Francisco, J. S.; Ruiz-Lopez, M. Theoretical Investigation of the Photoexcited $\text{NO}_2 + \text{H}_2\text{O}$ Reaction at the Air-Water Interface and Its Atmospheric Implications. *Chem. - Eur. J.* **2019**, *25*, 13899–13904.
- (7) Burkholder, J. B.; Sander, S. P.; Abbatt, J. P. D.; Barker, J. R.; Huie, R. E.; Kolb, C. E.; Kurylo, M. J.; Orkin, V. L.; Wilmouth, D. M.

Wine, P. H. *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies Evaluation Number 18*; Jet Propulsion Laboratory, 2015.

(8) Mozurkewich, M.; Calvert, J. G. Reaction Probability of N_2O_5 on Aqueous Aerosols. *J. Geophys. Res.* **1988**, *93*, 15889–15896.

(9) Mentel, T. F.; Bleilebens, D.; Wahner, A. A Study of Nighttime Nitrogen Oxide Oxidation in a Large Reaction Chamber - The Fate of NO_2 , N_2O_5 , HNO_3 , and O_3 at Different Humidities. *Atmos. Environ.* **1996**, *30*, 4007–4020.

(10) Wahner, A.; Mentel, T. F.; Sohn, M. Gas-Phase Reaction of N_2O_5 with Water Vapor: Importance of Heterogeneous Hydrolysis of N_2O_5 and Surface Desorption of HNO_3 in a Large Teflon Chamber. *Geophys. Res. Lett.* **1998**, *25*, 2169–2172.

(11) Voegele, A. F.; Tautermann, C. S.; Loerting, T.; Liedl, K. R. Toward Elimination of Discrepancies Between Theory and Experiment: The Gas-Phase Reaction of N_2O_5 with H_2O . *Phys. Chem. Chem. Phys.* **2003**, *5*, 487–495.

(12) Schwartz, S. Mass Transport Considerations Pertinent to Aqueous Phase Reactions of Gases in Liquid Water Clouds. In *Chemistry of Multiphase Atmospheric Systems*, NATO ASI Ser.; Jaeschke, W., Ed.; Springer-Verlag: New York, 1986; Vol. 6, pp 415–471.

(13) Bertram, T. H.; Thornton, J. A. Toward a General Parameterization of N_2O_5 Reactivity on Aqueous Particles: The Competing Effects of Particle Liquid Water, Nitrate and Chloride. *Atmos. Chem. Phys.* **2009**, *9*, 8351–8363.

(14) McNamara, J. P.; Hillier, I. H. Structure and Reactivity of Dinitrogen Pentoxide in Small Water Clusters Studied by Electronic Structure Calculations. *J. Phys. Chem. A* **2000**, *104*, 5307–5319.

(15) Wahner, A.; Mentel, T. F.; Sohn, M.; Stier, J. Heterogeneous Reaction of N_2O_5 on Sodium Nitrate Aerosol. *J. Geophys. Res.: Atmos.* **1998**, *103*, 31103–31112.

(16) Behnke, W.; George, C.; Scheer, V.; Zetzsch, C. Production and Decay of ClNO_2 from the Reaction of Gaseous N_2O_5 with NaCl Solution: Bulk and Aerosol Experiments. *J. Geophys. Res.: Atmos.* **1997**, *102*, 3795–3804.

(17) McCaslin, L. M.; Johnson, M. A.; Gerber, R. B. Mechanisms and Competition of Halide Substitution and Hydrolysis in Reactions of N_2O_5 with Seawater. *Sci. Adv.* **2019**, *5*, No. eaav6503.

(18) Staudt, S.; Gord, J. R.; Karimova, N.; McDuffie, E. E.; Brown, S. S.; Gerber, R. B.; Nathanson, G. M.; Bertram, T. H. Sulfate and Carboxylate Suppress the Formation of ClNO_2 at Atmospheric Interfaces. *ACS Earth Space Chem.* **2019**, *3*, 1987–1997.

(19) Becke, A. A New Mixing of Hartree-Fock and Local Density-Functional Theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.

(20) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104–154118.

(21) Vander Wall, A. C.; Lakey, P. S. J.; Rossich Molina, E.; Perraud, V.; Wingen, L. M.; Xu, J.; Soulsby, D.; Gerber, R. B.; Shiraiwa, M.; Finlayson-Pitts, B. J. Understanding Interactions of Organic Nitrates with the Surface and Bulk of Organic Films: Implications for Particle Growth in the Atmosphere. *Environ. Sci. Process. Impacts* **2018**, *20*, 1593–1610.

(22) Car, R.; Parrinello, M. Unified Approach for Molecular Dynamics and Density-Functional Theory. *Phys. Rev. Lett.* **1985**, *55*, No. 2471.

(23) Hirshberg, B.; Rossich Molina, E.; Götz, A. W.; Hammerich, A. D.; Nathanson, G. M.; Bertram, T. H.; Johnson, M. A.; Gerber, R. B. N_2O_5 at Water Surfaces: Binding Forces, Charge Separation, Energy Accommodation and Atmospheric Implications. *Phys. Chem. Chem. Phys.* **2018**, *20*, 17961–17976.

(24) Alecu, I. M.; Marshall, P. Computational Study of the Thermochemistry of N_2O_5 and the Kinetics of the Reaction $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3$. *J. Phys. Chem. A* **2014**, *118*, 11405–11416.

(25) Vaida, V. Perspective: Water Cluster Mediated Atmospheric Chemistry. *J. Chem. Phys.* **2011**, *135*, No. 020901.

(26) Bertram, T. H.; Thornton, J. A.; Riedel, T. P.; Middlebrook, A. M.; Bahreini, R.; Bates, T. S.; Quinn, P. K.; Coffman, D. J. Direct

Observations of N_2O_5 Reactivity on Ambient Aerosol Particles. *Geophys. Res. Lett.* **2009**, *36*, No. L19803.

(27) Miller, Y.; Thomas, J. L.; Kemp, D. D.; Finlayson-Pitts, B. J.; Gordon, M. S.; Tobias, D. J.; Gerber, B. R. Structure of Large Nitrate-Water Clusters at Ambient Temperatures: Simulations with Effective Fragment Potentials and Force Fields with Implications for Atmospheric Chemistry. *J. Phys. Chem. A* **2009**, *113*, 12805–12814.

(28) Jungwirth, P.; Tobias, J. D. Ions at the Air/Water Interface. *J. Phys. Chem. B* **2002**, *106*, 6361–6373.

(29) Varner, M. E.; Finlayson-Pitts, B. J.; Gerber, B. R. Reaction of a Charge-Separated ONONO₂ Species with Water in the Formation of HONO: An MP2 Molecular Dynamics Study. *Phys. Chem. Chem. Phys.* **2014**, *16*, 4483–4487.

(30) Gerber, R. B.; Varner, M. E.; Hammerich, A. D.; Riikonen, S.; Murdachaew, G.; Shemesh, D.; Finlayson-Pitts, B. J. Computational Studies of Atmospherically-Relevant Chemical Reactions in Water Clusters and on Liquid Water and Ice Surfaces. *Acc. Chem. Res.* **2015**, *48*, 399–406.

(31) Herrmann, H.; Ervens, B.; Jacobi, H.-W.; Wolke, R.; Nowacki, P.; Zellner, R. CAPRAM2.3: A Chemical Aqueous Phase Radical Mechanism for Tropospheric Chemistry. *J. Atmos. Chem.* **2000**, *36*, 231–284.

(32) Ervens, B.; et al. CAPRAM 2.4 (MODAC Mechanism): An Extended and Condensed Tropospheric Aqueous Phase Mechanism and Its Application. *J. Geophys. Res.* **2003**, *108*, 4426–4447.

(33) Ishikawa, Y.; Binning, R. C. *Computational Chemistry: Reviews of Current Trends*; Leszczynski, J., Ed.; World Scientific: Jackson, 2002; pp 187–244.

(34) Agmon, N. The Grotthuss Mechanism. *Chem. Phys. Lett.* **1995**, *244*, 456–462.