

Ionization of N₂O₄ in Contact with Water: Mechanism, Time Scales and Atmospheric Implications

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Abstract: Ionization of N₂O₄ in and on thin water films on surfaces is believed to be a key step in the hydrolysis of NO₂ which generates HONO, a significant precursor to the OH free radical in the lower atmosphere. Molecular dynamics simulations using “on the fly” high-level MP2 potentials are carried out for ONONO₂·(H₂O)_n clusters, $n \leq 8$, used to mimic the surface reaction, in order to investigate the ionization process and determine its time-scale and mechanism around room temperature. The results are (i) the isolated molecule does not convert to the NO⁺NO₃⁻ ion pair, even for long times; (ii) for ONONO₂·(H₂O)_n with $n = 1$ and 2, ionization takes place in several picoseconds; (iii) for $n \geq 3$, ionization is essentially immediate, implying that the neutral species does not have sufficient lifetime to be considered a significant intermediate in the reaction; and (iv) even at ice temperatures, $T \leq 250$ K, ionization for $n \geq 3$ is immediate. The implications for hydrolysis of oxides of nitrogen on surfaces in the atmosphere are discussed.

I. Introduction

Substantial experimental evidence points to the fact that the molecule NO₂ and its chemically bound dimer N₂O₄ are involved in important heterogeneous processes on surfaces in atmospheric and environmental chemistry.¹ In particular, the formation of HONO in the hydrolysis of NO₂ in water has been the topic of extensive experimental studies.^{1–17} Finlayson-Pitts and co-workers proposed a mechanism⁵ in which a sequence of

reactions beginning with dimerization of NO₂ to form N₂O₄ at the water–gas interface leads to the observed products, HONO and HNO₃. HONO is one of the main atmospheric sources of OH radicals that drive the chemistry of the troposphere.^{1,18} According to this mechanism, N₂O₄ is formed as its stable, symmetric isomer but undergoes conversion on the surface to an asymmetric, less stable form. Koel and co-workers had proposed isomerization occurs via the free O–H groups on amorphous ice,^{19–21} and it has been observed in a number of other studies.^{22–30} Various aspects of this chemistry have been studied using DFT calculations.^{31–33}

The asymmetric isomer is believed to undergo an ionization process to form the ion pair (NO⁺)·(NO₃⁻) which subsequently reacts with a water molecule to form HONO and HNO₃.⁵ This mechanism is partly supported by spectroscopic and kinetic

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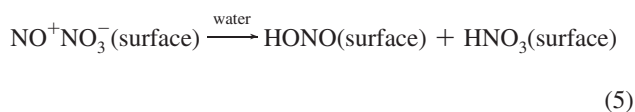
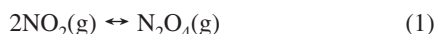
studies on NO₂ hydrolysis at thin water films and is also motivated by analogies with several other chemical reactions that correspond to the various steps. For example, the hydrolysis of N₂O₅ is believed to occur via ionization to NO₂⁺ + NO₃⁻ followed by reaction with water to form 2HNO₃.^{34,35} This reaction can be driven in the reverse direction by the presence of nitrate ions in the solution.³⁶ However, direct experimental evidence for the NO₂ hydrolysis mechanism is not yet at hand and presents a major challenge. In particular, the postulated step of conversion of asymmetric N₂O₄ into NO⁺ and NO₃⁻ raises many questions. Demonstration of this step and determination of its rate and other properties seems very desirable.

In the present study, we demonstrate computationally the ionization (or the autoionization) of asymmetric N₂O₄ in water clusters of different sizes to form NO⁺ and NO₃⁻. Clusters provide a reasonable model for surface reactions, which likely occur at the air–water interface and have different kinetics and mechanisms than bulk phase reactions.^{5,37,38} The approach taken is molecular dynamics (MD) simulations at the microscopic level and employs accurate, reliable potential surfaces that can adequately describe the process. These MD simulations, using MP2 potentials, are a demanding test of the feasibility of the proposed mechanism. Beyond testing the mechanism, our theoretical approach serves to characterize the process on the atomistic scale, determine its reaction time scale, and establish the role of water in the ionization.

The structure of the paper is as follows. We first describe the model system used, and the methodology of the simulation. Results and Analysis follow along with implications for atmospheric processes. Small clusters as a model for exploring chemical reactivity in at the water–air interface is discussed in Concluding Remarks.

II. Model System and Method

1. Assumed N₂O₄ Ionization in Hydrolysis of NO₂. It will be useful to consider briefly the current model of NO₂ hydrolysis at thin water films and the assumed step of N₂O₄ ionization in the kinetic sequence.⁵ The proposed mechanism is



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The HONO is subsequently released to the gas phase,^{16,39} while the HNO₃ remains on the surface in the form of complexes with water, the HNO₃ dimer, and the dissociated ions.¹⁷ Hydrolysis of NO₂ also occurs in bulk solution but is relatively slow.⁴⁰ The mechanism represented by reactions 1–5 suggests that ionization follows the formation of ONONO₂ as a well-defined neutral intermediate. For fundamental understanding of the process, it is important to establish whether ONONO₂ has a chemically meaningful lifetime before it dissociates into ions. It is also of interest to establish whether the process is thermally activated or rather spontaneous and immediate. The role of water in the process is also obviously of major interest.

The present paper explores the above questions by first-principles simulations in the framework of a simplifying model of finite cluster systems.

2. N₂O₄ in Water Clusters As a Model System. To carry out dynamics calculations with potential surfaces for a sufficiently high level of ab initio theory, restriction to finite cluster systems is required. For chemical reactions that are localized, such as reactions at the air–water interface, clusters are expected to provide at least a semiquantitative model. The water clusters studied in this paper are small ($n \leq 8$), but as will be seen later, the results strongly support the implied assumption of the very localized nature of the water environment effect upon ionization. The simulations described below begin with initial structures of the form ONONO₂·(H₂O)_n and compute the evolution of the systems in time. Sampling of the initial conditions for the trajectories is described later, but the computed equilibrium structure of both planar and nonplanar ONONO₂ were used in all cases. Obviously, if the ONONO₂ undergoes ionization after an exceedingly short time after the initiation of the dynamics, it is questionable whether this species should be considered as an intermediate in the reaction sequence of Section II.1.

3. Dynamics Using Directly Ab Initio MP2. The ab initio MP2 method has been used extensively for the structure, energetics, and vibrational spectroscopy of both neutral and ionic hydrogen-bonded clusters.^{41–47} Excellent agreement with experiments is generally found,⁴⁵ indicating the high quality of MP2 potential energy surfaces for water clusters.

Most recently, Miller and Gerber⁴⁸ used directly MP2 “on-the-fly” MD simulations of the recombination of protons and NO₃⁻ in water clusters ($n = 9$). Previously, only very few direct dynamics simulations using MP2 were reported, and these were for small isolated molecules.^{49–51} Recently, “on-the-fly” simulations have also been used with a high-level of theory (not MP2)

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on the pyruvic acid molecule.⁵² Careful selection of the initial states, as in ref 48, helps in efficient determination significant trajectories, and reduces the computational effort. The basis set used in our direct dynamics is DZV. Higher-level basis sets are computationally costly for the large clusters used here.

A first step for sampling the initial coordinates for the molecular dynamics, the local minima for *cis*-ONONO₂, *cis*-ONONO₂·H₂O, and *trans*-ONONO₂·(H₂O)₂ were calculated by using the MP2 electronic structure theory with the DZV basis set in the GAMESS package.^{53,54} A set of initial configurations were chosen with different positions of the ONONO₂ within the water cluster. Initial velocities for the molecular dynamics were computed by providing kinetic energy corresponding to a given temperature to each atom in the system, with sampling of different possible directions of the momenta. The trajectories were then propagated in time, where the time step size is 0.1 fs. Simulations were selected to stop when the ionization process occurs. The SCF convergence criterion which was used in the simulations is 10⁻⁹, whereas the default value which is employed in the standard GAMESS code^{53,54} is 10⁻⁵. The convergence criterion of 10⁻⁹ was tested and found to give accurate force calculations for all trajectories for all the current systems which have been studied here.

III. Results and Analysis

1. Initial States. The equilibrium geometries for *cis*-ONONO₂, *cis*-ONONO₂·H₂O, and *trans*-ONONO₂·(H₂O)₂ were calculated by using the MP2 electronic structure theory with the DZV basis set in the GAMESS package.^{53,54} The *cis* form was studied for *n* = 0 and 1 water molecules, but the *trans* for *n* = 2 because the *trans* conformer was obtained in all attempted optimizations of the initial state structure, suggesting that solvation stabilizes the *trans* compared with the *cis* conformer. The optimized geometries of *cis*-ONONO₂, *cis*-ONONO·H₂O, and *trans*-ONONO₂·(H₂O)₂ are shown in Figure 1. For the larger clusters (*n* = 3, 4, and 8), a set of initial configurations for the dynamics are local minima of the potential for the clusters. It should be noted here that the zero point energy of the species were not taken into account in the initial conditions. In our previous work,⁴⁸ initial configurations for the molecular dynamics simulations were also local minima of the potential for the clusters of NO₃⁻·H₃O⁺·(H₂O)_{*n*}, *n* = 8.

A detailed procedure for the MD simulations is presented in our previous work.⁴⁸ Kinetic energy corresponding to 200, 250, and 300 K, respectively, was provided to the atoms, with sampling of different possible directions of the momenta. The trajectories are then propagated in time. One trajectory was obtained for *cis*-ONONO₂·(H₂O)_{*n*}, *n* = 0, 1 at *T* = 200 K and *T* = 250 K, *trans*-ONONO₂·(H₂O)₂ at *T* = 200 and 250 K, and 14 trajectories were computed for *cis*-ONONO₂·(H₂O)_{*n*}, *n* = 3, 4, 8 at *T* = 200, 250, and 300 K. All trajectories, except those for *n* = 0, resulted ionization of ONONO₂·(H₂O)_{*n*} into NO⁺ and NO₃⁻ ions. Snapshots of a given set of trajectories (including partial charges and the HOMO orbitals of each snapshot) are shown in Figures 2–4.

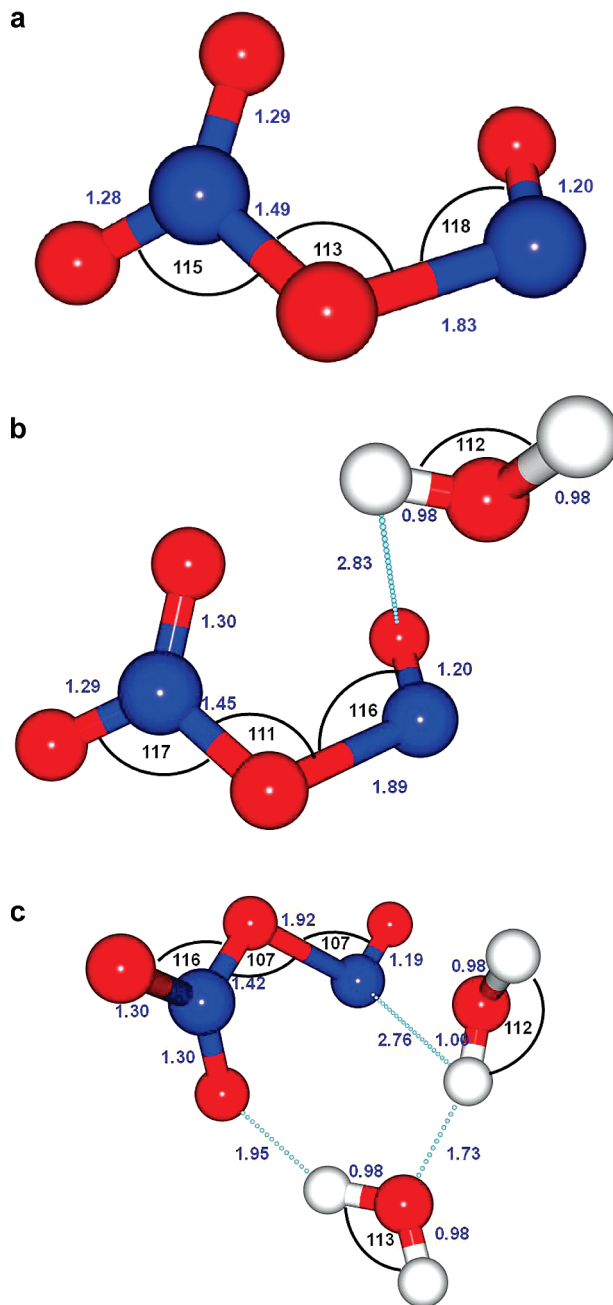


Figure 1. Optimized equilibrium structures of (a) *cis*-ONONO₂, (b) *cis*-ONONO₂·H₂O, and (c) *trans*-ONONO₂·(H₂O)₂. Bond lengths (in Å) and angles (in deg) are given for the MP2/DZV level of theory.

2. Dynamics in Time of ONONO₂·(H₂O)_{*n*}. Charge transfer within small molecules in clusters is an important process in physical and atmospheric chemistry. Cheshnovsky et al.⁵⁵ studied charge transfer in α -naphthol solvated in ammonia clusters. Jungwirth et al.⁵⁶ studied the charge transfer between sulfate ions and water. However, simulations of ONONO₂ in water clusters have not been reported.

Consider first the isolated ONONO₂ species. At equilibrium geometry, bonding in this species is partly ionic but largely covalent. This is seen from the computed partial charges on the atoms in the first snapshot of Figure 2a. The NO₃ and NO parts of the molecule are rather close in this configuration, the

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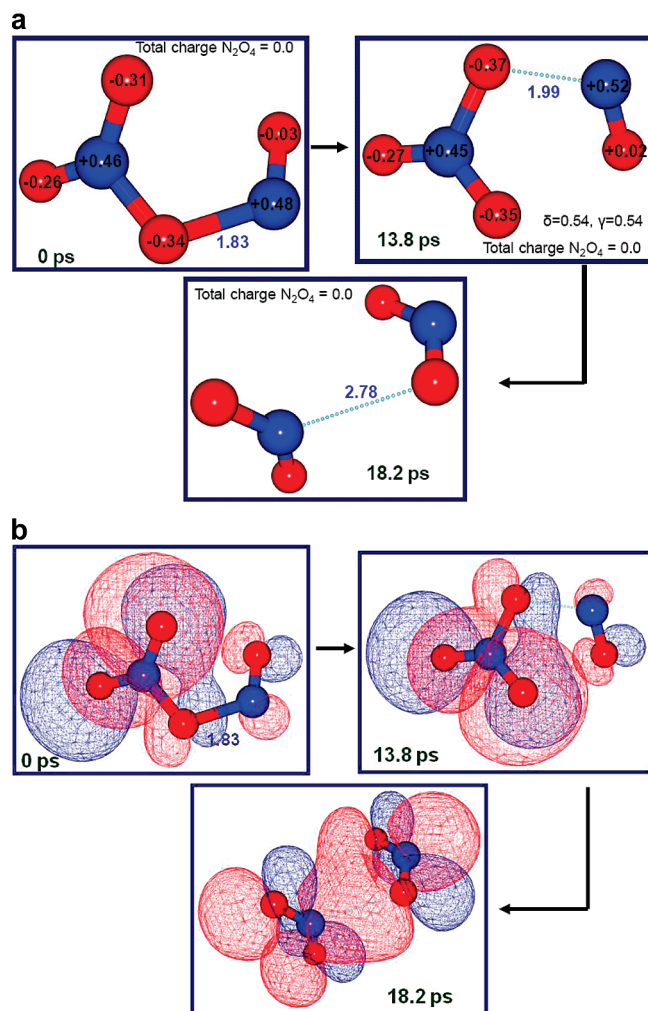


Figure 2. Snapshots of the dissociation process of $cis\text{-ONONO}_2$ into NO_2 at $T = 200$ K. (a) Partial charges on $\text{NO}^{+\delta}$ and $\text{NO}_3^{-\gamma}$ and for each atom of the $cis\text{-ONONO}_2$ (Mulliken charges) in a.u.; (b) HOMO orbital for each snapshot.

O–N distance between the two parts being only 1.83 Å. Further, there is an appreciable electronic density from the HOMO orbital between the two parts (which is being only 1.83 Å) at about equal distance from each (Figure 2b). Thus, at equilibrium geometry ONONO_2 obviously does not correspond to a pair of separate ions. This character of ONONO_2 seems to prevail for all computed trajectories in time and at all temperatures studied. Consider, for example, the snapshots of Figure 2a from one of the trajectories at 200 K. The largest O–N distance attained in this trajectory, at 13.8 ps, is 1.99 Å, not large enough to correspond to a separate pair. Moreover, the positive partial charge on the NO part, +0.54 au, is somewhat larger than at equilibrium (+0.45) but not enough for describing NO and NO_3 as a separate pair of ions. The shape of the HOMO orbital at 13.8 ps in Figure 2b, a sensitive indicator, is also not very different from that at equilibrium. Separation of ONONO_2 into fragments does take place in the trajectory of Figure 2, and is seen from the snapshot at 18.2 ps. However, this corresponds to dissociation into $\text{NO}_2 + \text{NO}_2$. Such dissociation is implied by the equilibrium $\text{N}_2\text{O}_4 \leftrightarrow 2\text{NO}_2$ at $T = 200$ K, but is a different process from ionization. In summary, ionization of isolated ONONO_2 into NO^+ and NO_3^- does not take place at room (or lower) temperature.

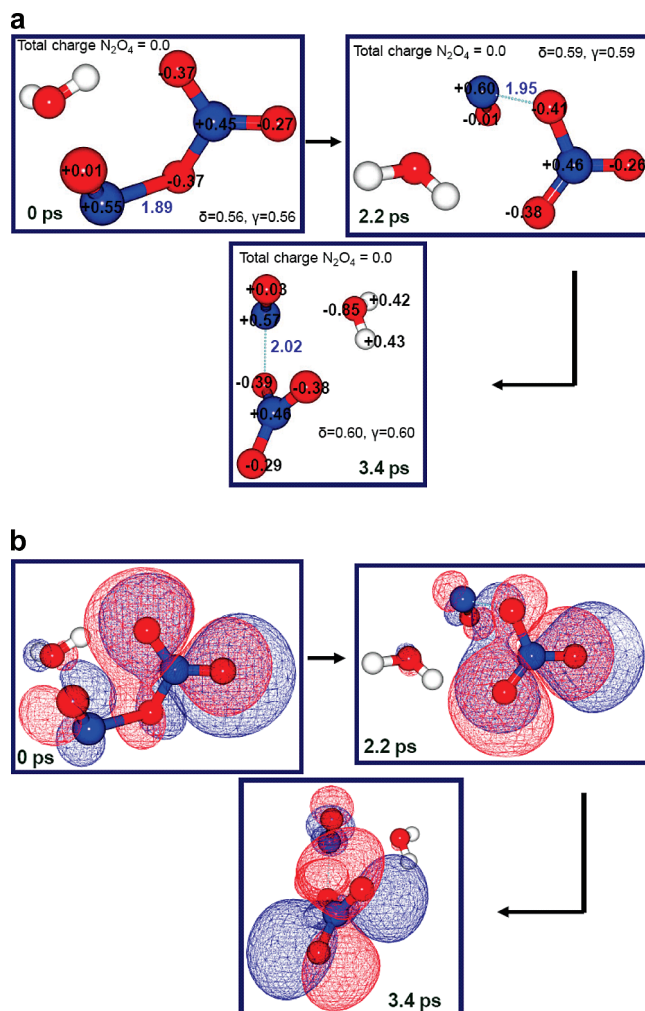


Figure 3. Snapshots of the ionization process of $cis\text{-ONONO}_2 \cdot (\text{H}_2\text{O})$ at $T = 250$ K. (a) Partial charges on $\text{NO}^{+\delta}$ and $\text{NO}_3^{-\gamma}$ and for each atom of the $cis\text{-ONONO}_2$ (Mulliken charges) in a.u.; (b) HOMO orbital for each snapshot.

The situation is dramatically different for the 1:1 complex of ONONO_2 with H_2O . Snapshots of the dynamics at 200 K are shown in Figure 3a. In the trajectory shown, the system reaches a transition state within 2.2 ps, in which the O–N bond between the NO and NO_3 parts of the molecule has grown to 1.95 Å. The partial charge on the NO group in this “transition state” is +0.59. Also, the shape of the HOMO orbital in the second snapshot of Figure 3b suggests that a chemical change is taking place, since this shape is significantly different from that in the first snapshot. This is another indication that the bond between the NO and NO_3 groups is breaking. The third snapshot in Figure 3a shows an increased distance between the $\text{NO}^{+\delta}$ and $\text{NO}_3^{-\gamma}$, though the separation is not complete. Further, the H_2O molecule has reoriented at this stage, 3.4 ps after the initial state, which probably allows for improved solvation of the $\text{NO}^{+\delta}$ (with $\delta \approx 0.6$). The electrostatic field due to the partial charges on the water molecule seems to provide the driving force for the ionic separation process in ONONO_2 . Other trajectories for this system also show (partial) ionic separation, within a time scale of several picoseconds. Temperature effects are briefly discussed later but are fairly modest for $\text{ONONO}_2 \cdot (\text{H}_2\text{O})$. The process of substantial, though not complete, separation of ONONO_2 into NO^+ and NO_3^- ions is found also for $\text{ONONO}_2 \cdot$

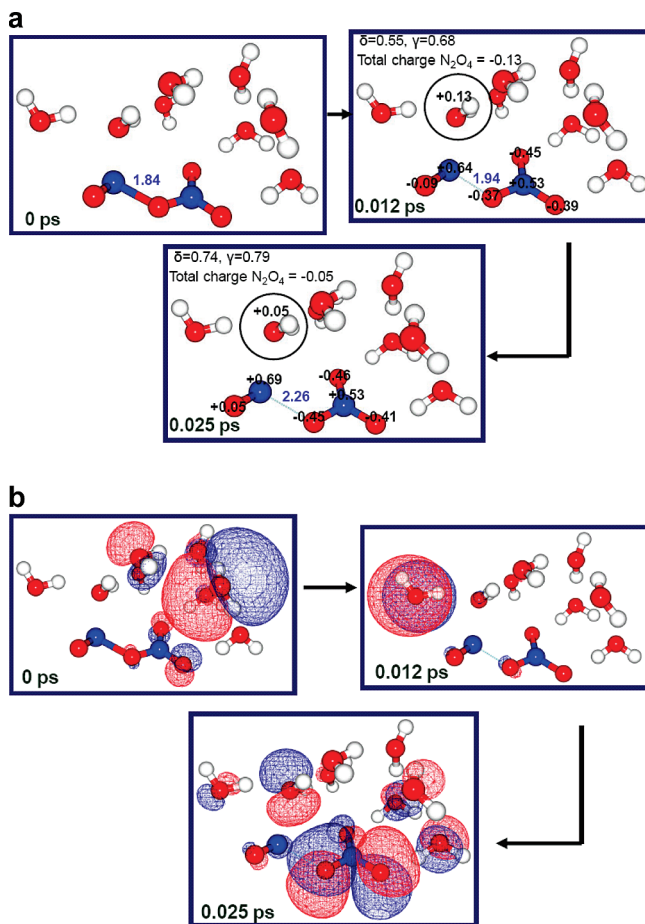


Figure 4. Snapshots of the ionization process of *cis*-ONONO₂·(H₂O)₈ at $T = 200$ K. (a) Partial charges on NO^{+ δ} and NO₃^{- γ} and for each atom of the *cis*-ONONO₂ (Mulliken charges) in a.u.; (b) HOMO orbital for each snapshot.

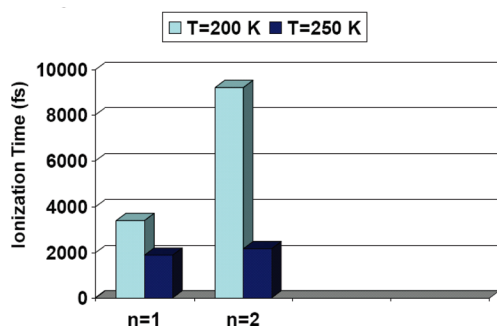


Figure 5. Ionization times for *cis*-ONONO₂·H₂O and *trans*-ONONO₂·(H₂O)₂ at $T = 200$ and 250 K.

(H₂O)₂. The time scale of several picoseconds is similar, though there are differences in the temperature effect.

A major change in the nature of the ionization process is found for ONONO₂·(H₂O)_n clusters with $n \geq 3$. We illustrate the process for $n = 8$ (Figure 4). One of the main differences compared to the small clusters is that after only 25 fs, the separation into ions is essentially complete and the partial charges on the NO^{+ δ} and NO₃^{- γ} groups are +0.74 and -0.79, respectively. This corresponds to an acceleration of the ionization process of more than 2 orders of magnitude compared with the smaller clusters with $n = 1$ and 2. An interesting aspect shown in Figure 4a, as well as of a fraction of the other trajectories for the large clusters, is that the partial charges on

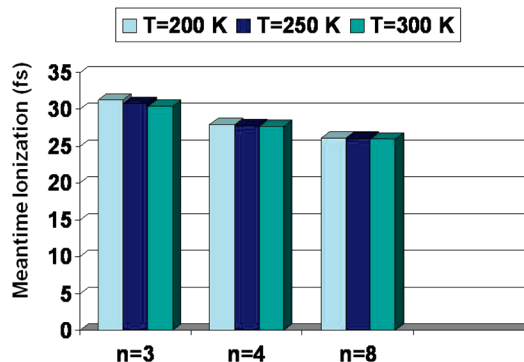


Figure 6. Mean ionization times for *cis*-ONONO₂·(H₂O)_n, $n = 3, 4,$ and 8, at different temperatures.

the NO^{+ δ} and NO₃^{- γ} are not the same throughout the process. For example, $\delta = 0.55$ and $\gamma = 0.68$ in the second snapshot of Figure 4a where partial ionization has occurred. The reason for this seems to be that the interactions between ONONO₂ and water in the larger clusters can involve a small, but significant, amount of charge transfer between the ion pair and water. Figure 4b indicates that the lone-pair electrons on some of the water molecules play a role in this, and in particular at $t = 25$ fs, a relatively strong interaction between the NO^{+ δ} species and the nearest water molecule involves some charge transfer (-0.05 au) from the water to the NO^{+ δ} . The extremely short time scale for the NO^{+ δ} ···NO₃⁻ ionic separation shows that this cannot be considered a thermally activated process but rather is a spontaneous one. While the first snapshots in Figure 4a,b correspond to a local minimum of the potential surface, the energy barrier against motion from this configuration is very small, essentially insignificant at the temperatures considered. The difference between the small clusters, $n = 1$ and 2, and the larger cluster ($n = 8$) is that the electrostatic field exerted by the partial charges for $n \geq 3$ are stronger, and essentially eradicate the barrier for the NO^{+ δ} ···NO₃⁻ charge separation.

In summary, for $n = 1$ and 2 the separation of ONONO₂ into ions is partial and is an activated process which takes picoseconds at the temperatures of interest. For $n \geq 3$ the separation into ions is nearly complete and spontaneous, occurring almost instantaneously when ONONO₂ is in contact with water. Implications of this for the hydrolysis mechanism of N₂O₄ are discussed below.

3. Temperature Effects and Cluster Size Effects. Figure 5 shows the mean ionization time computed for ONONO₂·(H₂O) and ONONO₂·(H₂O)₂ at $T = 200$ and 250 K. The interpretation of the results is straightforward. Basically, the ionization mechanism is the same for both clusters, as discussed in Section III.2 above. However, for $n = 2$ the structural rearrangement for reaching the transition state requires higher kinetic energy. Hence, the ionization for $n = 2$ is slower by a factor of ~ 5 for $T = 200$ K than for $T = 250$ K. For $n = 1$, where the required energy for structural rearrangement is smaller, the temperature effect is modest. Also, at $T = 250$ K, where the available kinetic energy is ample, the ionization rates for $n = 1$ and 2 are almost identical. The mean ionization times for the $n = 3, 4,$ and 8 clusters at $T = 200, 250,$ and 300 K are shown in Figure 6. In all of these cases the ionization is essentially spontaneous and instantaneous, as discussed in Section III.2. As expected in this case, since the process is not thermally activated, there is hardly any temperature effect. Further, the ionization rate increases only slightly with cluster size. This minor increase is due to the larger

electrostatic field of the solvent at the $ONONO_2$ when more water molecules are present.

The results suggest that the ionization process should also take place at extremely low temperatures. Given the cluster size effect found, this extrapolation is expected to hold for the air-water interface.

IV. Implications for Atmospheric Chemistry

These results are relevant to several important issues in atmospheric chemistry. We examine first the mechanism of hydrolysis of NO_2 (thus of N_2O_4) on thin water films on surfaces as discussed in Section III.1. The present results support the feasibility of the mechanism proposed by Finlayson-Pitts and co-workers⁵ in that the formation of $NO^+NO_3^-$ from the asymmetric dimer via reaction 4 is extremely fast in the presence of water. In fact, it is so fast that $ONONO_2$, as a well-defined transient with a chemically meaningful lifetime, cannot be formed on contact with more than two water molecules. Because of this, the presence of small $(ONONO_2) \cdot (H_2O)_n$ clusters is unlikely to be significant in realistic atmospheric systems. However, the $NO^+NO_3^-$ species that the clusters form so rapidly are likely to be important. Reaction of this ion pair with water will form $HONO$ and HNO_3 , and other reactions may also be possible.

These findings call for a reconsideration of the processes leading to formation of NO^+ and NO_3^- , in the hydrolysis of NO_2 , and especially in the isomerization of symmetric N_2O_4 , proposed in some cases to play a role. Chou et al.³¹ reported earlier that the direct reaction of symmetric N_2O_4 with water has too large a barrier to be important in the gas phase. Symmetric N_2O_4 has been reported from experiments to be converted to $ONONO_2$ on ice surfaces between 130 and 183 K,^{19–21} and theoretical calculations reported that the lifetime of symmetric N_2O_4 at room temperature with respect to isomerization is of the order of 500 s.³³ Our paper does not address the mechanism of conversion of symmetric O_2NNO_2 to $ONONO_2$, but the results presented here suggest that the lifetime of $ONONO_2$ in the presence of water is too short to consider it as an intermediate chemical species in the process. One possibility is motivated by the results of Pimentel et al.³² that show a formation of $ONONO_2$ directly from two NO_2 molecules in the gas phase is barrierless. Assuming such a mechanism, our results establish that in the presence of water $ONONO_2$ will ionize directly upon formation, and essentially be a transition state. It is also possible in principle that formation of NO^+ and NO_3^- takes place directly from symmetric N_2O_4 at the surface of water; as symmetric N_2O_4 “tries” to isomerize, it reaches a transition state like $ONONO_2$ and ionizes directly. Both of these suggestions are speculations at this stage and deserve future study.

Another issue of importance is the temperature effect. Symmetric N_2O_4 has been experimentally observed to be converted to $ONONO_2$ on ice surfaces between 130 and 183 K,^{19–21} and our simulations were performed at higher temperatures for small clusters that are very floppy, almost like liquid. Therefore, it is possible that ionization at, or in contact with, realistic ice is different than at a small cluster of water at 250

K. Future work on larger water clusters than studied here is justified to provide a more realistic model for ice in bulk. The results here predict that ionization at the ice-air interface should take place at essentially the same rate as at the water-air interface, suggesting that a detailed temperature study of the kinetics would be interesting.

Finally, and more broadly, the results point to a rich and interesting chemistry of NO_3 species in contact with water. The formation of ionic species and the role of solvation by water suggest that this is likely to lead to previously unrecognized chemical reactions that remain to be unraveled. This will be explored in the future through a combination of theoretical simulations and experiments on water films.

V. Concluding Remarks

Dynamics simulations of the separation of asymmetric N_2O_4 into NO^+ and NO_3^- ions were carried out in clusters of water. The calculations were carried out using the electronic structure method MP2, which is considered to be very reliable for water clusters.⁴⁸ Dynamics using directly the electronic structure method has been increasingly used in recent years to explore processes of atmospheric relevance.^{48,57,58}

The results show the utility of small clusters as a model for exploring chemical reactivity at the water-air interface. Several recent computational studies, specifically for water clusters and in an atmospheric chemistry context, also point in this direction.^{48,57,58} Interestingly, while none of the clusters investigated here is large, a transition in the nature of the process was found for $n \geq 3$ water molecules. This is a critical size effect, and such effects are of considerable interest in the physical chemistry of clusters.⁴⁵ More important for our purpose here is that quite small clusters seem to exhibit a chemical behavior that probably extrapolates to that expected for the corresponding water-air and ice-air interfaces, which are the systems of main relevance for atmospheric chemistry. In our model, the position of the water part of the larger clusters seems much like that expected at an interface.

The results presented support a key step in the hydrolysis of NO_2 at water, namely the separation of asymmetric N_2O_4 into NO^+ and NO_3^- . At the same time, the results provide insights into the nature of the process. Only for small water clusters is asymmetric $ONONO_2$ a well-defined intermediate. For large clusters (hence realistic water or ice on surfaces in the atmosphere), $ONONO_2$ has no significant lifetime. The simulations predict that the process takes place down to low temperatures, certainly ice temperatures, with the same rate as for room temperatures.

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