

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/51139488>

New Insights in the Atmospheric HONO Formation: New Pathways for N₂O₄ Isomerization and NO₂ Dimerization in the Presence of Water

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · JUNE 2011

Impact Factor: 2.69 · DOI: 10.1021/jp1123585 · Source: PubMed

CITATIONS

18

READS

12

2 AUTHORS:



Diogo Medeiros

University of Leeds

3 PUBLICATIONS 24 CITATIONS

[SEE PROFILE](#)



André S Pimentel

Pontifícia Universidade Católica do Rio de J...

46 PUBLICATIONS 370 CITATIONS

[SEE PROFILE](#)

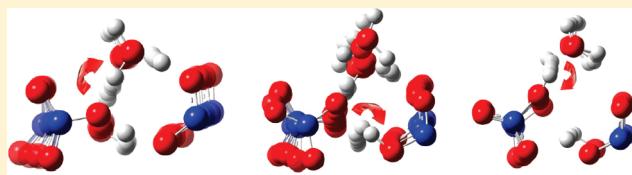
New Insights in the Atmospheric HONO Formation: New Pathways for N₂O₄ Isomerization and NO₂ Dimerization in the Presence of Water

Diogo de Jesus Medeiros and Andre Silva Pimentel*

Departamento de Química, Pontifícia Universidade Católica do Rio de Janeiro Rua Marquês de São Vicente, 225 Gávea, Rio de Janeiro, RJ, Brazil 22453-900

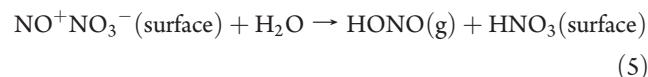
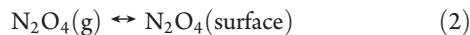
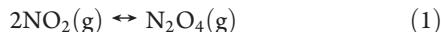
Supporting Information

ABSTRACT: Isomerization of N₂O₄ and dimerization of NO₂ in thin water films on surfaces are believed to be key steps in the hydrolysis of NO₂, which generates HONO, a significant precursor to the OH free radical in lower atmosphere and high-energy materials. Born–Oppenheimer molecular dynamics simulations using the density functional theory are carried out for NO₂(H₂O)_m, $m \leq 4$, and N₂O₄(H₂O)_n clusters, $n \leq 7$, used to mimic the surface reaction, to investigate the mechanism around room temperature. The results are (i) the NO₂ dimerization and N₂O₄ isomerization reactions occur via two possible pathways, the non-water-assisted and water-assisted mechanisms; (ii) the NO₂ dimerization in the presence of water yields either ONONO₂(H₂O)_m or NO₃[−]NO⁺(H₂O)_m clusters, but it is also possible to form the HNO₃(NO₂[−])(H₃O⁺)(H₂O)_{m−2} transition state to form HONO and HNO₃ directly; (iii) the N₂O₄ isomerization yields the NO₃[−]NO⁺(H₂O)_n cluster, but it does not hydrolyze faster than the NO₂⁺NO₂[−](H₂O)_n hydrolysis to directly form the HONO and HNO₃. New insights for hydrolysis of oxides of nitrogen in and on thin water films on surfaces in the atmosphere are discussed.



INTRODUCTION

The N₂O₄ isomerization and the NO₂ dimerization play an important role in fundamental, high-energy materials and atmospheric and environmental chemistries. In particular, the N₂O₄ molecule is a very important source of nitrous acids (HONO), which is the main source of OH radicals in the atmosphere. This subject has recently been present in several studies.^{1–8} Finlayson-Pitts et al.¹ have proposed the following mechanism to better understand the N₂O₄ hydrolysis:



Pimentel et al.^{5,6} have recently proposed that the N₂O₄ isomerization and NO₂ dimerization yield the formation of ONO[−]NO₂ directly in the presence of water. Miller et al.⁸ studied the ionization of ONONO₂ within finite water clusters to simulate the water interaction with ONONO₂ at room and low temperatures. Their results showed that the isolated ONONO₂ molecule may not be converted to the NO⁺NO₃[−] form in about 18 ps. They also found that the presence of small clusters ($n = 1–3$) is unlikely to be significant to ionize ONONO₂ in realistic

atmospheric systems. However, for $n \geq 3$, the ONONO₂ ionization is fast, on a time scale of 25–30 fs, even for low temperatures and the ONONO₂ molecule should not be considered an intermediate in the reaction.

The N₂O₄ isomerization and self-ionization and the NO₂ dimerization have been investigated,^{5,6,8} but the understanding of the chemical mechanism is still incomplete. For instance, the effect of water molecules on these reactions needs to be studied in more details. It is believed that water should increase the reaction rate of the N₂O₄ isomerization due to its transition state stabilization. Pimentel et al.⁶ investigated the N₂O₄ isomerization at gas phase and an implicit water model. The rate constant estimated for this reaction in the water model is $2.0 \times 10^{-3} \text{ s}^{-1}$ at 298 K, considerably faster than the one in gas phase.⁶

Pimentel et al.^{5,6} have investigated the N₂O₄ isomerization and NO₂ dimerization in a self-consistent reaction field model of solvation. The N₂O₄ isomerization is spontaneous in gas and water phases at 298 K. It was found that the NO₂ dimerization is nonspontaneous in the gas phase and spontaneous in the aqueous phase at 298 K. It would be important to further investigate if explicit water molecules would participate in the NO₂ dimerization and N₂O₄ isomerization steps of the chemical mechanism of HONO formation.

The recent findings of Miller et al.⁸ call for a reconsideration of the processes leading to formation of NO⁺ and NO₃[−], in the hydrolysis of NO₂, and especially in the isomerization of symmetric

Received: December 29, 2010

Revised: March 30, 2011

Published: May 18, 2011

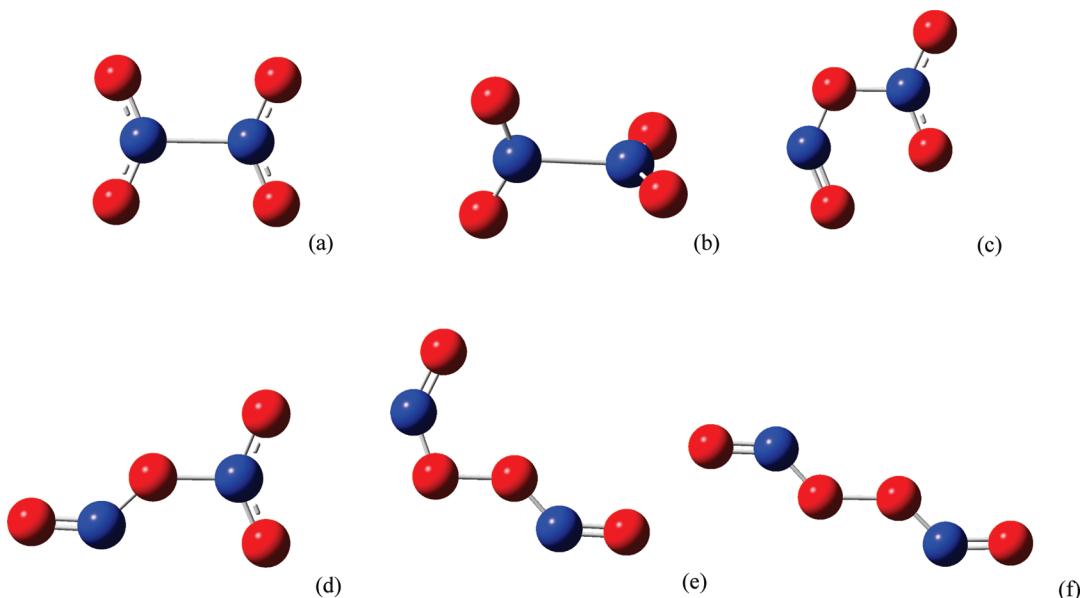


Figure 1. Main N_2O_4 isomers: (a) symmetric $\text{O}_2\text{N}-\text{NO}_2$, (b) coplanar $\text{O}_2\text{N}-\text{NO}_2$, (c) asymmetric *cis*- ONONO_2 , (d) asymmetric *trans*- ONONO_2 , (e) *cis*-*perp*-*trans*- ONOONO , and (f) *trans*-*perp*-*trans*- ONOONO .

N_2O_4 . While Chou et al.⁹ reported that the direct reaction of symmetric N_2O_4 with water has too large a barrier to be important in the gas phase and previous theoretical calculations reported by our group⁵ showed that the lifetime of symmetric N_2O_4 at room temperature with respect to isomerization is of the order of 500 s, symmetric N_2O_4 has been reported from experiments to be converted to ONONO_2 on ice surfaces between 130 and 183 K.^{10–12} Miller et al.⁸ presented that the lifetime of ONONO_2 in the presence of water is too short to consider it an intermediate chemical species in the process. Miller et al.⁸ establish that ONONO_2 will ionize directly upon formation in the presence of water. They also suggest that the formation of NO^+ and NO_3^- takes place directly from symmetric N_2O_4 at the surface of water. When the symmetric N_2O_4 isomerizes in water, it gets to a transition state that ionizes directly. On the other hand, our group⁶ previously showed that the formation of ONONO_2 may occur directly from two NO_2 molecules in the gas phase by a barrierless reaction.

The following questions are going to be investigated in the present study: (1) Would the NO_2 dimerization and the N_2O_4 isomerization be affected by explicit water molecules? (2) Is it possible that the NO_2 dimerization and the N_2O_4 isomerization in the presence of water directly yield to the end products (HONO and HNO_3), not passing through the ONONO_2 intermediate?

METHODOLOGY

The quantum chemical calculations were calculated using the B3LYP/6-311++G(3df,3pd) methodology.¹³ The geometries of the reactant, product, and transition state (TS) were fully optimized with the aid of analytical gradients using the Berny algorithm with redundant internal coordinates until a stationary point on the potential surface is found. The TS was searched by using standard methods and the TS structure was verified by the imaginary vibrational frequency related to the reaction path. The intrinsic reaction coordinate (IRC) was also calculated to follow the reaction path and reassure that TS is really a saddle

point of the reaction path. Then, the structures optimized with the B3LYP/6-311++G(3df,3pd) level of theory were submitted to Born–Oppenheimer molecular dynamics (BOMD) simulations.^{14–18}

All BOMD simulations^{14–18} in this work were performed using the B3LYP/6-31G methodology. Although these calculations were performed with the optimized geometries as starting configuration using a larger 6-311++G(3df,3pd) basis set, running 1.5 ps trajectories with 27 atoms with the larger basis set would be computationally prohibitive.^{19–22} The B3LYP/6-31G level of theory is not a good approach for thermodynamic calculation; however, it describes well the structure properties (bond length and angles) of the $\text{NO}_2(\text{H}_2\text{O})_m$ and $\text{N}_2\text{O}_4(\text{H}_2\text{O})_n$ clusters ($m = 0–4$ and $n = 0–7$). In BOMD, the potential energy surface (PES) and the forces are self-consistently calculated “on the fly”. Newton’s equations of motion are integrated by using a very accurate Hessian based algorithm that incorporates a predictor step on the local quadratic surface followed by a corrector step. The latter uses a fifth-order polynomial function fitted to the energy, gradient, and Hessian at the beginning and end points of each step. The integration scheme employed was the Bulirsch–Stoer method. The Hessian was updated for 5 steps before being recalculated analytically. An integration step size of 0.25 amu^{1/2} bohr was used for all of the calculations, and the trajectories were stopped when the products were found. In the isomerization path, the trajectory reached the products within a time that ranged from 250 to 350 fs. The total energy was conserved to 10^{-5} hartree and the total angular momentum to better than $10^{-9}\ \hbar$ because projection methods were used to remove the overall angular forces. Despite the real system contains protium in 99.98%, classical dynamics is used to propagate the nuclei by replacing all hydrogen atoms with deuterium atoms to minimize the error associated with neglecting quantum tunneling. This is a standard procedure in molecular dynamics that does not modify the underlying chemical mechanism of interest.^{19,20} However, several molecular dynamics simulations were also performed using H_2O molecules to check the reproducibility

of the chemical mechanism presented. As expected previously, the only difference between the simulations with D₂O and H₂O molecules was related to the reaction time due to the isotopic effect. For the N₂O₄ isomerization, trajectories starting from the transition state structure in the forward direction were run for about 1.5 ps. For each N₂O₄(H₂O)_n cluster, around 10 trajectories along the reaction coordinate were performed by thermal sampling and distribution at 298 K. The NO₂ dimerization was also run for less than 1 ps in the forward direction beginning from NO₂ molecules and NO₂(H₂O)_m clusters separated by about 5 Å. Several trajectories for the NO₂ dimerization were performed by randomly distributing the water around the NO₂ + NO₂ system. We acknowledge that many more trajectories would be required for a quantitative analysis of the reaction dynamics of these systems; however, it is prohibitive in terms of computational cost; the intention of our study is, at least, to gain qualitative insight into this complex reaction. The quantum

chemical calculations and molecular dynamics simulations were performed using the *Gaussian03* software.¹⁹

RESULTS AND DISCUSSION

In this investigation, a finite water cluster system was implied as model to simulate the water interaction on the air–water surface for both investigated steps: N₂O₄(H₂O)_n cluster with $n = 0–7$ for the N₂O₄ isomerization and NO₂ + NO₂(H₂O)_m cluster with $m = 0–4$ for the NO₂ dimerization. It is important to note that the choice of small gaseous water clusters NO₂ + NO₂(H₂O)_m/N₂O₄(H₂O)_n as model systems makes this study relevant for dimerization of NO₂ and isomerization of N₂O₄ in aqueous, thin films on surfaces, assuming that the structural constraints derived from an underlying surface structure are neglected.

Figure 1 presents the main N₂O₄ isomers formed in molecular dynamics simulation: (a) symmetric O₂N–NO₂, (b) coplanar O₂N–NO₂, (c) asymmetric *cis*-ONONO₂, (d) asymmetric *trans*-ONONO₂, (e) *cis*-*perp*-*trans*-ONOONO, and (f) *trans*-*perp*-*trans*-ONOONO. These structures were optimized using the B3LYP/6-311++G(3df,3pd) level of theory. This level of theory is appropriated for calculation of the structural and thermodynamic properties of NO₂(H₂O)_m and N₂O₄(H₂O)_n as compared with our previous studies.^{5,6} The main trajectories of the N₂O₄ isomerization and the NO₂ dimerization in the absence and presence of water molecules are discussed in the following.

NO₂ Dimerization. The NO₂ dimerization, which is the first step of the mechanism proposed by Finlayson-Pitts et al.,¹ is an essential source of the N₂O₄ molecule. Several trajectories departing from different initial configurations of the

Table 1. Products Formed in the NO₂ Dimerization in the Presence of H₂O and D₂O, Yield (%), Number of Trajectories That Reached the Product, and the Average Time (fs) Necessary for Product Formation

product	D ₂ O			H ₂ O		
	yield (%)	trajectories	average time (fs)	yield (%)	trajectories	average time (fs)
O ₂ N–NO ₂	20	4	378 ± 154	8	5	405 ± 68
ONONO ₂	45	9	529 ± 305	42	2	471 ± 160
ONOONO	30	6	985 ± 807	17	4	1586 ± 484
HONO + HNO ₃	5	1	606	3	1	238

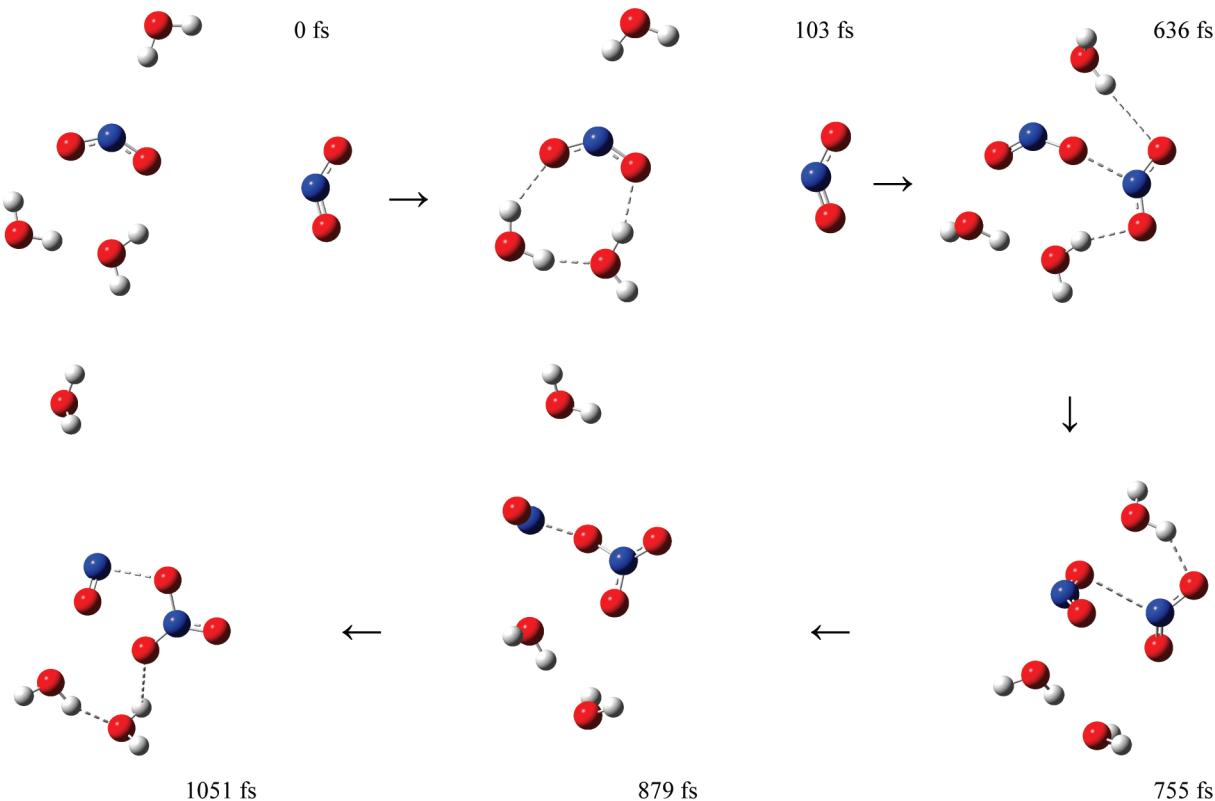


Figure 2. NO₂ dimerization in the presence of water: the formation of the asymmetric ONONO₂ isomer.

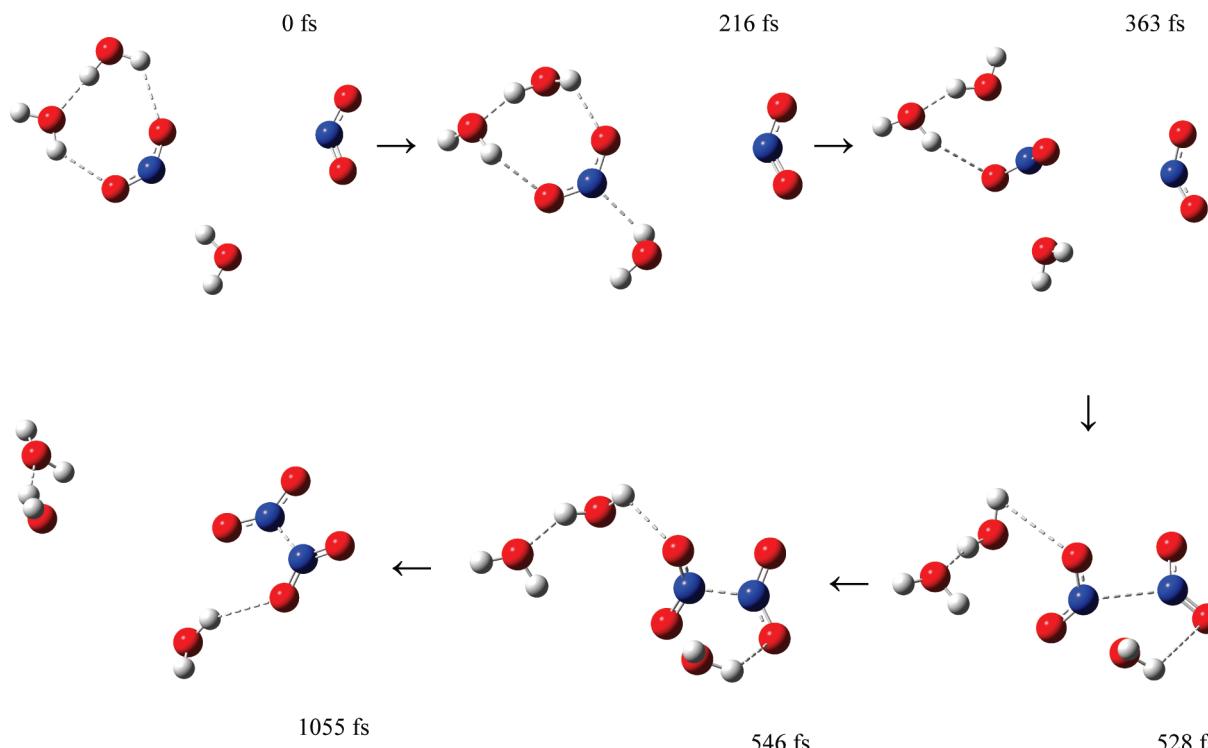


Figure 3. NO_2 dimerization in the presence of water: the formation of the symmetric $\text{O}_2\text{N}-\text{NO}_2$ isomer.

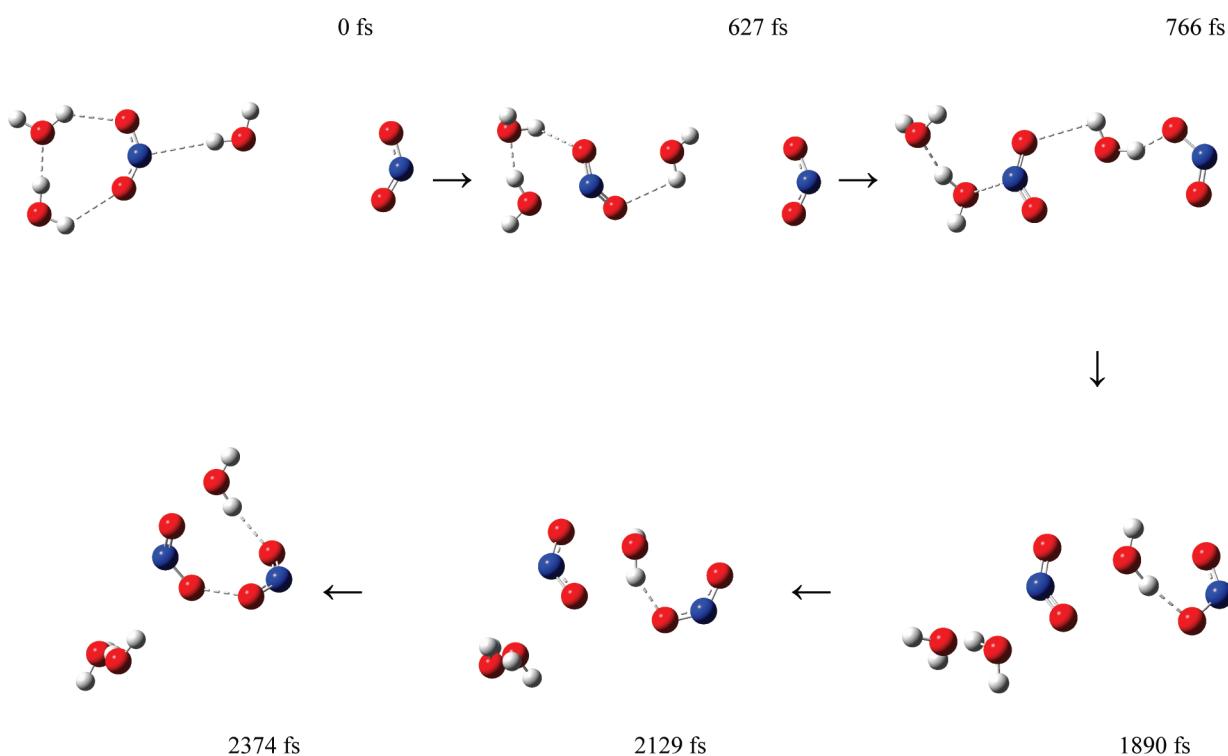


Figure 4. NO_2 dimerization in the presence of water: the formation of the ONOONO isomer.

$\text{NO}_2 + \text{NO}_2(\text{H}_2\text{O})_m$ ($m \leq 4$) system were investigated. The three main N_2O_4 isomers ($\text{O}_2\text{N}-\text{NO}_2$, ONONO_2 , and ONOONO) were found as products. The geometry of these molecules is presented in the Figure 1. From all trajectories performed in this

investigation, the results show that 45% formed ONONO_2 , 30% generated ONOONO , and 20% produced $\text{O}_2\text{N}-\text{NO}_2$ as presented in Table 1. The formation of the ONONO_2 isomer has a higher yield (45%), despite the fact that the $\text{O}_2\text{N}-\text{NO}_2$

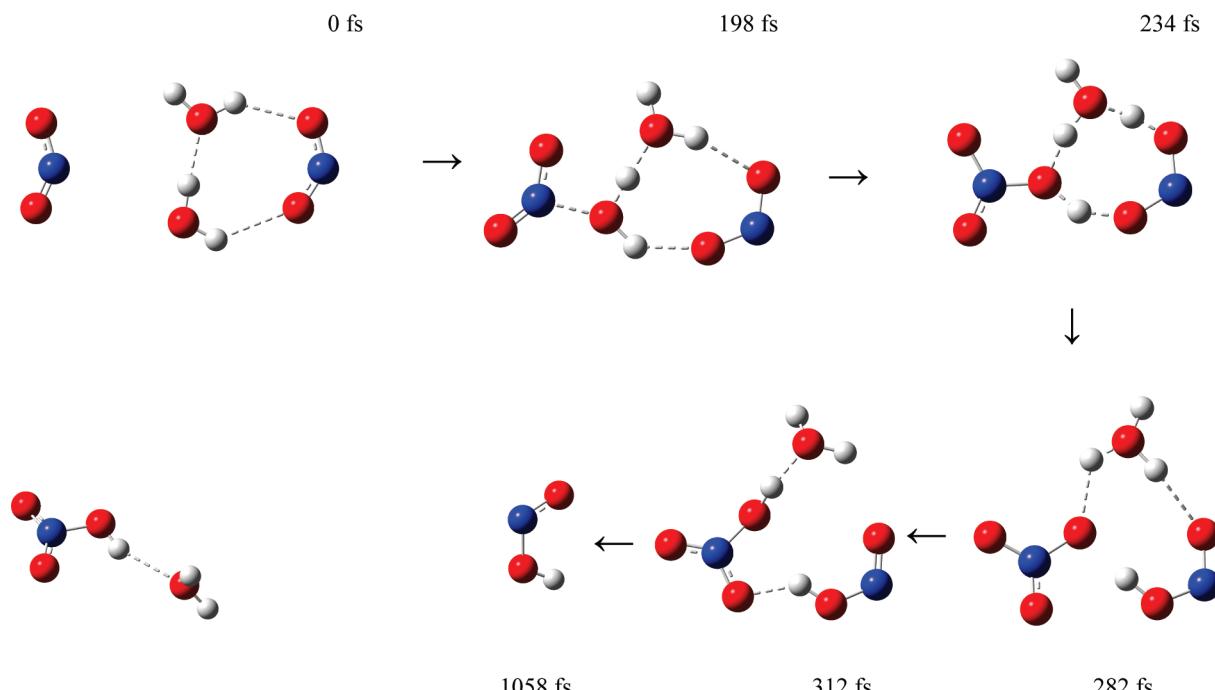


Figure 5. Formation of HNO_3 and HONO in the water-assisted mechanism from the collision of NO_2 with an $\text{NO}_2(\text{H}_2\text{O})_2$ cluster.

formation is considerably faster, around 378 fs, than that for the ONONO_2 formation, over 529 fs. These results elucidate that the direct formation of the asymmetric isomer upon NO_2 dimerization, presented in Figure 2, plays an important role as compared to the formation of the other isomers, $\text{O}_2\text{N}-\text{NO}_2$ and ONOONO , in Figures 3 and 4, respectively. Surprisingly, a trajectory for the $\text{NO}_2 + \text{NO}_2(\text{H}_2\text{O})_2$ reaction produced HONO and HNO_3 directly through a water-assisted mechanism with a time of about 312 fs. Figure 5 shows this water-assisted mechanism in details. Table 1 also presents information about the nondeuterated system.

The water-assisted mechanism of the NO_2 dimerization is quite different from that for the N_2O_4 isomerization (see in the next section). In the NO_2 dimerization, one of the water dissociates and the nitric acid is formed. Simultaneously, the H_3O^+ ion is formed. The charge distribution for the $\text{NO}_2 + \text{NO}_2(\text{H}_2\text{O})_2$ system is presented in the Figure 6. This charge distribution shows that there is a H_3O^+ formation in the NO_2 dimerization. After 50 fs, the nitric acid dissociates and transfers the proton to the nitrite ion (NO_2^-) forming the HONO . Then, the proton initially transferred from the water molecule to the other H_2O returns to the same original oxygen atom (which now pertains to the NO_3^- ion) and forms the nitric acid. Finally, the HONO is delivered to the gas phase and the HNO_3 continues interacting with water for a long period of time, about 1 ps.

N_2O_4 Isomerization. The TS Cartesian coordinates of $\text{N}_2\text{O}_4(\text{H}_2\text{O})_n$ also optimized with B3LYP/6-311++G(3df,3pd) level of theory are presented in Figure 7. For the N_2O_4 isomerization, trajectories beginning from the transition state, as starting configuration, were run for about 1.5 ps in the forward direction. The isomerization step consists of the conversion of the symmetric isomer $\text{O}_2\text{N}-\text{NO}_2$ into its asymmetric isomer ONONO_2 . The results show a remarkable decreasing trend of the barrier energy as the number of interacting water molecules increases. This behavior is due to

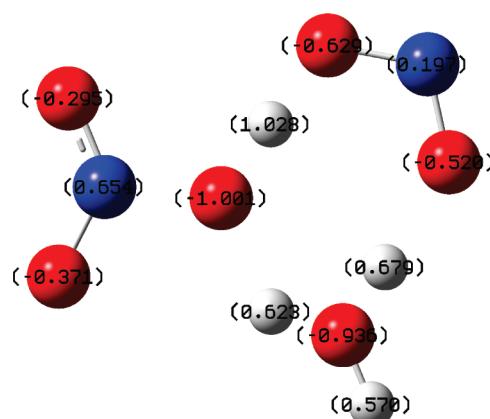


Figure 6. Charge distribution: H_3O^+ ion formation in the NO_2 dimerization.

the difficulties of finding the global minimum of the potential energy surface of $\text{O}_2\text{N}-\text{NO}_2(\text{H}_2\text{O})_n$. Intriguingly, it seems that it was only possible to find a local minima for $\text{O}_2\text{N}-\text{NO}_2-(\text{H}_2\text{O})_n$ cluster with odd numbers of water molecules ($n = 1, 3, 5$, and 7). It is also important to note that the N_2O_4 isomerization is only efficiently favored by the interaction of the asymmetric isomer with a certain number of water molecules. Although the ONONO_2 isomer is formed even without water molecules, the ONONO_2 stabilization is effectively observed for $n \geq 4$. This stabilization occurs via energy transfer by distributing the energy from N_2O_4 to water molecules in the $\text{N}_2\text{O}_4(\text{H}_2\text{O})_n$ cluster. Thus, the formed product is stabilized and energetically prevented from crossing the potential energy barrier of the inverse reaction. Surprisingly, some trajectories for $n = 7$ led to the direct formation of HNO_3 and HONO . Therefore, the HONO formation proposed by the mechanism

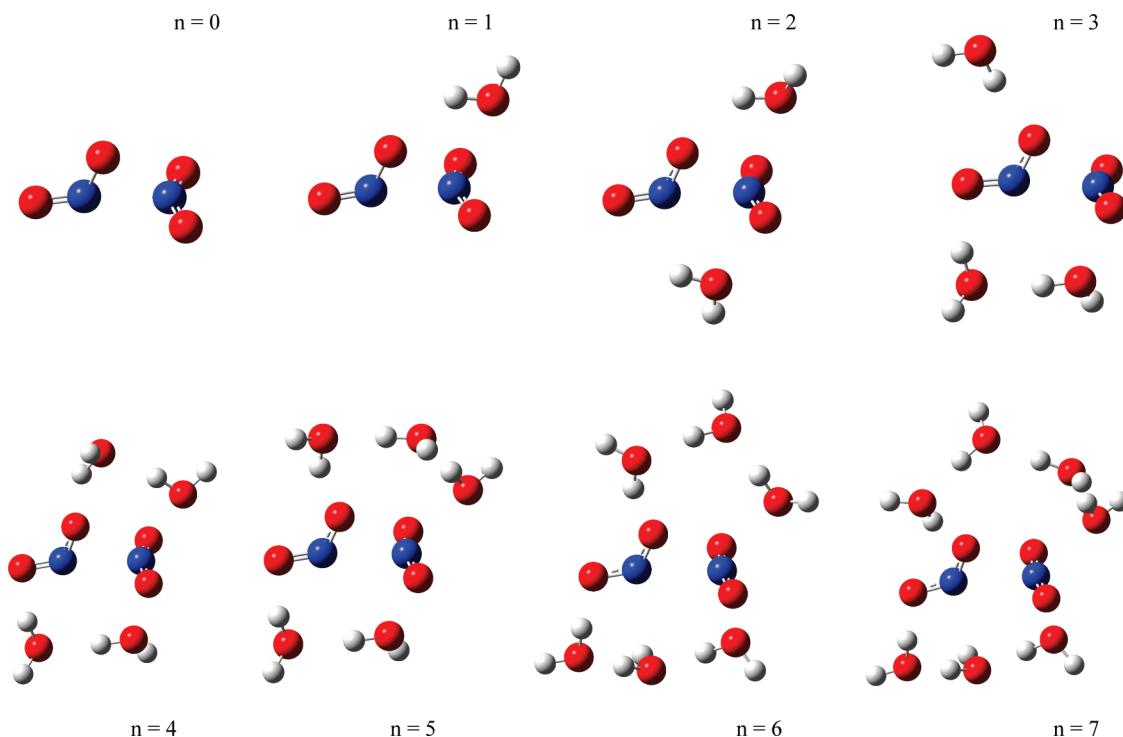


Figure 7. Transition state (TS) structures, $\text{N}_2\text{O}_4(\text{H}_2\text{O})_n$ ($n = 0-7$), optimized by using the B3LYP/6-311++G(3df,3pd) methodology.

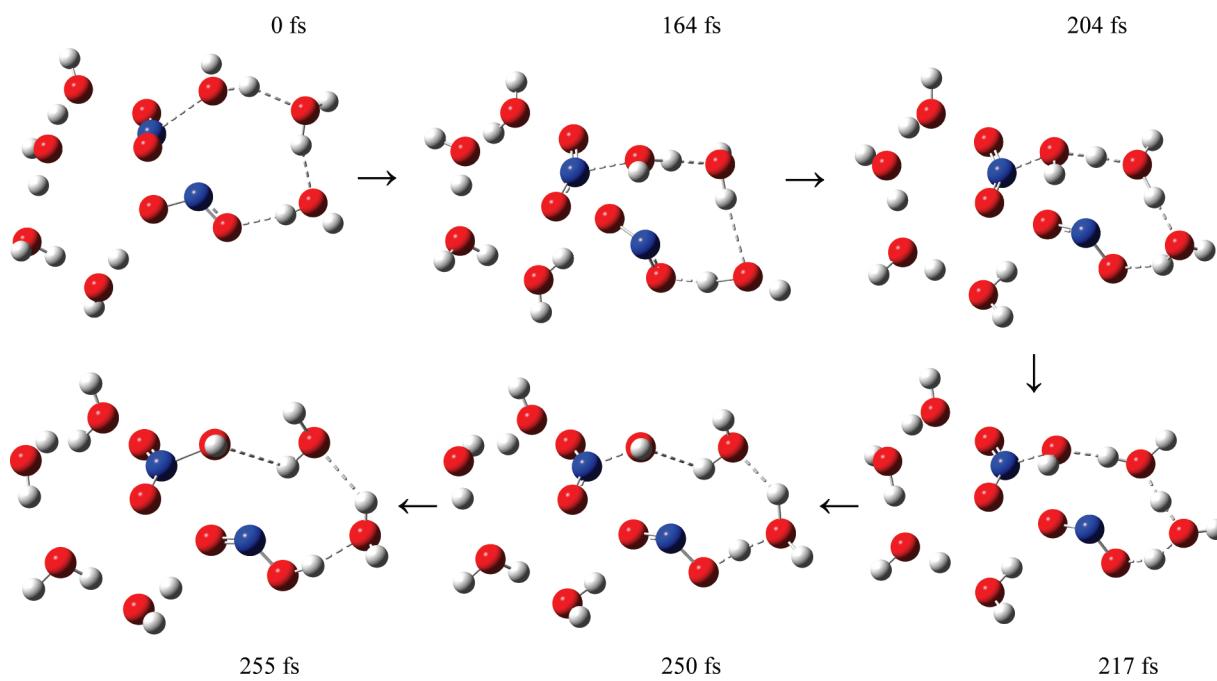


Figure 8. Formation of HNO_3 and HONO in the water-assisted mechanism before an imminent N_2O_4 isomerization.

of Finlayson-Pitts et al¹ is bypassed by a water-assisted mechanism presented in detail (Figure 8). In the following, it is presented a summary of results found for the N_2O_4 isomerization. Table 2 shows the products formed in the N_2O_4 isomerization, their average formation time and stability for both systems: $\text{N}_2\text{O}_4(\text{H}_2\text{O})_m$ and $\text{N}_2\text{O}_4(\text{D}_2\text{O})_m$.

The $\text{O}_2\text{N}-\text{NO}_2$ isomer is stable even without water molecules interacting with it. The results at 298 K elucidate that the thermal energy transfer may not be efficient to provide the energy necessary to cross the potential energy barrier of the N_2O_4 isomerization. As the number of water molecules increases, the energy barrier decreases, but the energy transfer from the

$\text{O}_2\text{N}-\text{NO}_2$ to the water molecules may prevent the N_2O_4 isomerization.

For $n = 0$, all trajectories converged to the asymmetric isomer in about 37 fs. However, when only one water molecule ($n = 1$) interacts with N_2O_4 , 92% of the trajectories generated the asymmetric isomer in about 45 fs. The other 8% formed $\text{O}_2\text{N}-\text{NO}_2$ in about 220 fs. On the other hand, when two molecules of water interact with N_2O_4 ($n = 2$), 60% of the trajectories generated the coplanar $\text{O}_2\text{N}-\text{NO}_2$ isomer in approximately 56 fs. The other trajectories (40%) formed ONONO_2 . For $n \leq 2$, the asymmetric isomers are not stabilized. For instance, Figure 9 shows that oxygen atom 4 bound to nitrogen atom 1 is transferred to nitrogen atom 2 in 46 fs, then transferred again to nitrogen 1 in 76 fs. In about 137 fs, the same oxygen atom moves back to the nitrogen atom to which it was bound in 45 fs. This behavior is repeated back and forth for a long period of time, 1.5 ps, which shows the

Table 2. Products Formed in the N_2O_4 Isomerization in the Presence of H_2O and D_2O , Formation Time (fs), Yield (%), and Product Stability

n	formed isomer	yield (%)		reaction time (fs)		stability	
		D_2O	H_2O	D_2O	H_2O	D_2O	H_2O
0	ONONO_2	100	100	37	37	unstable	unstable
1	ONONO_2	92	100	45	47	unstable	unstable
	$\text{O}_2\text{N}-\text{NO}_2$	8		220		stable	
2	coplanar $\text{O}_2\text{N}-\text{NO}_2$	60	100	56	58	unstable	unstable
	$\text{O}_2\text{N}-\text{NO}_2$	40		202		stable	
3	ONONO_2	90	86	42	46	small	small
	$\text{O}_2\text{N}-\text{NO}_2$	10		85		stable	
	coplanar $\text{O}_2\text{N}-\text{NO}_2$	14		90		small	
4	ONONO_2	100	100	93	70	stable	stable
5	$\text{O}_2\text{N}-\text{NO}_2$	60	100	138	188	stable	stable
	coplanar $\text{O}_2\text{N}-\text{NO}_2$	20		62		stable	
	ONONO_2	20		152		stable	
6	ONONO_2	100	100	229	143	stable	stable
7	ONONO_2	50	50	234	176	stable	stable
		33		211		stable	
	$\text{HNO}_3 + \text{HNO}_2$						
	$\text{O}_2\text{N}-\text{NO}_2$	17	33	190	221	stable	stable
	coplanar $\text{O}_2\text{N}-\text{NO}_2$	17		62		stable	

instability of the ONONO_2 isomer in the presence of few water molecules.

For $n = 3$ and 4, the isomer stabilization is slightly higher than it was found for $n \leq 2$. The trajectories performed for the $\text{O}_2\text{N}-\text{NO}_2(\text{H}_2\text{O})_3$ cluster formed 90% of the asymmetric isomer in about 42 fs and only 10% of the symmetric isomer in 85 fs. Similarly, 100% of the trajectories formed the ONONO_2 for $n = 4$. In this case, the isomer formed may be characterized as a product. The N_2O_4 isomerization occurs in about 93 fs for $n = 4$. The behavior presented in the previous paragraph occurs for the $\text{O}_2\text{N}-\text{NO}_2(\text{H}_2\text{O})_4$ cluster to a lesser extent, as presented in Figure 10, but not for $n = 7$, for instance, as shown in Figure 11.

The product stability is notably observed for $n > 4$. For $n = 5$, 60% of the trajectories generated the $\text{O}_2\text{N}-\text{NO}_2$ isomer with a formation time of about 138 fs. The other 20% yielded ONONO_2 in about 152 fs and another 20% produced the coplanar $\text{O}_2\text{N}-\text{NO}_2$ around 62 fs. Many trajectories were performed for simulating the trajectories of N_2O_4 isomerization for $n = 6$ and all of them produced ONONO_2 . When the N_2O_4 isomerizes with seven water molecules, an interesting water-assisted mechanism is found.²³ For $n = 7$, 55% of the trajectories produced the asymmetric isomer in an average time of 234 fs, 17% formed $\text{O}_2\text{N}-\text{NO}_2$ in about 190 fs, and surprisingly, 33% generated HNO_3 and HONO in over 211 fs. In this new mechanism, a water molecule dissociates into the OH ion, which interacts with a nitronium ion (NO_2^+) to form HNO_3 . Later, the H^+ ion is successively transferred to the nitrite ion (NO_2^-) via a proton transfer mechanism. The charge distribution for the $\text{N}_2\text{O}_4(\text{H}_2\text{O})_6$ cluster is presented in Figure 12. This charge distribution shows that there is a H_3O^+ formation in the N_2O_4 isomerization. It is interesting to note that the NO_2 group presented at 0 fs in Figure 8 is nearly linear, similar to the nitronium ion. In fact, all TS structures with water molecules in Figure 7 have a nearly linear NO_2 group. On the other hand, the other NO_2 group, shown in the same figure, is analogous to the nitrite ion, which is slightly more bent than a regular NO_2 molecule. This mechanism can be seen in detail in Figure 8.

Concluding Remarks: The Proposed Mechanism for the HONO Formation. The Born–Oppenheimer molecular dynamics was carried out using the density functional theory in $\text{NO}_2(\text{H}_2\text{O})_m$ and $\text{N}_2\text{O}_4(\text{H}_2\text{O})_n$ clusters, giving new insights on the HONO formation. The water-assisted mechanisms for the NO_2 dimerization and N_2O_4 isomerization are shown to be

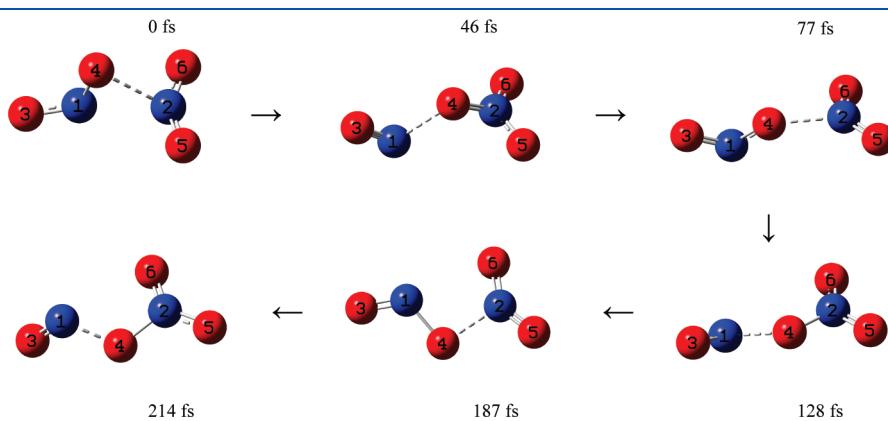
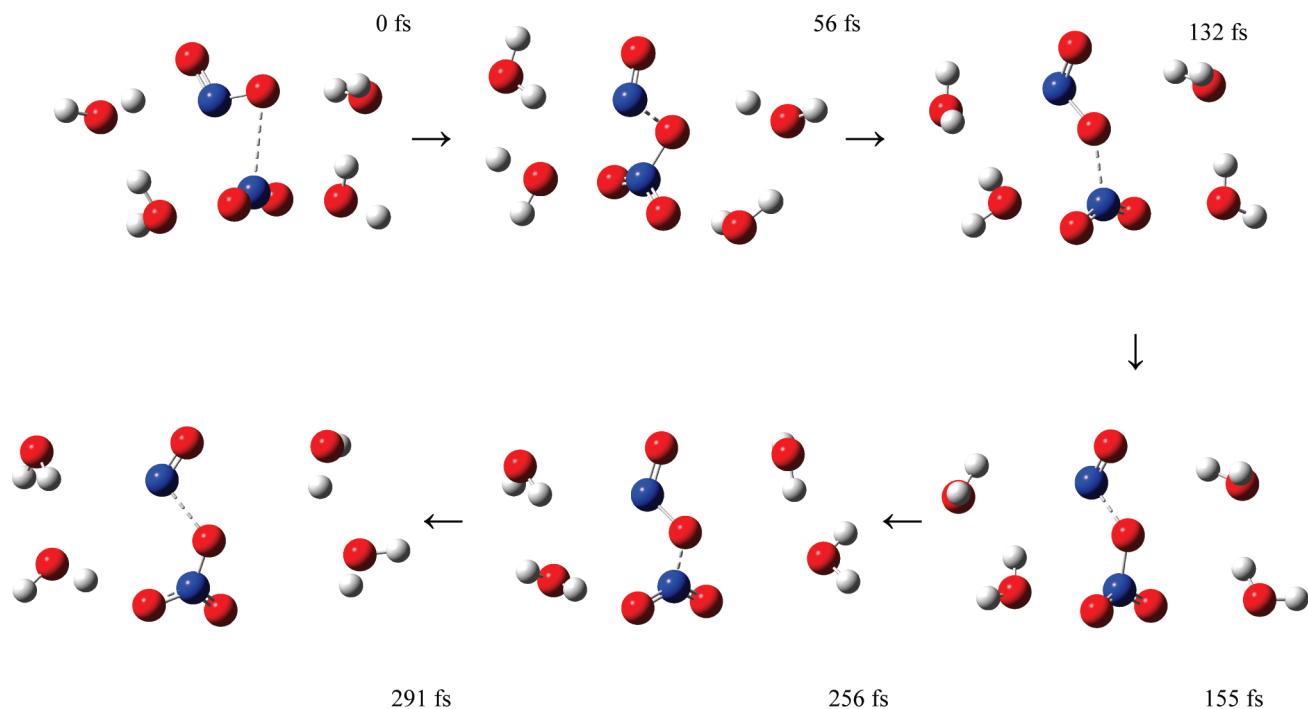
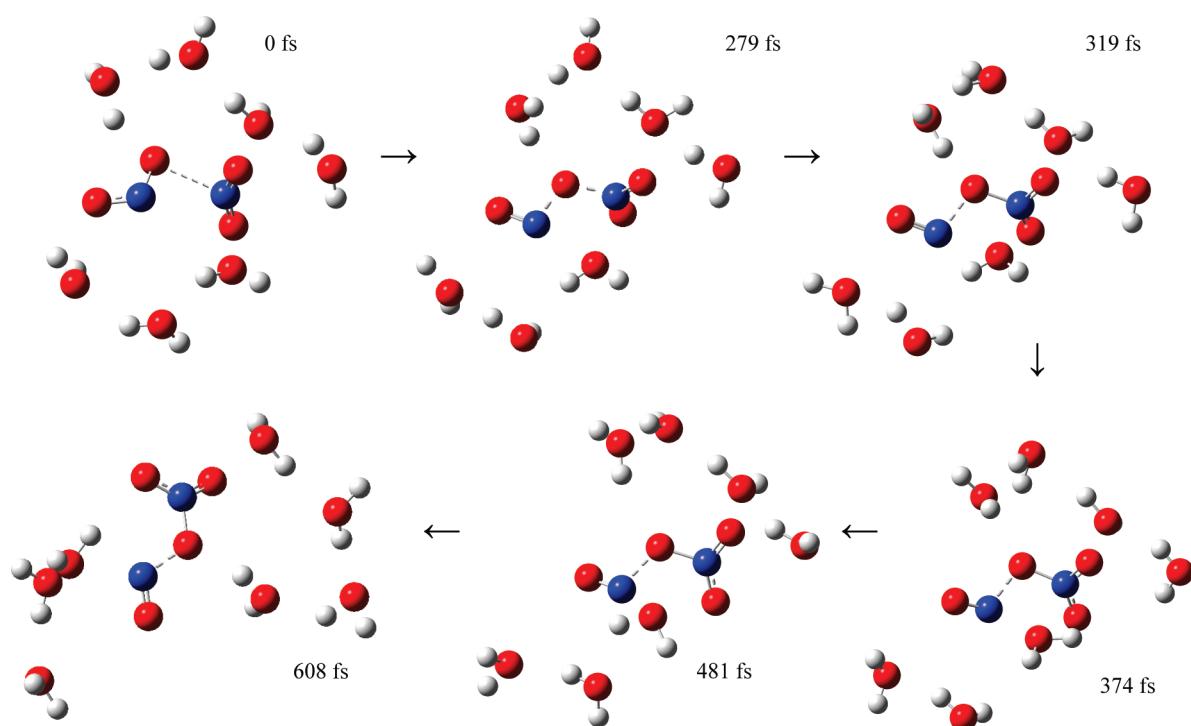
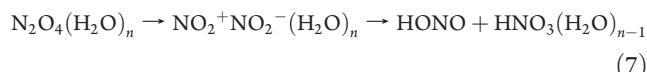
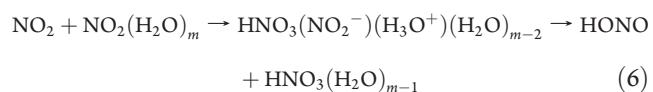


Figure 9. Back and forth behavior for the N_2O_4 stabilization in the absence of water.

Figure 10. Back and forth behavior for the $\text{N}_2\text{O}_4(\text{H}_2\text{O})_4$ stabilization.Figure 11. $\text{ONONO}_2(\text{H}_2\text{O})_7$ stabilization.

important direct sources of HONO and HNO_3 as presented in the following:



The molecular dynamics simulation presents that the NO_2 dimerization in the presence of water yields either $\text{ONONO}_2^-(\text{H}_2\text{O})_m$ or $\text{NO}_3^-\text{NO}^+(\text{H}_2\text{O})_m$. However, it is also possible to

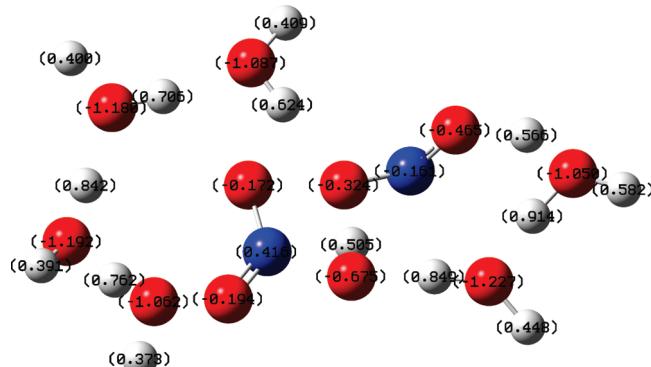


Figure 12. Charge distribution: H_3O^+ ion formation in the N_2O_4 isomerization.

form the intermediate $\text{HNO}_3(\text{NO}_2^-)(\text{H}_3\text{O}^+)(\text{H}_2\text{O})_{m-2}$ to yield HONO and HNO_3 (reaction 6). On the other hand, the results show that the N_2O_4 isomerization yields the $\text{NO}_3^-\text{NO}^+(\text{H}_2\text{O})_n$ cluster, but its hydrolysis is not faster than the $\text{NO}_2^+\text{NO}_2^-(\text{H}_2\text{O})_n$ hydrolysis to form the HONO and HNO_3 (reaction 7). However, it was not possible to confirm that the hydrolysis of the $\text{NO}_3^-\text{NO}^+(\text{H}_2\text{O})_n$ cluster does not happen after 1.5 ps. Finally, it was demonstrated that the NO_2 dimerization and N_2O_4 isomerization in the presence of water occur via two possible pathways: the non-water-assisted and water-assisted mechanisms. These new insights are relevant for the HONO formation on the hydrolysis of oxides of nitrogen in and on thin water films on surfaces in the atmosphere.

■ ASSOCIATED CONTENT

S Supporting Information. Optimized geometries in Cartesian coordinates for each transition state are presented here. The geometries were optimized at the B3LYP/6-311++G(3df,3pd) level of theory. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: a_pimentel@puc-rio.br.

■ ACKNOWLEDGMENT

We are grateful to the CNPq funding (No. 485364/2007-7). A.S.P. is a recipient of a CNPq productivity fellowship (No. 304187/2009-7) and another one awarded by the Pontifícia Universidade Católica at Rio de Janeiro. D.J.M. is thankful for a PIBIC/CNPq studentship. A.S.P. is also thankful for a FAPERJ young scientist fellowship (No. 101.452/2010).

■ REFERENCES

- (1) Finlayson-Pitts, B. J.; Wingen, L. M.; Sumner, A. L.; Syomin, D.; Ramazan, K. A. *Phys. Chem. Chem. Phys.* **2003**, *5*, 223.
- (2) Syomin, D.; Finlayson-Pitts, B. J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 5236.
- (3) Ramazan, K.; Syomin, D.; Finlayson-Pitts, B. J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3836.
- (4) Ramazan, K. A.; Wingen, L. M.; Miller, Y.; Chaban, G. M.; Gerber, R. B.; Xantheas, S. S.; Finlayson-Pitts, B. J. *J. Phys. Chem. A* **2006**, *110*, 6886.
- (5) Pimentel, A. S.; Lima, F. C. A.; da Silva, A. B. F. *Chem. Phys. Lett.* **2007**, *436*, 47.
- (6) Pimentel, A. S.; Lima, F. C. A.; da Silva, A. B. F. *J. Phys. Chem. A* **2007**, *111*, 2913.
- (7) Kamboures, M. A.; Raff, J. D.; Miller, Y.; Phillips, L. F.; Finlayson-Pitts, B. J.; Gerber, R. B. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6019.
- (8) Miller, Y.; Finlayson-Pitts, B. J.; Gerber, R. B. *J. Am. Chem. Soc.* **2009**, *131*, 12180.
- (9) Chou, A.; Li, Z. R.; Tao, F. M. *J. Phys. Chem. A* **1999**, *103*, 7848.
- (10) Wang, J.; Koel, B. E. *J. Phys. Chem. A* **1998**, *102*, 8573.
- (11) Wang, J.; Koel, B. E. *Surf. Sci.* **1999**, *436*, 15.
- (12) Wang, J.; Voss, M. R.; Busse, H.; Koel, B. E. *J. Phys. Chem. B* **1998**, *102*, 4693.
- (13) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, U.K., 1989.
- (14) Helgaker, T.; Uggerud, E.; Jensen, H. J. A. *Chem. Phys. Lett.* **1990**, *173*, 145.
- (15) Uggerud, E.; Helgaker, T. *J. Am. Chem. Soc.* **1992**, *114*, 4265.
- (16) Chen, W.; Hase, W. L.; Schlegel, H. B. *Chem. Phys. Lett.* **1994**, *228*, 436.
- (17) Millam, J. M.; Bakken, V.; Chen, W.; Hase, W. L.; Schlegel, B. H. *J. Chem. Phys.* **1999**, *111*, 3800.
- (18) Li, X.; Millam, J. M.; Schlegel, H. B. *J. Chem. Phys.* **2000**, *113*, 10062.
- (19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision A.1; Gaussian, Inc.: Pittsburgh, PA, 2003.
- (20) Andersen, A.; Carter, E. A. *J. Phys. Chem. A* **2006**, *110*, 1393.
- (21) Baptista, L.; Andrade, D. P. P.; Rocha, A. B.; Rocco, M. L. M.; Boechat-Roberty, H. M.; da Silveira, E. F. *J. Phys. Chem. A* **2010**, *114*, 6917.
- (22) Psciuk, B. T.; Tao, P.; Schlegel, H. B. *J. Phys. Chem. A* **2010**, *114*, 7653.
- (23) Scaldaferri, M. C. L.; Pimentel, A. S. *J. Phys. Chem. A* **2010**, *114*, 8993.