



# Article HONO Formation from the Oxidation Reactions of ClO, NO, and Water in the Gas-Phase and at the Air-Water Interface

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**Abstract:** Nitrous acid (HONO) plays a key role in atmospheric chemistry. Nevertheless, the HONO formation mechanism in the atmosphere, especially in the marine boundary layer, remains to be fully understood. Here, Born–Oppenheimer molecular dynamic and metadynamics simulations were performed to study the formation mechanism of HONO from the oxidation reactions of ClO radical and NO with the addition of  $(H_2O)_{1-2}$ , considering a monohydrated system ((ClO)(NO)(H<sub>2</sub>O)<sub>1</sub>) and dihydrated system ((ClO)(NO)(H<sub>2</sub>O)<sub>2</sub>), as well as at the air-water interface. This study shows that HONO formation follows a single-water mechanism in gas-phase and air-water interface systems. The free-energy barrier of the (ClO)(NO)(H<sub>2</sub>O)<sub>1</sub> system was 9.66 kJ mol<sup>-1</sup>, whereas the (ClO)(NO)(H<sub>2</sub>O)<sub>2</sub> system was a barrierless reaction. HONO formation at the air-water interface was faster than that in monohydrated and dihydrated systems. Although the concentration of ClO radical in the marine boundary layer is two orders higher than that of Cl radical, the production rates of HONO from the (ClO)(NO)(H<sub>2</sub>O)<sub>1</sub> system are six orders lower than that from the (Cl)(NO)(H<sub>2</sub>O)<sub>1</sub> system, which means that Cl radical dominates HONO formation rather than ClO radical in the marine boundary layer. These results can deepen our understanding of the HONO formation mechanism and be used to reduce HONO emissions and establish HONO-control strategies.

**Keywords:** nitrous acid; ClO radical; Born–Oppenheimer molecular dynamics; metadynamics simulation; marine boundary layer

# 1. Introduction

In the atmosphere, the hydroxyl radical (OH) is generally considered a "detergent" due to its contribution to atmospheric oxidizing capacity, which can clean up primary pollutants as well as initiate the photochemical process to further produce ozone and secondary pollutants [1–3]. Nitrous acid (HONO), an active nitrogen-containing component, is a significant reservoir of OH radicals. Field and modeling studies have evaluated that photolysis of HONO can contribute to 25–60% of the daytime OH radical on average (even about 90% during winter noon) [4–7]. Hence, HONO can indirectly affect atmospheric oxidizing capacity and influence regional air quality and global climate.

HONO has been detected in various environments, including ocean, rural, urban, forest, and polar [8–12]. For example, the average concentration of HONO was 0.44 ppb during a shipboard-based observation in the East China Sea [9] and 0.74 ppb at an urban site in Guangzhou [13]. The main sources of HONO can be categorized into direct emissions and secondary emissions. Direct emission sources contain vehicle exhaust [14,15], soil microbiological activities [16,17], biomass burning [18], and indoor combustion processes [19], as well as ship emissions in the marine [20]. The secondary emissions of HONO are mainly from homogeneous and heterogeneous chemical reactions of NO<sub>x</sub> (i.e., NO and NO<sub>2</sub>). During the daytime, HONO can be mainly produced through the reaction of



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). NO and OH radicals [21,22] and the reaction of NO and Cl radicals in the introduction of water molecules [23]. During nighttime, heterogeneous conversions of NO<sub>2</sub> on various wet surfaces, like aerosols, ground, vegetation, and sea, have always been considered the main nocturnal HONO formation route [10,24–27]. For example, HONO can be produced on indoor material surfaces by heterogeneous hydrolysis of NO<sub>2</sub> [28].

Despite the number of advances in exploring the HONO sources, the concentrations of HONO predicted by models and coefficient calculations based on current known HONO formation mechanisms are much lower than that of observed HONO. For example, the HONO concentration predicted by the Community Multiscale Air Quality (CMAQ) model only accounted for 60% of the observed HONO concentration [29]. The predicted HONO concentration calculated from the rate coefficient method was two and four times lower than the measured concentrations of HONO in severe haze and clean periods [30], respectively. Therefore, the sources and formation mechanisms of HONO are still unclearly and should be further investigated, especially in the marine boundary layer (MBL). For instance, the calculated production/loss rates of HONO in the East China Sea showed that the unknown HONO production rates at two monitoring sites are 1.52 ppb  $h^{-1}$  and 1.14 ppb  $h^{-1}$ , respectively [9]. Additionally, larger marine-derived HONO production rates in MBL than that in the land were detected in field observations [27,31]. Yang et al. revealed that the  $NO_2$ -to-HONO conversion rate in the "sea case" is four times faster than that in the "land case", where the sea surface microlayer is likely to be a medium for the formation of HONO [32]. Therefore, further investigations of the HONO formation mechanism in the MBL are much appreciated.

The air-water interfaces are ubiquitous and can influence most tropospheric chemical reactions in aerosols, fogs, and clouds [33]. The air-water interfaces can provide an effective adsorption and reaction site, which improves atmospheric reaction rates or creates novel mechanisms [34–37]. Previous studies have indicated that OH radical shows a higher potential to react with other species at the air-water interface than that in the gas phase [38–40]. Xia et al. unveiled a significant mechanism of HONO formation from NO<sub>2</sub> dimer catalyzed by CO<sub>2</sub> at the air-water interface by combining the simulation and flow system experiment [41]. Li et al. revealed that water droplets reduce the free-energy barrier to 0.5 kcal mol<sup>-1</sup> in HONO formation from NH<sub>3</sub>-promoted hydrolysis of NO<sub>2</sub> dimer, which can be ignored at room temperature [42]. Since oceans have more abundant water and air-water interfaces than inland areas, air-water interfaces in MBL likely play a more important role in the formation of HONO than that in inland areas.

Field observations found halogen sources in polar, open ocean, coastal areas, and salt lake regions [43]. Chlorine monoxide radical (ClO) is one of the reactive halogen species which can play an important role in stratospheric ozone depletion through a catalytic cycle [44,45]. In the coastal MBL, the average concentration for ClO radical is  $1.00 \times 10^7$  molecules cm<sup>-3</sup>, while the value is  $6.00 \times 10^5$  molecules cm<sup>-3</sup> for OH radical [46]. Interestingly, the rate constants of the oxidation reaction from OH and ClO radicals with caffeine showed a similar or close order of magnitude [47], indicating that OH and ClO radicals could have comparable reactivity and the importance of ClO in MBL should not be ignored. Meanwhile, the average concentration of Cl radical is  $3.00 \times 10^5$  molecules cm<sup>-3</sup> in the coastal MBL [46], which is two orders of magnitude lower than that of ClO radical. Our previous study proposed that the reaction of Cl radical, NO, and one water molecule can explain 40.3–53.8% of the unknown HONO production rate [23]. Considering the much higher concentration of ClO radical than that of Cl radical in MBL, as the following investigation, the HONO formation from ClO radical, NO, and water molecules need to be further explored.

Hence, in this study, the HONO formations from the reactions of CIO radical and NO with the addition of one to two water molecules and at the air-water interface in the MBL were simulated by using the Born–Oppenheimer molecular dynamics (BOMD) simulation and metadynamics (MTD) sampling. Density functional theory (DFT) calculations were further performed to verify the simulation results. The rate constants of CIO radical and

NO molecule in the presence of one water molecule were calculated by using the canonical variational transition-state theory (CVT) with the small curvature tunneling contribution (SCT) method. Furthermore, the contributions to HONO formation initiated by Cl and ClO radicals were compared to evaluate their atmospheric significance [23].

### 2. Materials and Methods

# 2.1. Born–Oppenheimer Molecular Dynamics (BOMD) Simulation

BOMD simulation for all reactions in gas-phase and at air-water interface was carried out using the Quickstep module of the CP2K program package [48]. The simulation systems in the gas-phase were (ClO)(NO)( $H_2O$ )<sub>n</sub> (n = 1–2), and the droplet system was consisted of 191 water molecules in a spherical model. A cubic box with  $20 \times 20 \times 20$  Å<sup>3</sup> was set for  $(ClO)(NO)(H_2O)_{1-2}$  systems, while  $35 \times 35 \times 35 \text{ Å}^3$  was chosen as cubic box for the droplet system to minimize the interactions between adjacent periodic units (Figure S1). By using the Becke–Lee–Yang–Parr (BLYP) correction functional [49,50], we treated the exchange and correction interactions. Grimme's dispersion correction (D3) method [51] was added to depict the weak dispersion interactions. To model the valence and core electrons, we chose a triple- $\zeta$  plus polarization level Gaussian basis set [52] and the Goedecker–Teter–Hutter (GTH) norm-conserved pseudopotentials [53], respectively. A 280 Ry energy cutoff was set for the plane-wave basis set, and a 40 Ry cutoff was selected for the Gaussian basis set. All BOMD simulations were employed under the canonical (NVT) ensemble with a temperature of 298 K, and the Nose-Hoover chain method [54] was adopted to control the temperature. The simulation step was set as 0.5 fs and 1 fs for gas-phase and air-water interface systems, respectively.

## 2.2. Metadynamics (MTD) Simulation

MTD simulation was employed using the PLUMED 2.4 plugin [55], combined with CP2K package. The distance between the O atom of ClO radical and H atom of water ( $d_{O-H}$ ) was chosen as the collective variable (CV) for the (ClO)(NO)(H<sub>2</sub>O)<sub>1–2</sub> systems. To reduce the unnecessary sampling, an upper wall was selected if the  $d_{O-H}$  was greater than 4.0 Å with force constant of 150.00 kcal mol<sup>-1</sup>. For the Gaussian functions, we set their height and width to 0.05 kcal mol<sup>-1</sup> and 0.1 Å, and every 100 steps will add a new Gaussian function.

# 2.3. Quantum Chemistry Calculations

To verify the results from dynamics simulations, a high-accuracy molecular orbital method was used to perform all density functional theory (DFT) calculations of reactants (R), pre-reaction compound (RC), transition state (TS), and product compound (PC) by using the Gaussian 16 software package [56], along with the hybrid meta function M06-2X method [57]. The geometric optimizations and vibrational frequency calculations were carried out at the 6-311++G(3df,3pd) level. The frequency calculations can ensure that there is only one imaginary frequency for TS. The intrinsic reaction coordinate (IRC) calculations [58] were also carried out at the same level to confirm that the TS is connected with desired RC and PC. For higher accuracy, the CCSD(T) method [59,60] with the aug-cc-pVTZ basis set was adopted to calculate single-point energies of the optimized geometries.

### 2.4. Rate Constant Calculations

The canonical variational transition-state (CVT) theory, along with the small curvature tunneling (SCT) contribution [61–64], was adopted to obtain the rate constant of the unimolecular reaction from RC to PC with the Polyrate 9.7 program [65]. Moreover, the KiSThelP program [66] was used to calculate the equilibrium constants between R and RC (details in the Supplementary Materials). It should be noted that all constants used in the study were based on a temperature range of 220–310 K.

# 3. Results and Discussion

HONO formation from oxidation reactions of ClO radical, NO, and water involves gas-phase reactions and air-water interface reactions. Two ab initio molecular dynamics simulations, BOMD simulation, and MTD simulation, as well as DFT quantum chemistry calculations, were used to present the dynamics and thermal analyses. For the gas-phase reactions, HONO formation from ClO radical, NO, and one water molecule (i.e., monohy-drated system or (ClO)(NO)(H<sub>2</sub>O)<sub>1</sub> system) and HONO formation from the ClO radical, NO, and two water molecules (i.e., dihydrated system or (ClO)(NO)(H<sub>2</sub>O)<sub>2</sub> system) were considered by using both ab initio molecular dynamics simulation and DFT calculation methods. For the air-water interface reactions, HONO formation was mainly analyzed by BOMD simulation.

## 3.1. HONO Formation from the Monohydrated System in the Gas-Phase

Figure 1 shows the variations of structures and key bond lengths in the HONO formation from the ClO radical, NO, and one water molecule by using BOMD simulation within 2.5 ps. Initially, the distance from the Cl atom of the ClO radical to the O atom of H<sub>2</sub>O (Cl-O2) and the distance from the N atom of NO to the O atom of H<sub>2</sub>O (N-O2) was kept at 3.00 Å. The distance from the O atom of ClO to the H atom of H<sub>2</sub>O (O1-H1) and the distance from the O atom of H<sub>2</sub>O to the H atom of H<sub>2</sub>O (O2-H1) fluctuated around 4.00 Å and 1.00 Å, respectively. Up to 1.20 ps, the O2-H1 bond length was 1.08 Å, while at approximately 1.23 ps, the H1 atom transferred to the O1 atom, forming a stable O1-H1 bond with a strength of 1.00 Å. After the H1 transferring, the O2-H2 group of H<sub>2</sub>O moved to the N atom of NO immediately at 1.24 ps, forming O2-N with a bond length of around 1.50 Å. These results can be interpreted as describing the dynamic process of HONO formation in the monohydrated system, which occurs at about 1.24 ps.



**Figure 1.** (a) BOMD simulation results of the monohydrated system. (b) Time evolution of the O1-H1, O2-H1, and O2-N bond lengths during the BOMD simulation. The white, blue, red, and green spheres represent H, N, O, and Cl atoms, respectively.

In order to calculate the free-energy variation of the dynamic process, a 28 ps MTD simulation was conducted based on the results of the BOMD simulation. As presented in Figure 2, there is a low free-energy barrier of 9.66 kJ mol<sup>-1</sup> for the monohydrated system considering the O1-H1 bond length as the Collective Variable (CV). It also can be seen from Figure S2a that the O1-H1 bond decreases from 4.00 Å to 1.00 Å in a dynamic equilibrium process after 0.80 ps.



**Figure 2.** The free energy variation versus the corresponding collective variable of the O1–H1 bond length in the monohydrated system. The white, blue, red, and green spheres represent H, N, O, and Cl atoms, respectively. The arrow is used to show the free energy value.

DFT calculations were carried out to confirm the results from the BOMD and MTD simulations. Figure 3 shows the free energy profile of the HONO formation from the monohydrated system at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(3df,3pd) level. Firstly, the ClO radical and NO molecule collide with the water molecule to form ClO-H<sub>2</sub>O and NO-H<sub>2</sub>O compounds, with a binding energy of 14.08 and 14.82 kJ mol<sup>-1</sup>, respectively. As pointed out in Figure 3, the subsequent formation of the ClO-NO-H<sub>2</sub>O pre-reaction compound (RC) is an endoergic reaction with a free energy of 23.71 kJ mol<sup>-1</sup>, followed by the formation of the product compound (PC) derived from the RC with a free energy of -51.57 kJ mol<sup>-1</sup>. This step can occur with a free-energy barrier of 18.75 kJ mol<sup>-1</sup>, resulting in the formation of HONO and HOCl, agreeing well with the MTD free-energy barrier of 9.66 kJ mol<sup>-1</sup> for the (ClO)(NO)(H<sub>2</sub>O)<sub>1</sub> system.

In our previous study, we simulated the HONO formation from the reaction of the Cl radical and the NO molecule with the addition of one water molecule [23]. It is interesting to compare the effect of Cl and ClO radicals on the HONO formation. For example, the MTD free-energy barrier of the HONO formation from the (Cl)(NO)(H<sub>2</sub>O)<sub>1</sub> system is 3.97 kJ mol<sup>-1</sup> [23], which is much lower than the value of 9.66 kJ mol<sup>-1</sup> for the (ClO)(NO)(H<sub>2</sub>O)<sub>1</sub> system in this study. Moreover, the DFT calculated free-energy barrier of the HONO formation in the (Cl)(NO)(H<sub>2</sub>O)<sub>1</sub> system is 16.26 kJ mol<sup>-1</sup>, which is also much lower than that in the (ClO)(NO)(H<sub>2</sub>O)<sub>1</sub> system. In addition, the formation of the RC from the ClO radical, NO, and one water molecule is endoergic by 23.71 kJ mol<sup>-1</sup>, while the formation of RC from the Cl radical, NO, and one water molecule is energetically more favorable than from the ClO radical, NO, and one water molecule, which matches well with the reported phenomenon that the Cl radical is more reactive than ClO radical [67,68].



**Figure 3.** The free energy profile and corresponding configurations of the monohydrated system at the CCSD(T)/cc-pVTZ//M06-2X/6-311++G(3df,3pd) level. The white, blue, red, and green spheres represent H, N, O, and Cl atoms, respectively.

### 3.2. HONO Formation from the Dihydrated System in the Gas-Phase

In a similar manner, the HONO formation from the ClO radical, NO, and two water molecules was also investigated by 2.5 ps BOMD and 28 ps MTD simulations, along with DFT calculations at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(3df,3pd) level. In the previous study of HONO forming through the NO<sub>2</sub> dimers hydrolysis reaction catalyzed by NH<sub>3</sub>, Li and coworkers had proposed a dual-water mechanism for their dihydrated system and believed that every water molecule was involved in the hydrogen transfer process [42]. However, in this study, Figure 4a clearly shows that the dihydrated system follows a single-water mechanism, which means only one water molecule is involved in the reaction of the ClO radical and the NO molecule, while the second water molecule acts as the "solvent". In Figure 4b, the O2-H1 bond in H<sub>2</sub>O remains at 1.00 Å at the beginning, and then the H1 transfers to the O atom of ClO to form a new hydrogen bond (O1-H1) at around 0.43 ps. In the next step, the remnant OH radical is connected quickly to the N atom of NO to form the HONO molecule.

To verify the effect of the "solvent" molecule, MTD simulation was employed to obtain the free energy variation of the dihydrated system. It can be obviously shown in Figure 5 that the HONO formation in the dihydrated system is a barrierless reaction, with the freeenergy barrier being much lower than that in the monohydrated system (9.66 kJ mol<sup>-1</sup>). This demonstrates that the HONO formation from the dihydrated system is energetically more favorable than that from the monohydrated system. Although the second water molecule does not directly participate in the HONO formation and does not provide the hydrogen bond for the reaction, it can decrease the free-energy barrier effectively and play a positive catalytic effect on HONO formation.



**Figure 4.** (a) BOMD simulation results of the dihydrated system. (b) Time evolution of the O1-H1, O2-H1, and O2-N bond lengths during the BOMD simulation. The white, blue, red, and green spheres represent H, N, O, and Cl atoms, respectively.



**Figure 5.** The free energy variation versus the corresponding collective variable of the O1–H1 bond length in the dihydrated system. The white, blue, red, and green spheres represent H, N, O, and Cl atoms, respectively.

The DFT calculation was also carried out to present the indirect evidence for the fact that the second water molecule serves as the "solvent". In the HONO formation mechanism, the NO<sub>2</sub> dimer hydrolyzes, and NH<sub>3</sub> acts as a catalyst proposed by Li and coworkers [42]; the free-energy barrier of the dihydrated system was calculated based on a loop structure formed by two water molecules participating in hydrogen transfer. However, as presented in Figure 6, the formation of the product (PC\_2) from the pre-reaction compound (RC\_2) with two water molecules directly participating in the reaction via a loop structure exhibits a free-energy barrier of 121.69 kJ mol<sup>-1</sup>, which is much higher than the value of 18.75 kJ mol<sup>-1</sup> in the monohydrated system. Therefore, the HONO formation from the dihydrated system tends to follow the single-water mechanism, which means that one water molecule participates in the hydrogen transfer process, and the second one acts as the "solvent" and has no interaction with other molecules. Overall, the HONO formation in both monohydrated and dihydrated systems follows the single-water mechanism rather than the dual-water mechanism [42].



**Figure 6.** The free energy profile and corresponding configurations of the dihydrated system at the CCSD(T)/cc-pVTZ//M06-2X/6-311++G(3df,3pd) level. The white, blue, red, and green spheres represent H, N, O, and Cl atoms, respectively.

# 3.3. HONO Formation at the Air-Water Interface

Considering the fact that the air-water interface is ubiquitous in MBL, the HONO formation from the ClO radical and the NO molecule at the air-water interface was studied by BOMD simulation. Through the 5 ps BOMD simulation presented in Figure 7, it is obvious that only one water molecule participates in the hydrogen transfer process, resulting in HONO and HOCl molecules. In other words, similar to the gas-phase reactions, the HONO formation from the ClO radical and the NO molecule at the air-water interface also exhibits a single-water mechanism. In the beginning, the ClO radical and the NO molecule were placed in the surface region without any interaction with neighboring water molecules. The distance from the O atom of the ClO radical to the H1 atom of H<sub>2</sub>O (O1-H1) decreased rapidly from 3.84 Å at 0.00 ps to 1.00 Å at 0.18 ps, resulting in the formation of the O1-H1 bond and the HOCl molecule. Next, the remnant OH group of the water molecule moved towards NO and yielded the HONO molecule, in which the distance between the O atom of H<sub>2</sub>O and the N atom of NO (O2-N) decreased from 2.56 Å to 1.50 Å until 0.19 ps. Subsequently, the bond lengths of O1-H1 and O2-N remained stable, indicating the reaction had stopped. It is necessary to compare the HONO formation in the gas-phase

systems with the HONO formation in the air-water interface system. HONO formation from the CIO radical and NO at the air-water interface only needs 0.19 ps, which is much faster than the formation in the monohydrated system (1.24 ps) and dihydrated system (0.45 ps), respectively, implying that air-water interface has a positive catalytic influence on the formation of HONO. This agrees well with the previous study that the time scale for the CH<sub>2</sub>OO reacting with water at the air-water interface was two to three orders of magnitude shorter than in the gas phase [69].



**Figure 7.** (a) BOMD simulation results of the reaction of the ClO radical and the NO molecule on the surface of a water droplet. (b) Time evolution of the O1-H1, O2-H1, and O2-N bond lengths during the BOMD simulation. The white, blue, red, and green spheres represent H, N, O, and Cl atoms, respectively.

As displayed in Figure S5, a 5 ps BOMD simulation was performed for the ClO radical and NO, initially placed in the interior of the droplet. During the whole process, there is no water molecule reacting with the ClO radical and the NO molecule, implying the weak reactivity of water molecules inside the droplet. This phenomenon is similar to previously published research [44], in which the ClO radical preferred to be adsorbed on the air-water interface rather than to be dissolved in bulk.

## 3.4. Atmospheric Implication

The unimolecular reaction rate constants for the reaction from RC to PC and total rate constants were calculated to determine the contribution of the monohydrated system in the marine atmosphere. The equilibrium constants ( $K_{eq}$ ) were calculated with the KisThelP program [66], and the unimolecular rate constants ( $k_{uni}$ ) were obtained by CVT/SCT theory by using the Polyrate program [65]. All equilibrium constants, unimolecular rate constants, and total rate constants with temperature ranges from 220 K to 310 K are listed in Table S1. From Table S1, the total rate constants of the (ClO)(NO)(H<sub>2</sub>O)<sub>1</sub> system vary from 4.65 × 10<sup>-40</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> (310 K) to 2.11 × 10<sup>-39</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> (220 K), which are 8–11 orders of magnitude lower than the (Cl)(NO)(H<sub>2</sub>O)<sub>1</sub> system from 6.10 × 10<sup>-32</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> (310 K) to 2.07 × 10<sup>-28</sup> cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup> (220 K) [23].

In addition to the rate constants, the reactant concentrations are also a critical element in evaluating the significance of the monohydrated system. According to field measurements, the average concentration of NO is 0.5 ppbv over the eastern Bohai Sea [70] and can reach approximately 350 ppbv in the East China Sea [9]. The average concentration of the ClO radical is  $1.00 \times 10^7$  molecules cm<sup>-3</sup> [46], with a maximum concentration of 15 pptv ( $3.67 \times 10^8$  molecules cm<sup>-3</sup>) in the coastal MBL [71]. The water molecule has a concentration of  $5.18 \times 10^{17}$  molecules cm<sup>-3</sup> [72]. Four cases were considered based on the concentrations of ClO, NO, and water molecule, namely cases 1–4. All the reaction rates at 300 K for the monohydrated system are depicted in Table S2. The highest production rate of HONO is  $1.25 \times 10^{-7}$  ppb h<sup>-1</sup> when the [NO] is 350 ppbv and [ClO] is  $3.67 \times 10^8$  molecules cm<sup>-3</sup>, which is six orders of magnitude lower than the value of  $6.13 \times 10^{-1}$  ppb h<sup>-1</sup> for the (Cl)(NO)(H<sub>2</sub>O)<sub>1</sub> system in the case of [NO] being 350 ppbv and [Cl] being  $8.00 \times 10^6$  molecule cm<sup>-3</sup> [23]. Although the concentration of the ClO radical in coastal MBL is two orders of magnitude higher than that of the Cl radical, the Cl radical dominates the HONO formation rather than the ClO radical in the MBL.

# 4. Conclusions

In this study, the HONO formation mechanisms from the CIO radical and the NO molecule in the presence of one to two water molecules and at the air-water interface were investigated by BOMD simulations and MTD samplings as well as DFT calculations. The monohydrated system exhibits a free-energy barrier of 9.66 kJ mol<sup>-1</sup>, whereas the dihydrated system is barrierless. All systems follow the single-water mechanism, which has one water molecule participating in the proton transfer of the reactions directly; other water molecules in the dihydrated system and in a water droplet just serve as the "solvent". The "solvent" water molecules can decrease the free-energy barrier in the dihydrated system or accelerate the simulation time at the air-water interface, which plays a positive catalytic effect on HONO formation. Although the concentration of the ClO radical in the MBL is two orders higher than that of the Cl radical, the production rates of HONO from the  $(ClO)(NO)(H_2O)_1$  system are six orders lower than that from the  $(Cl)(NO)(H_2O)_1$ system, which means that the Cl radical dominates the HONO formation rather than the ClO radical in the MBL. These new insights for the HONO formation can be input into HONO control and prediction models as detailed parameters and then narrow the gap between the predicted and measured values of the HONO concentration.

**Supplementary Materials:** The following supporting information can be downloaded at: https: //www.mdpi.com/article/10.3390/atmos14010030/s1, Figure S1: The BOMD simulation systems for (a) the monohydrated system, (b) the dihydrated system and (c) the air-water interface system with 191 water molecules; Figure S2: Length of O1-H1 versus time in the 28 ps metadynamics simulation for (a) the monohydrated system and (b) the dihydrated system; Figure S3: Snapshots of the system with ClO radical initially placed in the interior of the water droplet; Figure S4: Snapshots of the system with NO radical initially placed in the interior of the water droplet; Figure S5: Snapshots of the system with NO and the ClO radical initially placed in the interior of the water droplet; Table S1: The equilibrium constants ( $K_{eq}$ , cm<sup>3</sup> molecule<sup>-1</sup>), unimolecular rate constants ( $k_{uni}$ , s<sup>-1</sup>) and total rate constants ( $k_{total}$ , cm<sup>6</sup> molecule<sup>-2</sup> s<sup>-1</sup>) for the monohydrated system at 220–310 K; Table S2: The reaction rates (ppb h<sup>-1</sup>) for the monohydrated system under different concentrations of the ClO radical and the NO molecule (molecule cm<sup>-3</sup>) at 300 K.

**Author Contributions:** Conceptualization, F.X.; methodology, Q.Z. and X.Z.; software, X.Z. and M.H.H.; formal analysis, Q.Z.; investigation, X.W. and X.B.; data curation, Q.Z.; writing—original draft, Q.Z.; writing—review and editing, F.X. and M.H.H.; visualization, Y.S.; supervision, F.X.; funding acquisition, F.X. All authors have read and agreed to the published version of the manuscript.

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