



1 **Rapid formation of nitric acid during the daytime and its critical**
2 **contribution to methanesulfonic acid-methylamine nucleation in**
3 **coastal industrial areas**

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10 **Abstract**

11 Nitric acid (HNO₃) is critically involved in aerosol formation, acid deposition, and atmospheric
12 nitrogen cycling. However, the mechanisms underlying its daytime formation, particularly the
13 influences of gaseous and interfacial water molecules, and its effect on methanesulfonic acid-
14 methylamine (MSA-MA)-driven nucleation remains poorly understood. Here, we employed
15 quantum chemical calculations, atmospheric cluster dynamics code (ACDC) simulations, and Born-
16 Oppenheimer molecular dynamics (BOMD) to investigate how water catalyzes HNO₃ formation in
17 both gaseous and interfacial environments, as well as the contribution of HNO₃ to MSA-MA-driven
18 new particle formation (NPF). Results show that water-catalyzed HNO₃ formation in the gas phase
19 proceeds through a barrierless pathway and becomes significantly faster than the uncatalyzed NO₂
20 + OH reaction under typical atmospheric water vapor concentrations. At the air-water interface, NO₂
21 and OH not only show pronounced surface affinity, but also can lead to the rapid formation of HNO₃
22 within picoseconds. Against the backdrop of declining global SO₂ emissions, this work further
23 reveals that HNO₃ substantially promotes NPF and aerosol particle growth via two main
24 mechanisms (i) in high HNO₃ concentrations ($\sim 1.0 \times 10^{12}$ molecules·cm⁻³), such as the North China
25 Plain and New Delhi areas, HNO₃-involved pathways contribute up to 10% of the total nucleation
26 flux; (ii) NO₃⁻ exhibits a markedly enhanced capacity to promote aerosol hygroscopic growth by
27 facilitating vapor uptake and stabilizing molecular clusters, thereby driving aerosol nucleation and
28 growth. These findings offer molecular-level insights into the formation pathways of HNO₃ and the
29 growth of aerosol particles in polluted boundary layer.

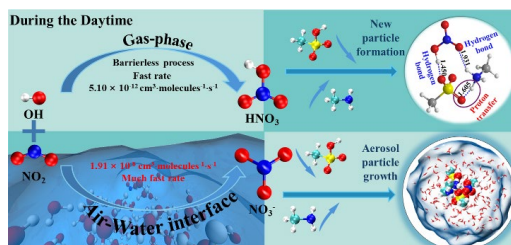
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30

Graphical Abstract



31



1. Introduction

Nitric acid (HNO_3 , NA), a key inorganic acid in atmospheric chemistry, plays an essential role in both tropospheric and stratospheric processes by influencing aerosol formation, acid deposition, and nitrogen cycling (Yang et al., 2019; Martins-Costa et al., 2019; Tang et al., 2024). It is primarily formed from the oxidation of nitrogen oxides (NO_x) emitted from anthropogenic and natural sources, including vehicle exhaust, coal combustion, petroleum refining, photochemical smog, and lightning (Hoffman et al., 2024; Mezuman et al., 2016; Driscoll et al., 2024). In heavily polluted regions, gaseous HNO_3 concentrations can reach levels as high as 10^{12} molecules $\cdot \text{cm}^{-3}$ (Driscoll et al., 2024; Kumar et al., 2018), highlighting its atmospheric significance (Mondal et al., 2021; Alecu and Marshall, 2014). Conventional pathways for atmospheric HNO_3 formation include the daytime gas-phase reaction of NO_2 with OH radicals (He et al., 2018; Xin et al., 2023), as well as the nighttime hydrolysis of N_2O_5 on aerosol surfaces following the $\text{NO}_3 + \text{NO}_2$ reaction (He et al., 2018; Xin et al., 2023; Hrdina et al., 2021). An additional pathway involves NO_3 radicals reacting with volatile organic compounds (VOCs) or dimethyl sulfide (DMS) (Ye et al., 2016). Among these, the $\text{NO}_2 + \text{OH}$ reaction is widely recognized as the dominant source of gas-phase NA in the atmosphere (Mondal et al., 2021; Mollner et al., 2010). Experimentally, Okimura et al. (Mollner et al., 2010) reported a rate coefficient of $9.2 (\pm 0.4) \times 10^{-12} \text{ cm}^3 \cdot \text{molecules}^{-1} \cdot \text{s}^{-1}$ at 298 K using spectroscopic techniques. In contrast, Percival et al. (Winiberg et al., 2020) obtained values ranging from 1.91×10^{-12} to $2.36 \times 10^{-11} \text{ cm}^3 \cdot \text{molecules}^{-1} \cdot \text{s}^{-1}$ using laser photolysis coupled with laser-induced fluorescence. Theoretically, Williams et al. (Williams et al., 2007) predicted a rate coefficient of $4.00 \times 10^{-11} \text{ cm}^3 \cdot \text{molecules}^{-1} \cdot \text{s}^{-1}$ at 300 K, which falls within the range of available experimental values.

In atmospheric oxidation processes, gaseous water (H_2O) can serve not only as a catalyst to accelerate reaction rates but also as a direct reactant that alters chemical pathways (Sun et al., 2016; Chen et al., 2025; Xu et al., 2024). For instance, in the $\text{HOSO} + \text{NO}_2$ reaction, H_2O has been shown to catalyze the formation of HONO and SO_2 , while also participating directly in channels leading to HNO_3 and H_2SO_3 (Sun et al., 2016). This dual role highlights the complex role of water in the atmospheric NO_x cycle and suggests that the current models of HNO_3 formation may need reassessment. A key unresolved question is whether H_2O significantly lowers the energy barrier of



61 the $\text{NO}_2 + \text{OH}$ reaction and what detailed mechanisms are involved. Beyond homogeneous gas-
62 phase chemistry, a growing body of evidence has highlighted the distinctive reactivity occurring at
63 the air-water interface (Zhong et al., 2017a; Zhong et al., 2017b; Kumar et al., 2017; Anglada et al.,
64 2020). For instance, organic acids reacting with SO_3 at such interface can form ion pairs such as
65 carboxylic sulfuric anhydride and hydronium ions (Zhong et al., 2019), a mechanism fundamentally
66 different from the gas-phase pathway. Similarly, Dong *et al.* (Dong et al., 2024) demonstrated that
67 the interfacial ammonolysis of glyoxal with amines on aqueous nanodroplets is both
68 thermodynamically and kinetically more favorable than the corresponding gas-phase and bulk-
69 phase reactions, resulting in more efficient glyoxal scavenging. Given these insights, it is essential
70 to explore the interfacial reaction mechanisms between NO_2 and OH radicals and to systematically
71 compare it with gas-phase pathways. Such a comparative approach will yield a more complete
72 understanding of HNO_3 formation and its role in atmospheric chemistry.

73 The role of NA in aerosol nucleation is well established (Perraud et al., 2015; Knattrup et al.,
74 2023). Molecular simulations by Liu et al. (Liu et al., 2018) demonstrated that NA enhances the
75 formation of sulfuric acid (SA)-ammonia (NH_3) cluster, particularly under low temperature, low-
76 SA and high- NH_3 conditions. This promoting effect was subsequently confirmed by Wang et al.
77 (Wang et al., 2020) in CLOUD chamber studies, which revealed enhanced SA- NH_3 nucleation
78 under clean and cold upper-tropospheric conditions. In polluted boundary layers, Liu et al. (Liu et
79 al., 2021b) further reported that NA can increase SA-dimethylamine (DMA) nucleation rates by up
80 to 80-fold. Against the backdrop of continually declining global SO_2 emissions, methanesulfonic
81 acid (MSA) is expected to play an increasingly important role in NPF (Perraud et al., 2015; Chen et
82 al., 2016; Shen et al., 2020; Liu et al., 2022; Lee et al., 2019; Hu et al., 2023), underscoring the need
83 to clarify the nucleation mechanisms in MSA-dominated systems under the influence of NA.
84 Notably, MSA exhibits a stronger binding affinity for methylamine (MA) than for NH_3 or DMA
85 (Chen et al., 2016; Chen and Finlayson-Pitts, 2017; Shen et al., 2019). Further studies indicated that
86 adding MA to MSA-based nucleation pathways significantly improves the efficiency of new particle
87 formation over the corresponding binary MSA mechanism (Zhang et al., 2022; Hu et al., 2023).
88 Despite these insights, the influence of NA on MSA-MA driven new particle formation (NPF)
89 remains unclear.

90 In this work, we elucidate the formation mechanism of HNO_3 , via the daytime $\text{NO}_2 + \text{OH}$



91 reaction and its influence on NPF driven by MSA-MA. A multiscale computational strategy is
 92 employed to achieve this objective. First, quantum chemical calculations are performed to assess
 93 HNO_3 formation from the gaseous $\text{NO}_2 + \text{OH}$ reaction, both in the absence and presence of H_2O .
 94 Subsequently, Born-Oppenheimer molecular dynamics (BOMD) simulations were employed to
 95 probe the interfacial reaction between NO_2 and OH at the air-water interface (Zhong et al., 2017a;
 96 Zhong et al., 2017b; Kumar et al., 2017; Limmer et al., 2024; Anglada et al., 2020). Finally, the
 97 impact of HNO_3 on MSA-MA-driven NPF under varied atmospheric conditions is quantitatively
 98 assessed using the Atmospheric Clusters Dynamic Code (ACDC). Overall, this study will
 99 provide molecular-level insight into daytime HNO_3 formation and clarifies the role of HNO_3 in
 100 promoting particle nucleation within MSA-MA systems.

101 2 Computational methods

102 **2.1 Quantum Chemical Details.** The M06-2X functional (Mardirossian and Head-Gordon,
 103 2016; Pereira et al., 2017) has proven effective in accurately describing weak intermolecular
 104 interactions and reliably predicting thermochemical properties and equilibrium geometries in
 105 atmospheric cluster systems. To explore the $\text{NO}_2 + \text{OH}$ reaction, both in the absence and
 106 presence of H_2O , we conducted geometry optimizations and vibrational frequency calculations
 107 at the M06-2X/6-311++G(2df,2pd) level using Gaussian 09 (Frisch et al., 2009). Intrinsic
 108 reaction coordinate (IRC) calculations were further performed to verify the connectivity
 109 between transition states and their associated reactant or product complexes. The relative
 110 Gibbs free energies were subsequently refined through single-point calculations at the
 111 DLPNO-CCSD(T)/aug-cc-pVTZ level using ORCA (Neese, 2012).

112 The energetically favored geometries of $(\text{MSA})_x(\text{MA})_y(\text{NA})_z$ ($z \leq x + y \leq 3$) clusters were
 113 obtained through a systematic multi-step approach. First, the ABcluster program (Zhang and Dolg,
 114 2015) was employed to generate $n \times 1000$ random isomers ($1 \leq n \leq 3$), which were pre-screened
 115 at the PM6 level using MOPAC 2016 (Partanen et al., 2016). From this set, the $n \times 100$ lowest-
 116 energy candidates were selected and optimized at the M06-2X/6-31+G(d,p) level. The top $n \times 10$
 117 structures then underwent further refinement via preoptimization at the M06-2X/6-311++G(2df,2pd)
 118 level to determine the global minima. Finally, single-point energies calculations were performed at
 119 the DLPNO-CCSD(T)/aug-cc-pVTZ level (Tchinda T. N. et al., 2022) using ORCA (Neese, 2012).



120 The resulting lowest-energy geometries and their corresponding Gibbs free energies are summarized
 121 in Fig. S12 and Table S7. In addition, electrostatic potential (ESP) and localized orbital locator (LOL)
 122 maps were analyzed using the Multiwfn 3.8 program (Lu and Chen, 2012), with computational
 123 details provided in Supporting Information Part S3.

124 **2.2 Classical Molecular Dynamics Simulation.** The solvation behavior of NO₂ and OH at
 125 the air-water interface was investigated using classical molecular dynamics (MD) simulations. A
 126 periodic water slab model with two interfaces was constructed, containing 2165 TIP3P water
 127 molecules and a single NO₂ or OH molecule, in a 4 × 4 × 9 nm³ simulation box. The generalized
 128 GAFF force field (Li et al., 2024a; Zhao et al., 2019) was used to model NO₂ and OH. The free
 129 energy profile for transferring each molecule from the gas phase across the air-water interface into
 130 bulk water was computed using umbrella sampling coupled with MD simulations. Each sampling
 131 window included 10 ns of equilibration under a harmonic restraint applied along the Z-axis between
 132 the center of mass (COM) of the molecule and the COM of the water slab. Free energy profiles were
 133 reconstructed using the weighted histogram analysis method (WHAM) (Hub et al., 2010).
 134 Additionally, 150 ns NVT simulations were performed to monitor molecular diffusion and estimate
 135 phase-specific residence probabilities. All simulations were conducted with the GROMACS
 136 package (Abraham et al., 2015) under the NVT ensemble, maintained at 300 K using the Nosé-
 137 Hoover chain thermostat. Electrostatic interactions were treated with the particle-mesh Ewald (PME)
 138 method (Darden et al., 1993) using a 1.0 nm real-space cutoff. The LINCS algorithm (Hess et al.,
 139 1997) was applied to constrain bond lengths, and a 1 fs time step was used.

140 **2.3 BOMD simulations.** BOMD simulations based on density functional theory (DFT) were
 141 performed using the CP2K package (Varandas and Pansini, 2014). Cubic simulation cells with side
 142 lengths of 15 Å (gas phase) and 35 Å (air-water interface) were constructed to minimize periodic
 143 image interactions. The interfacial system, consistent with previous studies (Kumar et al., 2018;
 144 Kumar and Francisco, 2019; Ma et al., 2020b; Ding et al., 2024), contained 191 water molecules,
 145 NO₂ and OH. The BLYP functional (Becke, 1988; Lee et al., 1988) combined with Grimme's D3
 146 dispersion correction (Grimme et al., 2010) was adopted to describe exchange-correlation and van
 147 der Waals interactions, respectively. Valence electrons were treated with a double- ζ Gaussian basis
 148 set (DZVP) (Vandevondele and Hutter, 2007), while core electrons were represented using GTH
 149 pseudopotentials (Goedecker et al., 1996; Hartwigsen et al., 1998). A constant-volume NVT



ensemble at 300 K was employed using a Nosé-Hoover chain thermostat (Zhong et al., 2019; Kumar et al., 2018; Kumar et al., 2017) to control the temperature. The plane-wave and auxiliary basis set cutoffs were set to 280 Ry and 40 Ry, respectively. All simulations were conducted in the NVT ensemble at 300 K with a time step of 1 fs. Metadynamics simulations were performed using the CP2K package interfaced with PLUMED package (Tribello et al., 2014), with Gaussian bias potentials of 0.1 kcal·mol⁻¹ height and 1.0 Å width deposited every 0.05 ps. Each gas-phase BOMD simulation lasted 100 ps, while interfacial runs were 10 ps. To mitigate potential bias from initial configurations, five independent gas-phase and twenty interfacial simulations were conducted.

2.4 Atmospheric Cluster Dynamics Code (ACDC) Model. The ACDC (Mcgrath et al., 2012) was applied to simulate the formation rates and growth pathways of (MSA)_x(MA)_y(NA)_z clusters. Thermodynamic parameters, including binding free energies, were derived from quantum chemical calculations at the M06-2X/6-311++G(2df,2pd) level. The temporal evolution of cluster populations was described by a set of birth-death equations, which explicitly consider all possible collision and evaporation processes:

$$\frac{dc_i}{dt} = \frac{1}{2} \sum_{j < i} \beta_{j,(i-j)} C_j C_{(i-j)} + \sum_j \gamma_{(i+j) \rightarrow i} C_{i+j} - \sum_j \beta_{i,j} C_i C_j - \frac{1}{2} \sum_{j < i} \gamma_{i \rightarrow j} C_i + Q_i - S_i \quad (1)$$

Here, c_i represents the concentration of cluster i ; $\beta_{i,j}$ is the collision coefficient between clusters i and j ; and $\gamma_{(i+j) \rightarrow i}$ denotes evaporation rate coefficient for the dissociation of cluster $i + j$ into i and j . Q_i represents external source of cluster i , while coagulation losses were modeled with a sink coefficient of $2 \times 10^{-2} \text{ s}^{-1}$, reflecting polluted atmospheric conditions (Liu et al., 2021a). Detailed procedures for calculating the collision and evaporation rates are provided in Supporting Information Part S4. Within the ACDC framework, boundary clusters were defined as sufficiently stable to permit sustained atmospheric growth. So, the clusters of (MSA)₄(MA)₃ and (MSA)₄(MA)₄ were selected as boundary clusters in the MSA-MA-NA system.

3. Results and Discussion

3.1 Reactions in the gas phase

To evaluate the catalytic effect of water in the gas phase as well as at the air-water interface, we first reinvestigated the gas phase $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$ reaction using quantum chemical methods of DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(2df,2pd) and master equation modeling.



As shown in Fig. 1(a), the potential energy surface (PES) features no distinct transition state, which is consistent with the relaxed scan of the weakly bound $\text{NO}_2 \cdots \text{HO}$ complex and previous calculation results at different levels (Mollner et al., 2010; Golden et al., 2003). The reaction is strongly exothermic, with a reaction energy of $-47.1 \text{ kcal}\cdot\text{mol}^{-1}$, in close agreement with earlier theoretical values (Williams et al., 2007). The computed rate coefficient at 298 K is $5.10 \times 10^{-12} \text{ cm}^3\cdot\text{molecules}^{-1}\cdot\text{s}^{-1}$ (Table 1), consistent with experimental values $(9.2 (\pm 0.4) \times 10^{-12} \text{ cm}^3\cdot\text{molecules}^{-1}\cdot\text{s}^{-1})$ ¹⁴ and previous theoretical results $(4.00 \times 10^{-11} \text{ cm}^3\cdot\text{molecules}^{-1}\cdot\text{s}^{-1})$ (Williams et al., 2007). Additionally, BOMD simulations (Fig. 1(b) and Movie S1) confirmed rapid HNO_3 formation from the $\text{NO}_2 + \text{OH}$ reaction within 1 ps.

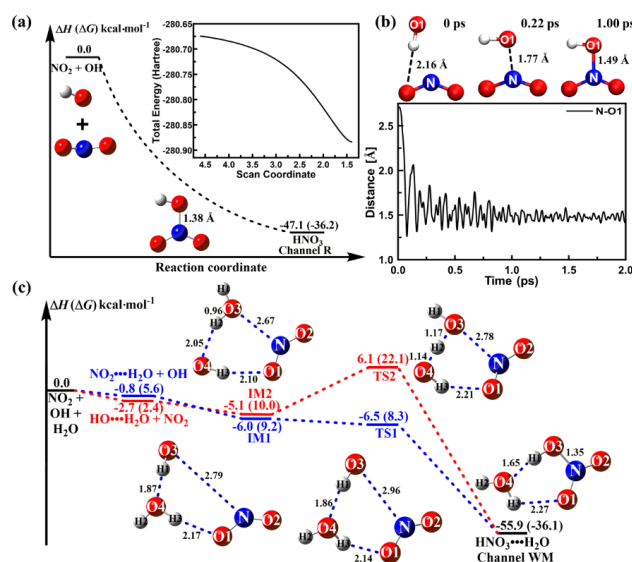


Fig. 1 (a) Potential energy surface for the $\text{NO}_2 + \text{OH}$ reaction at the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(2df,2pd) level, along with a scan of the loose $\text{NO}_2 \cdots \text{OH}$ complex at the M06-2X/6-311++G(2df,2pd) level; (b) BOMD trajectories depicting the reaction dynamics of $\text{NO}_2 + \text{OH}$ in the gas phase; (c) Potential energy profiles for the H_2O -assisted $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$ reaction calculated at the DLPNO-CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(2df,2pd) level of theory.

Given its typical atmospheric abundance ($\sim 10^{17} \text{ molecules}\cdot\text{cm}^{-3}$ (Anglada et al., 2013)), water vapor serves as both a hydrogen-bond donor and acceptor, effectively catalyzing numerous proton-transfer reactions (Ding et al., 2024; Cheng et al., 2025; Mu et al., 2024). We identified two sequential bimolecular routes: (i) $\text{NO}_2 \cdots \text{H}_2\text{O} + \text{HO}$ (Path 1) and (ii) $\text{HO} \cdots \text{H}_2\text{O} + \text{NO}_2$ (Path 2). Under typical atmospheric concentrations ($[\text{NO}_2] = 8.80 \times 10^9 \text{ molecules}\cdot\text{cm}^{-3}$ (Dieudonné et al., 2013), $[\text{OH}] = 3.00 \times 10^6 \text{ molecules}\cdot\text{cm}^{-3}$ (Fuentes et al., 2000), and $[\text{H}_2\text{O}] = 7.70 \times 10^{17}$



199 molecules·cm⁻³ (Anglada et al., 2013)) the calculated concentrations of NO₂···H₂O, H₂O···HO and
 200 HO···H₂O complexes at 298 K are 2.67×10^4 , 5.81×10^3 and 7.13×10^3 molecules·cm⁻³,
 201 respectively (Table S3). Notably, Path 1 is barrierless and exhibits an activation energy 11.2
 202 kcal·mol⁻¹ lower than that of Path 2, establishing it as the favorable route for water-catalyzed HNO₃
 203 formation. At a water vapor concentration of 7.70×10^{17} molecules·cm⁻³ (Anglada et al., 2013), as
 204 listed in Table 1, the effective rate coefficients for Path 1 obtained using the Master Equation Solver
 205 for Multi-Energy Well Reactions (Supporting Information Part S1) are calculated to be in the range
 206 of 2.21×10^{-13} - 6.67×10^{-13} cm³·molecule⁻¹·s⁻¹, which are comparable to that of the uncatalyzed
 207 reaction (5.10×10^{-12} cm³·molecule⁻¹·s⁻¹). These results indicate that the H₂O-catalyzed pathway
 208 makes a non-negligible contribution to atmospheric HNO₃ formation. Detailed effective rate
 209 coefficients are summarized in Table S4.

210 To quantitatively assess the catalytic effect of water molecules, the total rate coefficient k_{tot} was
 211 defined according to Eqns (2). As summarized in Table 1, the resulting enhancement factor $k'_{\text{WM1}}/k_{\text{tot}}$
 212 ranges from 3.71% to 13.15% across 280-320 K, indicating that the role of H₂O is non-negligible
 213 in atmospheric HNO₃ formation.

$$214 \quad k_{\text{tot}} = k_{\text{R}} + k'_{\text{WM1}} \quad (2)$$

215 **3.2 Reactions at the air-water interface**

216 ***Molecular uptake at the air-water interface.*** To determine whether the reaction between NO₂
 217 and OH preferentially occurs at the air-water interface, we first evaluated their surface affinity by
 218 computing the free energy profile as a function of the vertical distance (Z-axis) from the geometric
 219 center of the water slab to each molecule (Fig. 2). As the molecule moves from the gas phase toward
 220 the aqueous interior, the free energy decreases, reaching a minimum in the interfacial region (Z =
 221 19.0-24.0 Å), before rising again into the bulk water phase. Complementing these findings, 150 ns
 222 molecular dynamics simulations show that NO₂ and OH reside within the interfacial region for 29.2%
 223 and 41.7% of the time, respectively (Fig. S1). In addition, independent 5 ps BOMD simulations at
 224 the droplet interface confirm that both NO₂ and OH can stably reside at the interface. Together, these
 225 results confirm a clear interfacial preference for both NO₂ and OH, supporting the likelihood of
 226 interfacial reaction initiation.

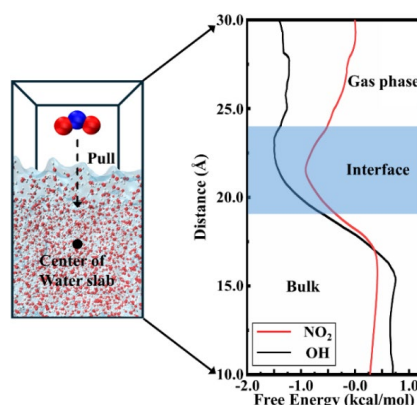


Fig. 2 Schematic diagram of umbrella sampling and free energy profile for the migration of NO_2 and OH from the gas phase into bulk water along the Z axis.

Mechanistic insights of reactions at the air-water interface. Similar to previously studied interfacial reactions involving SO_3 or Criegee intermediates (Sun et al., 2016; Li et al., 2024a; Lv and Sun, 2020; Ma et al., 2020a), three potential pathways were initially considered for the $\text{NO}_2 + \text{OH}$ reaction at the air-water interface: (i) collision of gaseous NO_2 with adsorbed OH , (ii) collision of gaseous OH with adsorbed NO_2 , and (iii) reaction via the $\text{NO}_2 \cdots \text{HO}$ complex at the interface. However, as demonstrated in Fig. 1(b), the $\text{NO}_2 \cdots \text{HO}$ complex rapidly converts to HNO_3 in the gas phase before reaching the surface. Consequently, only pathways (i) and (ii) were considered in the subsequent analysis.

Radial distribution functions (RDFs) analysis (Fig. 3(a) and Fig. 3(b)) indicates that NO_2 adsorption at the interface is primarily driven by van der Waals interactions between the nitrogen atom of NO_2 and oxygen atoms of interfacial water molecules. So, collision of gaseous OH with interfacial NO_2 on the aqueous surface (Path 3), illustrated in Fig. 3, Fig. S2 and Movie S2, begins with the reaction of gaseous OH with hydrated NO_2 ($(\text{NO}_2)\text{N} \cdots \text{O}(\text{H}_2\text{O})$) at the interface. As HO gradually approaches a water molecule within the hydrated NO_2 at the air-water interface, proton transfer from interfacial water to HO . At 0.23 ps, a new water molecule and an OH radical are formed, accompanied by $\text{N}-\text{O}1$ shortening to 2.78 Å and crossing a free energy barrier of 2.10 kcal·mol⁻¹. Subsequently, at 0.76 ps, the $\text{N}-\text{O}1$ bond shortened further to 1.75 Å, indicating the formation of HNO_3 with an energy release of 16.84 kcal·mol⁻¹. As compared to the gas phase formation of HNO_3 assisted by water molecule (Fig 1(c)), the reaction barrier of Path 3 at the air-water interface is reduced by 10.0 kcal·mol⁻¹. Furthermore, owing to the strong acidity of HNO_3 ,



spontaneous proton transfer readily occurs at the interface, leading to the formation of a stable $\text{NO}_3^- \cdots \text{H}_3\text{O}^+$ ion pair. Notably, in Path 3, interfacial water molecules act not only as a reactant but also as both a proton donor and acceptor, thereby facilitating the overall reaction process. The rate constant for Path 3 was further calculated using Eqns. (3):

$$k_i = \frac{\sigma T k_B}{h} \exp\left(-\frac{\Delta G_i}{RT}\right) \quad (3)$$

where, σ is the reaction path degeneracy, T is temperature, k_B is the Boltzmann constant, h is Planck constant and ΔG_i is the Gibbs free energy barrier. The calculated rate coefficient k_{i1} is $4.59 \times 10^7 \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, which is significantly higher than the rate constants of the gaseous $\text{NO}_2 + \text{OH}$ reaction without and with H_2O , predict that the interfacial Path 3 represents a significant source of atmospheric HNO_3 .

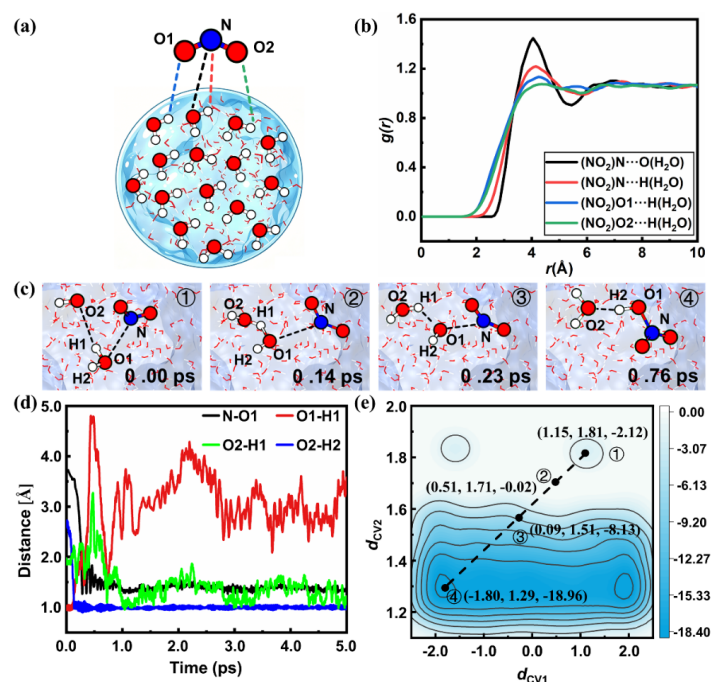


Fig. 3 (a) Schematic illustration of the interaction modes between NO_2 and interfacial water molecules; (b) radial distribution functions obtained for NO_2 at the air-water interface; (c) key reaction snapshots, (d) evolution of key bond lengths and (e) corresponding free energy profiles for the reaction of HNO_3 formation at the air-water interface from the collision of gaseous OH with interfacial NO_2 .

In contrast, Path 4 involves the direct reaction of gaseous NO_2 with adsorbed OH at the interface, leading to the formation of HNO_3 (Fig. 4, Fig. S3, and Movie S3). Notably, the adsorption of OH at the air-water interface is mainly stabilized through hydrogen-bond interactions involving



the oxygen center of OH and nearby interfacial water molecules (Fig. 4(b)), producing a hydrated
 HO ((OH)H...O(H₂O)). As NO₂ approaches the interfacial OH moiety of hydrated HO, the N-O1
 bond gradually shortens to 1.46 Å at 0.29 ps, accompanied by a significant energy release of 32.72
 kcal·mol⁻¹, indicating a barrierless reaction pathway as show in Fig. 4(e). Throughout Path 4,
 interfacial water molecules act as proton acceptors, thereby facilitating the overall reaction. The
 interfacial rate constant of Path 4 was evaluated using a reaction-diffusion framework (Johnson et
 al., 2024). Detailed calculations are provided in the Supporting Information Part S2. The
 corresponding rate constant k_{t2} is $3.36 \times 10^8 \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$, which is seven times greater than
 that for Path 3. Moreover, the rate ratio between Path 4 and Path 3 was evaluated (Supporting
 Information Part S2), revealing that Path 4 is 4.50×10^3 times faster than Path 3. This result
 indicates that HNO₃ is predominantly formed via the reaction of gaseous NO₂ with adsorbed OH at
 the gas-liquid interface.

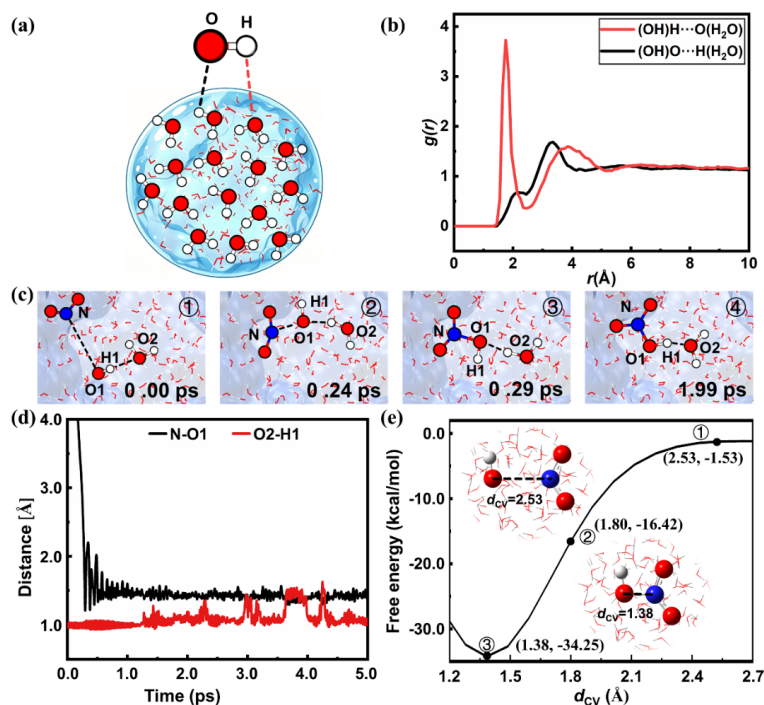


Fig. 4 (a) Schematic illustration of the interaction modes between OH and interfacial water molecules; (b) radial distribution functions obtained for OH at the air-water interface; (c) key reaction snapshots, (d) evolution of key bond lengths and (e) corresponding free energy profiles for the reaction of HNO₃ formation at the air-water interface from the collision of gaseous NO₂ with interfacial OH.

Atmospheric implications of reactions at the air-water interface. To further evaluate the



relative importance of gas-phase and interfacial pathways, the rate ratio between gaseous NO₂ reacts with the adsorbed OH at the air-water interface (Path 4) and the reaction of NO₂ + OH in the gas phase (Channel R) was compared using Eqns. (4):

$$r = \frac{k_{i2} \cdot c_{\text{OH-}i} \cdot c_{\text{NO}_2\text{-}g}}{k_R \cdot c_{\text{OH-g}} \cdot c_{\text{NO}_2\text{-}g}} \cdot \eta \cdot d \quad (4)$$

where k_{i2} is the reaction rate constant of Path 4, while k_R is the reaction rate constant of NO₂ + OH at the gas phase. The gas-phase and interfacial concentrations of reactants are denoted as $c_{x\text{-}g}$ (e.g., $c_{\text{OH-g}}$) and $c_{x\text{-}i}$ (e.g., $c_{\text{OH-i}}$), respectively. For typical cloud environments, the interfacial surface density η and the corresponding water-film thickness d are taken as $4 \times 10^{-3} \text{ cm}^2 \cdot \text{cm}^{-3}$ (Ravishankara, 1997) and 1 nm.

At 300 K, the calculated ratio (r) is 1.62×10^3 , indicating that the reaction between NO₂ and OH at the air-water nanodroplet interface is markedly faster than the corresponding gas-phase reaction. These results demonstrate that, under humid conditions with elevated NO₂ and OH concentrations (e.g., East Asia (Stone et al., 2012; Stavrakou et al., 2013) and the Indian subcontinent (Li et al., 2018)), the reaction between gaseous NO₂ and adsorbed OH at the air-water interface constitutes a dominant pathway for HNO₃ formation. This mechanism complements the conventional understanding of daytime nitric acid production and highlights the critical role of air-water interfaces in regulating multiphase atmospheric chemistry.

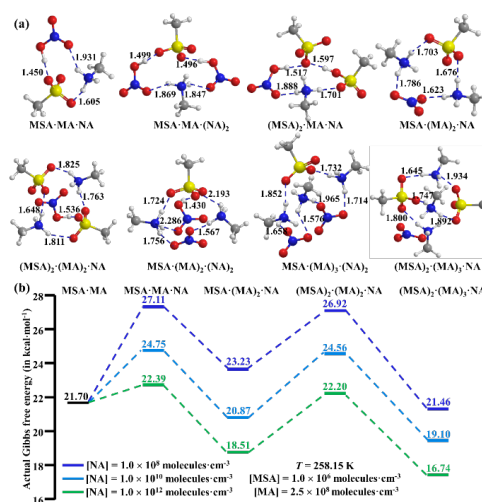
3.3 New particle formation and growth from atmospheric nitric acid

3.3.1 Enhancement effect of NA on NPF in the gas phase

Cluster structures and stability analysis. Intermolecular interactions are essential for stabilizing nucleation precursors in molecular clusters. ESP analysis (Fig. S4) shows that the -OH hydrogen atoms of NA (+72.10 kcal·mol⁻¹) act as strong hydrogen-bond (HB) donors, while the oxygen atoms of NA (-19.37 kcal·mol⁻¹) serve as acceptors, enabling NA to form HBs with both MSA and MA. As illustrated in Fig. 5(a), the lowest-energy MSA-MA-NA ternary clusters are stabilized by extensive HB networks (blue dashed lines), with NA embedded within the MSA-MA framework. As the cluster size increases, the structures evolve from ring-like to more compact cage-like geometries, indicating enhanced stability. At the same time, steric hindrance from the -CH₃ groups of MA drives these molecules to preferentially occupy peripheral positions, with the methyl groups oriented outward. Beyond hydrogen bonding, proton transfer further contributes to cluster



315 stabilization. Specifically, MA first undergoes proton transfer with the more acidic MSA, and the
 316 remaining MA can subsequently interact with NA through additional proton transfer. This is
 317 supported by LOL analysis (Fig. S5), which shows no proton transfer in the binary MSA·MA cluster
 318 but clear transfer in NA-containing clusters (MSA·MA·NA and MSA·MA·(NA)₂), as evidenced by
 319 the increase in the H1-N LBO from 0.581 to 0.739. Consistently, the higher electron density (ρ) and
 320 more negative Laplacian ($\nabla^2\rho$) in MSA·MA·(NA)₂ further confirm that NA strengthens
 321 intermolecular interactions. In summary, NA enhances cluster stability by promoting both hydrogen-
 322 bonding networks and proton transfer processes.



323 **Fig. 5** (a) The most stable configurations of ternary clusters of (MSA)_x(MA)_y(NA)_z ($y \leq x + z \leq 3$) clusters at the
 324 M06-2X/6-311++G(2df,2pd) level; (b) the actual Gibbs free energies of formation (ΔG_{actual} , kcal·mol⁻¹) of selected
 325 clusters in MSA-MA-NA system.
 326

327 To further elucidate the stabilizing role of NA in MSA-MA nucleation, the actual Gibbs free
 328 energy of formation (ΔG_{actual} , Fig. 5(b)) was evaluated for (MSA)_x(MA)_y(NA)_z ($y \leq x + z \leq 3$) clusters.
 329 As shown in Fig. 5(b), along the MSA-MA-NA growth pathway, the conversion from the MSA·MA
 330 cluster to (MSA)₂·(MA)₃·NA is exothermic, indicating a thermodynamically favorable growth
 331 process. Furthermore, with increasing NA concentration, the energy barriers are progressively
 332 reduced and the Gibbs free energy become more negative, underscoring the energetic advantage of
 333 NA incorporation. To further assess cluster stability from a kinetic perspective, total evaporation
 334 rates ($\sum \gamma$, Table S11) were analyzed. At 258.15 K, more than 20% of the investigated clusters exhibit
 335 $\sum \gamma < 10^{-2} \text{ s}^{-1}$, indicative of relatively high stability. Notably, NA-containing clusters such as
 336 (MSA)₂·(MA)₃·NA, MSA·(MA)₂·NA and (MA)₂·(NA)₂ display particularly low evaporation rates



(1.37×10^{-6} to $6.74 \times 10^{-3} \text{ s}^{-1}$), together with $\beta C/\Sigma\gamma > 1$, suggesting favorable growth propensity. Taken together, these results demonstrate that NA not only thermodynamically stabilizes MSA-MA clusters but also kinetically promotes their growth, thereby playing an active role in atmospheric nucleation.

Enhancement mechanism of NA. The growth pathways of MSA-MA-NA clusters were investigated under varying temperatures and precursor concentrations. At 258.15 K (Fig. 6(a), $[\text{MSA}] = 10^6 \text{ molecules}\cdot\text{cm}^{-3}$ (Berresheim et al., 2002; Davis et al., 1998), $[\text{MA}] = 2.5 \times 10^8 \text{ molecules}\cdot\text{cm}^{-3}$ (Zhou et al., 2019; Hirai and Matsumoto, 2021; Du et al., 2021) and $[\text{NA}] = 10^{11} \text{ molecules}\cdot\text{cm}^{-3}$ (Brown et al., 2006; Xu et al., 2015; Acker et al., 2010)), pathway involving NA, where it acts either as a “catalyst” or a “participant”, become dominant. In the participant route, MA and NA monomers first collide to form the MA·NA complex. Subsequently, this complex sequentially collides with $(\text{MSA})_2(\text{MA})_2$ and MA monomers, ultimately yielding $(\text{MSA})_3(\text{MA})_3\text{NA}$. In the catalytic route, the $(\text{MSA})_2(\text{MA})_3\text{NA}$ trimer collides with MA monomers to form $(\text{MSA})_3(\text{MA})_3\text{NA}$. Subsequently, one NA molecule evaporates, yielding $(\text{MSA})_3(\text{MA})_3$, which eventually grows beyond the system scope. At elevated temperatures (278.15-298.15 K; Fig. 6(a)), NA did not participate in MSA-MA nucleation due to its enhanced evaporation, demonstrating the strong temperature dependence of its role in MSA-MA nucleation.

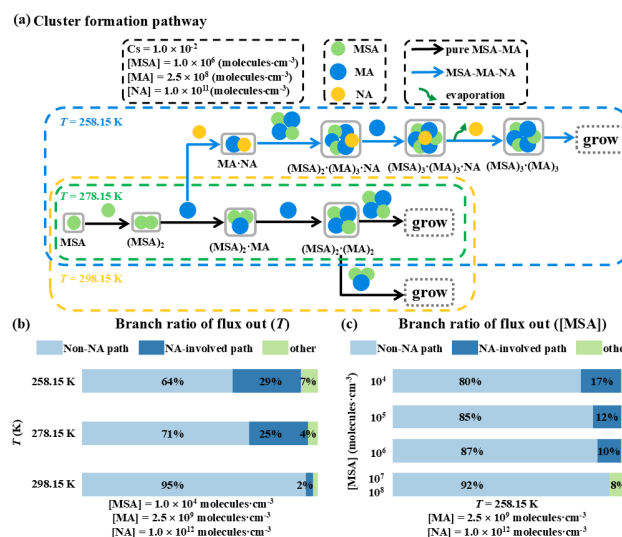


Fig. 6 Nucleation mechanism of the MSA-MA-NA system: (a) proposed cluster formation pathway, and the branch ratio of outward flux under varying (b) T (238.15-298.15 K) and (c) MA concentrations (1.0×10^7 - $1.0 \times 10^9 \text{ molecules}\cdot\text{cm}^{-3}$).



To quantitatively assess the influence of temperature and precursor concentrations on NA participation, we analyzed its contribution rate across conditions. As shown in Fig. 6(b), NA-mediated pathways are negligible at 298.15 K but contribute up to 29% at 258.15 K, highlighting its increased participation at low temperature. Beyond temperature, precursors (MSA and MA) concentrations also modulate NA's impact: its contribution declines with rising [MSA] (17% at 1×10^4 molecules·cm⁻³) (Fig. 6(c)) but increases with [MA], from 0% at 2.5×10^7 to 12% at 2.5×10^9 molecules·cm⁻³ (Fig. S12), attributed to the greater availability of MA binding partners. Therefore, NA exerts the strongest influence under conditions of low temperature, low [MSA], and high [MA].

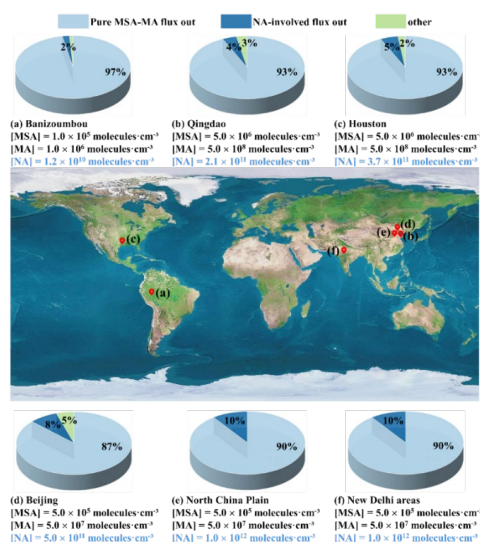


Fig. 7 Branching ratios of the MSA-MA-NA (navy blue pie) and MSA-MA (light blue pie) growth pathways across different regions with varying NA concentrations. Data in blue and black are from field observations and the optimal concentration set in this work, respectively. Basemap © Google Maps (<https://www.google.com/maps>, last access: 15 July 2025).

Atmospheric implications. To further evaluate the influence of NA on atmospheric MSA-MA nucleation, the contributions of MSA-MA cluster growth pathways to NPF, with and without the involvement of NA, were quantified under the corresponding regional environmental conditions (Fig. 7). The concentrations of MSA and MA employed in this analysis are selected to reflect typical ambient levels in the corresponding regions, thereby ensuring the realism of the simulations. Field measurements reveal considerable regional variability in [NA], ranging from 1.0×10^{10} molecules·cm⁻³ to 1.0×10^{12} molecules·cm⁻³. In low [NA] environments, such as Banizoumbou (1.2×10^{10} molecules·cm⁻³) (Ossouhou et al., 2019), NA contributes negligibly to MSA-MA cluster



formation. At moderate [NA] levels, observed in regions including Qingdao (2.1×10^{11} molecules·cm⁻³) (Li et al., 2014), Houston (3.7×10^{11} molecules·cm⁻³) (Neuman et al., 2002), and Beijing (5.0×10^{11} molecules·cm⁻³) (Li et al., 2024b), the contribution of NA-involved pathway increases markedly from 4% to 8%. Under high [NA] conditions, as in the North China Plain and New Delhi (up to 1.0×10^{12} molecules·cm⁻³) (Chen et al., 2024), NA-driven nucleation accounting for up to 10 % of the total nucleation rate. These findings confirm that elevated [NA] strongly promotes MSA-MA nucleation. Therefore, in regions characterized by low temperature, low [MSA], high [MA] and high [NA], such as the Yangtze River Delta in China, southern Bangladesh, and southern Italy, NA is expected to play a substantial role in NPF dynamics.

3.3.2 The contribution of interfacial NO₃⁻ to aerosol hygroscopic growth

The formation of NO₃⁻·(H₂O)_n clusters listed in Table S16 is thermodynamically more favorable than that of NO₂·(H₂O)_n and OH·(H₂O)_n, indicating substantially stronger hydration of the ionic product relative to its neutral precursors. This distinction is consistently supported by the hydration distribution analysis (Fig. 8, Fig. S13-S14, and Table S17), which shows that NO₃⁻ remains predominantly hydrated across a wide range of conditions (T = 258.15-298.15 K; RH = 25-100%), whereas NO₂ and OH largely persist in their bare forms. Specifically, at 258.15 K under dry conditions (RH = 25%) (Fig. 8), NO₂ and OH exist almost exclusively as unhydrated species, while HNO₃ exhibits only weak hydration, with a minor fraction forming HNO₃·(H₂O). In contrast, NO₃⁻ is already substantially hydrated, primarily forming clusters with 2-3 water molecules, along with a non-negligible contribution from higher-order hydrates such as NO₃⁻·(H₂O)₅. As relative humidity increases, NO₃⁻ progressively shifts toward larger cluster sizes, with $n = 3-5$ species becoming dominant under humid conditions. With increasing temperature, as shown in Fig. S13-S14, the hydration distributions of NO₃⁻ shift toward smaller cluster sizes. At 278.15 K, the population of higher-order hydrates decreases slightly, accompanied by an increase in $n = 2-3$ clusters. This trend becomes more pronounced at 298.15 K, where NO₃⁻ is primarily distributed as NO₃⁻·(H₂O)₁₋₃, and the contribution of larger clusters ($n \geq 4$) is significantly reduced. In contrast, over the same temperature range (258.15-298.15 K), NO₂ and OH remain essentially unhydrated across all conditions, and HNO₃ continues to show only limited hydration. Collectively, these results demonstrate that NO₃⁻ formed via the interfacial NO₂ + OH reaction possesses markedly enhanced hygroscopicity compared to its neutral counterparts. Its strong propensity to associate with multiple



water molecules, particularly under low-temperature and high-humidity conditions, facilitates efficient water uptake and underscores its potential role in promoting aerosol growth at the air-water interface.

Beyond its strong hydration, interfacial NO_3^- also enhances vapor uptake and cluster stability. In particular, it effectively attracts gas-phase species such as MSA and HNO_3 to the interface. Gibbs free energy calculations (Fig. S15) at the CCSD(T)/aug-cc-pVTZ//M06-2X/6-311++G(2df,2pd) level show that interactions of NO_3^- with MSA or HNO_3 are significantly stronger than the benchmark $\text{MSA} \cdots \text{MA}$ interaction, with binding free energies enhanced by $16.1 \text{ kcal} \cdot \text{mol}^{-1}$. This stronger interaction translates into enhanced cluster stabilization. As shown in Table S18, the $(\text{MSA})_1(\text{MA})_1(\text{NO}_3^-)_1$ cluster is more stable than analogous systems containing other common organic acids (e.g., HCOOH , CH_3COOH , and dicarboxylic acids), with formation free energies lower by $7.5\text{-}10.6 \text{ kcal} \cdot \text{mol}^{-1}$.

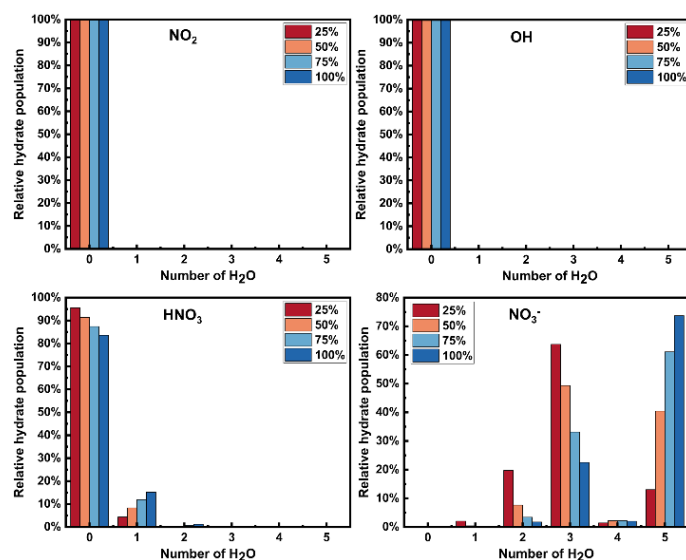


Fig. 8 Hydration distribution (%) of studied heterogeneous reactants (NO_2 and OH) and products (HNO_3 and NO_3^-) at different relative humidity ($\text{RH} = 25\text{-}100\%$) and $T = 258.15 \text{ K}$.

Overall, the interfacial $\text{NO}_2 + \text{OH}$ reaction not only produces highly hygroscopic NO_3^- but also promotes vapor uptake, cluster stabilization, and nucleation, providing a direct pathway for enhanced aerosol particle growth.

4. Summary and Conclusions

In this study, we employed a combined approach of quantum chemical calculations, BOMD



simulations, and the ACDC kinetic model to elucidate the daytime formation pathways of NA in both the gas phase and at the air-water interface, and to evaluate its influence on MSA-MA nucleation and aerosol hygroscopic growth.

In the gas phase, the water-catalyzed $\text{NO}_2 + \text{OH}$ reaction proceeds via a barrierless mechanism, releasing approximately $50 \text{ kcal}\cdot\text{mol}^{-1}$ of energy. Rate coefficients calculations confirm efficient HNO_3 formation, with water-catalyzed pathways competing effectively with the direct reaction within the 280-320 K temperature range. ACDC kinetic simulations further demonstrate that HNO_3 substantially enhances NPF by accelerating MSA-MA cluster formation. Growth pathway analysis identifies NA as an active participant, particularly under polluted coastal and industrial conditions such as those in the North China Plain and New Delhi.

At the air-water interface, MD simulations reveal that the preferential accumulation of NO_2 and OH near the water surface, where NA formation occurs through two competing pathways: (i) NO_2 collision with adsorbed OH, and (ii) OH collision with adsorbed NO_2 . Both mechanisms rapidly produce HNO_3 , which undergoes picosecond-scale dissociation into $\text{NO}_3^- \cdots \text{H}_3\text{O}^+$ ion pairs. Kinetic analysis identifies NO_2 collision with adsorbed OH as the most favorable interfacial route, with comparative rate analysis highlighting the catalytic role of the interface. Moreover, NO_3^- not only exhibits enhanced aerosol hygroscopic growth, but also promotes vapor uptake and stabilizes molecular clusters, thereby facilitating aerosol nucleation and growth.

Overall, this work elucidates key daytime HNO_3 formation mechanisms and establishes the significant role of HNO_3 in promoting both new particle formation and aerosol particle growth under ambient atmospheric conditions.

Data Availability.

The data used in this study could be available upon request from the corresponding author.

Video Supplement

Gaseous and interfacial reaction between NO_2 and OH. (MP4)

Supporting Information

The supplement related to this article is available online at Supplementary Material (PDF)

Author Contributions.

GW: methodology, investigation, writing (original draft). CZ: writing (editing), data curation, visualization, investigation. XG: writing (review), data curation, methodology, investigation. RS:



459 methodology, data curation. XC: data computation, investigation. YZ: data curation, visualization.

460 TZ: writing (review and editing), funding acquisition.

461 **Competing Interests.**

462 The authors declare that they have no conflict of interest.

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Table. 1 Rate constants (k , $\text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}$) for the $\text{NO}_2 + \text{OH}$ reaction in the absence and presence of a water molecule, and the effective rate constants (k' , $\text{cm}^3\cdot\text{molecule}^{-1}\cdot\text{s}^{-1}$) for water-catalyzed reaction calculated using master equation within the range of 212.6–320.0 K and 0–10 km

Altitude	P (Torr)	T (K)	k_R	k_{WM1}	k'_{WM1}	$k'_{\text{WM1}}/k_{\text{tot}}$ (%)
0 km	760.00	280.00	5.72×10^{-12}	2.27×10^{-10}	2.21×10^{-13}	3.71
		290.00	5.37×10^{-12}	2.13×10^{-10}	3.05×10^{-13}	5.37
		298.15	5.10×10^{-12}	2.03×10^{-10}	3.92×10^{-13}	7.15
			$(9.2 \pm 0.4) \times 10^{-12} \text{ }^a$			
			$4.00 \times 10^{-11} \text{ }^b$			
			$(10.6 \pm 3.7) \times 10^{-12} \text{ }^c$			
		300.00	5.04×10^{-12}	2.00×10^{-10}	4.14×10^{-13}	7.59
		310.00	4.71×10^{-12}	1.86×10^{-10}	5.38×10^{-13}	10.24
		320.00	4.41×10^{-12}	1.73×10^{-10}	6.67×10^{-13}	13.15
5 km	406.75	258.30	4.78×10^{-12}	2.20×10^{-10}	2.44×10^{-14}	0.51
10 km	202.16	229.70	4.11×10^{-12}	2.21×10^{-10}	1.11×10^{-15}	0.03

k_R and k_{WM1} was denoted the rate constants for the $\text{NO}_2 + \text{OH}$ reaction without and with water molecule, respectively;

k'_{WM1} was denoted the effective rate constants for the $\text{NO}_2 + \text{OH}$ reaction with water molecule.

^a The experimental values were reported from *Winiberg et al., 2020*;

^b The theoretical values were reported from *Sun et al., 2016*;

^c The experimental values were reported from *Berresheim et al., 2002*.