



# Mechanistic insights into nitric acid-enhanced iodic acid particle nucleation in the upper troposphere and lower stratosphere

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**Abstract.** In the upper troposphere and lower stratosphere (UTLS), new particles frequently form to seed cloud condensation nuclei (CCN), thereby affecting radiative forcing and global climate. Iodic acid (IA) particles have been widely detected in the UTLS; however, how they form is still largely unknown. Given the abundance of nitric acid (NA) and ammonia (NH<sub>3</sub>) in the UTLS and their nucleation potential, we explore the influence of NA and NH<sub>3</sub> on IA nucleation by quantum chemical calculations and cluster dynamics simulations. The structural analysis indicates that NA and NH<sub>3</sub> can cluster with IA via hydrogen bonds, halogen bonds, and electrostatic attractions between ions. The small-sized IA–NA–NH<sub>3</sub> clusters have lower free energies than typical sulfuric acid (SA)–NA–NH<sub>3</sub> clusters in the upper troposphere, exhibiting greater stability and higher nucleation efficiency. Moreover, the NA-enhanced effect on the established efficient IA–NH<sub>3</sub> nucleation is more evident at lower temperatures, especially with richer NA and NH<sub>3</sub>. In the extremely low-temperature UTLS, the proposed IA–NA–NH<sub>3</sub> ternary pathway dominates nucleation, while in the mid-troposphere with higher temperatures, the role of NA is minor due to its rapid evaporation. These findings underscore the important role of NA in iodine particle formation in the UTLS, offering mechanistic insights into the missing secondary particle sources.

## 1 Introduction

Globally occurring new particle formation (NPF) events contribute significantly to the formation of cloud condensation nuclei (CCN) (Kerminen et al., 2018; Nieminen et al., 2018; Kulmala et al., 2022), which further affects climate and radiative force (Zhang et al., 2012). The first and key process in NPF is the clustering of gas-phase precursors into nanoparticles, known as the nucleation stage (Zhang et al., 2012; Kulmala et al., 2013). Despite the importance of particle nucleation, the origin of NPF is unclear due to limited understanding of its molecular mechanisms, especially in the upper troposphere and lower stratosphere (UTLS), which contributes

over one-third of global CCN population (Williamson et al., 2019; Wang et al., 2022). However, due to the challenges of long-term field measurements in the UTLS, the lack of field data has led to some underlying nucleation mechanisms remaining undiscovered.

Prior studies primarily focused on particle nucleation driven by sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, SA) (Kirkby et al., 2011; Almeida et al., 2013; Glasoe et al., 2015; Elm, 2019, 2021). Despite the involvement of water (H<sub>2</sub>O) and ammonia (NH<sub>3</sub>), the resulting SA–H<sub>2</sub>O/SA–NH<sub>3</sub> nucleation cannot fully account for the observed high nucleation rates in most locations (Zhang et al., 2012; Elm, 2021). Even being further enhanced by nitric acid (HNO<sub>3</sub>, NA), the SA–

NA–NH<sub>3</sub> ternary nucleation can only explain nucleation in limited regions, e.g., the Asian monsoon zone (Wang et al., 2022). In fact, apart from SA particles, significant levels of iodic acid (HIO<sub>3</sub>, IA) particles have also been widely detected in the troposphere and even the stratosphere (Koenig et al., 2020; Frege et al., 2017; Beck et al., 2022; Salignat et al., 2024). Although the critical role of IA in NPF in the marine boundary layer (MBL) has been extensively identified (Rauch et al., 2002; Sipilä et al., 2016; Yu et al., 2019; Baccharini et al., 2020), its impacts on NPF in the high-altitude UTLS remain largely unknown. Crucially, the recent CERN CLOUD (Cosmics Leaving Outdoor Droplets) experiments provided solid evidence that IA-driven nucleation is highly temperature-dependent, showing a remarkable efficiency at low temperatures, even surpassing the well-established SA–NH<sub>3</sub> system (He et al., 2021). Notably, the high-altitude atmosphere like UTLS is characterized by not only low temperatures but also sparse background particles (i.e., low condensation sinks CS: 10<sup>−4</sup>–10<sup>−5</sup> s<sup>−1</sup>), both of which facilitate IA nucleation (He et al., 2021), but the underlying mechanisms in the UTLS are still poorly understood.

Given the base stabilization of NH<sub>3</sub> on acidic IA (Rong et al., 2020; Xia et al., 2020) and its high levels in the upper troposphere (about 30 pptv to 1.4 ppbv) (Wang et al., 2022; Höpfner et al., 2016; Höpfner et al., 2019), our previous study found that NH<sub>3</sub> can effectively promote IA nucleation via their acid–base reactions, especially at higher altitudes (Li et al., 2024a). However, the real atmosphere is complex, meaning that such IA–NH<sub>3</sub> binary nucleation likely overlooks the impacts of other chemicals, particularly those with nucleation potential and high concentrations in the UTLS, e.g., NA. NA is abundant, accounting for up to 50 % of reactive nitrogen in the tropical upper troposphere, with its gas-phase mixing ratios ranging from 0.1 to 2 ppbv (Laaksonen et al., 1997; Popp et al., 2006). Moreover, as mentioned earlier, NA has been proven to work with NH<sub>3</sub> to synergistically enhance SA nucleation, which plays a dominant role in NPF process in the upper troposphere over Asian monsoon regions (Wang et al., 2022, 2023; Liu et al., 2018). However, whether NA can enhance IA nucleation through its synergy with NH<sub>3</sub> and the molecular mechanisms remain unknown despite the detection of NA and IA in the field-collected particles in the upper troposphere (Frege et al., 2017; Beck et al., 2022).

In this study, we performed both quantum chemical calculations and atmospheric cluster dynamic code (ACDC) simulations to investigate (IA)<sub>x</sub>(NA)<sub>y</sub>(NH<sub>3</sub>)<sub>z</sub> (1 ≤ x + y + z ≤ 6, x + y ≥ z) nucleation. The molecular clustering process was explored through wave function analysis. Specifically, we analyzed the reactive binding sites as well as the type and strength of intermolecular interactions. The stability of the formed IA–NA–NH<sub>3</sub> clusters was investigated through thermodynamic analysis. Additionally, a series of ACDC kinetic simulations were conducted to further calculate the cluster formation rate, steady-state concentration, and formation

pathways of the IA–NA–NH<sub>3</sub> system. To better evaluate the nucleation efficiency of the IA–NA–NH<sub>3</sub> system, we further conducted a comparative analysis with the well-established SA–NA–NH<sub>3</sub> system under UTLS conditions.

## 2 Methods

### 2.1 Quantum chemistry calculations

A multistep conformation search was employed to determine the global minima of (IA)<sub>x</sub>(NA)<sub>y</sub>(NH<sub>3</sub>)<sub>z</sub> (1 ≤ x + y + z ≤ 6, x + y ≥ z) clusters, and the details are shown in the Supplement. The final lowest-energy structures were optimized at the ωB97X-D/6-311++G(3df,3pd) (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) level of theory (Francl et al., 1982; Peterson et al., 2003) using the Gaussian 09 package (Frisch et al., 2009). Further single-point energy calculations were performed on the identified lowest-free-energy conformations employing the Domain-based Local Pair Natural Orbital Coupled Cluster method (DLPNO-CCSD(T)) in combination with the aug-cc-pVTZ(-PP) basis set and TightPNO/TightSCF settings, using the ORCA 5.0.4 program (Neese, 2011). Moreover, given the heavy-atom nature of iodine, the spin–orbit coupling (SOC) corrections were taken into account in the Gibbs free formation energies (Δ*G*) of all iodine-containing clusters (Zaki et al., 2023; Verstraete et al., 2008; Engsvang et al., 2024). These corrections were calculated at the ωB97X-D/6-311++G(3df,3pd) (for H, O, and N atoms) + dhf-TZVP-2c (for I atom) level of theory (Kuhn and Weigend, 2015; Sarr et al., 2021; Holzer et al., 2022; Chan and Yim, 2013) using the Gaussian 16 package (Frisch et al., 2016). Herein, we calculated Δ*G*<sub>ref</sub> (kcal mol<sup>−1</sup>) of the IA–NA–NH<sub>3</sub> systems at the reference pressure (*P*<sub>ref</sub> = 1 atm) as in Eq. (1):

$$\Delta G_{\text{ref}} = \Delta G_{\text{thermal}}^{\omega\text{B97X-D}} + \Delta E_{\text{DLPNO-CCSD(T)}} + \Delta E_{\text{SOC}}, \quad (1)$$

where Δ*G*<sub>thermal</sub><sup>ωB97X-D</sup> and Δ*E*<sub>DLPNO-CCSD(T)</sub> are the thermal contribution and electronic contribution to Gibbs free energy, respectively. Δ*E*<sub>SOC</sub> is the spin–orbit coupling energies in the formation of iodine-containing clusters. The Δ*G*<sub>thermal</sub><sup>ωB97X-D</sup> values at different temperatures (220–260 K) were calculated using the Shermo 2.0 package (Lu and Chen, 2021), and the final Gibbs formation free energies are presented in Table S1. When considering the effect of the concentrations of nucleation precursors, Δ*G*<sub>ref</sub> can be further converted to Δ*G* using Eq. (2):

$$\Delta G(P_1, P_2, \dots, P_n) = \Delta G_{\text{ref}} - k_B T \sum_{i=1}^n N_i \ln \left( \frac{P_i}{P_{\text{ref}}} \right), \quad (2)$$

where Δ*G*<sub>ref</sub> is the Gibbs formation free energy calculated at the reference pressure *P*<sub>ref</sub> (1 atm), *k<sub>B</sub>* is the Boltzmann constant, and *T* is the temperature. *N<sub>i</sub>* denotes the number of molecules *i* within the cluster, and *P<sub>i</sub>* represents the partial pressure of vapor *i*. Additional theoretical methods and computational details are provided in the Supplement.

## 2.2 Wave function analysis

The intrinsic stability of the cluster is essentially determined by the intermolecular interactions among the molecules forming the cluster. Therefore, we performed the wave function analysis on the IA–NA–NH<sub>3</sub> clusters using Multiwfn 3.7 code (Lu and Chen, 2012) to further understand the interactions within the clusters. Initially, the electrostatic potential (ESP) mapped on the molecular van der Waals (vdW) surface was calculated to predict the potential interaction sites of the nucleation precursor molecules (i.e., IA, NA, and NH<sub>3</sub>). Subsequently, reduced density gradient (RDG) analysis was performed to reveal the nature and characteristics of noncovalent interactions. Finally, the atoms-in-molecule (AIM) theory (Lane et al., 2013) was applied to further quantify the strength of intermolecular interactions.

## 2.3 Atmospheric cluster dynamic simulations

The atmospheric cluster dynamic code (ACDC) (McGrath et al., 2012) was employed to investigate the cluster formation rates, formation pathways, and steady-state concentrations of the IA–NA–NH<sub>3</sub> clusters by solving the birth–death equation (Eq. 3).

$$\frac{dC_i}{dt} = \frac{1}{2} \sum_{j < i} \beta_{j,(i-j)} C_j C_{(i-j)} + \sum_j \gamma_{(i+j) \rightarrow i} C_{i+j} - \sum_j \beta_{i,j} C_i C_j - \frac{1}{2} \sum_{j < i} \gamma_{i \rightarrow j} C_i + Q_i - S_i, \quad (3)$$

where  $\beta_{i,j}$  denotes the collision rate coefficient between clusters  $i$  and  $j$ ,  $C_i$  is the concentration of cluster  $i$ , and  $\gamma_{(i+j) \rightarrow i}$  indicates the rate coefficient for the evaporation of cluster  $(i+j)$  into smaller clusters  $i$  and  $j$ .  $Q_i$  and  $S_i$  correspond to the external source and possible loss term of cluster  $i$ . Further details on the calculation of  $\beta_{i,j}$  and  $\gamma_{(i+j) \rightarrow i}$  can be found in the Supplement. Moreover, a cluster is considered stable when the collision frequency ( $\beta \cdot C$ ) exceeds the total evaporation rate coefficients ( $\Sigma \gamma$ ; Table S2). This criterion was used to establish the boundary conditions for the simulation system, which are detailed in Table S3.

In addition, we applied a collision factor of 2.3 to account for the enhancement of intermolecular van der Waals forces on  $\beta_{i,j}$  in the ACDC simulation (Halonen et al., 2019) based on its application in previous research (Cai et al., 2021; Li et al., 2023; Stolzenburg et al., 2020; Ning et al., 2024). Furthermore, we employed a size-dependent coagulation sink ( $\text{CoagS}_i$ ) (Lehtipalo et al., 2016) in this study, which is calculated as follows:

$$\text{CoagS}_i = \text{CS}_{\text{ref}} \times (d_i/d_{\text{ref}})^{-m}, \quad (4)$$

where  $\text{CS}_{\text{ref}}$  is the condensation sink (CS) of the reference monomer (i.e., IA monomer) and  $d$  is the diameter of the monomer or cluster. The exponent  $m$ , with a value of 1.7,

varies based on the background distribution and is within the common range observed for atmospheric aerosols (Lehtinen et al., 2007).

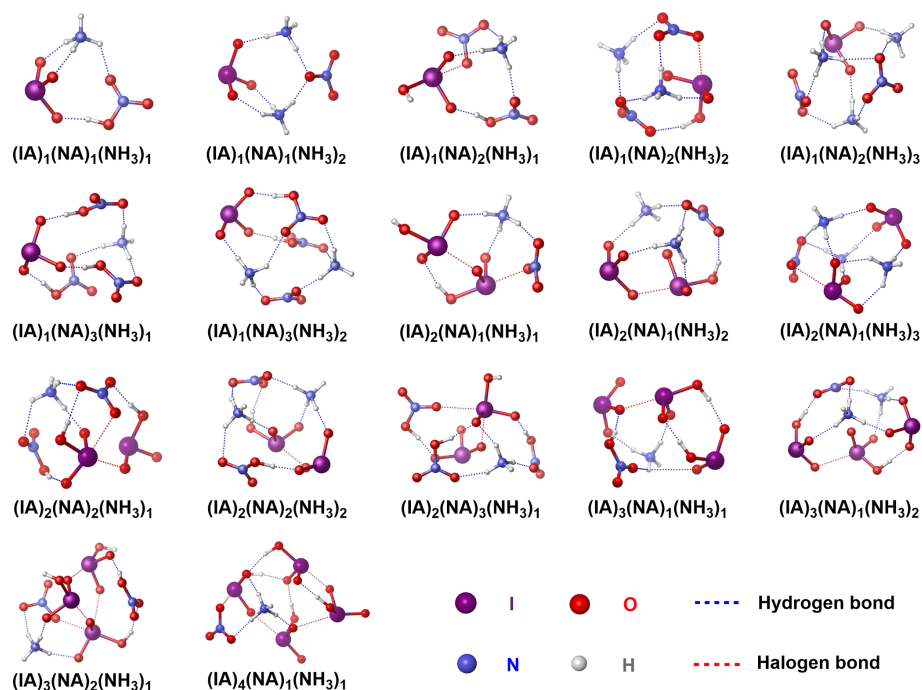
## 3 Results and discussion

### 3.1 Cluster structure and stability

The formation of stable pre-nucleation clusters relies on robust intermolecular interactions such as hydrogen bonds (HB) and halogen bonds (XB). Here, we mainly probed the newly identified ternary IA–NA–NH<sub>3</sub> clusters since the binary clusters (IA–NH<sub>3</sub> and NA–NH<sub>3</sub>) and pure-IA clusters were discussed in previous studies (Rong et al., 2020; Liu et al., 2018). Furthermore, all clusters investigated in this study comprise an equal or greater number of acid molecules relative to base molecules as previous studies have demonstrated that such compositions generally exhibit enhanced thermodynamic stability (Xie and Elm, 2021). To reveal the clustering potential of IA, NA, and NH<sub>3</sub>, their electrostatic potential (ESP) mapped on van der Waals (vdW) surfaces was calculated and presented in Fig. S1 in the Supplement. And the results suggest that all these precursors possess donor or acceptor sites for HB and XB. Thus, NA is expected to jointly cluster with IA and NH<sub>3</sub> molecules via HB and XB.

As depicted in Fig. 1, in the identified stable IA–NA–NH<sub>3</sub> clusters (Cartesian coordinates in Table S6), NA and NH<sub>3</sub> interact with IA via a network of HBs (blue dashed lines) and XBs (red dashed lines). NA molecules tend to localize at the periphery of the cluster, likely limited by their planar geometry. If positioned at the center of such sub-nanometer cluster, it may increase steric hindrance. More specifically, statistical analysis suggests that the prevalence of HBs (84 %) is inherently higher than that of XBs (Fig. S2), which arises from the ability of NH<sub>3</sub> to form up to four HBs, resulting in more N–H...O HBs. Despite most sites being involved in HB and XB, there remain vacant sites for further adsorption and growth, as shown in the ESP analysis of the large-size pre-nucleation (IA)<sub>2</sub>(NA)<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub> cluster (Fig. S3). During the IA–NA–NH<sub>3</sub> clustering, acid–base reactions always occur. When acids outnumber or equal NH<sub>3</sub>, all NH<sub>3</sub> molecules are fully protonated. Due to the stronger acidity of NA compared to IA, most NH<sub>3</sub> (60 %) in ternary clusters is more prone to be protonated by NA first, yielding NO<sub>3</sub><sup>−</sup>–NH<sub>4</sub><sup>+</sup> ion pairs. Overall, the IA–NA–NH<sub>3</sub> clusters are simultaneously stabilized by intermolecular HBs, XBs, and robust electrostatic interactions between the acid–base ions, which are similar to the features of other studied IA-containing clusters (Rong et al., 2020; Ning et al., 2022a, b; Li et al., 2024a, b).

In the IA–NA–NH<sub>3</sub> system, the presence of IA introduces XBs, allowing NA to be stabilized simultaneously by HBs, XBs, and electrostatic interactions. In contrast, in the SA–NA–NH<sub>3</sub> clusters, a typical high-efficiency system in the UTLS (Liu et al., 2018; Wang et al., 2022), NA only participates in HB formation and the protonation of NH<sub>3</sub>. To



**Figure 1.** The identified  $(\text{IA})_x(\text{NA})_y(\text{NH}_3)_z$  ( $x + y + z \leq 6$ ,  $z \leq x + y$ ) cluster conformation with lowest Gibbs free energies at the  $\omega\text{B97X-D/6-311++G(3df, 3pd)}$  (for H, O, and N atoms) + aug-cc-pVTZ-PP (for I atom) level of theory.

further assess the cluster stability, we compared the Gibbs free energies ( $\Delta G$ ) of the  $\text{IA-NA-NH}_3$  and  $\text{SA-NA-NH}_3$  cluster formation at  $T = 220\text{ K}$ , as shown in Fig. S4. Overall, under the condition of same number of molecules, the  $\Delta G$  values of the  $\text{IA-NA-NH}_3$  clusters are relatively lower than those of the  $\text{SA-NA-NH}_3$  clusters, especially for clusters with fewer molecules (Table S4). This suggests that like the well-established  $\text{SA-NA-NH}_3$  system, the  $\text{IA-NA-NH}_3$  system may also play an important role in particle nucleation in the UTLS. Specifically, as to the clusters with one  $\text{NH}_3$  molecule, the  $\text{IA-NA-NH}_3$  clusters exhibit lower energies compared to the  $\text{SA-NA-NH}_3$  clusters. For example, the  $\Delta G$  of  $(\text{IA})_2(\text{NA})_1(\text{NH}_3)_1$  cluster is even lower than that of  $(\text{SA})_2(\text{NA})_1(\text{NH}_3)_1$  cluster by  $4.03\text{ kcal mol}^{-1}$ . To probe the cause of the energy difference, herein we employ reduced density gradient (RDG) analysis to uncover the bonding nature of the  $(\text{IA})_2(\text{NA})_1(\text{NH}_3)_1$  and  $(\text{SA})_2(\text{NA})_1(\text{NH}_3)_1$  clusters. As presented in Fig. 2, the blue regions indicate strong attractions like HB and XB, and the green regions signifies vdW interaction, while the red regions indicate repulsive interactions. The structure of  $(\text{IA})_2(\text{NA})_1(\text{NH}_3)_1$  cluster (Fig. 2a) features four HBs (three  $\text{N-H}\cdots\text{O}$  and one  $\text{O-H}\cdots\text{O}$ ) and two XBs ( $\text{O-I}\cdots\text{O}$ ). The RDG analysis of  $(\text{IA})_2(\text{NA})_1(\text{NH}_3)_1$  cluster (bottom-left panel) presents six prominent blue spikes. Further combined with the AIM analysis, the spikes located at  $\text{sign}(\lambda_2)\rho = -0.062$  and  $-0.054\text{ au}$  are attributed to the two XBs, while the remaining four spikes correspond to HBs. In contrast, the  $(\text{SA})_2(\text{NA})_1(\text{NH}_3)_1$  cluster contains only HBs, and all blue spike values in its RDG

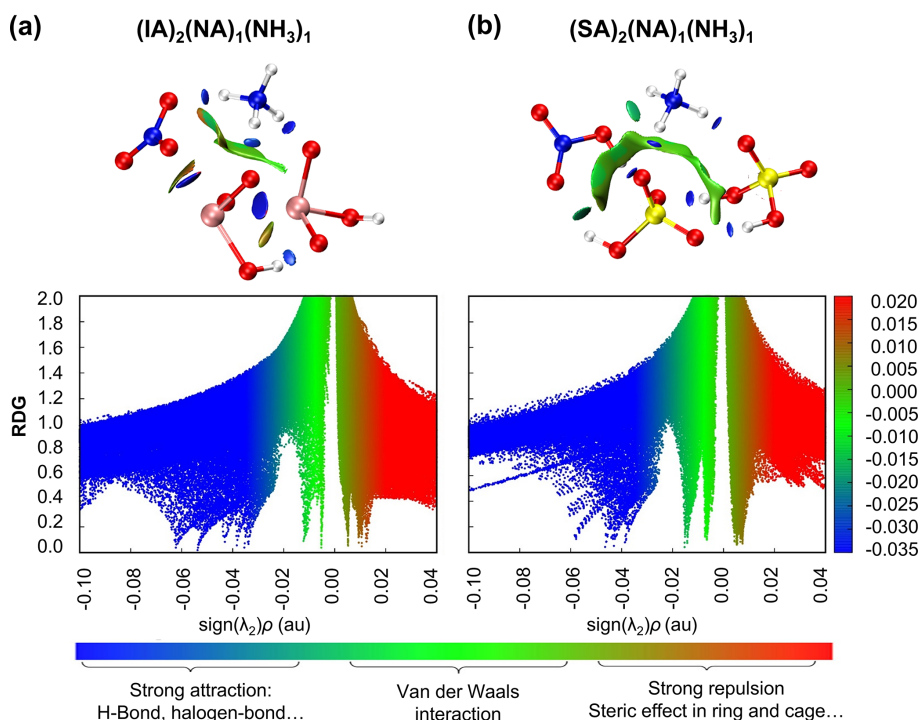
plot (bottom-right panel) are greater than  $-0.06\text{ au}$ . Generally, the smaller  $\text{sign}(\lambda_2)\rho$  values indicate stronger interactions. Thus, the presence of XBs in the  $(\text{IA})_2(\text{NA})_1(\text{NH}_3)_1$  cluster likely contributes to stronger attractions compared to  $(\text{SA})_2(\text{NA})_1(\text{NH}_3)_1$  cluster, resulting in a lower free energy of the  $(\text{IA})_2(\text{NA})_1(\text{NH}_3)_1$  cluster.

### 3.2 Cluster formation rate

To further evaluate the nucleation efficiency of the  $\text{IA-NA-NH}_3$  system, we performed ACDC simulations to calculate cluster formation rates ( $J$ ,  $\text{cm}^{-3}\text{ s}^{-1}$ ) under the UTLS conditions. The concentrations of the nucleation precursors (IA, NA, and  $\text{NH}_3$ ) used in this study were primarily based on currently available field observations and model simulation data.

#### 3.2.1 Concentration of IA

Sipilä et al. (2016) reported that atmospheric IA concentrations range from  $10^6$  to  $10^8\text{ molec. cm}^{-3}$  during new particle formation events at the Mace Head site in the boundary layer. Moreover, Salignat et al. (2024) reported an average IA concentration of  $2.9 \times 10^5\text{ molec. cm}^{-3}$  at the Maïdo Observatory (2150 m a.s.l.) over the Indian Ocean, with peak values reaching up to  $3.3 \times 10^6\text{ molec. cm}^{-3}$ . Although, to our knowledge, gaseous IA levels at higher altitudes have not yet been reported, and vertical profiles of IO radicals, a key intermediate in IA formation, are available across differ-



**Figure 2.** The reduced density gradient (RDG) color-filled maps and isosurface of (a)  $(\text{IA})_2(\text{NA})_1(\text{NH}_3)_1$  and (b)  $(\text{SA})_2(\text{NA})_1(\text{NH}_3)_1$  clusters.

ent elevations. Importantly, CLOUD experimental evidence shows a strong correlation between IA concentrations ( $[\text{IA}]$ ) and IO radical levels, and IA formation of in this process appears to be insensitive to variations in  $\text{O}_3$ ,  $\text{H}_2\text{O}$ , and temperature (Finkenzeller et al., 2023). Notably, the mixing ratio of IO radicals exhibits minimal variation with altitude, particularly above 2 km (Saiz-Lopez et al., 2014; Karagodin-Doyennel et al., 2021). This suggests that at high altitudes, IA might exhibit similar concentrations at  $\sim 2$  km altitude ( $\sim 10^6$  molec.  $\text{cm}^{-3}$ ), although lower IA levels are also possible. This issue warrants further investigation in future studies. Given the limited field observations of IA concentrations in the UTLS, this study adopts an IA concentration range of  $10^5$  to  $10^6$  molec.  $\text{cm}^{-3}$ , which are comparable to or even lower than those observed at around 2 km altitude.

### 3.2.2 Concentration of NA

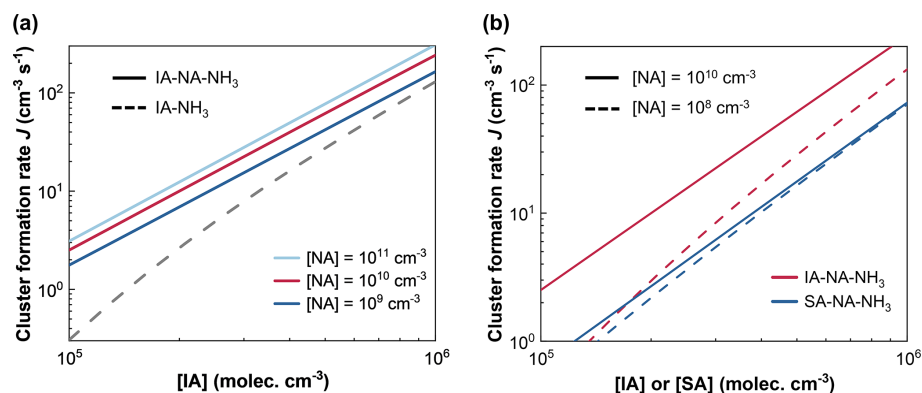
NA mixing ratios at an altitude of approximately 10 km range from 100 to 2500 pptv, with average values exceeding 1000 pptv (Singh et al., 1996). Meanwhile, theoretical model investigations indicated that NA mixing ratios in the upper troposphere range from 0.1 to 2 ppbv (Laaksonen et al., 1997). In addition, gas-phase NA concentrations observed in the tropical lower stratosphere were typically 0.1 ppbv or lower (Popp et al., 2006). Therefore, based on the environmental conditions such as temperature and pressure in the UTLS, the concentration of NA in this study

was set to a broad range from 10 pptv to 10 ppbv ( $10^8$ – $10^{11}$  molec.  $\text{cm}^{-3}$ ).

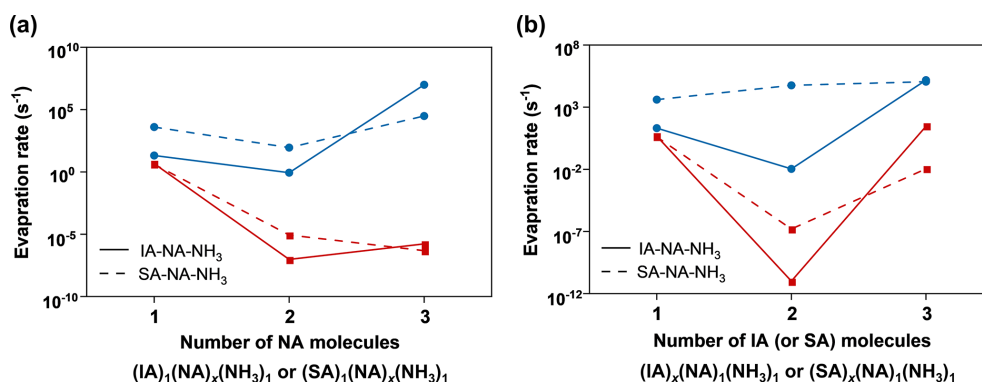
### 3.2.3 Concentration of $\text{NH}_3$

Based on satellite observations and high-altitude aircraft measurements,  $\text{NH}_3$  mixing ratios in the upper troposphere over the Asian monsoon region can reach up to 30 pptv as a 3-month average and up to 1.4 ppbv in hotspots (Höpfner et al., 2016; Höpfner et al., 2019). Accordingly, the  $\text{NH}_3$  concentration was set to 30 pptv in this study based on the typical conditions of the UTLS. Under these conditions, specifically at a temperature of 220 K and a pressure of 0.2 atm, 30 pptv corresponds to  $3 \times 10^8$  molec.  $\text{cm}^{-3}$ .

As illustrated in Fig. 3a, at  $T = 220$  K,  $\text{CS} = 10^{-4} \text{ s}^{-1}$ ,  $[\text{IA}] = 10^5$ – $10^6$  molec.  $\text{cm}^{-3}$ , and  $[\text{NH}_3] = 3 \times 10^8$  molec.  $\text{cm}^{-3}$ , NA exhibits a significant enhancing effect on IA– $\text{NH}_3$  nucleation. Even when the NA concentration is as low as  $10^9$  molec.  $\text{cm}^{-3}$ , it can enhance  $J(\text{IA}–\text{NH}_3)$  by up to a factor of 6, increasing from 0.3 to  $1.8 \text{ cm}^{-3} \text{ s}^{-1}$ . Under the conditions of  $[\text{IA}] = 10^5$  molec.  $\text{cm}^{-3}$  and  $[\text{NA}] = 10^{11}$  molec.  $\text{cm}^{-3}$  (light blue line),  $J(\text{IA}–\text{NA}–\text{NH}_3)$  is approximately 10 times higher than  $J(\text{IA}–\text{NH}_3)$ . This suggests that the enhancement of NA on IA– $\text{NH}_3$  nucleation is pronounced in high-altitude regions characterized by low  $[\text{IA}]$  and high  $[\text{NA}]$ . Moreover, we have calculated the enhancement strength  $R$  (Fig. S5) to quantify the rate enhancement of IA–NA– $\text{NH}_3$  ternary nucleation



**Figure 3.** (a) Cluster formation rate  $J$  ( $\text{cm}^{-3} \text{s}^{-1}$ ) as a function of  $[\text{IA}]$  of  $\text{IA-NH}_3$  and  $\text{IA-NA-NH}_3$  systems at the conditions of  $T = 220 \text{ K}$ ,  $\text{CS} = 10^{-4} \text{ s}^{-1}$ ,  $[\text{NA}] = 10^9\text{--}10^{11} \text{ molec. cm}^{-3}$ , and  $[\text{NH}_3] = 3 \times 10^8 \text{ molec. cm}^{-3}$ . (b)  $J$  of  $\text{IA-NA-NH}_3$  and  $\text{SA-NA-NH}_3$  systems at  $T = 220 \text{ K}$ ,  $\text{CS} = 10^{-4} \text{ s}^{-1}$ ,  $[\text{IA}] = 10^5\text{--}10^6 \text{ molec. cm}^{-3}$ ,  $[\text{NA}] = 10^8$  or  $10^{10} \text{ molec. cm}^{-3}$ , and  $[\text{NH}_3] = 3 \times 10^8 \text{ molec. cm}^{-3}$ .

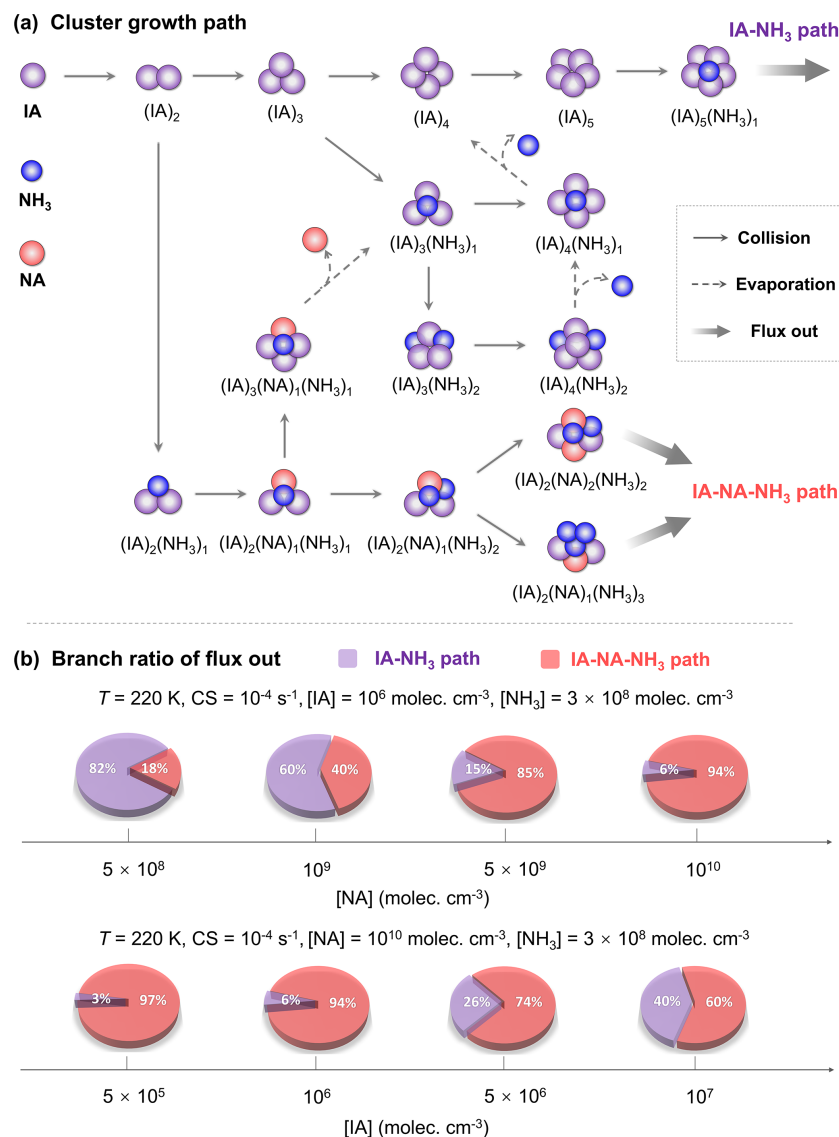


**Figure 4.** Evaporation rates of NA (blue lines) and IA/SA (red lines) molecules from  $\text{IA-NA-NH}_3$  (solid lines) and  $\text{SA-NA-NH}_3$  (dashed lines) clusters. (a) The results for  $(\text{IA})_1(\text{NA})_x(\text{NH}_3)_1$  and  $(\text{SA})_1(\text{NA})_x(\text{NH}_3)_1$  clusters and (b) the results for  $(\text{IA})_x(\text{NA})_1(\text{NH}_3)_1$  and  $(\text{SA})_x(\text{NA})_1(\text{NH}_3)_1$  clusters.

compared to the established  $\text{IA-NH}_3$  and  $\text{NA-NH}_3$  binary nucleation in a broader array of atmospheric conditions (see details in the Supplement). The role of  $\text{IA-NA-NH}_3$  nucleation is stronger in regions with lower temperatures and higher concentrations of NA and  $\text{NH}_3$ , which corresponds to the UTLS conditions. This suggests that  $\text{IA-NA-NH}_3$  nucleation may provide a plausible explanation for the unknown sources of CCN in the UTLS. In addition, considering the potential uncertainties in quantum chemical calculations, we also investigated the effect of the uncertainty in the calculated  $\Delta G$  on the cluster formation rate  $J$ . As shown in Fig. S6, under NA concentrations ranging from  $10^8$  to  $10^{10} \text{ molec. cm}^{-3}$ , adjusting the  $\Delta G_{220\text{K}}$  of clusters by subtracting  $1 \text{ kcal mol}^{-1}$  results in a minor variation in  $J$ . Although an increase in  $\Delta G_{220\text{K}}$  by adding  $1 \text{ kcal mol}^{-1}$  may cause a slight offset in  $J$  values, the DLPNO method tends to underestimate binding energies to some extent, indicating that the present results ( $J_{\Delta G, 220\text{K}}$ ) are at a low limit. Therefore, the scenario of adding  $1 \text{ kcal mol}^{-1}$  may be unlikely to occur. Taken together, the uncertainty of

calculated quantum chemistry does not significantly impact the conclusions of this study.

Furthermore, under the conditions of  $T = 220 \text{ K}$ ,  $\text{CS} = 10^{-4} \text{ s}^{-1}$ ,  $[\text{IA}] = 10^5\text{--}10^6 \text{ molec. cm}^{-3}$ ,  $[\text{NA}] = 10^8$  or  $10^{10} \text{ molec. cm}^{-3}$ , and  $[\text{NH}_3] = 3 \times 10^8 \text{ molec. cm}^{-3}$ , we simulated  $J$  for the  $\text{IA-NA-NH}_3$  and  $\text{SA-NA-NH}_3$  systems and conducted a comparative analysis, as shown in Fig. 3b. The results reveal that, at the same  $[\text{NA}]$  levels,  $J(\text{IA-NA-NH}_3)$  (red line) consistently surpasses  $J(\text{SA-NA-NH}_3)$  (blue line), with this difference becoming more pronounced when  $[\text{NA}]$  reaches  $10^{10} \text{ molec. cm}^{-3}$  (closer to actual UTLS conditions). Considering that the  $[\text{IA}]$  in the actual UTLS atmospheric environment may be slightly lower than  $[\text{SA}]$ , we also simulated the scenarios where  $[\text{IA}]$  is lower than  $[\text{SA}]$ . The results show that when  $[\text{IA}] = 50\%[\text{SA}]$ ,  $J(\text{IA-NA-NH}_3)$  is already comparable to  $J(\text{SA-NA-NH}_3)$  (Fig. S7). This observation indicates that, although the  $\text{SA-NA-NH}_3$  system is widely regarded as an efficient nucleation mechanism in the UTLS, the  $\text{IA-NA-NH}_3$  system achieves notably higher nucleation efficiency under similar conditions. To reveal the underlying



**Figure 5.** (a) Main clustering pathways of the IA–NA–NH<sub>3</sub> system. (b) Branch ratio of flux out at  $T = 220 \text{ K}$ ,  $CS = 10^{-4} \text{ s}^{-1}$ ,  $[IA] = 5 \times 10^5$ – $10^7 \text{ molec. cm}^{-3}$ ,  $[NA] = 5 \times 10^8$ – $10^{10} \text{ molec. cm}^{-3}$ , and  $[NH_3] = 3 \times 10^8 \text{ molec. cm}^{-3}$ .

reasons for higher  $J(\text{IA–NA–NH}_3)$ , we further analyzed the evaporation rates of the clusters in both systems. Figure 4 presents the evaporation rates of NA and IA (or SA) from the cluster versus clusters sizes for different clusters compositions. For both cluster types, the evaporation of the NA molecule (blue lines) is faster than that of the IA (or SA) molecule (red lines). For the clusters containing three–four molecules, NA and IA evaporate more slowly within the IA–NA–NH<sub>3</sub> clusters, while for larger-size clusters with five–six molecules, the evaporation rates of NA and SA are lower in the SA–NA–NH<sub>3</sub> cluster (see Tables S2 and S5). Based on the resulting  $J(\text{IA–NA–NH}_3)$  and the corresponding results for evaporation, it can be inferred that smaller clusters containing two to four molecules formed early have a greater effect on the cluster formation rate. Similar

behavior has also been observed in the SA–NH<sub>3</sub>–H<sub>2</sub>O system (Napari et al., 2002). Therefore, understanding the gas-to-cluster process at the molecular level, especially the formation of initial clusters that underpin subsequent growth but are challenging to reveal experimentally, is essential for atmospheric nucleation.

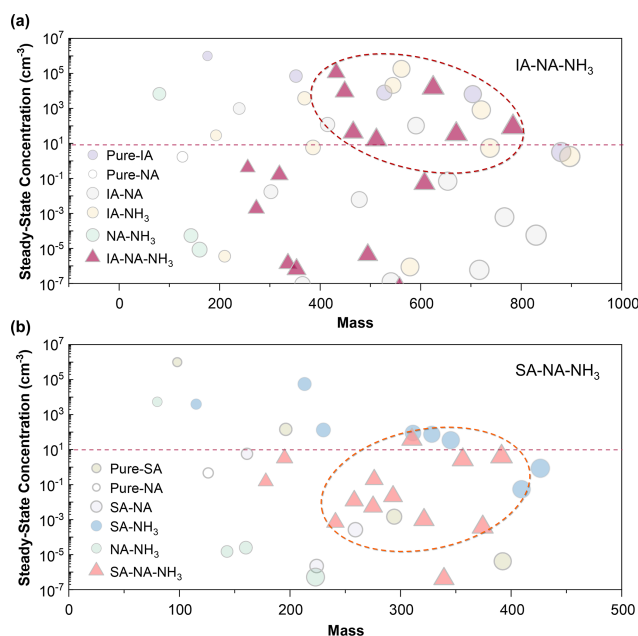
### 3.3 Cluster formation pathway

To gain deeper insights into the impact of NA and NH<sub>3</sub> on IA nucleation, we have performed the ACDC simulations under the UTLS conditions to track the detailed dynamics of the NA–IA–NH<sub>3</sub> clustering process. As shown in Fig. 5a, the nucleation process of IA–NA–NH<sub>3</sub> system can proceed through two types of pathways: (i) IA–NH<sub>3</sub> and (ii) IA–NA–

$\text{NH}_3$  pathways. The  $\text{IA-NH}_3$  pathway primarily involves the initial self-collision of IA molecules to form the  $(\text{IA})_5$  cluster, which further collides with  $\text{NH}_3$  to grow into the  $(\text{IA})_5(\text{NH}_3)_1$  cluster. Interestingly, NA and  $\text{NH}_3$  also participate in initial cluster formation and subsequently evaporate out, acting like “catalysts” to promote clustering. In the  $\text{IA-NA-NH}_3$  pathway, the clustering process primarily proceeds via the sequential addition of acid or base monomers. Furthermore, given the impacts of atmospheric conditions on nucleation pathways, we calculated the branch ratio of different pathways under UTLS conditions. As illustrated in Fig. 5b, the contribution of the  $\text{IA-NA-NH}_3$  pathway increases with rising  $[\text{NA}]$  and declining  $[\text{IA}]$ . Notably, when  $[\text{NA}]$  reaches  $10^{10} \text{ molec. cm}^{-3}$  or  $[\text{IA}]$  decreases to  $5 \times 10^5 \text{ molec. cm}^{-3}$ , the contribution of  $\text{IA-NA-NH}_3$  pathway can reach nearly 95 %. This finding indicates that the  $\text{IA-NA-NH}_3$  ternary pathway dominates in regions where IA level is limited, while NA is abundant, aligning well with the conditions in the focused UTLS. More broadly, such scenario characterized by scarce IA and rich NA also exists in higher atmosphere, such as  $\sim 20 \text{ km}$  (i.e., the bottom of near space). This NA-enhanced mechanism is likely a vital source of fresh particles in this region. Therefore, the  $\text{IA-NA-NH}_3$  mechanism may have significant implications for the formation of aerosols or ice particles at the high altitude, which provides deeper insights into the origin of global CCN and helps to improve atmospheric modeling.

In addition to the UTLS, here we also investigate the formation mechanism of  $\text{IA-NA-NH}_3$  clusters in the low-mid free troposphere with higher temperatures and precursor concentrations. However, in the mid free troposphere with  $T = 240 \text{ K}$  (Fig. S8), the nucleation process proceeds mainly through the pure IA and  $\text{IA-NH}_3$  binary pathway. While NA contributes to the initial stages of cluster formation, it subsequently evaporates from the pre-nucleation cluster, ultimately functioning in a catalyst-like capacity. Moreover, at  $T = 260 \text{ K}$  in the lower free troposphere, NA plays a negligible role in cluster formation due to its rapid evaporation at an elevated temperature. Consequently, we conclude that the  $\text{IA-NA-NH}_3$  ternary nucleation pathway can play a vital role in iodine particle nucleation under extremely low-temperature conditions, such as the high-altitude UTLS.

To provide a baseline for future experimental study, we have calculated the steady-state concentrations of clusters formed in the  $\text{IA-NA-NH}_3$  and  $\text{SA-NA-NH}_3$  system under the typical UTLS conditions in Fig. 6. The simulated results indicate that the concentrations of most  $\text{IA-NA-NH}_3$  clusters exceed  $10 \text{ cm}^{-3}$ , while those of  $\text{SA-NA-NH}_3$  clusters remain below this threshold (dashed line). This suggests that under equivalent conditions, the number concentrations of  $\text{IA-NA-NH}_3$  cluster are generally higher, showing a potentially greater contribution to particle formation. Although  $[\text{SA}]$  may be higher than that of  $[\text{IA}]$  under the UTLS conditions, the resulting impact of the  $\text{IA-NA-NH}_3$  system is likely comparable to that of the  $\text{SA-NA-NH}_3$  system. Thus,



**Figure 6.** Simulated steady-state concentrations ( $\text{cm}^{-3}$ ) of (a)  $\text{IA-NA-NH}_3$  and (b)  $\text{SA-NA-NH}_3$  clusters against cluster mass at the conditions of  $T = 220 \text{ K}$ ,  $\text{CS} = 10^{-4} \text{ s}^{-1}$ ,  $[\text{IA}] = 10^6 \text{ molec. cm}^{-3}$ ,  $[\text{SA}] = 10^6 \text{ molec. cm}^{-3}$ ,  $[\text{NA}] = 10^9 \text{ molec. cm}^{-3}$ , and  $[\text{NH}_3] = 3 \times 10^8 \text{ molec. cm}^{-3}$ . For better clarify, the concentrations of ternary clusters in the  $\text{IA-NA-NH}_3$  and  $\text{SA-NA-NH}_3$  systems are highlighted with circles, respectively.

these results further highlight that the  $\text{IA-NA-NH}_3$  nucleation mechanism is potentially significant in the UTLS.

## 4 Conclusion

High-altitude NPF serves as an essential source of global CCN, thereby impacting climate. Iodic acid (IA) particles are widely found in the UTLS; however, their formation mechanism is yet unknown. Given the abundance of NA and  $\text{NH}_3$  in the UTLS and their nucleation potential, they may jointly affect IA nucleation. To probe their nucleation process, we performed quantum chemical calculations and cluster dynamics simulations to investigate the  $\text{IA-NA-NH}_3$  ternary system under the UTLS conditions. The structural analysis shows that NA, IA, and  $\text{NH}_3$  can bind together via HBs, XBs, and electrostatic attraction between the formed ion pairs ( $\text{NO}_3^- - \text{NH}_4^+$  and  $\text{IO}_3^- - \text{NH}_4^+$ ) to form stable nanoscale clusters. In contrast to the role of NA in the well-established  $\text{SA-NA-NH}_3$  clusters in the UTLS, which only engages in HB formation, NA additionally forms XB with IA in the  $\text{IA-NA-NH}_3$  system. Notably, the resulting small-sized  $\text{IA-NA-NH}_3$  clusters (three–four molecules) exhibit lower free energies than  $\text{SA-NA-NH}_3$  clusters, with the reduced evaporation rates indicating greater stability. As a result, the simulated rate  $J(\text{IA-NA-NH}_3)$  is even higher than  $J(\text{SA-NA-NH}_3)$  at the same precursor concentrations, showing higher nucle-

ation efficiency. Furthermore, we found that the enhancement strength is sensitive to temperature as well as NA and  $\text{NH}_3$  concentrations. In regions characterized by lower temperatures and high levels of NA and  $\text{NH}_3$ , such as the UTLS, the impact of IA–NA– $\text{NH}_3$  nucleation is more pronounced. At a lower temperature of 220 K in the UTLS, the ternary IA–NA– $\text{NH}_3$  clustering pathway dominates during nucleation. However, as the temperature rises to 240 K, NA facilitates IA– $\text{NH}_3$  nucleation through functioning as a quasi-catalyst precursor by initially participating in cluster formation and then evaporating out. However, in the lower free troposphere with a higher temperature of 260 K, NA evaporates rapidly, ceasing to participate in clustering process.

Our findings highlight the significant role of NA in IA nucleation, which potentially helps explain the missing source of the detected fresh IA particles in the UTLS. Even in the higher stratosphere (e.g.,  $\sim 20$  km, the lower near space), NA (Orsolini et al., 2009; Fahey et al., 2001; Wespes et al., 2007),  $\text{NH}_3$  (Xenofontos et al., 2024; Johansson et al., 2024), and IA particles (Koenig et al., 2020) were also frequently detected (Wen-Qin, 2009), suggesting that the IA–NA– $\text{NH}_3$  nucleation could also be a significant source of near-space iodine particles. Further, these ultrafine particles can participate in the formation of CCN or ice nuclei, which alters high-altitude cloud microphysical properties, thereby affecting radiation balance and global climate.

**Data availability.** The data in this article are available from the corresponding author upon reasonable request (anning@bit.edu.cn and zhangxiuhui@bit.edu.cn).

**Supplement.** The supplement related to this article is available online at <https://doi.org/10.5194/acp-25-14237-2025-supplement>.

**Author contributions.** XZ designed and supervised the research. JL, XD, and AN performed the quantum chemical calculations and the ACDC simulations. JL, AN, FB, and LL analyzed data. JL, AN, and XZ wrote the paper. YZ, PL, and QH reviewed the paper. All authors commented on the paper.

**Competing interests.** The contact author has declared that none of the authors has any competing interests.

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