# Synergistic Effect of Ammonia and Methylamine on Nucleation in the Earth's Atmosphere. A Theoretical Study

Chun-Yu Wang,[†,‡] Shuai Jiang,[‡] Yi-Rong Liu,[‡] Hui Wen,[†] Zhong-Quan Wang,[†,‡] Ya-Juan Han,[†] Teng Huang,[†] and Wei Huang*,[†,‡,§]

[†]Laboratory of Atmospheric Physico-Chemistry, Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences, Hefei, Anhui 230031, China

[‡]School of Information Science and Technology, University of Science and Technology of China, Hefei, Anhui 230026, China

[§]CAS Center for Excellence in Regional Atmospheric Environment, Xiamen, Fujian 361021, China

**S** *Supporting Information*

**ABSTRACT:** Ammonia and amines are important common trace atmospheric species that can enhance new particle formation (NPF) in the Earth's atmosphere. However, the synergistic effect of these two bases involving nucleation is still lacking. We studied the most stable geometric structures and thermodynamics of quaternary $(NH_3)(CH_3NH_2)$-$(H_2SO_4)_m(H_2O)_n$ ($m = 1–3$, $n = 0–4$) clusters at the PW91PW91/6-311++G(3df,3pd) level of theory for the first time. We find that the proton transfer from $H_2SO_4$ molecule to $CH_3NH_2$ molecule is easier than to $NH_3$ molecule in the free or hydrated $H_2SO_4$-base clusters, and thus leads to the stability. The energetically favorable formation of the $(NH_3)(CH_3NH_2)(H_2SO_4)_m(H_2O)_n$ ($n = 0–4$) clusters, by hydration or attachment of base or substitution of ammonia by methylamine at 298.15 K, indicate that ammonia and methylamine together could enhance the stabilization of small binary clusters. At low RH and an ambient temperature of 298.15 K, the concentration of total hydrated $(NH_3)(CH_3NH_2)(H_2SO_4)_2$ clusters could reach that of total hydrated $(NH_3)(H_2SO_4)_2$ clusters, which is the most stable ammonia-containing cluster. These results indicate that the synergistic effect of $NH_3$ and $CH_3NH_2$ might be important in forming the initial cluster with sulfuric acid and subsequently growth process. In addition, the evaporation rates of $(NH_3)(CH_3NH_2)(H_2SO_4)(H_2O)$, $(NH_3)(CH_3NH_2)(H_2SO_4)_2$ and $(NH_3)(CH_3NH_2)(H_2SO_4)_3$ clusters, three relative abundant clusters in $(NH_3)(CH_3NH_2)(H_2SO_4)_m(H_2O)_n$ system, were calculated. We find the stability increases with the increasing number of $H_2SO_4$ molecules.
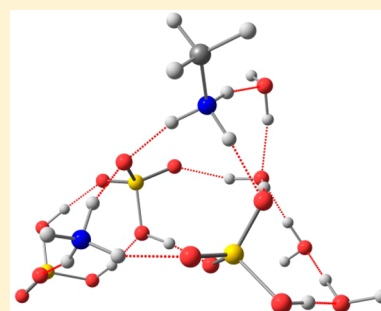
## 1. INTRODUCTION

Atmospheric aerosols affect the climate and human life by absorbing and scattering radiation and acting as cloud condensation nuclei (CCN).[1] Gas-to-particle conversion via nucleation is an important source of atmospheric aerosol particles.[2,3] However, there remains much uncertainty related to their actual birth-mechanism and composition.[4−6]

Atmospheric nucleation typically correlates with sulfuric acid concentration under a large variety of conditions;[7,8] thus, molecular clusters containing sulfuric acid are likely the precursors to stable particles. Extensive theoretical[9,10] and experimental[11−13] investigations into the atmospheric chemistry of sulfuric acid have been conducted. Yet, the binary homogeneous nucleation of sulfuric acid and water alone cannot explain the rate of new particle formation (NPF) observed, particularly in the lower regions of the troposphere,[14−16] and other species are also involved in nucleation. Zhang et al.[17] have pointed out, and then Nadykto et al.[18] have affirmed, the crucial role of organic compounds in atmospheric aerosol formation. Organic compounds, such as amines,[19−32] organic acids,[17,33−37] amino acid,[38,39] aldehydes,[40] and highly oxidized multifunctional organic molecules (HOMs)[41] have

been focused on. Atmospheric bases are key species for stabilizing sulfuric acid clusters mediated via proton transfer reactions. It has been seen in earlier modeling studies that amines could stabilize $H_2SO_4$ clusters significantly more than ammonia,[22,42] although different quantum-chemistry methods give somewhat different results concerning the magnitude of the stability difference.[24,43]

Ammonia, the most common base in the Earth's atmosphere, has been considered as a potential stabilizer of $H_2SO_4$−$H_2O$ clusters and atmospheric nucleation catalyst since 1990s.[44−48] Amount of data from quantum chemical calculations and experiments for the ternary clusters containing ammonia is available at the present time. Typically, atmospheric levels of ammonia are hundreds to thousands of pptv, while amines can be tens of pptv.[49−51] On the basis of smog chamber experiments and field measurements, amine chemistry plays a significant role in particle formation in regions. A 2011 study using the CLOUD chamber at the European Organization for

Nuclear Research (CERN) concluded that atmospherically relevant concentrations of ammonia and amines enhanced aerosol nucleation rates by a factor of 100−1000 in the lower troposphere.[15]

Yu et al.[52] examined the enhancing effect of amines, such as methylamine (MA), dimethylamine, trimethylamine, triethylamine, and *tert*-butylamine in a flow tube and compared with ammonia, they found that the enhancement factor of amines increased with increasing alkalinity of amines, implying that acid−base reactions play a role in aerosol formation and growth. However, other factors, such as steric hindrance and the number and strength of hydrogen bonds a base molecule formed, could also affect cluster ability and then aerosol formation.[53] The ease of affinity of amines and hydration during cluster formation and immediate growth should be compared. So, meaningful conclusion could be reached with a thorough interactions and thermodynamics study.

Lots of experimental and computational studies have been devoted to ammonia[45,46,54−57] or amine separately, the conclusion implies that amines are more effective than ammonia at enhancing nucleation.[22,24,42] Recently, Glasoe et al.[58] found that there is an increase in particle formation experimentally when $NH_3$ was added along with single-digit pptv levels of methylamine or dimethylamine, which was called synergistic effect. It has recently been inferred that species in concert might have a greater enhancement effect on NPF.[59] However, as far as we know, there has been no theoretical study on the mechanism of this synergistic effect. The most accurate way to study this effect is by quantum chemistry.

In the current work, we wish to uncover the synergistic effect of $CH_3NH_2$ and $NH_3$ at a molecular level. Using density functional theory methods, we investigate the structures, relative stabilities of the clusters and the process of initial quaternary particle formation. To obtain the dominant clusters in different atmospheric environments, the hydrate distribution has been analyzed. Then, the evaporation rates of these dominant clusters have been calculated, which can be used in the atmospheric cluster dynamics code (ACDC) to simulate the particle formation processes.[41,60−62]

## 2. METHODS

The initial geometries were obtained using a basin-hopping (BH) algorithm,[63−65] a generalized gradient approximation in the Perdue−Burke−Ernzerhof (PBE) functional and the double numerical plus d-functions (DND) basis set, which was implemented in DMol3.[66] This was employed in the density functional theory (DFT) module coupled with BH, which includes two procedures: (1) a new structure, which was generated via the random displacement of molecules, was optimized to the local minimum, and (2) the local minimum was used as a criterion to accept the initial structure spaces with the Boltzmann weight at a finite temperature. This method has been validated to perform well in our previous studies when we have explored atomic and molecular systems.[67−71]

Then, the results were optimized at the PW91PW91/6-31+G* level. The stable isomers within 6 kcal mol$^{-1}$ of the stable global minimum were reoptimized using the 6-311++G(3df, 3pd) basis set to determine the final configurations. Thus, much less time is required to obtain the final structures than via direct optimization using the PW91PW91/6-311++G(3df, 3pd) method. The performance of the PW91PW91/6-311++G (3df, 3pd) method has been systematically validated against experimental Gibbs free energies for clusters relevant to

the Earth's atmosphere[18,72−75] and has shown a very good agreement with the experiments and higher level ab initio studies.[76−80] All the geometry optimization and frequency calculations have been done in Gaussian 09. To assess the performance of the chosen methodology, we have done a benchmark about the methods employed in atmospheric cluster calculations, and a brief discussion of computational details is available in part S1 in the Supporting Information. The relative Gibbs free energies within 6 kcal mol$^{-1}$ of the global minimum with the number of isomers for each composition (part S2 in the Supporting Information) and Cartesian coordinates with energies (part S3 in the Supporting Information) of all isomers are reported in the Supporting Information.

## 3. RESULTS AND DISCUSSION

**3.1. Structures and Energetics.** Proton transfer reaction in hydrated sulfuric acids, leading to cluster stabilization, has been noticed by many researchers.[81,82] The number of proton transfers in $(NH_3)(MA)(H_2SO_4)_m(H_2O)_n$ ($m = 1-3$, $n = 0-4$) clusters and simpler clusters containing the same number of acid and base is summarized in Table 1. It is interesting to find

**Table 1. Number of Proton Transfers within Clusters at $T = 298.15$ K**

|  | $n = 0$ | $n = 1$ | $n = 2$ | $n = 3$ | $n = 4$ |
|---|---|---|---|---|---|
| $(NH_3)_2(H_2SO_4)_2(H_2O)_n$ | 2 | 2 | 2 | 2 | 2 |
| $(NH_3)_2(H_2SO_4)_3(H_2O)_n$ | 2 | 2 | 2 | 2 | 3 |
| $(MA)_2(H_2SO_4)_2(H_2O)_n$ | 2 | 2 | 2 | 2 | 2 |
| $(MA)_2(H_2SO_4)_3(H_2O)_n$ | 2 | 2 | 2 | 2 | 2 |
| $(NH_3)(MA)(H_2SO_4)(H_2O)_n$ | 1 | 1 | 1 | 1 | 1 |
| $(NH_3)(MA)(H_2SO_4)_2(H_2O)_n$ | 2 | 2 | 2 | 2 | 2 |
| $(NH_3)(MA)(H_2SO_4)_3(H_2O)_n$ | 2 | 2 | 3 | 2 | 2 |

that proton transfer occurs in all these sulfuric acid-containing clusters, the amount of proton transfers cannot exceed the amount of sulfuric acid molecules and does not dependent on the number of base molecules; Then, no matter how many $H_2O$ molecules are added to the clusters containing two $H_2SO_4$ and two base molecules (i.e., $(NH_3)_2(H_2SO_4)_2(H_2O)_n$, $(MA)_2(H_2SO_4)_2(H_2O)_n$, and $(NH_3)(MA)(H_2SO_4)_2(H_2O)_n$), the number of proton transfer remains two. These two findings may be due to the fact that $H_2SO_4$ is easy to bind $H_2O$, while the bases can hardly bind water. So, the number of $H_2SO_4$ molecules directly restricts the number of proton transfer within these small clusters. The $(NH_3)(MA)(H_2SO_4)_m(H_2O)_n$ clusters are more ionic than $(NH_3)_2(H_2SO_4)_m(H_2O)_n$ counterparts but less than $(MA)_2(H_2SO_4)_m(H_2O)_n$ counterparts due to the higher basicity of methylamine compared to ammonia. This ionic character is further corroborated by a middle dipole moment and polarizability compared to the $(NH_3)_2(H_2SO_4)_m(H_2O)_n$ and $(MA)_2(H_2SO_4)_m(H_2O)_n$ clusters (for more details see S4 in the Supporting Information). The optimized structures of $(NH_3)_2(H_2SO_4)_m(H_2O)_n$ ($m = 2-3$, $n = 0-4$) and $(MA)_2(H_2SO_4)_m(H_2O)_n$ ($m = 2-3$, $n = 0-4$) are shown in Figure S1 and Figure S2 in the Supporting Information, respectively, and these stable binary and ternary conformers found in this work agree well with previous works.[28,29,83]

Figure 1 presents the optimized global minimum clusters of $(NH_3)(MA)(H_2SO_4)(H_2O)_n$ ($n = 0-4$). Proton transfer to a methylamine molecule is more favorable than that to an ammonia molecule. For example, one proton transfers from the
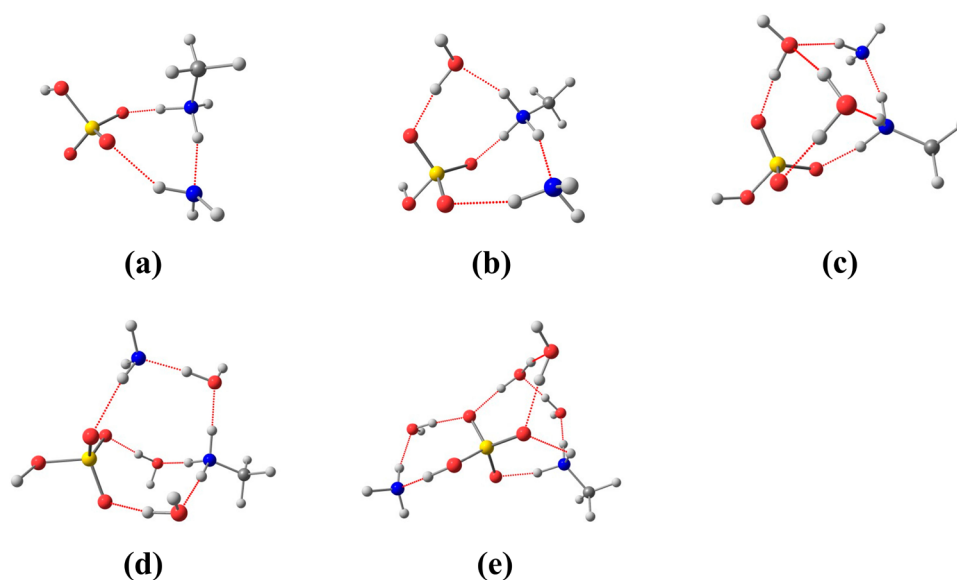
**Figure 1.** Global minima for $(NH_3)(MA)(H_2SO_4)(H_2O)_n$ ($n = 0-4$) optimized at the PW91PW91/6-311++G(3df, 3pd) level of theory.
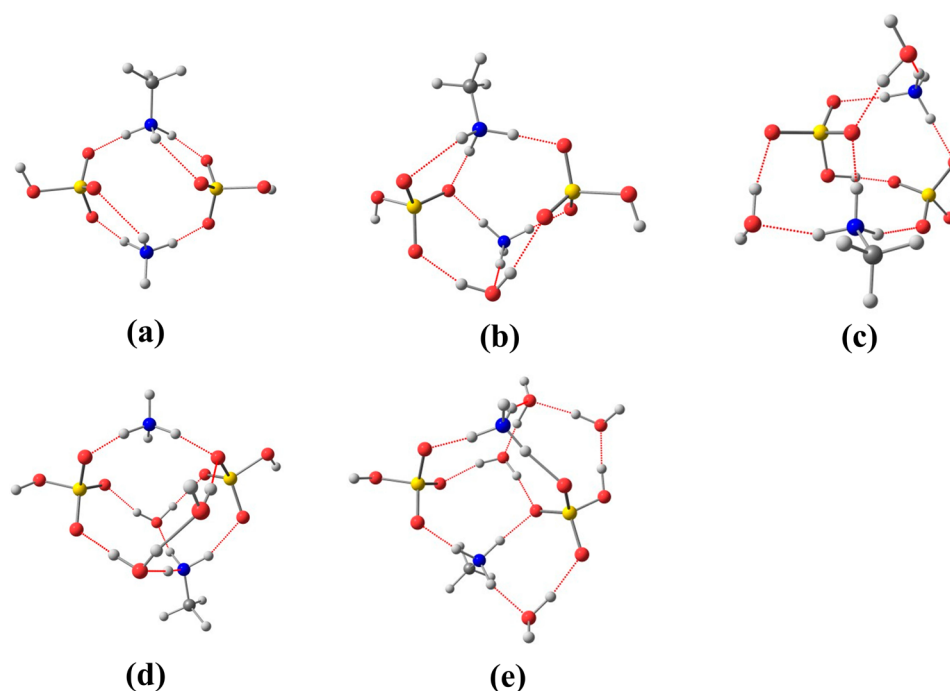


**Figure 2.** Global minima for $(NH_3)(MA)(H_2SO_4)_2(H_2O)_n$ ($n = 0-4$) optimized at the PW91PW91/6-311++G(3df, 3pd) level of theory.

$H_2SO_4$ molecule to the $CH_3NH_2$ molecule rather than the $NH_3$ molecule, forming $HSO_4^-$ and $CH_3NH_3^+$ in all these structures, as reflected by the higher gas-phase basicity of amines. The number of hydrogen bonds and the complexity of geometry increase with the number of water molecule increasing.

The optimized global minimum clusters of $(NH_3)(MA)-(H_2SO_4)_2(H_2O)_n$ ($n = 0-4$) are shown in Figure 2. Both bases and sulfuric acid are present in the ionic form, and all clusters contain one protonated amine-$HSO_4^-$ ion pair and one protonated ammonium-$HSO_4^-$ ion pair. For $(NH_3)(MA)-(H_2SO_4)_2$ cluster, each acid molecule interacts between two base molecules and each base molecule interacts between two acid molecules, forming a ring shape.

The optimized most stable conformations of $(NH_3)(MA)-(H_2SO_4)_3(H_2O)_n$ ($n = 0-4$) are depicted in Figure 3. Proton

transfer, two detached protons from two $H_2SO_4$ molecules transfer to an ammonia molecule and a methylamine molecule, respectively, occurs in all of the clusters. In particular, the third $H_2SO_4$ molecule is also deprotonated and the detached proton transfers to one $H_2O$ molecule in $(NH_3)(MA)-(H_2SO_4)_3(H_2O)_2$ cluster. The hydrogen bond network appears as a cage-like configuration in all five clusters.

By comparing Figures 1−3, it is apparent that one can obtain two conclusions: first, the attachment of water molecule to preexisting cluster occurs without proton transfer, which is likely a sign of weak or moderately weak hydration. The only exception is the $(NH_3)(MA)(H_2SO_4)_3(H_2O)_2$ cluster, in which one water molecule acts as receptor of proton. Second, the interaction of methylamine with the free or hydrated sulfuric acid leads to the deprotonation of the sulfuric acid and
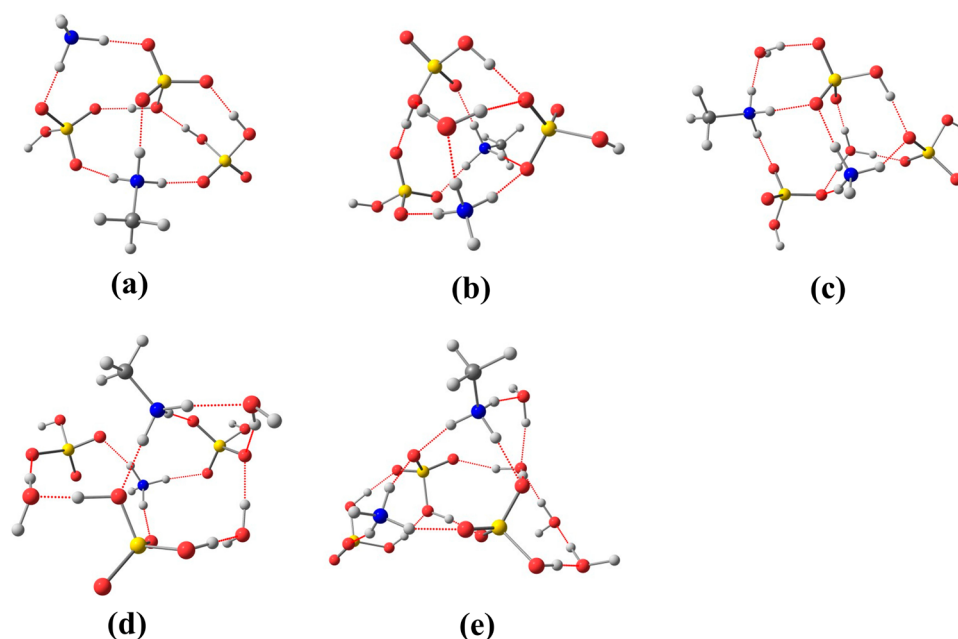
**Figure 3.** Global minima for $(NH_3)(MA)(H_2SO_4)_3(H_2O)_n$ ($n = 0-4$) optimized at the PW91PW91/6-311++G(3df, 3pd) level of theory.

transference of the detached proton toward $-NH_2$ of methylamine, and then the $-NH_2$ binds with the sulfuric acid or water to form hydrogen bonds. Additionally, comparing the most stable geometry of the different size $(NH_3)(MA)$-$(H_2SO_4)_m$ ($m = 1-3$) clusters, we found the sulfuric acid molecule/molecules connects/connect the two mutually exclusive base molecules as a bridge to form hydrogen bonds.

**3.2. Thermodynamics Analysis.** *Stepwise Hydration.* Table 2 presents reaction enthalpies, entropies, and Gibbs free

**Table 2. Reaction Enthalpies, Entropies, and Gibbs Free Energy Changes Associated with Hydration of Nucleating $(NH_3)(MA)(H_2SO_4)_m(H_2O)_n$ Clusters at 298.15 K and 101.3 KPa**

| $m$ | $n$ | $\Delta H$ (kcal mol$^{-1}$) | $\Delta S$ (cal mol$^{-1}$ K$^{-1}$) | $\Delta G$ (kcal mol$^{-1}$) |
|---|---|---|---|---|
| $(NH_3)(MA)(H_2SO_4)(H_2O)_{n-1} + H_2O \Leftrightarrow (NH_3)(MA)(H_2SO_4)(H_2O)_n$ | | | | |
| 1 | 1 | −13.49 | −34.08 | −3.32 |
|   | 2 | −11.50 | −36.42 | −0.64 |
|   | 3 | −10.05 | −29.52 | −1.25 |
|   | 4 | −12.21 | −35.70 | −1.57 |
| $(NH_3)(MA)(H_2SO_4)_2(H_2O)_{n-1} + H_2O \Leftrightarrow (NH_3)(MA)(H_2SO_4)_2(H_2O)_n$ | | | | |
| 2 | 1 | −12.83 | −37.29 | −1.71 |
|   | 2 | −13.92 | −41.73 | −1.48 |
|   | 3 | −8.50 | −27.48 | −0.31 |
|   | 4 | −15.76 | −40.06 | −3.82 |
| $(NH_3)(MA)(H_2SO_4)_3(H_2O)_{n-1} + H_2O \Leftrightarrow (NH_3)(MA)(H_2SO_4)_3(H_2O)_n$ | | | | |
| 3 | 1 | −9.87 | −33.28 | 0.05 |
|   | 2 | −13.25 | −35.18 | −2.76 |
|   | 3 | −8.35 | −31.19 | 0.95 |
|   | 4 | −14.58 | −45.19 | −1.11 |

energies changes associated with hydration of a shell containing $H_2O$ around $(NH_3)(MA)(H_2SO_4)_m$ core. As shown in Table 2, for $(NH_3)(MA)(H_2SO_4)$ and $(NH_3)(MA)(H_2SO_4)_2$ systems, the Gibbs free energy change ($\Delta G$) for each hydration step is invariably negative. For $(NH_3)(MA)(H_2SO_4)(H_2O)_n$ clusters, the $(NH_3)(MA)(H_2SO_4)(H_2O)$ cluster is most favorable to form, the following step-by-step addition of water molecule is

less thermodynamically favorable. The small change in Gibbs free energy per hydration is driven by changes in the electrostatic network upon hydration due to the increase in size or volume and the loss of entropy as more water molecules add to the parent cluster. Each hydration step of $(NH_3)(MA)$-$(H_2SO_4)_3$ is weaker than that of $(NH_3)(MA)(H_2SO_4)$ and $(NH_3)(MA)(H_2SO_4)_2$. The addition of the first water molecule is unfavorable, which is consistent with changes in $(MA)$-$(H_2SO_4)_3$ clusters.[29] The addition of the second water molecule significantly changes the relative energy as the number of hydrogen bonds that can be formed with water increases shown in Table 1.

*Affinity of $NH_3$ together with $CH_3NH_2$ to Nucleating $(H_2SO_4)_2(H_2O)_n$ Clusters.* Paasonen et al.[84] have modeled formation rate of clusters and shown that the formation rate of clusters with at least two of both sulfuric acid and amine molecules might be the rate-limiting step for atmospheric particle formation. Therefore, we specially studied the formation of $H_2SO_4$ dimers containing bases. Table 3 presents the comparison of reaction enthalpies, entropies, and Gibbs free energies changes describing the affinity of $NH_3$ and/or $CH_3NH_2$ to nucleating $(H_2SO_4)_2(H_2O)_n$ clusters. As shown in Table 3, the attachment of $NH_3$ molecules, $CH_3NH_2$ molecules, and the two bases together to $(H_2SO_4)_2(H_2O)_n$ clusters are all seen to be favorable. The affinity of $NH_3$ together with $CH_3NH_2$ to $(H_2SO_4)_2(H_2O)_n$ clusters is much higher than that of $NH_3$ molecules but less than that of $CH_3NH_2$ molecules, which is also due to the higher basicity of methylamine compared to ammonia.

*Substitution of $NH_3$ by $CH_3NH_2$ in $(NH_3)_2(H_2SO_4)_m(H_2O)_n$ Clusters.* Table 4 presents the substitution of $NH_3$ by $CH_3NH_2$ in $(NH_3)_2(H_2SO_4)_2(H_2O)_n$ and $(NH_3)_2(H_2SO_4)_3(H_2O)_n$ clusters. As shown in Table 4, the substitution of $NH_3$ by $CH_3NH_2$ in these two clusters is favorable due to the fact that $CH_3NH_2$ is more basic than $NH_3$. In other words, $(NH_3)$-$(MA)(H_2SO_4)_m(H_2O)_n$ clusters are more stable than $(NH_3)_2(H_2SO_4)_m(H_2O)_n$ clusters. Recently, Bzdek et al.[85] found that base displacement on the cluster surface is both thermodynamically and kinetically barrierless via experiment

**Table 3. Comparison of Reaction Enthalpies, Entropies, and Gibbs Free Energy Changes Describing the Affinity of $NH_3$, MA, and $NH_3$ together with MA to Nucleating $(H_2SO_4)_2(H_2O)_n$ Clusters at 298.15 K and 101.3 KPa**

| $n$ | $\Delta H$ (kcal mol$^{-1}$) | $\Delta S$ (cal mol$^{-1}$ K$^{-1}$) | $\Delta G$ (kcal mol$^{-1}$) |
|---|---|---|---|
| | $(H_2SO_4)_2(H_2O)_n + 2NH_3 \Leftrightarrow (NH_3)_2(H_2SO_4)_2(H_2O)_n$ | | |
| 0 | −45.10 | −71.76 | −23.71 |
| 1 | −42.45 | −74.77 | −20.15 |
| 2 | −44.66 | −78.17 | −21.36 |
| 3 | −40.66 | −72.91 | −18.92 |
| 4 | −34.42 | −61.30 | −16.14 |
| | $(H_2SO_4)_2(H_2O)_n + 2MA \Leftrightarrow (MA)_2(H_2SO_4)_2(H_2O)_n$ | | |
| 0 | −52.12 | −66.62 | −32.25 |
| 1 | −49.77 | −68.10 | −29.47 |
| 2 | −48.74 | −70.13 | −27.83 |
| 3 | −45.61 | −66.46 | −25.80 |
| 4 | −42.48 | −60.71 | −24.38 |
| | $(H_2SO_4)_2(H_2O)_n + NH_3 + MA \Leftrightarrow (NH_3)(MA)(H_2SO_4)_2(H_2O)_n$ | | |
| 0 | −47.49 | −64.95 | −28.13 |
| 1 | −44.55 | −67.56 | −24.41 |
| 2 | −46.22 | −76.10 | −23.53 |
| 3 | −40.40 | −65.82 | −20.77 |
| 4 | −40.69 | −61.92 | −22.23 |

**Table 4. Reaction Enthalpies, Entropies, and Gibbs Free Energy Changes for Substitution of $NH_3$ by MA in $(NH_3)_2(H_2SO_4)_m(H_2O)_n$ Clusters at Temperature of 298.15 K and Pressure of 101.3 KPa**

| $m$ | $n$ | $\Delta H$ (kcal mol$^{-1}$) | $\Delta S$ (cal mol$^{-1}$ K$^{-1}$) | $\Delta G$ (kcal mol$^{-1}$) |
|---|---|---|---|---|
| | | $(NH_3)_2(H_2SO_4)_2(H_2O)_n + MA \Leftrightarrow (NH_3)(MA)(H_2SO_4)_2(H_2O)_n + NH_3$ | | |
| 2 | 0 | −2.39 | 6.81 | −4.42 |
| | 1 | −2.10 | 7.21 | −4.25 |
| | 2 | −1.56 | 2.07 | −2.18 |
| | 3 | 0.26 | 7.09 | −1.85 |
| | 4 | −6.28 | −0.62 | −6.09 |
| | | $(NH_3)_2(H_2SO_4)_3(H_2O)_n + MA \Leftrightarrow (NH_3)(MA)(H_2SO_4)_3(H_2O)_n + NH_3$ | | |
| 3 | 0 | −5.60 | 2.07 | −6.21 |
| | 1 | −0.80 | 8.30 | −3.27 |
| | 2 | −1.77 | −2.90 | −0.91 |
| | 3 | 1.58 | 6.44 | −0.34 |
| | 4 | −2.52 | 0.69 | −2.72 |

and computation. The potential of $NH_3$ and $CH_3NH_2$ in enhancing sulfuric acid-induced new particle formation and the favorable conditions for the existence of quaternary clusters are discussed in section 3.3.

In conclusion, the $(NH_3)(MA)(H_2SO_4)_m(H_2O)_n$ cluster could form via hydration step-by-step or via attaching a $NH_3$ together with a $CH_3NH_2$ molecule or via substitution of $NH_3$ by $CH_3NH_2$. The basicity of the base will highly influence the formation of the initial $(Base)_2(H_2SO_4)_2$ clusters regardless of the several types of base. For bases with high basicity, the growth process via acid−base reactions is barrierless, and new particle formation will be at the kinetic limit. The synergistic effect observed in the experiment may be more attributed to kinetics. The negative Gibbs free energy changes of the $(NH_3)(MA)(H_2SO_4)_m(H_2O)_n$ ($m$ = 1−3, $n$ = 0−4) clusters via addition of a $NH_3$ molecule together with a $CH_3NH_2$ molecule to $(H_2SO_4)_2(H_2O)_n$ clusters indicate that the coexistence of $NH_3$ and $CH_3NH_2$ is able to enhance the stability of cluster containing $H_2SO_4$ and/or no water.

**3.3. Effect of the Ammonia Together with Methylamine on Formation of Nucleating Clusters under Atmospheric Conditions.** In this section, we use the thermochemical data to estimate the effect of $NH_3$ together with $CH_3NH_2$ on the formation of stable clusters containing $H_2SO_4$ and $H_2O$ under atmospheric conditions. Figure 4 presents the distributions of hydrated $(NH_3)(MA)(H_2SO_4)$, $(NH_3)(MA)(H_2SO_4)_2$ and $(NH_3)(MA)(H_2SO_4)_3$ clusters at an ambient temperature of 298.15 K and variable RH. As seen in Figure 4, most of $(NH_3)(MA)(H_2SO_4)$ clusters are hydrated under typical atmospheric conditions, hence, the RH dependency of the cluster distributions is obvious. The fraction of the hydrated $(NH_3)(MA)(H_2SO_4)$ clusters grows quickly with increasing RH, reaching almost 90% at RH = 80%. The hydration of $(NH_3)(MA)(H_2SO_4)_2(H_2O)_n$ clusters is much weaker, however, fraction of hydrated clusters reaches ~40% at RH = 80%. The hydration of $(NH_3)(MA)(H_2SO_4)_3(H_2O)_n$ clusters is the weakest, it stays almost completely dry no matter how RH increases. Hydrate distribution for $(NH_3)(MA)$-$(H_2SO_4)$, $(NH_3)(MA)(H_2SO_4)_2$ and $(NH_3)(MA)(H_2SO_4)_3$ clusters has maximum at $n$ = 1, $n$ = 0, and $n$ = 0, respectively.

The formation of stable $H_2SO_4$ dimers is the first step in acid−base cluster formation, and molecules consisting of two $H_2SO_4$, two base molecules and multiple water are assumed to
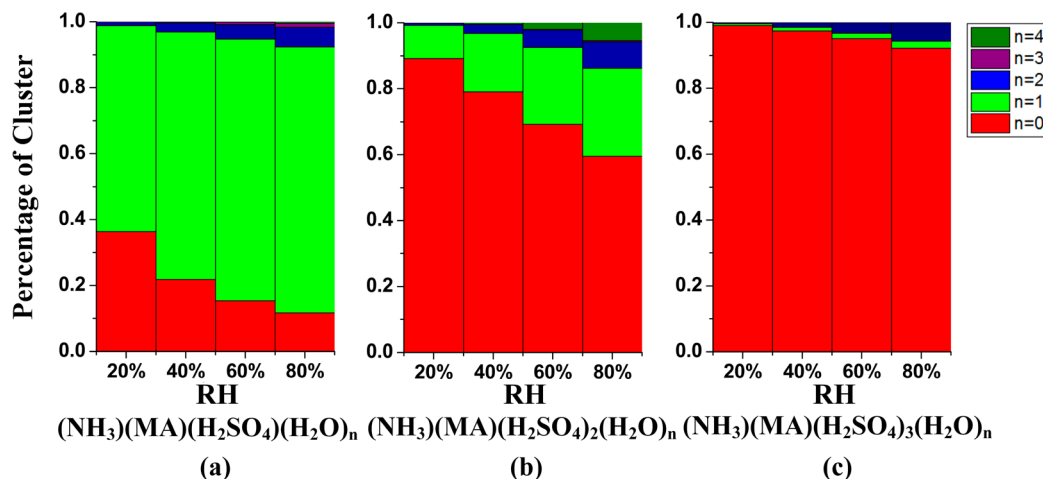


**Figure 4.** Fraction distribution of $(NH_3)(MA)(H_2SO_4)_m(H_2O)_n$ ($m$ = 1−3, $n$ = 0−4) at ambient temperature (298.15 K) and variable RH.
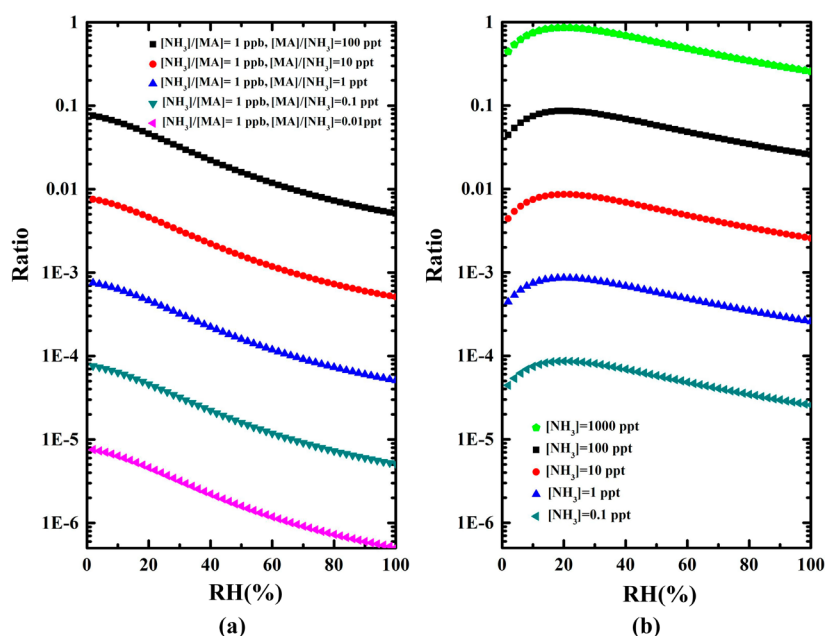
**Figure 5.** Concentration ratios of $(NH_3)(MA)(H_2SO_4)_2(H_2O)_n$ and $(NH_3)(H_2SO_4)_2(H_2O)_n$ clusters to binary $(H_2SO_4)_2(H_2O)_n$ clusters as a function of RH at an ambient temperature of 298.15 K. Different symbols in part a refer to the 1 ppb background concentration of ammonia at different concentration of methylamine or 1 ppb background concentration of methylamine at different concentration of ammonia. The data for ammonia were adopted from ref 83.

**Table 5. Evaporation Rates ($1\ s^{-1}$) for Different Clusters[a]**

|  | $(NH_3)(MA)(H_2SO_4)(H_2O)$ | $(NH_3)(MA)(H_2SO_4)_2$ | $(NH_3)(MA)(H_2SO_4)_3$ |
|---|---|---|---|
| $\gamma$ | $2.41 \times 10^8$ | $3.88 \times 10^4$ | 24.10 |
| $\gamma$ of $NH_3$ | $1.85 \times 10^8$ | $3.88 \times 10^4$ | 1.18 |
| $\gamma$ of MA | $3.86 \times 10^5$ | 22.27 | $1.31 \times 10^{-3}$ |
| $\gamma$ of $H_2SO_4$ | $2.84 \times 10^{-5}$ | $2.83 \times 10^{-5}$ | 16.21 |
| $\gamma$ of $(NH_3)(MA)$ | $6.67 \times 10^{-3}$ | $5.30 \times 10^{-14}$ | $1.82 \times 10^{-19}$ |
| $\gamma$ of $(NH_3)(H_2SO_4)$ | $4.97 \times 10^3$ | 0.19 | 6.41 |
| $\gamma$ of $(MA)(H_2SO_4)$ or $(NH_3)(H_2O)$ | $2.33 \times 10^5$ | 0.19 | 0.27 |
| $\gamma$ of $H_2O$ or $(H_2SO_4)_2$ | $5.52 \times 10^7$ | $5.30 \times 10^{-14}$ | $1.16 \times 10^{-11}$ |

[a] $\gamma$ refers to the total evaporation rate including monomer evaporation and fission (non-monomer evaporation) rate.

be reactive enough to grow further via collisions with acids other than $H_2SO_4$.[84] So, it is important to get the relative concentration of $(Base)_2(H_2SO_4)_2(H_2O)_n$ clusters. Nadykto et al.[23] have studied the concentration ratios of ternary dimers (dimers with $NH_3$ or $CH_3NH_2$) to binary sulfuric acid–water dimers. However, the relative concentration of clusters containing two different bases was lacked. Here, the concentration ratio of $(NH_3)(MA)(H_2SO_4)_2(H_2O)_n$ to binary $(H_2SO_4)_2(H_2O)_n$ was studied, which can be used to estimate the maximum new particle production and its sensitivity to the concentration of base, RH and other relevant parameters.

Previous evaporation rates calculations for $(NH_3)_m(H_2SO_4)_n$ ($m = 1–4$, $n = 1–4$) clusters at 298.15 K, used the formation free energies obtained with the combination of B3LYP/CBSB7 optimized geometries and frequency calculations with an RI-CC2/aug-cc-pVTZ single point energy calculation, showed that the most stable ammonia-containing cluster is $(NH_3)$-$(H_2SO_4)_2$,[86] and the concentration of relevant $(NH_3)(H_2SO_4)_2$ clusters are relatively high in atmosphere. So, we also calculated the concentration ratio of $(NH_3)(H_2SO_4)_2(H_2O)_n$ clusters to binary $(H_2SO_4)_2(H_2O)_n$ to intuitively characterize the impacts of $NH_3$ on the formation of binary sulfuric acid–water clusters. The favorable conditions for the existence of quaternary

clusters can be also obtained by comparing the two ratios. Here, parts a and (in Figure 5 present the concentration ratio of $(NH_3)(MA)(H_2SO_4)_2(H_2O)_n$ and $(NH_3)(H_2SO_4)_2(H_2O)_n$ cluster to binary $(H_2SO_4)_2(H_2O)_n$ cluster, respectively. The plots here are for the sum of n from 1 to infinity, detailed method and explanations of the calculations are provided in S5 in the Supporting Information.

For the ratio of $(NH_3)(MA)(H_2SO_4)_2(H_2O)_n$ to binary $(H_2SO_4)_2(H_2O)_n$, the contribution of $NH_3$ concentration is equal to that of $CH_3NH_2$ concentration. As can be seen in the curves shown in Figure 5, the concentration ratio of $(NH_3)(MA)(H_2SO_4)_2(H_2O)_n$ to binary $(H_2SO_4)_2(H_2O)_n$ decreases with the increase of RH, low RH is clearly favorable condition at which the strongest effect of $CH_3NH_2$ and $NH_3$ on the formation of stable $(NH_3)(MA)(H_2SO_4)_2(H_2O)_n$ clusters is achieved, while, the concentration ratio of $(NH_3)$-$(H_2SO_4)_2(H_2O)_n$ clusters to binary $(H_2SO_4)_2(H_2O)_n$ has the maximum value when RH is approximately equal to 20%. Comparing parts a and b, we found the concentration of total hydrated $(NH_3)(MA)(H_2SO_4)_2$ clusters is similar to that of total hydrated $(NH_3)(H_2SO_4)_2$ clusters at typical concentration of 1 ppb methylamine, the same concentration of ammonia and RH approximately of 7%.

**3.4. Evaporation Rates.** $(NH_3)(MA)(H_2SO_4)(H_2O)$, $(NH_3)(MA)(H_2SO_4)_2$ and $(NH_3)(MA)(H_2SO_4)_3$ are relatively stable clusters under atmosphere conditions based on calculations of hydrate distributions above. However, to directly compare with experimental results, we need to include kinetics, where the cluster evaporation rate based on the formation free energy is a critical parameter. Table 5 presents monomer evaporation and fission (nonmonomer evaporation) rates (1 s$^{-1}$) for above three clusters according to the method reported by Ortega et al.[86] Comparing evaporation rates of these three clusters, two conclusions can be obtained. First, the evaporability decreases with increasing number of $H_2SO_4$ molecules as proton transfer from sulfuric acid to base molecule stabilizes the cluster. Then, the fission rate is obviously smaller than monomer evaporation rate for all these clusters.

For $(NH_3)(MA)(H_2SO_4)(H_2O)$ and $(NH_3)(MA)(H_2SO_4)_2$ clusters, the evaporation of $NH_3$ is the most significant, which also proves that the $(MA)(H_2SO_4)(H_2O)$ cluster is more stable than the $(NH_3)(H_2SO_4)(H_2O)$ cluster and that the $(MA)(H_2SO_4)_2$ cluster is more stable than the $(NH_3)(H_2SO_4)_2$ cluster. For the $(NH_3)(MA)(H_2SO_4)_3$ cluster, evaporation of one sulfuric acid molecule is preferred than that of ammonia and methylamine due to the fact that the third $H_2SO_4$ molecule is absent from deprotonation to form the hydrogen bond.

## 4. CONCLUSIONS

Our study serves as the first investigation of synergistic effect with quantum chemistry. The structures of $(NH_3)_2(H_2SO_4)_m(H_2O)_n$ ($m = 2-3$, $n = 0-4$) and $(MA)(H_2SO_4)_m(H_2O)_n$ ($m = 1-3$, $n = 0-4$) agreed well with earlier reports; the thermochemical formation, the abundance of quaternary $(NH_3)(MA)(H_2SO_4)_m(H_2O)_n$ ($m = 1-3$, $n = 0-4$) clusters under ambient conditions, and the evaporability of relatively stable clusters were discussed. The following conclusions were obtained from the present study:

Sulfuric acid deprotonates and the detached proton transfers toward $CH_3NH_2$ in all clusters consisting of free or hydrated $H_2SO_4$, and the added $H_2SO_4$ molecule will directly connect to $CH_3NH_2$ molecule to form hydrogen bond.

The negative Gibbs free energy changes of the $(NH_3)(MA)(H_2SO_4)_m(H_2O)_n$ ($m = 1-3$, $n = 0-4$) clusters via addition of a $NH_3$ molecule together with a $CH_3NH_2$ molecule indicate that the coexistence of $NH_3$ and $CH_3NH_2$ is able to enhance the stability of clusters containing $H_2SO_4$ and/or no water. Though $(NH_3)_2(H_2SO_4)_3$ cluster is stable in the sulfuric acid−ammonia system, one $CH_3NH_2$ molecule is easy to substitute one $NH_3$ molecule under atmospheric conditions, and strong bases are important chemical species in the initial formation of new particles.

The hydrate distributions for $(NH_3)(MA)(H_2SO_4)(H_2O)_n$, $(NH_3)(MA)(H_2SO_4)_2(H_2O)_n$, and $(NH_3)(MA)(H_2SO_4)_3(H_2O)_n$ clusters have maximum at $n = 1$, $n = 0$, and $n = 0$, respectively. The concentration of total hydrated $(NH_3)(MA)(H_2SO_4)_2$ clusters is similar to that of total hydrated $(NH_3)(H_2SO_4)_2$ clusters at methylamine concentration of 1 ppb and RH approximately of 7%. The evaporation rates of these three relatively stable clusters decrease with increasing number of $H_2SO_4$ molecules.

Because of the interesting effect of ammonia and methylamine on small $(H_2SO_4)_m(H_2O)_n$ clusters, further quantitative experimental studies and theoretical simulations are required to investigate the synergistic effect on the cluster formation and its

dependence on ambient conditions. Specifically, we need to compare the nucleation rate and process under coexist of ammonia and methylamine conditions with that presence of only one base. Thus, the nature of synergistic effect could be accurately obtained. In addition, the synergistic effect caused by other species is also worth exploring.

## ■ ASSOCIATED CONTENT

### ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.8b00681.

Details about method validation, all the optimized Cartesian coordinates and energies of $(NH_3)(MA)(H_2SO_4)_m(H_2O)_n$ ($m = 1-3$, $n = 0-4$), all the structures, dipole moments and polarizabilities of $(NH_3)_2(H_2SO_4)_m(H_2O)_n$ ($m = 2-3$, $n = 0-4$) and $(MA)_2(H_2SO_4)_m(H_2O)_n$ ($m = 2-3$, $n = 0-4$), and the method of calculating the concentration ratios (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

*(W.H.) E-mail: huangwei6@ustc.edu.cn. Telephone: +86-551-63606711.

### ORCID ⊕

Wei Huang: 0000-0001-8147-386X

### Notes

The authors declare no competing financial interest.

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