Molecular-Level Understanding of Synergistic Effects in Sulfuric Acid–Amine–Ammonia Mixed Clusters

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Abstract

The abundance and basicity of a stabilizing base have shown to be key factors in sulfuric acid-driven atmospheric new-particle formation. However, since experiments indicate that a low concentration of ammonia enhances particle formation from sulfuric acid and dimethylamine, which is a stronger base, there must be additional factors affecting the particle formation efficiency. Using quantum chemistry, we provide a molecular-level explanation for the synergistic effects in sulfuric acid–dimethylamine–ammonia cluster formation. Due to the capability of ammonia to form more intermolecular interactions than dimethylamine, it can act as a bridge-former in sulfuric acid–dimethylamine clusters. In many cluster compositions, ammonia is more likely to be protonated than dimethylamine, although it is a weaker base. By nanoparticle formation rate simulations, we show that due to the synergistic effects, ammonia can increase the particle formation rate by up to five orders of magnitude compared to the two-component sulfuric acid–amine system.

1 - Introduction

The ability to understand and to mitigate human-caused climate change requires understanding the factors that determine atmospheric composition and their implications for climate.[1] Of these, the largest uncertainties are attributed to the impacts of atmospheric aerosol particles on the Earth's radiative balance. Particles can directly absorb or scatter sunlight and can also act as cloud condensation nuclei and ice nuclei, thereby affecting cloud properties and lifetimes.[2] Since clouds have an overriding global relevance in regulating the Earth's radiative balance, understanding the processes that regulate atmospheric particle populations is a key step in addressing the scientific challenges associated with climate change.

Sulfuric acid is known to be a key player in atmospheric new-particle formation, but it requires additional stabilizing components in order to yield observed particle formation rates.[3] Both ammonia and amines lead to significant increases in particle formation rates compared to pure sulfuric acid or sulfuric acid–water systems. The reason for this increase is attributed to acid–base chemistry, meaning proton transfer reactions and hydrogen bonding interactions between acid and base molecules. Higher new-particle formation rates due to amines compared to ammonia are reported in field and laboratory measurements as well as in theoretical studies.[4–9] This is explained through stronger interactions of sulfuric acid with amines due to fact that amines are stronger bases than ammonia.

Experimental studies have shown that when combining amines and ammonia together with sulfuric acid, new-particle formation rates are 10–100 times higher compared to two-component sulfuric acid–amine mixtures.[10,11] This cannot be explained by the aqueous-phase base constant or the gas-phase proton affinity, and thus the reason for this synergy is not understood. One logical explanation can be that atmospheric ammonia concentration is typically several orders of magnitude higher than that of amines. However, it was observed in laboratory measurements, in which ammonia was present at lower levels than dimethylamine, that reactions of sulfuric acid with bases yields nanoparticles that contain more ammonia than dimethylamine molecules.[12] This implies that the uptake of ammonia is not related to relative concentrations, but to some physico-chemical effect in the initial steps of particle formation. Indeed, Temelso *et al.* found theoretical evidence for synergy by studying Gibbs free formation energies of three-component sulfuric acid–amine–ammonia molecular clusters. They showed that the addition of sulfuric acid to a cluster containing sulfuric acid, dimethylamine or trimethylamine and ammonia is thermodynamically more favorable than adding sulfuric acid to a cluster containing only sulfuric acid and dimethylamine or trimethylamine.[13] Here we explore the structural properties of sulfuric acid–dimethylamine–ammonia clusters by quantum chemistry in order to explain the synergistic effects at a molecular level.

2 - Computational Methods

The cluster structures and thermochemistry were calculated applying a multi-step approach. For clusters consisting of several molecules, the potential energy surface becomes highly complicated and thus finding the global minimum free energy structure is challenging. To find these structures, we explored the potential energy surface of all the acid–base clusters using ABCluster program.[14,15] Monomer structures are rigid in the ABCluster structure search, meaning that proton transfer reactions are not concidered in the initial cluster structures. We have overcome this issue by using both neutral molecules as well as anions and cations to build cluster structures, which allows the examination of configurational space with different protonation states. We started by creating 1000 cluster structures, and used the PM7 semiempirical method[16] for initial optimization and vibrational frequency calculations. Based on the obtained Gibbs free energies and dipole moments, we separated different conformers, which were then optimized using the range-separated and dispersion-corrected density functional ωB97X-D with Pople's valence double-zeta basis set 6-31+G*.[17,18] For 5–10 lowest energy conformations, the ωB97X-D/6-31++G** level of theory was used for final optimization and vibrational frequency calculation. In previous studies, the ωB97X-D/6-31++G** level has shown to yield good geometries and thermochemical parameters for non-covalently bound molecular clusters.[19] In order to obtain highly accurate binding energies, we calculated electronic energy corrections on top of the ωB97X-D/6-31++G** structures using the domain-based local pair natural orbital coupled cluster singles, doubles and perturbative triples method DLPNO–CCSD(T) applying tight PNO criteria with augmented correlation consistent triple-zeta basis set aug-cc-pVTZ.[20–23] Gibbs free energies were calculated at the DLPNO–CCSD(T)/aug-cc-pVTZ//ωB97X-D/6-31++G** level, and the global minimum energy structure for each cluster was identified. The particle formation rate simulations were conducted using the Gibbs free energies as input in the Atmospheric Cluster Dynamic Code (ACDC). ACDC is a theoretical tool to study nanoparticle formation dynamics at given ambient conditions, and its details are explained in supporting information and Ref. 24. Briefly, it calculates the rate coefficients for all collision and evaporation processes within a given set of clusters and vapor molecules, and solves the birth–death equations that describe the dynamics of the cluster population.

For simplicity we refer sulfuric acid as A, ammonia as N and dimethylamine as D, and the number of molecules is before its name, i.e., 3A2N refers to the cluster with three sulfuric acid and two ammonia molecules. All geometries were optimized and vibrational frequencies were calculated using Gaussian 16 RevA.03.[25], and single point energy corrections were performed in Orca version 4.0.1.2.[26] Thermochemistry was calculated using the rigid rotor–harmonic oscillator approximation. All the Gibbs free binding energies (in kcal/mol and at 298.15 K) for the minimum energy clusters, electronic energies, thermal corrections and single point energy corrections for all clusters and monomers as well as the structures in xyz format are available in the supporting information. The ACDC code is available from the authors upon request.

3 - Results and Discussion

3.1 - Structural Effects in Mixed Clusters

We have studied the following structural effects of three-component clusters: number of intermolecular bonds, proton transfer and symmetry. We found that even though dimethylamine is a stronger base, in some cluster structures ammonia is more likely to be protonated (see the supporting information for the molecular pictures of all three-component clusters). This can be explained by the fact that ammonium is T_d symmetric and capable of forming four intermolecular bonds, whereas dimethylaminium can form only two bonds due to the steric hindrance of methyl groups. Therefore, a protonated ammonia molecule is likely to be placed in the center of the cluster structure and form stable bridge complexes between surrounding molecules. The smallest cluster in which the protonation of ammonia over dimethylamine is detected is 1A2N1D as shown in Figure 1. It should be noted that small clusters with a larger number of base than acid molecules tend to be unstable against evaporation in atmospheric conditions. However, since ammonium is always capable of forming a larger number of intermolecular interactions than dimethylaminium, the protonation effect can be assumed to apply also for larger particles, which are stable also at higher base:acid ratios.

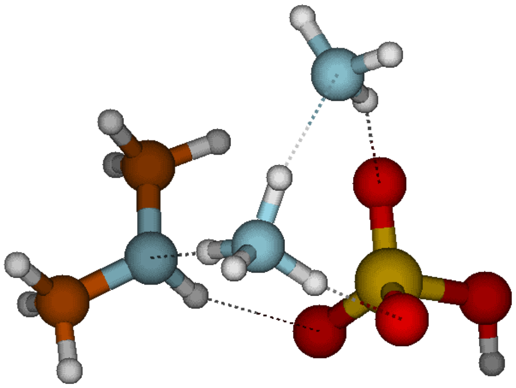

Figure 1: Molecular structure of 1A2N1D cluster in which ammonia has taken a proton from sulfuric acid. Color coding: brown is carbon, blue is nitrogen, red is oxygen, yellow is sulfur and white is hydrogen.

In addition to the protonation of ammonia over dimethylamine, in some cases the number of proton transfer reactions is "against the base strength", meaning that for clusters in which the number of base molecules is higher than the number of sulfuric acid molecules, bases might be able to take both protons from an acid molecule. The number of proton transfer reactions depends on the identities of the base molecules: for instance, the 2A2N1D cluster exhibits three proton transfers, whereas the 2A1N2D cluster shows only two, as shown in Figure 2. The 2A2N1D cluster structure, in which a sulfate ion with a point group of T_d has formed, is more spherical compared to the 2A1N2D cluster in which only dimethylamines are protonated and ammonia binds to the cluster via a single hydrogen bond interaction with the hydroxyl group of a bisulfate. These structural effects are able to explain the observations of high levels of particulate ammonium in nanometer-sized particles by Lawler *et al.*[12]

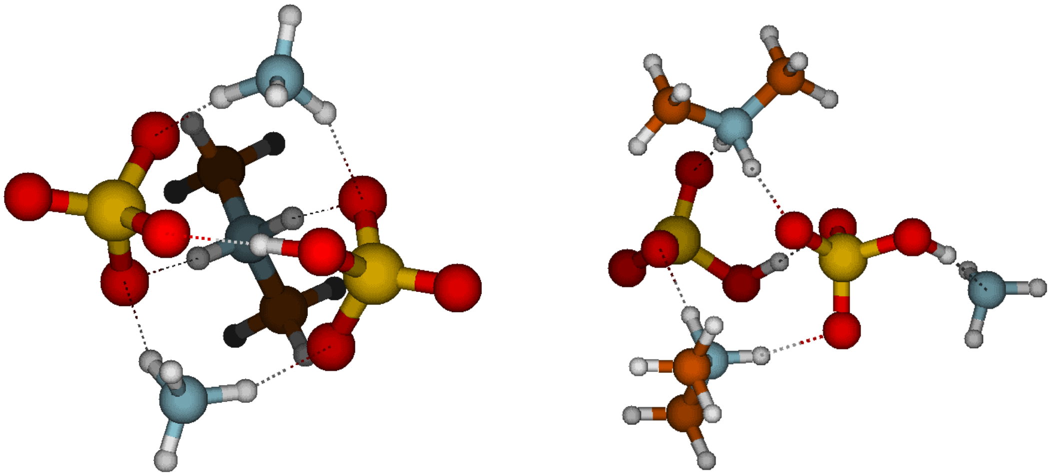

Figure 2: Molecular structures of 2A2N1D (left) and 2A1N2D (right) clusters. Color coding: brown is carbon, blue is nitrogen, red is oxygen, yellow is sulfur and white is hydrogen.

The importance of structural effects increases with cluster size as the molecules are able to form more strong intermolecular bonds. For instance, in the 4A4D cluster structure, there is a total of 12 intermolecular bonds, of which eight are between a bisulfate and a dimethylammonium and four are between bisulfate ions. The 4A2N2D cluster, on the other hand, contains 13 intermolecular interactions, of which 11 are between a bisulfate and an ammonium or a dimethylaminium and only two between bisulfate ions. It is clear that the interaction between an anion and a cation is much stronger than that between two anions, which might promote the formation of three-component clusters over two-component clusters (Figure 3).

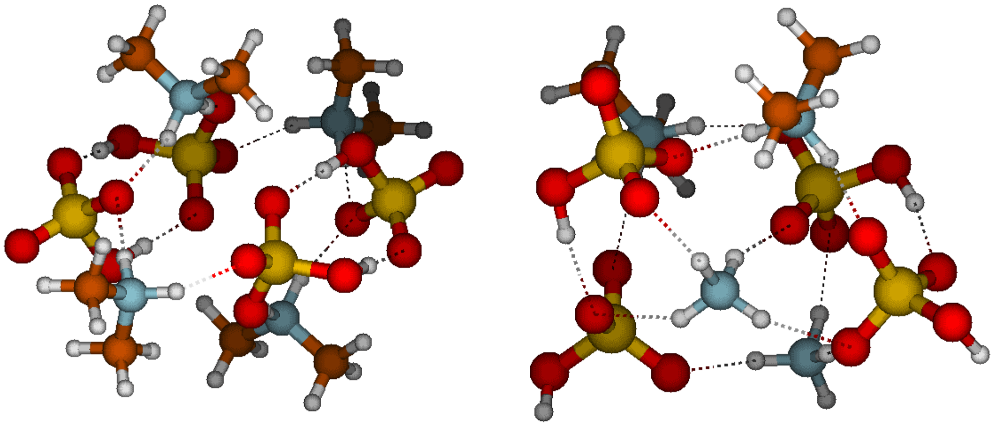

Figure 3: Molecular structures of 4A4D (left) and 4A2N2D (right) clusters. Color coding: brown is carbon, blue is nitrogen, red is oxygen, yellow is sulfur and white is hydrogen.

While previous studies have reported observations of amine substitution into small sulfuric acid–ammonia clusters, it should be kept in mind that the Gibbs free reaction energies and substitution energies are a different concept. For instance, we can compare the formation of 4A4D and 4A2N2D via monomeric sulfuric acid or dimethylamine additions as:

4A3D + 1D → 4A4D, ΔG=−19.6 kcal/mol

4A2N1D + 1D → 4A2N2D, ΔG=−20.5 kcal/mol.

That is, the formation of a 4(acid)4(base) cluster by addition of monomeric dimethylamine is 0.9 kcal/mol more favorable in the case of 4A2N2D. For the reactions

3A4D + 1A → 4A4D, ΔG=−22.4 kcal/mol

3A2N2D + 1A → 4A2N2D, ΔG=−23.4 kcal/mol

the formation of a 4(acid)4(base) cluster by addition of monomeric sulfuric acid is 1.0 kcal/mol more favorable in the case of 4A2N2D, but the substitution reaction of

4A4D + 2 1N → 4A4N + 2 1D, ΔG=14.7 kcal/mol

is thermodynamically highly unfavorable. A similar trend for substitution reactions has been shown, for instance by Waller *et al.*[27]

It can be mentioned that structural effects are likely to be related also to hydration of sulfuric acid–base clusters. The effect of hydration on particle formation is expected to depend on the strength of the base, in that the effect is larger for a weaker base: computational studies have shown a large hydration effect on ammonia clusters, a medium effect on methylamine clusters and a very small effect on dimethylamine or trimethylamine clusters.[7,28] However, a recent study by Yang *et al.* indicates that the water uptake effects may be due to the number of available hydrogen bonds in the cluster structure,[29] suggesting that structural effects have a role over the base strength also in hydration.

3.2 - Particle Formation Rates

To quantify the synergistic effects on nanoparticle formation, we used a cluster population model to simulate new-particle formation rates based on our computed Gibbs free formation energies (see supporting information and Ref. 24 for details). Figure 4 shows the new-particle formation rates as a function of sulfuric acid vapor concentration at different dimethylamine concentrations (1) without ammonia, and (2) at an atmospherically relevant ammonia concentration of 1000 ppt_V. To be consistent with experiments, the sulfuric acid "monomer" concentration here corresponds to the measurable concentration, which includes sulfuric acid monomers as well as all clusters containing one sulfuric acid molecule and any number of base ligands, *i.e.*, $\sum[1\text{A}n\text{Base}]$, where n=0–4. The enhancing effect of ammonia is seen in Figure 4: at low sulfuric acid and dimethylamine concentrations, the presence of ammonia increases the new-particle formation rate by several orders of magnitude. For a given sulfuric acid concentration, the absolute increase depends on the dimethylamine concentration, demonstrating the synergistic effects. At high acid and amine concentrations the particle formation rate is close to the theoretical maximum (*i.e.* kinetic limit) and thus the role of ammonia is small. Solely ammonia-enhanced particle formation rates are simulated in order to demonstrate that two-component sulfuric acid–ammonia particle formation is very slow and the three-component rates are not simply the sum of dimethylamine- and ammonia-based particle formation rates.

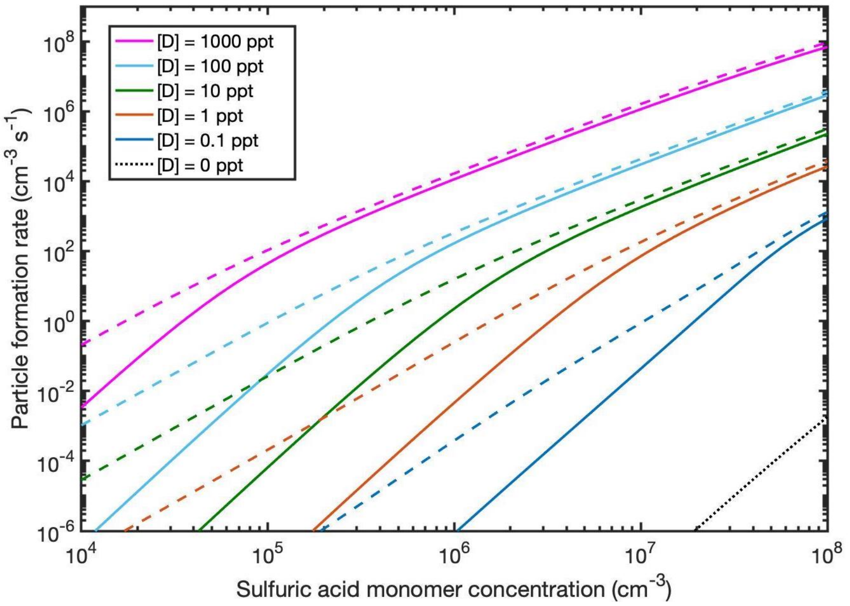

Figure 4: Particle formation rates as a function of measurable sulfuric acid vapor concentration. Solid lines represent solely dimethylamine-stabilized particle formation without ammonia, and dashed lines represent the synergistic particle formation at an ammonia concentration of 1000 ppt$_V$. The black dotted line (with negligibly low values at most simulated conditions) corresponds to two-component sulfuric acid–ammonia particle formation at an ammonia concentration of 1000 ppt$_V$.

Under atmospheric relevant conditions ([A]=10^7 cm^{-3}, [D]=1 ppt$_V$ and [N]=1000 ppt$_V$ at 298.15 K), cluster growth begins via the two-component sulfuric acid–dimethylamine channel as: 1A1D → 2A1D → 2A2D → 3A2D. When the 3A2D cluster has formed, there exist competing parallel growth pathways: the system can continue via the two-component pathway by either forming 3A3D which can collide with another cluster and grow out of the system, or grow to 4A4D via monomer additions and further out of the simulation box. In the present simulations, clusters are allowed to grow out of the system as stable particles when they contain at least five acid and four base molecules. The three-component pathway proceeds via the formation of 3A1N2D which then grows into the 4A1N2D cluster. 4A1N2D can grow to either 4A1N3D or 4A2D2N, which can grow out of the simulation box via a monomeric collision. Approximately half of the particles grow out via the three-component pathway. Although also the two-component ammonia–sulfuric acid pathway is possible in the simulations, its role is negligible as demonstrated in Figure 4.

We studied the effect of substituting some amount of dimethylamine vapor by ammonia while still keeping the total base concentration constant. Figure 5 shows the particle formation rates for total base concentrations of 10 ppt$_V$ and 100 ppt$_V$ with ammonia composing 0, 10, 50 and 90% of the total base concentration. In the case of [total Base]=10 ppt$_V$, the highest new-particle formation rate at low sulfuric acid concentrations occurs when the system contains 10% of ammonia. When sulfuric acid concentration is higher than ca. 10^6 cm^{-3}, 10% of ammonia has no effect compared to the 0% case. At equal ammonia and dimethylamine concentrations, the particle formation rate is slightly higher than for the two-component sulfuric acid–dimethylamine case at low sulfuric acid concentrations, and when sulfuric acid concentration increases, the two-component formation rate slightly exceeds the three-component rate. 90% of ammonia leads to 1–3 orders of magnitude lower particle formation rates compared to the other simulated cases.

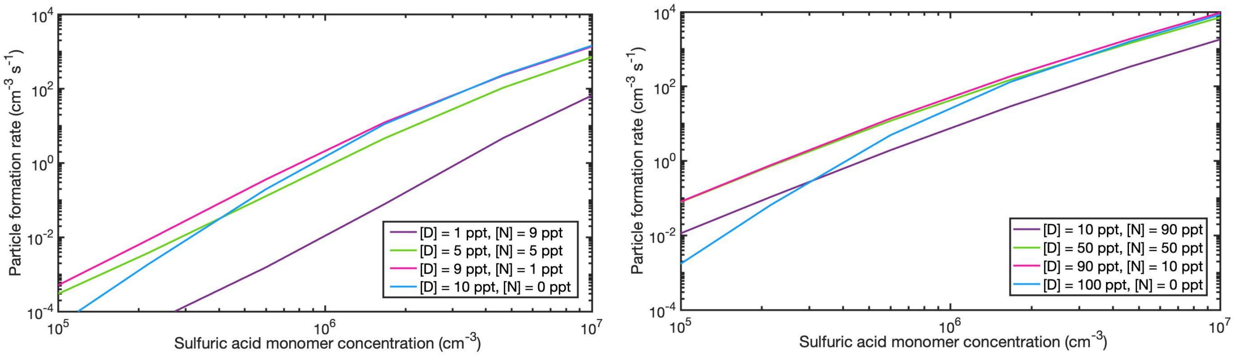

Figure 5: Particle formation rates as a function of measurable sulfuric acid vapor concentration. The total concentration of base vapor is kept constant at 10 ppt$_V$ (left) and at 100 ppt$_V$ (right), and different dimethylamine–ammonia ratios are simulated.

At [total Base]=100 ppt$_V$, ammonia fractions of 10% and 50% lead to equally high particle formation rates. The two-component sulfuric acid–dimethylamine system shows two orders of magnitude lower formation rates than 10% and 50% of ammonia at low sulfuric acid concentration, but when sulfuric acid concentration reaches ca. 10^7 cm^{-3}, the two-component rates become equal to the rates at 10% and 50% of ammonia. In the case of 90% of ammonia, the system yields constantly an order of magnitude lower particle formation rate compared to the 10% and 50% cases.

The particle formation rate simulations show a trend similar to experimental studies by Yu *et al.* and Glasoe *et al.*, who demonstrated an order of magnitude increase in particle number concentrations in the presence of ammonia compared to a two-component sulfuric acid–dimethylamine case.[10,11] Our results indicate that even when ammonia is present only as a contaminant, the synergistic effects with amine may lead to ca. an order of magnitude increase in the particle formation rate. At atmospheric conditions where ammonia concentration can be at $\mathrm{ppb_V}$ level and dimethylamine concentration at $\mathrm{ppt_V}$ level, the base synergy may lead up to five orders of magnitude increase in particle formation rates compared to the two-component sulfuric acid–dimethylamine system.

4 - Conclusions

In this paper we have provided a molecular-level explanation for synergistic effects between sulfuric acid, amines and ammonia. Since ammonia is able to form more intermolecular interactions than amines, it can act as a bridge-former in sulfuric acid–amine clusters. We demonstrated that ammonia is often more likely to be protonated than dimethylamine, even though it is a weaker base. The ammonium ion locates itself in the center of the cluster structure and thereby forms strong intermolecular interactions with surrounding molecules and ions.

Our findings demonstrate that the particle formation potential cannot be determined solely by the strengths of the involved bases: due to base synergy, replacing a fraction of the gas-phase concentration of a relatively strong base with a weaker base may enhance particle formation instead of reducing it. Bzdek *et al.* have showed that the displacement of ammonia by dimethylamine is likely to occur very fast for small clusters, meaning that if the smallest sulfuric acid–ammonia clusters form, the rapid displacement yields more stable sulfuric acid–dimethylamine clusters.[30–32] When clusters grow, however, the structural effects become more important and ammonia enhances cluster growth more effectively than dimethylamine, which is confirmed by increased particle formation rates. This is consistent with the findings of Temelso *et al.* who demonstrated that clusters larger than 2(acid)2(base) need to be studied in order to rationalize the synergistic effects since in the very smallest clusters the Gibbs free reaction energy correlates directly with the base strength.[13] This also supports the hypothesis that the strength of acids and bases in the particle phase decreases when particle size increases.[33]

It should be noted that the synergy is likely to occur also in other systems than presented in this study. Bases containing hydrocarbon groups are likely to benefit from the presence of ammonia due to more favorable structural arrangement. We showed that ammonia is capable of becoming protonated instead of a stronger base, which can be assumed to be related to the T_d symmetry of ammonium ion. This leads to the question whether the deprotonation of acid molecules in clusters containing different acidic species follows the same trend. For instance, sulfuric acid is a stronger acid than nitric acid, but the deprotonation of nitric acid leads to the trigonal planar nitrate ion with a point group of D_{3h}, whereas bisulfate ion is only C_s symmetric (meaning less symmetry operations than in the case of nitrate). Indeed, Yacovitch *et al.* have studied small anionic clusters containing sulfuric acid and nitric acid. They demonstrated that depending on the cluster composition, the cluster can contain either HSO_4^- or NO_3^- ion, meaning that the charge localization does not directly follow the acid strength.[34] Hou *et al.* focused on the structure of an anionic sulfuric acid–formic acid complex and showed that both conformers $(HCOOH)(HSO_4{}^-)$ and $(H_2SO_4)(HCOO^-)$ exist, and their abundances are dependent on the temperature. They suggest that electron delocalization by means of multiple hydrogen bonds might affect the stabilization of the $(H_2SO_4)(HCOO^-)$ complex, because the $(HCOOH)(HSO_4{}^-)$ complex should be the stable one based on monomer acidities.[35] In addition, both monomers in the $(H_2SO_4)(HCOO^-)$

complex as well as the complex itself have a C_{2v} symmetry whereas $(HCOOH)(HSO_4^-)$ does not have any symmetry operations. In order to prove the effects of internal symmetry, a systematic study over different multicomponent cluster structures is needed, and the size of the studied clusters needs to be large enough for the structural effects to have a role over the acid or base strength.

Our study shows the importance of synergistic effects in atmospheric new-particle formation. The results suggest that synergy should be taken into account in atmospheric models, since its effects might impact particle formation rates by up to several orders of magnitude. The atmosphere is a complex mixture containing a plethora of potential contributors to particle formation, and thus investigating the role of synergy for other mixtures is mandatory in order to understand and predict its importance in different atmospheric environments.

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Supporting Information Available

- Cartesian coordinates for each global minimum energy structure
- Electronic energies, thermal corrections and single point energy corrections for each monomer and cluster
- Gibbs free binding energies for the studied clusters

- Details about cluster population model
- Molecular structures of the three-component clusters

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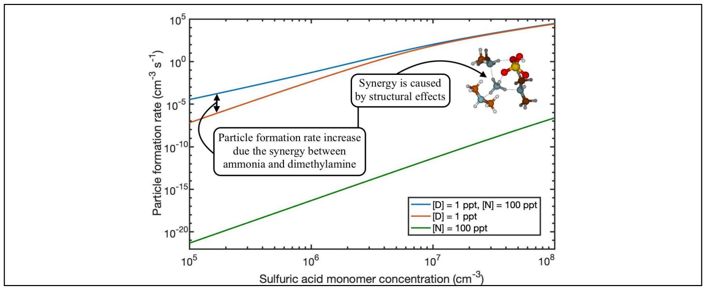
Graphical TOC Entry



Synergy is caused by structural effects

Particle formation rate increase due the synergy between ammonia and dimethylamine