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Amines in the Earth's Atmosphere: A Density Functional Theory Study of the Thermochemistry of Pre-Nucleation Clusters

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Abstract: The impact of organic species which are present in the Earth's atmosphere on the burst of new particles is critically important for the understanding of the molecular nature of atmospheric nucleation phenomena. Amines have recently been proposed as possible stabilizers of binary pre-nucleation clusters. In order to advance the understanding of atmospheric nucleation phenomena, a quantum-chemical study of hydrogen-bonded complexes of binary sulfuric acid-water clusters with methyl-, dimethyl- and trimethylamines representing common atmospheric organic species, vegetation products and laboratory impurities has been carried out. The thermochemical stability of the sulfuric acid-amines-water complexes was found to be higher than that of the sulfuric acid-ammonia-water complexes, in qualitative agreement with the previous studies. However, the enhancement in stability due to amines appears to not be large enough to overcome the difference in typical atmospheric concentrations of ammonia and amines. Further research is needed in order to address the existing uncertainties and to reach a final conclusion about the importance of amines for the atmospheric nucleation.

Keywords: amines; thermochemistry; clusters; nucleation precursors; sulfuric acid; water

1. Introduction

Aerosol particles formed in the Earth's atmosphere via nucleation [1,2] influence the Earth's climate by affecting cloud properties and precipitation. They play an important role in global climate changes [3,4] and are responsible for the adverse public health impacts of airborne ultrafine particles, including various cardiovascular diseases, lung cancer and enhanced mortality rates [5–7]. The atmospheric nucleation process can be described schematically as nucleation of $\text{H}_2\text{SO}_4\text{-H}_2\text{O-X}$. In other words, atmospheric nucleation involves sulfuric acid, the key atmospheric nucleation precursor, water, the dominant constituent of the mixture of condensable vapours in the Earth's atmosphere, and something else [8–15]. A perfectly logical question “What else is involved in the atmospheric nucleation?” has yet to be answered and a consensus on the dominant nucleation mechanism/mechanisms in the Earth's atmosphere is yet to be achieved. Since the 1990s ammonia, the most common base in the Earth's atmosphere, has been considered as a principle stabilizer of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ clusters. The somewhat excessive initial enthusiasm about the ternary homogeneous $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ nucleation theory (THN) disappeared, when it was discovered that the widely used THN model [11] grossly overestimates nucleation rates [12]. Kulmala *et al.* have revised the original THN model [13], but the revised model THN predicts negligible THN rates under typical atmospheric conditions. Other candidate nucleation mechanisms include ion mediated nucleation of $\text{H}_2\text{SO}_4\text{-H}_2\text{O-ion}$ (IMN) [10], nucleation of iodine-containing vapours [14] and organics-enhanced nucleation [15].

It is well-known that atmospheric organic species may be involved in nucleation. The presence of common organic species in the aerosol particles has been corroborated in a number of observations [16–23]. However, the role of organics in the atmospheric nucleation has long been underestimated or neglected due to the complexity of laboratory experiments and the absence of theoretical instruments, which would be able to account for the complex intermolecular interactions occurring in nucleating vapours. The importance of organic species has been pointed out in the pioneering experiments of Zhang *et al.* [15], in which a considerable enhancement in nucleation rates due to organic species has been observed. The ability of computational quantum chemical methods to provide an adequate description of molecular interactions in nucleating vapours has been pointed out in Nadykto *et al.* [24], in which the classical problem of the ion sign preference established in back 1897 by Wilson [1] has been solved. Recently, computational chemical studies of atmospheric species have become a focus of intense activity [24–36]. Although a large number of the computational quantum studies considering atmospheric clusters has been published within the last five years, only a few are dedicated to the interaction of common organics with atmospheric nucleation precursors [32,34,35]. The ability of common low-molecular carboxylic formic and acetic acids to stabilize $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ clusters has been pointed in our recent work [34]. The conclusion about the importance of organic species for the stabilization of atmospheric pre-nucleation clusters has been confirmed in independent studies [32,35].

Amines are common atmospheric species originating mainly from vegetation and common laboratory impurities. The activity of amines as potential nucleation agents has been indicated in a number of experiments and observations [37–45]. Typically, the atmospheric concentrations of amines are much lower than those of ammonia; however, a number of sites with high amine concentration exist in the boundary layer. Angelino *et al.* [43] have concluded, based on smog chamber experiments and field measurements, that amine chemistry plays “a significant role in particle formation in regions

with high amine concentrations". Laboratory experiments and quantum chemical calculations of crystal structures of Murphy *et al.* [44] showed that diethylamine is more efficient in catalyzing the nucleation of nitric acid than ammonia. Observations of Makela *et al.* [45] have indicated that dimethylammonium ion, the ionic form of dimethylamine, was present in aerosol particles formed during nucleation events and/or subsequent particle growth process in Hyytiälä, Southern Finland. Although the potential relevance of amines to nucleation in the Earth's atmosphere is well-established, their roles in the gas-to-particle conversion and the extent at which they can affect atmospheric nucleation rates are unknown. More recently, several experimental studies and reviews concerning the role of amines in atmospheric nucleation have been published [37–42].

Recently, amines have been proposed as potential stabilizers of sulfuric acid-water clusters [32]. The conclusion about the potential importance of amines for atmospheric nucleation made in Kurten *et al.* [32] is based solely on the RI-MP2/CC2 formation free energies of H₂SO₄-amine complexes, which appeared to be more stable than the ammonia bisulfate formed via the NH₃ + H₂SO₄ ⇌ (NH₃)(H₂SO₄) reaction. Although the enhancement in dimerization free energies may be an important indicator of the stability in simple unitary systems, the stability of complex, essentially multicomponent, H₂SO₄-H₂O-amine complexes is controlled by three somewhat competing factors: attachment of the sulfuric acid, affinity of amines to clusters being formed and hydration. Therefore, no meaningful conclusion can be reached without a thorough study of the interactions of all three species.

In the present paper, the hydrogen bonded complexes of common amines, methylamine (CH₃)NH₂, dimethylamine (CH₃)₂NH and trimethylamine (CH₃)₃N, with sulfuric acid and water have been studied using the Density Functional Theory (DFT). The properties of mixed dimers, trimers, tetramers and pentamers have been investigated and a comprehensive thermochemical analysis has been carried out. The impact of amines on the stability of binary pre-nucleation clusters has been investigated and possible involvement of amines in the atmospheric nucleation has been discussed.

2. Methods

At the present time, DFT is the only option for studying large clusters due to the enormously large computational expenses associated with the application of *ab initio* MP2 and higher level methods [46]. However, the relative importance of different nucleation pathways is primarily related to the difference in stepwise free energy changes associated with the formation of different types of clusters, which is predicted by different methods in good agreement with each other. For example, it has been shown that the difference in binding energies of (H₂SO₄)(NH₃) and (H₂SO₄)(H₂O) complexes given by different *ab initio* and DFT methods, with and without counterpoise corrections, is several times lower than the difference in the absolute values of the binding energy of (H₂SO₄)(NH₃) or (H₂SO₄)(H₂O) clusters [47]. In the present study, the initial/generated geometries have been treated using the semi-empirical PM3 [46] method and then optimized at the PW91PW91/6-31+G* level of theory. The most stable isomers (within 2 kcal mole⁻¹ of the most stable isomer/global minimum) obtained at the PW91PW91/6-31+G* level have been optimized using the PW91PW91/6-311+G(3df,3pd) method to obtain the final results. The choice of the computational method is based on the satisfactory performance of the PW91PW91 [46] on atmospheric clusters, including predicting the Gibbs free energies, structural characteristics and vibrational spectra in a very good agreement with experiments

and *ab initio* studies, and availability of large amount of data for different atmospheric species/clusters computed at PW91PW91/6-311+G(3df,3pd) level of theory for comparison [24–30,34]. The availability of data for ternary sulfuric acid-water-ammonia clusters computed at the same level of theory is a very important factor because the assessment of different nucleation pathways, which is based on the analysis of the reaction free energies computed using the same method, is clearly more legitimate than that based on the comparison of results obtained at different levels of theory [47].

3. Results and Discussion

Figures 1 and 2 present the equilibrium geometries of the most stable isomers of $(\text{CH}_3\text{NH}_2)_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ and $[(\text{CH}_3)_2\text{NH}]_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ complexes. The equilibrium geometries of all the $(\text{CH}_3\text{NH}_2)_2$, $(\text{CH}_3\text{NH}_2)_3$, $[(\text{CH}_3)_2\text{NH}]_2$, $[(\text{CH}_3)_2\text{NH}]_3$, $(\text{CH}_3\text{NH}_2)(\text{H}_2\text{SO}_4)$, $[(\text{CH}_3)_2\text{NH}](\text{H}_2\text{SO}_4)$, and $[(\text{CH}_3)_3\text{N}](\text{H}_2\text{SO}_4)$ are in good agreement with the previous *ab initio* MP2 studies [32,48–50]. A comparison of geometries of $\text{CH}_3\text{NH}_2\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$, $(\text{CH}_3)_2\text{NH}\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ and $(\text{CH}_3)_3\text{N}\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ complexes presented in Figures 1 and 2 reveals a number of similarities. For example, the attachment of water molecules to both CH_3NH_2 and $(\text{CH}_3)_2\text{NH}$ occurs without the proton transfer, which is likely a sign of weak or moderately weak hydration. The interaction of both amines with both the free and hydrated H_2SO_4 leads to the deprotonation of the sulfuric acid and transfer of the detached proton towards NH_2 and NH groups of CH_3NH_2 and $(\text{CH}_3)_2\text{NH}$, respectively. Both amines and sulfuric acid are present in the binary amine-sulfuric acid and ternary amine-sulfuric acid-water clusters in the ionic form. The proton transfer and number of ionic structures in the aforementioned clusters depend strongly on the cluster size and composition. All the mixed dimers, trimers and tetramers at $n = 1; 2$ and $m = 1; 2$, which contain less than two amines and water, include single ion pairs CH_3NH_3^+ and HSO_4^- or $(\text{CH}_3)_2\text{NH}_2^+$ and HSO_4^- , while tetramers and pentamers with $n \geq 2$ and $m \geq 2$ contain two protonated amine- HSO_4^- ion pairs.

Figure 1. Equilibrium geometries of the most stable isomers of $(\text{CH}_3\text{NH}_2)_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ complexes. Distances and angles are given in angstroms and degrees, respectively.

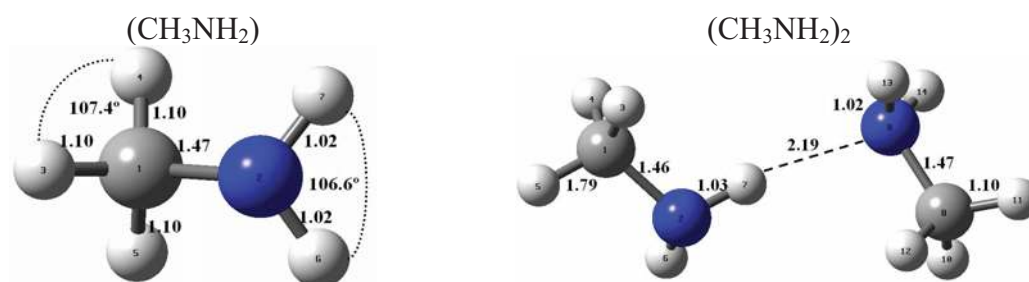


Figure 1. Cont.

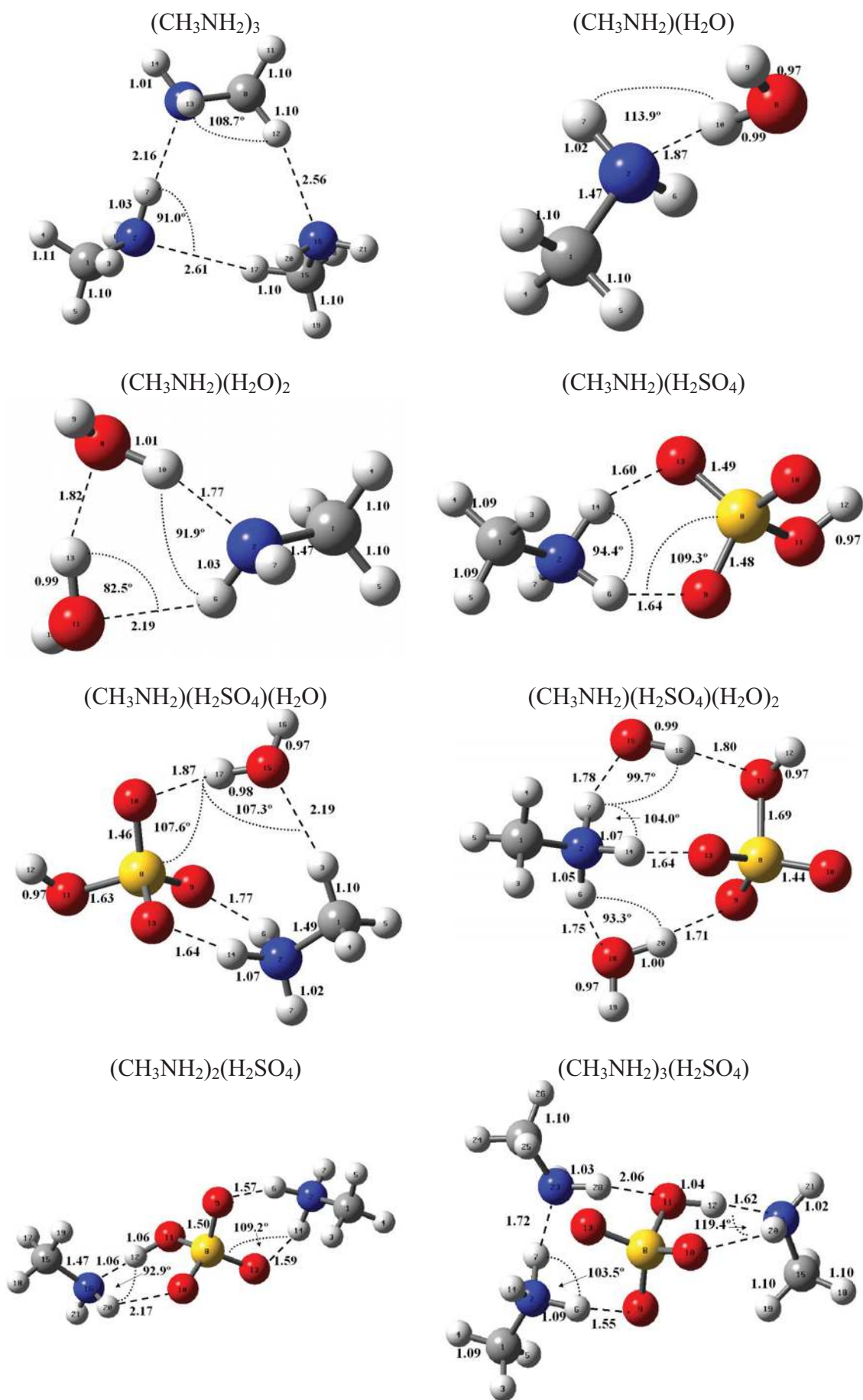


Figure 1. Cont.

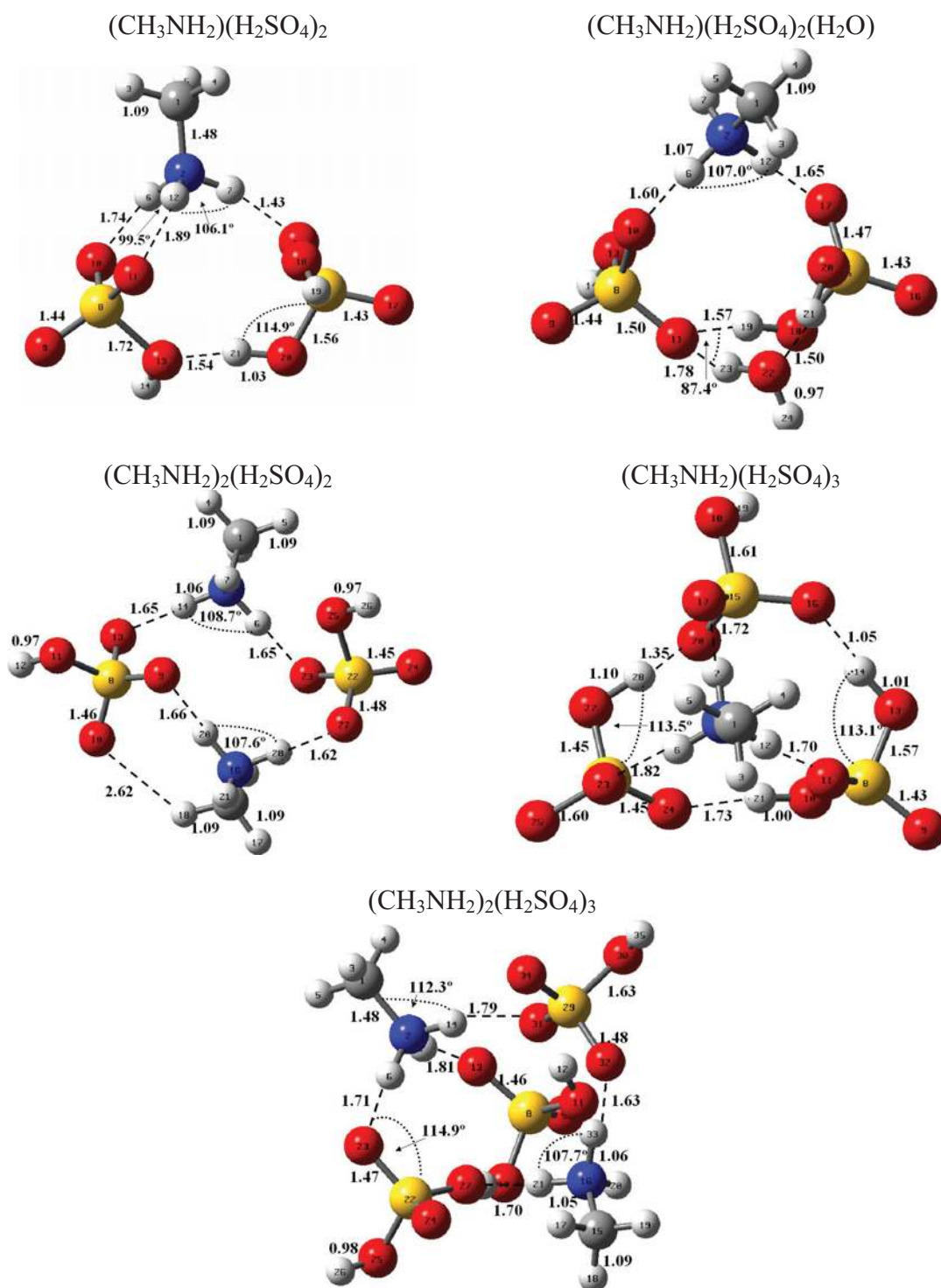


Figure 2. Equilibrium geometries of the most stable isomers of $[(\text{CH}_3)_2\text{NH}]_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ complexes. Distances and angles are given in angstroms and degrees, respectively.

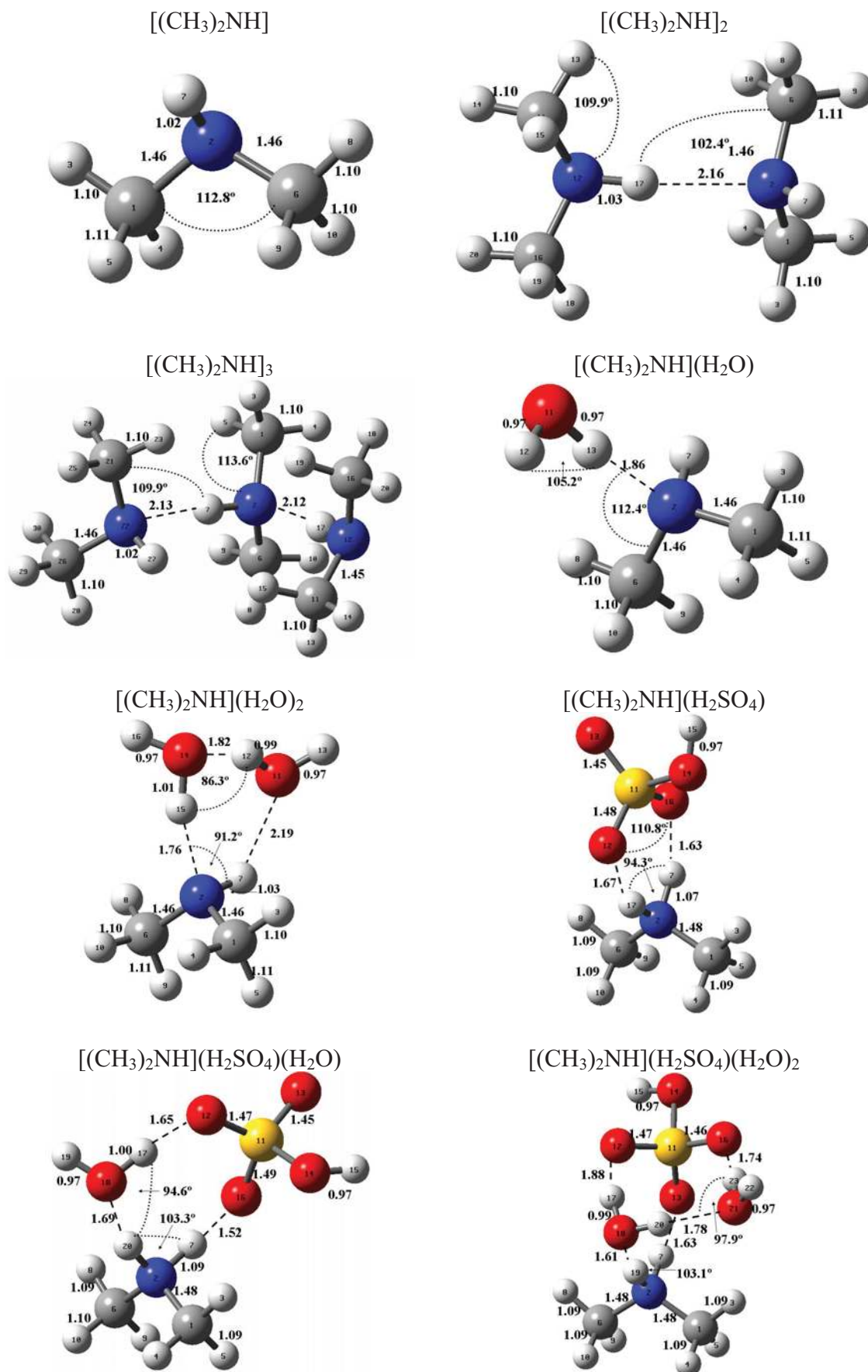
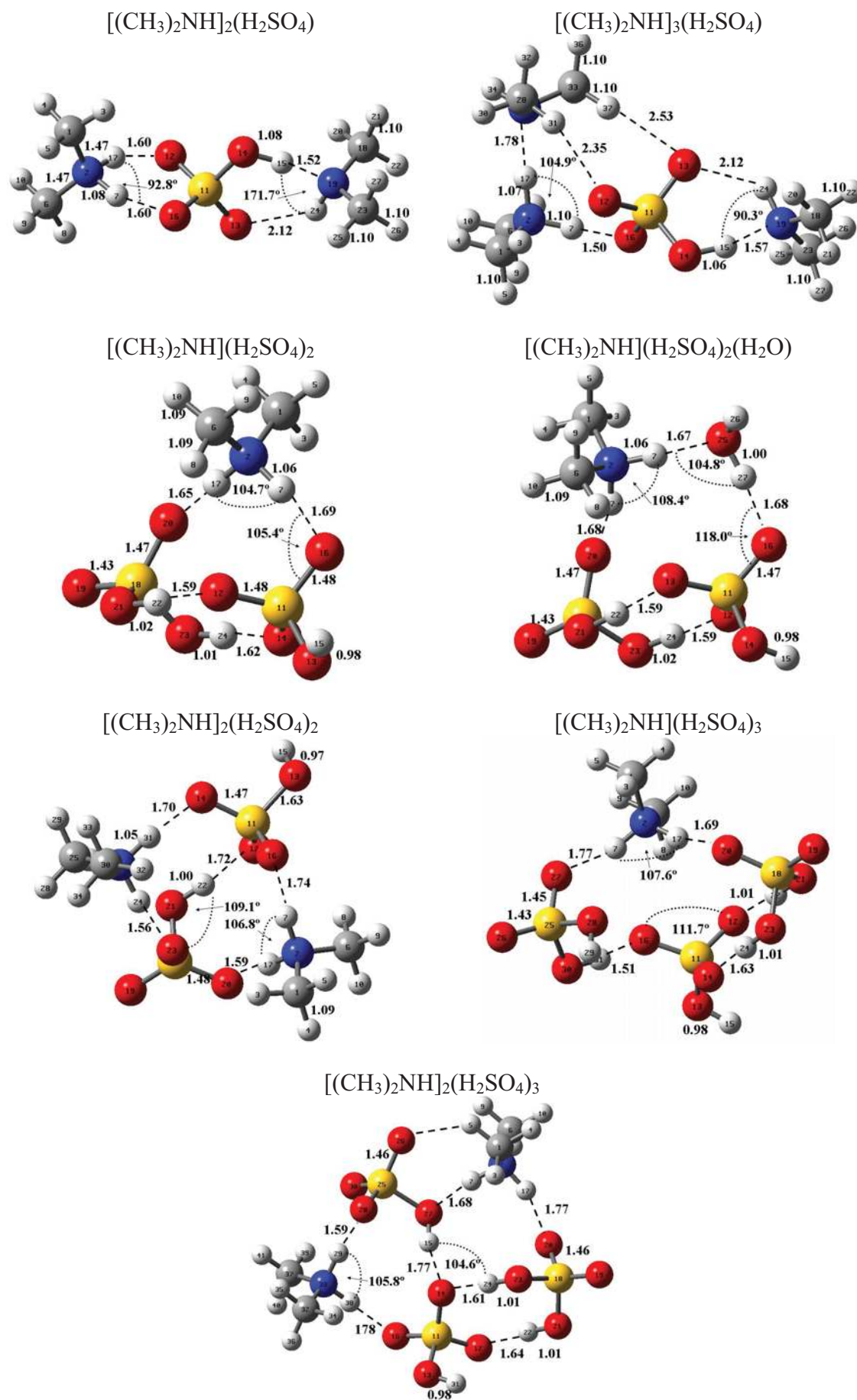


Figure 2. Cont.



Tables 1, 2, and 3 present the key thermochemical properties controlling the thermodynamic stability: attachment of H_2SO_4 , affinity of amines to clusters being formed, and hydration. As may be seen from Table 1, the qualitative conclusion about the hydration of amines made based on the structural data agrees well with the obtained thermochemical data. The hydration of amines is weak, and, thus, hydrated sulfuric acid-amine clusters are thermodynamically unstable under typical atmospheric conditions. The above-mentioned conclusion is also applicable to the weakly hydrated $(\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH}_2)(\text{H}_2\text{O})$ and $(\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}](\text{H}_2\text{O})$ complexes. In contrast, the hydration of both the $(\text{H}_2\text{SO}_4)(\text{CH}_3\text{NH})$ and $(\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}]$, and $(\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH})(\text{H}_2\text{O})$ and $(\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}](\text{H}_2\text{O})$ is strong enough to expect the existence of such clusters in the Earth's atmosphere. On average, the hydration of amine-sulfuric acid-water complexes is moderately weak and is close to that of ammonia-sulfuric acid-water complexes, for which the hydration is considered to be much less important than the attachment of the sulfuric acid and ammonia. As seen from Tables 2 and 3, the bonding energies associated with attachment of CH_3NH_2 and $(\text{CH}_3)_2\text{NH}$ to clusters of identical chemical composition are very close. The difference between them is less than $0.7 \text{ kcal mole}^{-1}$ on average. The hydration affects the attachment of both sulfuric acid and amines; however, its effect is weak. The comparison of affinities of amines and ammonia to the pre-nucleation clusters is favorable for amines because the free energies of $[(\text{CH}_3)_2\text{NH}]_{m-1}(\text{H}_2\text{SO}_4)_n + (\text{CH}_3)_2\text{NH} \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_m(\text{H}_2\text{SO}_4)_n$ reactions are in most cases higher than those of the $(\text{NH}_3)_{m-1}(\text{H}_2\text{SO}_4)_n + \text{NH}_3 \Leftrightarrow (\text{NH}_3)_m(\text{H}_2\text{SO}_4)_n$ reactions. In some cases, the replacement of ammonia with amines leads to a considerable (up to $2\text{--}3.5 \text{ kcal mole}^{-1}$) enhancement in the affinity of the sulfuric acid, the key atmospheric nucleation precursor, to the pre-nucleation clusters.

It is important to note that the enhanced thermodynamic stability does not necessarily imply stronger stabilizing effects under the real atmospheric conditions. The stabilizing effect is controlled by two different factors: stepwise Gibbs free energy changes and concentration ratio of amines with respect to ammonia, which is $\sim 10^{-2}\text{--}10^{-3}$ under typical atmospheric conditions [32,37–42]. As it may be seen from Tables 2 and 3, the difference in formation free energies of (amine)(H_2SO_4) and (ammonia- H_2SO_4) clusters is $\sim 3\text{--}4 \text{ kcal mole}^{-1}$, which may imply the possibility of the domination of clusters containing amines over ammonia bisulfate clusters under favorable condition (high concentration of amines and low temperatures). However, the difference in the free energies of (amine)(H_2SO_4) + $\text{H}_2\text{SO}_4 \Leftrightarrow$ (amine)(H_2SO_4)₂ and $(\text{NH}_3)(\text{H}_2\text{SO}_4) + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{NH}_3)(\text{H}_2\text{SO}_4)_2$ reaction underlining the further cluster growth does not exceed $\sim 2.5 \text{ kcal mole}^{-1}$ and tends to decrease with hydration. Another important details are that the free energies of (amine)(H_2SO_4) + amine \Leftrightarrow (amine)₂(H_2SO_4) are very small ($3.7\text{--}4.7 \text{ kcal mole}^{-1}$) and that the (amine)₂(H_2SO_4) clusters, to which the sulfuric acid could easily attach, are unstable thermodynamically. Other possible pathways of the formation of large clusters such as $(\text{H}_2\text{SO}_4)_2 + \text{amine} \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{amine})$ or $(\text{amine})_2 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)(\text{amine})_2$ are impossible under the atmospheric conditions due to the insufficient stability of $(\text{H}_2\text{SO}_4)_2$ and amine dimers. The obtained results lead us to conclude that under typical atmospheric conditions $(\text{H}_2\text{SO}_4)_2(\text{amine})$ formation is the limiting stage of the pre-nucleation cluster formation.

Table 1. Comparison of changes in enthalpies ΔH (kcal mole⁻¹), entropies ΔS (cal mole⁻¹ K⁻¹), and Gibbs free energies ΔG (kcal mole⁻¹) associated with formation of $(\text{CH}_3\text{NH}_2)_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$, $((\text{CH}_3)_2\text{NH})_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ and $((\text{CH}_3)_3\text{N})_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ complexes via hydration with those associated with the formation of $(\text{NH}_3)_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ at temperature of 298.15K and pressure of 101.3 KPa.

	ΔH	ΔS	ΔG
$\text{CH}_3\text{NH}_2 + \text{H}_2\text{O} \Leftrightarrow (\text{CH}_3\text{NH})_1(\text{H}_2\text{O})_1$	-7.73	-22.25	-1.10
$(\text{CH}_3)_2\text{NH} + \text{H}_2\text{O} \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{O})_1$	-6.58	-23.75	0.50
$\text{H}_2\text{SO}_4 + \text{H}_2\text{O} \Leftrightarrow (\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1$	-11.76 ^a	-31.80 ^a	-2.28 ^a
$(\text{CH}_3\text{NH})_1(\text{H}_2\text{O})_1 + \text{H}_2\text{O} \Leftrightarrow (\text{CH}_3\text{NH})_1(\text{H}_2\text{O})_2$	-8.70	-34.42	1.56
$[(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{O})_1 + \text{H}_2\text{O} \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{O})_2$	-8.77	-34.74	1.59
$(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1 + \text{H}_2\text{O} \Leftrightarrow (\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2$	-12.57 ^a	-32.08 ^a	-3.00 ^a
$(\text{CH}_3\text{NH})_1(\text{H}_2\text{SO}_4)_1 + \text{H}_2\text{O} \Leftrightarrow (\text{CH}_3\text{NH})_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1$	-13.02	-32.50	-3.33
$[(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{SO}_4)_1 + \text{H}_2\text{O} \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1$	-12.65	-30.11	-3.67
$(\text{NH}_3)_1(\text{H}_2\text{SO}_4)_1 + \text{H}_2\text{O} \Leftrightarrow (\text{NH}_3)_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1$	-10.96 ^a	-32.03 ^a	-1.41 ^a
$(\text{CH}_3\text{NH})_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1 + \text{H}_2\text{O} \Leftrightarrow (\text{CH}_3\text{NH})_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2$	-13.85	-34.66	-3.52
$[(\text{CH}_3)_3\text{N}]_1(\text{H}_2\text{SO}_4)_1 + \text{H}_2\text{O} \Leftrightarrow [(\text{CH}_3)_3\text{N}]_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1$	-10.88	-32.51	-1.19
$[(\text{CH}_3)_3\text{N}]_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1 + \text{H}_2\text{O} \Leftrightarrow [(\text{CH}_3)_3\text{N}]_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2$	-10.74	-32.76	-0.97
$[(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1 + \text{H}_2\text{O} \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2$	-12.66	-36.13	-1.89
$(\text{NH}_3)_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1 + \text{H}_2\text{O} \Leftrightarrow (\text{NH}_3)_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2$	-11.92 ^a	-32.34 ^a	-2.28 ^a
$(\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH})_1 + \text{H}_2\text{O} \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH})_1(\text{H}_2\text{O})_1$	-10.50	-31.47	-1.13
$(\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}]_1 + \text{H}_2\text{O} \Leftrightarrow (\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{O})_1$	-9.82	-30.09	-0.85
$(\text{H}_2\text{SO}_4)_2(\text{NH}_3)_1 + \text{H}_2\text{O} \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{NH}_3)_1(\text{H}_2\text{O})_1$	-11.68	-31.32	-2.31

^a [34].

It is also important to note that the difference in the absolute values of the dimerization free energies between PW91PW91 and RI-MP2/CC2 [8] is quite large. The absolute free energies of the formation $(\text{H}_2\text{SO}_4)(\text{amine})$ dimers obtained using these two methods deviate by 1.5–5 kcal mole⁻¹. This finding is quite surprising, because in the case of clusters composed of H_2SO_4 , NH_3 and H_2O the agreement between PW91PW91 and RI-MP2/CC2 is very good. RI-MP2/CC2 energies [32] are higher than those produced by PW91PW91; however, they were obtained neglecting the Basis Set Superposition Error (BSSE), which is significant and may reach several Kcal mole⁻¹. In contrast, the BSSE at the DFT level with large basis sets is very small, and seldom exceed 0.5 kcal mole⁻¹. This means that absolute RI-MP2/CC2 reaction free energies [32] would be significantly lower, and thus, in better agreement with the DFT results in the case, when the BSSE in the previous RI-MP2/CC2 work [32] is corrected. It is important to note that while BSSE affect mainly the absolute values, the basis set dependency of the MP2 calculations exceeding 6 kcal mole⁻¹ in the case of $(\text{CH}_3)_3\text{N} + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{CH}_3)_3\text{N}(\text{H}_2\text{SO}_4)$ reaction [32,33] and anharmonic correction are essential sources of uncertainties in both absolute and relative energies. These uncertainties may significantly affect the conclusions about the role of amines in the atmospheric nucleation, and, therefore, further research is needed in order to reach a final conclusion about the importance of amines for atmospheric nucleation.

Table 2. Comparison of changes in enthalpies ΔH (kcal mole⁻¹), entropies ΔS (cal mole⁻¹ K⁻¹), and Gibbs free energies ΔG (kcal mole⁻¹) associated with formation of $(\text{CH}_3\text{NH}_2)_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$, $((\text{CH}_3)_2\text{NH})_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ and $((\text{CH}_3)_3\text{N})_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ complexes via the attachment of amines with those associated with the formation of $(\text{NH}_3)_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ at temperature of 298.15K and pressure of 101.3 KPa.

	ΔH	ΔS	ΔG
$(\text{H}_2\text{SO}_4)(\text{H}_2\text{O}) + \text{CH}_3\text{NH} \Leftrightarrow (\text{CH}_3\text{NH})_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1$	-21.66	-32.11	-12.08
$(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1 + (\text{CH}_3)_2\text{NH} \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1$	-22.24	-31.78	-12.76
$(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1 + (\text{CH}_3)_3\text{N} \Leftrightarrow [(\text{CH}_3)_3\text{N}]_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1$	-19.37	-35.69	-8.73
$(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1 + \text{NH}_3 \Leftrightarrow (\text{NH}_3)_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_1$	-15.91 ^a	-30.23 ^a	-6.90 ^a
$(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2 + \text{CH}_3\text{NH} \Leftrightarrow (\text{CH}_3\text{NH})_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2$	-22.94	-34.69	-12.59
$(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2 + (\text{CH}_3)_2\text{NH} \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2$	-22.33	-35.84	-11.65
$(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2 + (\text{CH}_3)_3\text{N} \Leftrightarrow [(\text{CH}_3)_3\text{N}]_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2$	-17.51	-36.37	-6.66
$(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2 + \text{NH}_3 \Leftrightarrow (\text{NH}_3)_1(\text{H}_2\text{SO}_4)_1(\text{H}_2\text{O})_2$	-15.27 ^a	-30.49 ^a	-6.18 ^a
$(\text{H}_2\text{SO}_4)_1(\text{CH}_3\text{NH})_1 + \text{CH}_3\text{NH} \Leftrightarrow (\text{H}_2\text{SO}_4)_1(\text{CH}_3\text{NH})_2$	-15.93	-39.96	-4.02
$(\text{H}_2\text{SO}_4)_1[(\text{CH}_3)_2\text{NH}]_1 + (\text{CH}_3)_2\text{NH} \Leftrightarrow (\text{H}_2\text{SO}_4)_1[(\text{CH}_3)_2\text{NH}]_2$	-14.53	-35.61	-3.92
$(\text{H}_2\text{SO}_4)_1[(\text{CH}_3)_3\text{N}] + (\text{CH}_3)_3\text{N} \Leftrightarrow (\text{H}_2\text{SO}_4)_1[(\text{CH}_3)_3\text{N}]_2$	-14.18	-35.64	-3.56
$(\text{H}_2\text{SO}_4)_1(\text{NH}_3)_1 + \text{NH}_3 \Leftrightarrow (\text{H}_2\text{SO}_4)_1(\text{NH}_3)_2$	-13.68	-29.96	-4.74
$(\text{H}_2\text{SO}_4)_2 + \text{CH}_3\text{NH} \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH})_1$	-31.65	-40.13	-19.69
$(\text{H}_2\text{SO}_4)_2 + (\text{CH}_3)_2\text{NH} \Leftrightarrow (\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}]$	-32.56	-41.79	-20.10
$(\text{H}_2\text{SO}_4)_2 + \text{NH}_3 \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{NH}_3)$	-25.67 ^a	-39.68 ^a	-13.83 ^a
$(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_1 + \text{CH}_3\text{NH} \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH})_1(\text{H}_2\text{O})_1$	-27.72	-34.60	-17.40
$(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_1 + (\text{CH}_3)_2\text{NH} \Leftrightarrow (\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{O})_1$	-27.94	-34.89	-17.55
$(\text{H}_2\text{SO}_4)_2(\text{H}_2\text{O})_1 + \text{NH}_3 \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{NH}_3)_1(\text{H}_2\text{O})_1$			-15.9 ^b
$(\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH})_1 + \text{CH}_3\text{NH} \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH})_2$	-20.13	-28.86	-11.52
$(\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}]_1 + (\text{CH}_3)_2\text{NH} \Leftrightarrow (\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}]_2$	-24.45	-36.25	-13.64
$(\text{H}_2\text{SO}_4)_2(\text{NH}_3)_1 + \text{NH}_3 \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{NH}_3)_2$	-18.16	-19.87	-8.74
$(\text{H}_2\text{SO}_4)_3 + \text{CH}_3\text{NH} \Leftrightarrow (\text{H}_2\text{SO}_4)_3(\text{CH}_3\text{NH})_1$	-32.44	-32.08	-22.88
$(\text{H}_2\text{SO}_4)_3 + (\text{CH}_3)_2\text{NH} \Leftrightarrow (\text{H}_2\text{SO}_4)_3[(\text{CH}_3)_2\text{NH}]_1$	-31.63	-30.68	-22.48
$(\text{H}_2\text{SO}_4)_3 + \text{NH}_3 \Leftrightarrow (\text{H}_2\text{SO}_4)_3(\text{NH}_3)_1$	-25.58	-32.17	-16.01
$\text{CH}_3\text{NH} + \text{CH}_3\text{NH} \Leftrightarrow (\text{CH}_3\text{NH})_2$	-4.93	-21.07	1.35
$(\text{CH}_3\text{NH})_2 + \text{CH}_3\text{NH} \Leftrightarrow (\text{CH}_3\text{NH})_3$	-3.17	-24.50	4.13
$(\text{CH}_3)_2\text{NH} + (\text{CH}_3)_2\text{NH} \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_2$	-2.83	-23.58	4.20
$[(\text{CH}_3)_2\text{NH}]_2 + \text{CH}_3\text{NH} \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_3$	-3.83	-32.22	5.77

^a [34]; ^b [30].

Table 3. Comparison of changes in enthalpies ΔH (kcal mole⁻¹), entropies ΔS (cal mole⁻¹ K⁻¹), and Gibbs free energies ΔG (kcal mole⁻¹) associated with formation of $(\text{CH}_3\text{NH}_2)_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$, $((\text{CH}_3)_2\text{NH})_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ and $((\text{CH}_3)_3\text{N})_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ complexes via the attachment of the sulfuric acid with those associated with the formation of $(\text{NH}_3)_m(\text{H}_2\text{SO}_4)_n(\text{H}_2\text{O})_k$ at temperature of 298.15K and pressure of 101.3 KPa.

	ΔH	ΔS	ΔG
$\text{CH}_3\text{NH}_2 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{CH}_3\text{NH})_1 (\text{H}_2\text{SO}_4)_1$	-20.40 (-20.87)	-31.42 (-36.62)	-11.03 (-9.95)
$(\text{CH}_3)_2\text{NH} + \text{H}_2\text{SO}_4 \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_1 (\text{H}_2\text{SO}_4)_1$	-21.36 (-24.73)	-33.48 (-37.14)	-11.38 (-13.66) -7.28*
$(\text{CH}_3)_3\text{N} + \text{H}_2\text{SO}_4 \Leftrightarrow [(\text{CH}_3)_3\text{N}]_1 (\text{H}_2\text{SO}_4)_1$	-20.58 (-26.01)	-33.61 (-36.08)	-10.56 (-15.26)
$\text{NH}_3 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{NH}_3)_1 (\text{H}_2\text{SO}_4)_1$	-16.72 ^a	-30.01 ^a	-7.77 ^a
$(\text{CH}_3\text{NH})(\text{H}_2\text{O}) + (\text{H}_2\text{SO}_4) \Leftrightarrow (\text{CH}_3\text{NH})_1 (\text{H}_2\text{SO}_4)_1 (\text{H}_2\text{O})_1$	-25.69	-13.91	-13.26
$[(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{O})_1 + (\text{H}_2\text{SO}_4) \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_1 (\text{H}_2\text{SO}_4)_1 (\text{H}_2\text{O})_1$	-27.43	-39.84	-15.55
$(\text{CH}_3\text{NH})_1 (\text{H}_2\text{O})_2 + (\text{H}_2\text{SO}_4) \Leftrightarrow (\text{CH}_3\text{NH})_1 (\text{H}_2\text{SO}_4)_1 (\text{H}_2\text{O})_2$	-30.83	-41.91	-18.34
$[(\text{CH}_3)_2\text{NH}]_1 (\text{H}_2\text{O})_2 + (\text{H}_2\text{SO}_4) \Leftrightarrow [(\text{CH}_3)_2\text{NH}]_1 (\text{H}_2\text{SO}_4)_1 (\text{H}_2\text{O})_2$	-31.32	-41.23	-19.02
$(\text{H}_2\text{SO}_4)_1(\text{CH}_3\text{NH})_1 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH})_1$	-27.42	-44.17	-14.25
$(\text{H}_2\text{SO}_4)_1[(\text{CH}_3)_2\text{NH}]_1 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}]_1$	-27.36 (-32.70)	-43.77 (-44.97)	-14.30 (-19.29)
$(\text{H}_2\text{SO}_4)_1[(\text{CH}_3)_3\text{N}]_1 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_3\text{N}]_1$	-22.88	-41.79	-10.41
$(\text{H}_2\text{SO}_4)_1(\text{NH}_3)_1 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{NH}_3)_1$	-25.11 ^a	-45.14 ^a	-11.65 ^a
$(\text{H}_2\text{SO}_4)_1(\text{CH}_3\text{NH})_1(\text{H}_2\text{O})_1 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH})_1 (\text{H}_2\text{O})_1$	-24.91	-43.14	-12.05
$(\text{H}_2\text{SO}_4)_1 [(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{O})_1 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}]_1(\text{H}_2\text{O})_1$	-24.54	-43.76	-11.49
$(\text{H}_2\text{SO}_4)_1(\text{NH}_3)_1(\text{H}_2\text{O})_1 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_2 (\text{NH}_3)_1(\text{H}_2\text{O})_1$	-25.83	-44.42	-12.59
$(\text{H}_2\text{SO}_4)_1 (\text{CH}_3\text{NH})_2 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH})_2$	-31.62	-33.06	-21.76
$(\text{H}_2\text{SO}_4)_1[(\text{CH}_3)_2\text{NH}]_2 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}]_2$	-37.28	-44.41	-24.04
$(\text{H}_2\text{SO}_4)_1 (\text{NH}_3)_2 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_2(\text{NH}_3)_2$	-29.59	-46.77	-15.66
$(\text{H}_2\text{SO}_4)_2(\text{CH}_3\text{NH})_1 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_3(\text{CH}_3\text{NH})_1$	-17.05	-35.39	-6.50
$(\text{H}_2\text{SO}_4)_2[(\text{CH}_3)_2\text{NH}]_1 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_3[(\text{CH}_3)_2\text{NH}]_1$	-15.33	-32.34	-5.69
$(\text{H}_2\text{SO}_4)_2(\text{NH}_3)_1 + \text{H}_2\text{SO}_4 \Leftrightarrow (\text{H}_2\text{SO}_4)_3(\text{NH}_3)_1$	-16.20	-35.93	-5.49

^a [34];* [33]; () [32].

4. Conclusions

In the present paper, the hydrogen-bonded complexes of binary sulfuric acid-water clusters with methylamine, dimethylamine and trimethylamine—common atmospheric organic species, vegetation products and laboratory impurities, have studied using the computational quantum methods. The present study shows that amines form strongly hydrogen-bonded complexes with the pre-nucleation sulfuric acid-water clusters. The replacement of ammonia with amines leads to a moderately large enhancement in the stabilization of pre-nucleation clusters and sulfuric acid- pre-nucleation clusters

bonding energies. However, the difference in the formation free energies between the critically important $(\text{H}_2\text{SO}_4)(\text{amine}) + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{H}_2\text{SO}_4)_2(\text{amine})$ and $(\text{H}_2\text{SO}_4)(\text{NH}_3) + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{H}_2\text{SO}_4)_2(\text{NH}_3)$ reactions is not large enough to account for the large (a factor of 10^2 – 10^3 [37–42]) difference in atmospheric typical concentrations of amines and ammonia. This leads us to a logical conclusion that under atmospheric conditions the formation of $(\text{H}_2\text{SO}_4)_2(\text{amine})$ is a limiting stage. This indicates that under typical atmospheric conditions the stabilizing effect of amines is unlikely to exceed that of ammonia.

We also found that the difference in the dimerization free energies between the present study and earlier work [32] is considerable. There exist several sources of uncertainties, the basis set dependency of the MP2 calculations, which exceeds 6 kcal mole^{-1} in the case of $(\text{CH}_3)_3\text{N} + \text{H}_2\text{SO}_4 \rightleftharpoons (\text{CH}_3)_3\text{N}(\text{H}_2\text{SO}_4)$ reaction [32,33], the vibrational anharmonicity, moderately large BSSE in the MP2/CC2 study [32] and possible problems of the PW91PW91 method in describing the hydrogen bonding. The aforementioned uncertainties directly affect the conclusions about the importance of amines for the atmospheric nucleation. It is important to note the qualitative conclusions appear to be quite sensitive to moderately large differences between calculated thermodynamic data of the present study and Kurten *et al.* [32]. While the present more comprehensive study concludes that the presence of amines does not enhance the cluster stability enough to overcome a concentration difference (in favour of ammonia) of around 2–3 orders of magnitude, the predictions of Kurten *et al.* [32], which are based on the dimerization free energies only, leads to the opposite conclusion. In contrast to [32], the recent experimental study [37] shows that in the case of trimethylamine the threshold $[\text{H}_2\text{SO}_4]$ needed to produce the unity nucleation rate ($[\text{H}_2\text{SO}_4]$ of 10^6 – 10^7 cm^{-3}) and the number of precursor molecules in the critical cluster ($n_{\text{H}_2\text{SO}_4} = 4$ – 6 ; $n_{\text{TMA}} = 1$) are surprisingly similar to those found in the ammonia (NH_3) ternary nucleation study [51]. At lower RH some enhancement in nucleation rates due to trimethylamine was observed; however, its value was up to an order of magnitude only. The recent experimental study [37] agrees with our theoretical results and supports our conclusion that under typical atmospheric conditions the stabilizing effect of amines is unlikely to exceed that of ammonia. Further computations using the high level *ab initio* or compound methods taking both the BSSE and anharmonic correction into accounts are needed to address these issues and to clarify the role of amines in the atmospheric nucleation.

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References

1. Wilson, C.T.R. Condensation of water vapour in the presence of dust-free air and other gases. *Phil. Trans. R. Soc. Lond. A* **1897**, *189*, 265–307.
2. Becker, R.; Doring, W. Kinetische Behandlung der Keimbildung in übersättigten Dämpfen. *Ann. Physik* **1935**, *24*, 719–752.

3. Charlson, R.J.; Seinfeld, J.H.; Nenes, A.; Kulmala, M.; Laaksonen, A.; Facchini, M.C. Atmospheric science: Reshaping the theory of cloud formation. *Science* **2001**, *292*, 2025–2026.
4. Kulmala, M. How particles nucleate and grow. *Science* **2003**, *302*, 1000–1001.
5. Saxon, D.; Diaz-Sanchez, D. Air pollution and allergy: You are what you breathe. *Nature Immunol.* **2005**, *6*, 223–226.
6. Penttinen, P.; Timonen, K.L.; Tiittanen, P.; Mirme, A.; Ruuskanen, J.; Pekkanen, J. Ultrafine particles in urban air and respiratory health among adult asthmatics. *Euro. Respir. J.* **2001**, *17*, 428–435.
7. Oberdorster, G.; Utell, M. Ultrafine particles in the urban air: To the respiratory tract—Ang beyond? *Environ. Health. Persp.* **2002**, *110*, A440–A441.
8. Hamill, P.; Turco, R.P.; Kiang, C.S.; Toon, O.B.; Whitten, R.C. An analysis of various nucleation mechanisms for sulfate particles in the stratosphere. *J. Aerosol Sci* **1982**, *13*, 561–585.
9. Berndt, T.; Böge, O.; Stratmann, F.; Heintzenberg, J.; Kulmala, M. Rapid formation of sulfuric acid particles at near-atmospheric conditions. *Science* **2005**, *307*, 698–700.
10. Yu, F.; Turco R.P. Ultrafine aerosol formation via ion-mediated nucleation. *Geophys. Res. Lett.* **2000**, *27*, 883–886.
11. Napari, I.; Noppel, M.; Vehkamäki, H.; Kulmala, M. Parametrization of ternary nucleation rates for H₂SO₄-NH₃-H₂O vapors. *J. Geophys. Res.* **2002**, *107*, 4381–4386.
12. Yu, F. Effect of ammonia on new particle formation: A kinetic H₂SO₄-H₂O-NH₃ nucleation model constrained by laboratory measurements. *J. Geophys. Res.* **2006**, *111*, D01204.
13. Merikanto, J.; Napari, I.; Vehkamäki, H.; Anttila, T.; Kulmala, M. New parameterization of sulfuric acid-ammonia-water ternary nucleation rates at tropospheric conditions. *J. Geophys. Res.* **2007**, *112*, D1520.
14. O'Dowd, C.D.; Jimenez, J.L.; Bahreini, R.; Flagan, R.C.; Seinfeld, J.H.; Hämerl, K.; Pirjola, L.; Kulmala, M.; Jennings, S.G.; Hoffmann, T. Marine aerosol formation from biogenic iodine emissions. *Nature* **2002**, *417*, 632–636.
15. Zhang, R.; Suh, I.; Zhao, J.; Zhang, D.; Fortner, E.C.; Tie, X.; Molina, L.T.; Molina, M.J. Atmospheric new particle formation enhanced by organic acids. *Science* **2004**, *304*, 1487–1490.
16. Sun, J.; Ariya, P.A. Atmospheric organic and bio-aerosols as cloud condensation nuclei (CCN): A review. *Atmos. Environ.* **2006**, *40*, 795–807.
17. Adachi, K.; Buseck, P.R. Internally mixed soot, sulfates, and organic matter in aerosol particles from Mexico City. *Atmos. Chem. Phys.* **2008**, *8*, 6469–6487.
18. Smith, J.N.; Dunn, M.J.; VanReken, T.M.; Iida, K.; Stolzenburg, M.R.; McMurry, P.H.; Huey, L.G. Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: Evidence for an important role for organic species in nanoparticle growth. *Geophys. Res. Lett.* **2008**, *35*, L04808.
19. Sellegri, K.; Hanke, M.; Umann, B.; Arnold, F.; Kulmala, M. Measurements of organic gases during aerosol formation events in the boreal forest atmosphere during QUEST. *Atmos. Chem. Phys.* **2005**, *5*, 373–384.
20. Boy, M.; Karl, T.; Turnipseed, A.; Mauldin, R.L.; Kosciuch, E.; Greenberg, J.; Rathbone, J.; Smith, J.; Held, A.; Barsanti, K.; *et al.* New particle formation in the front range of the Colorado Rocky Mountains. *Atmos. Chem. Phys.* **2007**, *7*, 15581–15617.

21. Bonn, B.; Hirsikko, A.; Hakola, H.; Kurtén, T.; Laakso, L.; Boy, M.; Dal Maso, M.; Mäkelä, J.M.; Kulmala, M. Ambient sesquiterpene concentration and its link to air ion measurements. *Atmos. Chem. Phys.* **2007**, *7*, 2893–2916.
22. Parshintsev, J.; Nurmi, J.; Kilpeläinen, I.; Hartonen, K.; Kulmala, M.; Riekkola, M.-L. Preparation of β -caryophyllene oxidation products and their determination in ambient aerosol samples. *Analytic. Bioanalytic. Chem* **2008**, *390*, 3, 913–927.
23. Bonn, B.; Kulmala, M.; Riipinen, I.; Sihto, S.-L.; Ruuskanen, T.M. How biogenic terpenes govern the correlation between sulfuric acid concentrations and new particles formation. *J. Geophys. Res. D Atmos.* **2008**, *113*, D12209.
24. Nadykto, A.B.; Al Natsheh, A.; Yu, F.; Mikkelsen, K.V.; Ruuskanen, J. Quantum nature of the sign preference in ion-induced nucleation. *Phys. Rev. Lett.* **2006**, *98*, 125701.
25. Nadykto, A.B.; Al Natsheh, A.; Yu, F.; Mikkelsen, K.V.; Ruuskanen, J. Sulfuric acid and sulfuric acid hydrates in the gas phase: A DFT investigation. *J. Phys. Chem. A* **2004**, *108*, 8914–8923.
26. Nadykto, A.B.; Du, H.; Yu, F. Quantum DFT and DF-DFT study of vibrational spectra of sulfuric acid, sulfuric acid monohydrate, formic acid and its cyclic dimer. *Vibr. Spectr.* **2007**, *44*, 2, 286–296.
27. Lewandowski, H.; Koglin, E.; Meier, R.J. Computational study of the infrared spectrum of acetic acid, its cyclic dimer, and its methyl ester. *Vibr. Spec.* **2005**, *39*, 15–22.
28. Ding, C.-G.; Laasonen, K.; Laaksonen, A. Two sulfuric acids in small water clusters. *J. Phys. Chem. A* **2003**, *107*, 8648–8658.
29. Kurtén, T.; Sundberg, M.R.; Vehkamäki, H.; Noppel, M.; Blomqvist, J.; Kulmala, M. Ab initio and density functional theory reinvestigation of gas-phase sulfuric acid monohydrate and ammonium hydrogen sulfate. *J. Phys. Chem. A* **2006**, *110*, 7178–7188.
30. Kurtén, T.; Torpo, L.; Ding, C.-G.; Vehkamäki, H.; Sundberg, M.R.; Laasonen, K.; Kulmala, M. A density functional study on water-sulfuric acid-ammonia clusters and implications for atmospheric cluster formation. *J. Geophys. Res.* **2007**, *112*, D04210.
31. Ortega, I.K.; Kurtén, T.; Vehkamäki, H.; Kulmala, M. The role of ammonia in sulfuric acid ion induced nucleation. *Atmos. Chem. Phys.* **2008**, *8*, 2859–2867.
32. Kurtén, T.; Loukonen, V.; Vehkamäki, H.; Kulmala, M. Amines are likely to enhance neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia. *Atmos. Chem. Phys.* **2008**, *8*, 4095–4103.
33. Kurtén, T.; Ortega, I.K.; Vehkamäki, H. The sign preference in sulfuric acid nucleation. *J. Mol. Structure: Theochem.* **2009**, *15901*, 169–176.
34. Nadykto, A.B.; Yu, F. Strong hydrogen bonding between atmospheric nucleation precursors and common organics. *Chem. Phys. Lett.* **2007**, *435*, 14–18.
35. Zhao, J.; Khalizov, A.; Zhang, R.; McGraw, R. Hydrogen-bonding interaction in molecular complexes and clusters of aerosol nucleation precursors. *J. Phys. Chem. A* **2009**, *113*, 680–689.
36. Nadykto, A.B.; Yu, F.; Herb, J. Towards understanding the sign preference in binary atmospheric nucleation. *Phys. Chem. Chem. Phys.* **2008**, *10*, 7073–7078.
37. Erupe, M.E.; Viggiano, A.A.; Lee, S.-H. The effect of trimethylamine on atmospheric nucleation involving H_2SO_4 . *Atmos. Chem. Phys. Disc.* **2006**, *10*, 27673–27693.

38. Kerminen, V.-M.; Petäjä, T.; Manninen, H.E.; Paasonen, P.; Nieminen, T.; Sipilä, M.; Junninen, H.; Ehn, M.; Gagné, S.; Laakso, L.; Riipinen, I.; *et al.* Atmospheric nucleation: Highlights of the EUCAARI project and future directions *Atmos. Chem. Phys.* **2010**, *10*, 10829–10848.
39. Berndt, T.; Stratmann, F.; Sipilä, M.; Vanhanen, J.; Petäjä, T.; Mikkilä, J.; Grüner, A.; Spindler, G.; Lee Mauldin, R., III.; Curtius, J.; *et al.* Laboratory study on new particle formation from the reaction OH + SO₂: Influence of experimental conditions, H₂O vapour, NH₃ and the amine tert-butylamine on the overall process. *Atmos. Chem. Phys. Disc.* **2010**, *10*, 6447–6484.
40. Ge, X.; Wexler, A.S.; Clegg, S.L. Atmospheric amines—Part I. A review. *Atmos. Env.* **2011**, *45*, 524–546.
41. Ge, X.; Wexler, A.S.; Clegg, S.L. Atmospheric amines—Part II. Thermodynamic properties and gas/particle partitioning. *Atmos. Env.* **2011**, *45*, 561–577.
42. Bzdek, B.R.; Ridge, D.P.; Johnston, M.V. Amine exchange into ammonium bisulfate and ammonium nitrate nuclei. *Atmos. Chem. Phys.* **2010**, *10*, 3495–3508.
43. Angelino, A.; Suess, D.T.; Prather, K. Formation of aerosol particles from reactions of secondary and tertiary alkylamines: Characterization by aerosol rime-of-flight mass spectrometry. *Environ. Sci. Technol.* **2001**, *35*, 3130–3138.
44. Murphy, S.M.; Sorooshian, A.; Kroll, J.H.; Ng, N.L.; Chhabra, P.; Tong, C.; Surratt, J.D.; Knipping, E.; Flagan, R.C.; Seinfeld, J.H. Secondary aerosol formation from atmospheric reactions of aliphatic amines. *Atmos. Chem. Phys.* **2007**, *7*, 2313–2337.
45. Makela, J.M.; Yli-Koivisto, S.; Hiltunen, V.; Seidl, W.; Swietlicki, E.; Teinila, K.; Sillanpaa, M.; Koponen, I.K.; Paatero, J.; Rosman, K.; Hameri, K. Chemical composition of aerosol during particle formation events in boreal forest. *Tellus* **2001**, *53B*, 380–393.
46. Cook, D.B. *Handbook of Computational Quantum Chemistry*; Oxford University Press: New York, NY, USA, 1998.
47. Kurtén, T.; Vehkamäki, H. Investigating atmospheric sulfuric acid-water-ammonia particle formation using quantum chemistry. *Adv. Quant. Chem.* **2008**, *55*, 407–427.
48. Cabaleiro-Lago, E.M.; Rios, M.A. Ab initio study of interactions in methylamine clusters. The significance of cooperative effects. *J. Chem. Phys.* **2000**, *112*, 2155–2163.
49. Cabaleiro-Lago, E.M.; Rios, M.A. An *ab initio* study of the interaction in dimethylamine dimer and trimer. *J. Chem. Phys.* **2000**, *113*, 9523–9531.
50. Sverdlov, L.M.; Kovner, M.A.; Krainov, E.P. *Vibrational Spectra of Polyatomic Molecules*; Wiley: New York, NY, USA, 1974.
51. Benson, D.; Markovich, A.; Lee, S. Atmospheric homogeneous nucleation of H₂SO₄ and H₂O. *Atmos. Chem. Phys. Discuss.* **2010**, *10*, 22395–22414.