Properties and Atmospheric Implication of Methylamine–Sulfuric Acid–Water Clusters

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Supporting Information

ABSTRACT: The presence of amines can increase aerosol formation rates. Most studies have been devoted to dimethylamine as the representative of amine; however, there have been a few works devoted to methylamine. In this study, theoretical calculations are performed on $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 0-3, n = 0-3) clusters. In addition to the structures and energetics, we focused on determining the following characteristics: (1) the growth mechanism, (2) the hydrate distributions and the influences of humidity and temperature, (3) Rayleigh scattering properties. We explored the cluster growth mechanism from a thermodynamics aspect by calculating the Gibbs free energy of adding a water or sulfuric acid molecule step by step at three atmospherically relevant temperatures. The relative ease of the reaction at each step is discussed. From the analysis of hydrate



distributions, we find that $CH_3NH_2(H_2SO_4)(H_2O)_2$, $CH_3NH_2(H_2SO_4)_2$, and $CH_3NH_2(H_2SO_4)_3$ are most likely to exist in the atmosphere. The general trend of hydration in all cases is more extensive with the growing relative humidity (RH), whereas the distributions do not significantly change with the temperature. Analysis of the Rayleigh scattering properties showed that both H_2SO_4 and H_2O molecules could increase the Rayleigh scattering intensities and isotropic mean polarizabilities, with greater influence by the sulfuric acid molecules. This work sheds light on the mechanism for further research on new particle formation (NPF) containing methylamine in the atmosphere.

INTRODUCTION

Atmospheric aerosols affect our life in a number of ways, in terms of their effect on health¹ and climate patterns.^{2,3} Aerosols arise to a large degree from particles formed through the condensation of gas-phase molecules.⁴ However, the very first steps of electrically neutral cluster formation are only roughly understood.⁵

Sulfuric acid is generally considered to play a key role in the atmospheric nucleation precursor, and water is likely to be involved, as its concentration exceeds that of other condensable gases, often by 8–10 orders of magnitude.⁶ However, 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,^{7–9} and other ternary species are also involved in nucleation. On the basis of experimental and modeling results, ternary bases such as ammonia and amines,^{10–19} as well as organics,^{20–23} enhance the nucleation rate. The role of charged particles (ion-induced nucleation)^{24–26} is expected to be minimal in the lower troposphere,^{8,27} although it might be

important in the upper troposphere and lower stratosphere.²⁸ Recent experimental results indicate that neutral mechanisms are likely to dominate nucleation, at least in boreal forest areas, with ion-induced nucleation playing only a small role.²⁹

Amines are common atmospheric species. There have been a number of experiments and observations studying the role of amines in NPF. On the basis of experimental results, ammonia and amines as base molecules stabilize small particles in a process called base stabilization, and they can enhance aerosol nucleation rates by a factor of 100-1000 in the lower troposphere.⁷ Yu et al.¹⁵ found that both the size and concentrations of $(CH_3)_2NH-H_2SO_4$ clusters increased with the concentrations of constituent molecules. Dimethylamine enhanced the concentrations of clusters larger than 1 nm by a factor of 5 and the concentrations of clusters larger than 2 nm by approximately 2 orders of magnitude. The enhancement

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factors of amines increased with their relative basicity. Zhang et al.^{30,31} found that although the typical concentrations of amines are 2-3 orders of magnitude smaller than that of ammonia, they can reach hundreds of micrograms per cubic meter or many parts per million in areas of large industrial, sewage treatment, or animal husbandry activity. In these places, amines may participate in gas-phase reactions and in heterogeneous reactions with a condensed or aerosol phase.³¹ On the basis of the theoretical results, Kurtén et al.¹² found that amines bind more strongly to H_2SO_4 and HSO_4^- than to ammonia because of their higher proton affinities, and they have a greater effect on enhancing overall nucleation in comparison to ammonia. However, Nadykto et al.³² agreed that amines are more effective than ammonia in enhancing nucleation but stated that the difference in binding energies is insufficient to overcome ammonia's mass-balance advantage. Thus, they concluded that ammonia should play a larger role in new particle formation. Furthermore, Loukonen et al.³³ found that dimethylamine's strong binding could promote the growth of clusters including sulfuric acid. As mentioned above, most experimental and computational studies have been devoted to dimethylamine as the representative amine and there have been only a few works devoted to methylamine. The methylamine in the atmosphere comes mainly from animal husbandry, fish processing, industry, automobiles, sewage treatment, biomass burning, bacteria culture, and oceans.¹⁶ Its global emission is approximately 83 \pm 26 Gg N a⁻¹, in comparison to 50000 \pm 30000 Gg N a⁻¹ for ammonia, 33 ± 19 Gg N a⁻¹ for dimethylamine, and 169 ± 33 Gg N a⁻¹ for trimethylamine.³⁴

It has recently become evident that the atmosphere contains a large pool of neutral molecular clusters with sizes below 2 nm.^{29,35–37} The concentration reported is in the range of 100– 100000 cm⁻³.^{35–37} For individual molecules, clusters, and particles with diameters much lower than the wavelength of the incoming radiation, the phenomenon of Rayleigh scattering is apparent.^{38,39} However, the current understanding of the lightscattering properties of this pool of clusters is lacking.

In this work, we study $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 0-3, n = 0-3) clusters using a basin-hopping (BH) algorithm with density functional theory (DFT). To understand the very first steps of particle formation, i.e., the clustering of the first few molecules from the gas phase, the Gibbs free energies of adding a water or sulfuric acid molecule step by step at three atmospherically relevant temperatures were calculated. The results give detailed information on the structures and relative stabilities of the clusters, which can be used in the direct modeling of the particle formation processes. For obtaining information on which clusters are dominant in different atmospheric environments, we analyzed the hydrate distributions and the influence of humidity and temperature. In addition, the Rayleigh scattering properties, including isotropic mean polarizabilities, anisotropic polarizabilities, depolarization ratios, and Rayleigh scattering intensities of these atmospheric prenucleation clusters, have also been discussed.

METHODS

The BH algorithm coupled with DFT was employed to search for low-lying structures of the $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 0-3, n = 0-3) system. The BH algorithm has been turned out to be efficient for exploring atomic and molecular systems.^{40–45} This algorithm fundamentally combined the MC algorithm and local optimization procedures. Two steps were included in this method: a new structure was generated via the random displacement of molecules and then optimized to the local minimum, and then this local energy minimum was used as a criterion to accept the initially generated structure spaces with Boltzmann weight at a finite temperature. The number of BH searches ranged from 2 to 5 according to the cluster size. Every search was performed with 200-300 MC steps with 200 randomly generated initial structures. At each MC step, all of the molecules were translated and rotated, and the maximum translational and rotational displacements were 2 Å and $\pi/2$, respectively. To prevent the divergence of the clusters, we compiled a function to check whether the intermolecular distances exceeded the range defined after the structure perturbation caused by the MC sampling. After each MC step, this function automatically determined whether the molecule moved more than 3 Å, which could cause the optimization to fail. If a large divergence occurred, then this function automatically moved the molecules closer together. The atoms in different molecules were not permitted to be closer than 2 Å to prevent the self-consistent field calculation from failing to converge. During this process, generalized gradient approximation in the Perdue-Burke-Ernzerhof (PBE)⁴⁶ functional and the double-numerical plus d functions (DND) basis set, implemented in the DMol³ code,⁴⁷ were chosen for structure optimization. Then the top 50 lowest-lying isomers of each size were reoptimized using the functional PW91⁴⁸ and the 6-311++G(3df,3pd) basis set for all elements using the Gaussian 09 software package.⁴⁹ In this study, we only focus on the lowest-energy structures we calculated. There is no imaginary frequency for the optimized structures. Finally, single-point energies were calculated at the DF-MP2-F12/vdzf12 level of theory, implemented in Molpro 2010.1.^{50,51} Zeropoint corrected energies were evaluated using thermodynamic corrections at the PW91/6-311++G(3df,3pd) level of theory. The choice of the PW9148 computational method is based on its satisfactory performance on atmospheric clusters, including the prediction of Gibbs free energies and structural characteristics, 26,32,52-56 and the availability of a large amount of data for different atmospheric species/clusters computed at the PW91/ 6-311+G(3df,3pd) level of theory for comparison.⁵⁷⁻⁶³ We have done a benchmark about the methods employed in atmospheric cluster calculations. Detailed information is given in the Supporting Information.

The Gibbs free energies of cluster formation have been calculated at three atmospherically relevant temperatures: the temperature of the tropopause (216.65 K), the average temperature of the troposphere (273.15 K), and room temperature (298.15 K).¹⁹ The Gibbs free energies $\Delta G(T)$ and binding energies $\Delta E(T)$ were obtained by subtraction between the energy of the products and reactants. Standard state conditions are 1 atm and the stated temperature.

In addition, to find a suitable methodology for calculating the optical properties of $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 0-3, n = 0-3) clusters, a DFT functional and basis set analysis was performed for the smallest cluster subunits: H_2SO_4 , CH_3NH_2 , and H_2O . The performance of calculating the mean isotropic polarizability was tested using CCSD(T), CAM-B3LYP, B3LYP, M06-2X, and PW91 with various correlation consistent basis sets. On the basis of the results of this calculation, we found that CAM-B3LYP/aug-cc-pVDZ is a good compromise between efficiency and accuracy, yielding good agreement with that of CCSD(T). A complete basis set and functional analysis is available in the Supporting Information. Furthermore, the CAM-B3LYP functional has been successfully employed in the



Figure 1. Global minima of $CH_3NH_2(H_2O)_n$ (n = 1-3) calculated at the PW91/6-311++G(3df,3pd) level of theory.



Figure 2. Global minima of $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 1-3, n = 0-3) calculated at the PW91/6-311++G(3df,3pd) level of theory.

calculation of various response properties such as polarizabilities,^{64,65} absorption properties,⁶⁶ van der Waals C6 coefficients,⁶⁴ and natural⁶⁷ and magnetic circular dichroism.^{68,69} Very recently, CAM-B3LYP showed adequate performance in calculating the hyper-Rayleigh scattering of large chromophores.⁷⁰ All presented calculated properties are given in atomic units (au).

Optical properties such as depolarization ratios and Rayleigh scattering intensities for natural light were then calculated. For the elastic Rayleigh scattering the depolarization ratio of natural light σ_n , the light scattering intensities R_n , and the isotropic mean polarizabilities $\overline{\alpha}$ as well as the anisotropic polarizabilities $\Delta \alpha$ are calculated as

$$\sigma_{\rm n} = \frac{6(\Delta \alpha)^2}{45(\overline{\alpha})^2 + 7(\Delta \overline{\alpha})^2} \tag{1}$$

$$R_{\rm n} = 45(\overline{\alpha})^2 + 13(\Delta \alpha)^2 \tag{2}$$

$$\overline{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{3}$$

$$(\Delta \alpha)^{2} = \frac{1}{2} [(\alpha_{xx} - \alpha_{yy})^{2} + (\alpha_{yy} - \alpha_{zz})^{2} + (\alpha_{zz} - \alpha_{xx})^{2}] + 3 [(\alpha_{xy})^{2} + (\alpha_{xz})^{2} + (\alpha_{yz})^{2}]$$
(4)

RESULTS AND DISCUSSION

A. Structures and Energetics. Figures 1 and 2 show the structures of the global minima of $CH_3NH_2(H_2O)_n$ (n = 1-3) and $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 1-3, n = 0-3), respectively. The structures were optimized at the PW91/6-311++G(3df,3pd) level. As shown in these two figures, there is no proton transfer in the $CH_3NH_2(H_2O)_n$ clusters (n = 1-3), whereas there is one proton transfer in the clusters $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 1-3, n = 0-3). If there is a sulfuric acid molecule, then one proton transfers from the CH_3NH_2 molecule to the H_2SO_4 molecule, forming HSO_4^- and $CH_3NH_3^+$. The number of proton transfers in each cluster, as obtained from electronic structure calculations, is summarized in Table 1. There are one to two proton transfers in the

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

	n = 0	n = 1	n = 2	n = 3
$CH_3NH_2(H_2O)_n$		0	0	0
$CH_3NH_2(H_2SO_4)(H_2O)_n$	1	1	1	2
$CH_3NH_2(H_2SO_4)_2(H_2O)_n$	1	1	2	2
$CH_3NH_2(H_2SO_4)_3(H_2O)_n$	1	2	2	

clusters of $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 1-3, n = 0-3) from Table 1. In addition, we can conclude that the larger the sizes of the clusters, the more proton transfers occur. Generally, proton transfer within a cluster can lead to additional stabilization of hydrates.

In addition, as shown in Figure 2d-k, in most of the clusters, sulfuric acid molecules contact with methylamine directly because of the acid-base reaction mechanism, expect for the

 $CH_3NH_2(H_2SO_4)(H_2O)_3$ cluster (as shown in Figure 2f), in which the water molecules separate the acid and base molecules to form bridging hydrogen bonds (HBs). In our study, we also got many local minima of the $CH_3NH_2(H_2SO_4)(H_2O)_3$ cluster in which the sulfuric acid contacts with methylamine directly. We selected the lowest-energy structure of these local minima (as shown in Figure 3b). Comparisons of structures and the energies of this local minimum and the global minimum are shown in Figure 3 and Table 2, respectively. As shown in Table

Table 2. Electronic Energies (*E*) and Gibbs Free Energies (*G*) of the Global Minimum and the Local Minimum of $CH_3NH_2(H_2SO_4)(H_2O)_3$ in kcal/mol

	Ε	G
global minimum	-642754.57	-642783.36
local minimum	-642754.25	-642782.21

2, the deviation of the electronic energies is smaller than 1 kcal/ mol. However, the deviation of the Gibbs free energies is relatively large at 1.15 kcal/mol. This may be due to the effects of temperature.

Recently Henschel et al. studied the hydration of sulfuric acid–dimethylamine clusters.⁷¹ The structural patterns of these two kinds of base clusters are consistent except for the $(H_2SO_4)(H_2O)_2$ -base, $(H_2SO_4)(H_2O)_3$ -base, and $(H_2SO_4)_2(H_2O)_3$ -base clusters. Unlike the case for the corresponding dimethylamine clusters, the water molecules in the $CH_3NH_2(H_2SO_4)_2(H_2O)_2$, $CH_3NH_2(H_2SO_4)(H_2O)_3$, and $CH_3NH_2(H_2SO_4)_2(H_2O)_3$ clusters distribute in a dispersed fashion. This may be due to the fact that methylamine is more weakly alkaline than dimethylamine, resulting in a loose connection of methylamine and sulfuric acid.

Moreover, as shown in Table 3, the energies of the single sulfuric acid cluster in this work are in qualitative agreement with previous studies.^{19,32} Our $\Delta G(298.15 \text{ K})$ values compare well with Nadykto et al.'s PW91/6-311++G(3df,3pd) results.³² In comaprison with the work of Bustos et al. (using a RI-MP2/aug-cc-pVDZ functional with scaled frequencies),¹⁹ we found the same global minima and relatively low difference in energies, which can be attributed to the levels of theory and basis sets used as well as the vibrational anharmonicity corrections, indicating that the calculation method we used performs well for molecule clusters.

B. Hydration of Methylamine Clusters. Table 4 shows the energy changes upon the stepwise addition of water to $CH_3NH_2(H_2SO_4)_m(H_2O)_{n-1}$ (m = 0-3, n = 1-4) at a standard state of 1 atm and three given temperatures.



Figure 3. Global minimum (a) and the local minimum (b) of $CH_3NH_2(H_2SO_4)(H_2O)_3$ calculated at the PW91/6-311++G(3df,3pd) level of theory.

Table 3. Comparison of the Gibbs Free Energy of Formation of Global Minima at T = 298.15 K in kcal/mol with Previous Literature Values for $CH_3NH_2(H_2SO_4)(H_2O)_n$, Where n = 0-2

	this work ^a	Bustos et al. ^b	Nadykto e al. ^c
$H_2SO_4 + CH_3NH_2$	-11.7834	-10.63	-11.03
$CH_3NH_2(H_2SO_4) + H_2O$	-3.5685	-3.53	-3.33
$CH_3NH_2(H_2SO_4)H_2O + H_2O$	-3.0943	-3.95	-3.52
$CH_3NH_2(H_2SO_4)(H_2O)_2 + H_2C_4$	-1.2304	0.23	
$CH_3NH_2(H_2SO_4)_2 + H_2O$	-0.9646		-1.13

^{*a*}DF-MP2-F12/VDZ-F12 and PW91/6-311++G(3df,3pd) without anharmonicity corrections. ^{*b*}Reference 19. RI-MP2/CBS with anharmonicity corrections. ^{*c*}Reference 32. PW91/6-311++G(3df,3pd) without anharmonicity corrections.

Table 4. Energy Change upon the Stepwise Addition of Water to $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 0-3, n = 0-3) at a Standard State of 1 atm and the Given Temperature in kcal/mol

n	$\Delta E(0 \text{ K})$	$\Delta G(216.65 \text{ K})$	$\Delta G(273.15 \text{ K})$	$\Delta G(298.15 \text{ K})$	
	$\mathrm{CH}_{3}\mathrm{NH}_{2}(\mathrm{H}_{2}\mathrm{O})_{n-1} + \mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{CH}_{3}\mathrm{NH}_{2}(\mathrm{H}_{2}\mathrm{O})_{n}$				
1	-5.6069	-0.8539	0.5058	1.0955	
2	-7.0061	-0.2542	1.6997	2.8753	
3	-8.2019	-2.2340	-0.3726	0.1258	
$CH_3NH_2(H_2SO_4)(H_2O)_{n-1} + H_2O \rightarrow CH_3NH_2(H_2SO_4)(H_2O)_n$					
1	-12.5419	-6.2492	-4.3853	-3.5685	
2	-12.3677	-5.8174	-3.9222	-3.0943	
3	-9.8072	-3.7653	-2.0019	-1.2304	
$CH_3NH_2(H_2SO_4)_2(H_2O)_{n-1} + H_2O \rightarrow CH_3NH_2(H_2SO_4)_2(H_2O)_n$					
1	-10.0811	-3.6653	-1.7882	-0.9646	
2	-10.4050	-4.5144	-2.7770	-2.0127	
3	-11.3083	-3.7099	-1.4045	-0.3890	
$\mathrm{CH}_{3}\mathrm{NH}_{2}(\mathrm{H}_{2}\mathrm{SO}_{4})_{3}(\mathrm{H}_{2}\mathrm{O})_{n-1} + \mathrm{H}_{2}\mathrm{O} \rightarrow \mathrm{CH}_{3}\mathrm{NH}_{2}(\mathrm{H}_{2}\mathrm{SO}_{4})_{3}(\mathrm{H}_{2}\mathrm{O})_{n}$					
1	-8.2278	-2.2027	-0.4189	0.3672	
2	-10.8970	-4.3512	-2.4539	-1.6237	

As shown in Table 4, for the CH₃NH₂-H₂O system, the free energies of addition of one water molecule at standard state are positive at T = 298.15 K, change from positive to negative at 273.15 K, and are all negative at T = 216.65 K. This result demonstrates that the free energy of association of water with methylamine is favorable at T = 216.65 K but not at higher temperatures, specifically at 298.15 K. However, this result does not imply that the $CH_3NH_2(H_2O)_n$ (n = 1-3) clusters never form at 298.15 K but rather that one would find a much smaller number of these hydrates in comparison to that at lower troposphere temperatures. The exact values depend on the initial concentrations of water and methylamine as well as the pressure. Moreover, from the trend of ΔG , adding another water molecule to the complex containing two water molecules is easier than the other two steps. This result is consistent with the lower binding energy of $CH_3NH_2(H_2O)_3$ in comparison to the other two clusters.

Table 4 shows that the associations of water with the clusters of methylamine and one sulfuric acid are favorable at these three temperatures. According to the data, the addition of a water molecule leads to an increase in molar Gibbs free energy, which shows that the subsequent addition of water molecules to an existing cluster is less thermodynamically favorable in comparison with the cluster of $CH_3NH_2(H_2SO_4)(H_2O)$.

For the cluster containing one methylamine and two sulfuric acid molecules, the energies for each hydration step are invariably negative. However, these hydration results tend to be somewhat higher than the hydration results of the clusters containing one methylamine and one sulfuric acid, implying that adding another sulfuric acid molecule makes the hydration of the cluster harder. In addition, adding another water molecule to the $CH_3NH_2(H_2SO_4)_2(H_2O)$ cluster exhibits a rather small Gibbs free energy. This result can be attributed to the extraordinary stability of the second hydrate.

The hydration energies for the cluster consisting of three sulfuric acid molecules are also found to be higher than those for the clusters containing one or two sulfuric acid molecules. The hydration energies of systems containing three sulfuric acid molecules derived from the electronic structure calculations follow the same pattern as the hydration energies of the clusters containing two sulfuric acid molecules.

Here we also compared the free energies of water molecule addition and structural patterns of $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 1-3, n = 0-3) and $((CH_3)_2NH)(H_2SO_4)_m(H_2O)_n$ (m = 1-3, n = 0-3)1-3, n = 0-3) clusters. The free energies of water molecule addition for $CH_3NH_2(H_2SO_4)(H_2O)_n$ (n = 0-3) and $CH_3NH_2(H_2SO_4)_3(H_2O)_n$ (n = 0-2) clusters increase with the number of water molecules, which is consistent with changes in dimethylamine clusters according to Henschel et al.'s work.⁷¹ The situations are quite different when both of the base clusters containing two sulfuric acid molecules are considered. Adding another water molecule to the cluster of $CH_3NH_2(H_2SO_4)_2(H_2O)$ exhibits a relatively low Gibbs free energy in comparison with $CH_3NH_2(H_2SO_4)_2$ and $CH_3NH_2(H_2SO_4)_2(H_2O)_2$, implying that the second hydrate is relatively stable, which is just the opposite with dimethylamine hydrate.

As in the analysis above, the $\Delta G(T)$ values of the formation of CH₃NH₂(H₂O)_n (n = 1-3) are all positive at 298.15 K, whereas the $\Delta G(T)$ values of the formation of CH₃NH₂(H₂SO₄)_m(H₂O)_n (m = 1-3, n = 0-3) are negative, implying that the H₂SO₄ molecule plays a crucial role in the hydration of the cluster containing CH₃NH₂ molecules in certain cases, such as addition of a water molecule to CH₃NH₂ at 298.15 K. In addition, the cluster containing one sulfuric acid molecule and one base molecule is slightly more strongly hydrated than the clusters containing multiple sulfuric acid molecules and one base molecule. Moreover, as shown in Table 4, the value of $\Delta G(T)$ decreases with decreasing temperature, indicating that the hydration of the CH₃NH₂-H₂SO₄ cluster occurs more easily at low temperature.

C. Composite Methylamine Hydration with Sulfuric Acid Molecules. Apart from growth by hydration, it is entirely possible to grow the clusters of $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 0-3, n = 0-3) by adding sulfuric acid molecules. As in the above analysis of the step-by-step hydration, we study adding sulfuric acid molecules step by step for each size of methylamine hydration.

Table 5 presents the energy change upon the stepwise addition of sulfuric acid to $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 0-3, n = 0-3) at 1 atm and the given temperatures. In Table 5, as for the $CH_3NH_2-H_2SO_4$ system, the process of forming the cluster containing two sulfuric acid molecules has a more favorable Gibbs free energy, indicating the stability of this cluster. The clusters containing more water molecules have lower Gibbs free energies for adding the first sulfuric acid molecule and higher Gibbs free energies for adding the second

Table 5. Energy Change upon the Stepwise Addition of Sulfuric Acid to $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 0-3, n = 0-3) at 1 atm and the Given Temperature in kcal/mol

п	$\Delta G(216.65 \text{ K})$	$\Delta G(273.15 \text{ K})$	$\Delta G(298.15 \text{ K})$		
	$CH_3NH_2(H_2SO_4)_{n-1}$	+ $H_2SO_4 \rightarrow CH_3NH_2$	$(H_2SO_4)_n$		
1	-14.4189	-12.5833	-11.7834		
2	-22.3052	-19.8591	-18.7879		
3	-13.4112	-11.0809	-10.0643		
$\mathrm{CH}_{3}\mathrm{NH}_{2}(\mathrm{H}_{2}\mathrm{O})(\mathrm{H}_{2}\mathrm{SO}_{4})_{n-1} + \mathrm{H}_{2}\mathrm{SO}_{4} \rightarrow \mathrm{CH}_{3}\mathrm{NH}_{2}(\mathrm{H}_{2}\mathrm{O})(\mathrm{H}_{2}\mathrm{SO}_{4})_{n}$					
1	-19.8142	-17.4744	-16.4475		
2	-19.7213	-17.2620	-16.1840		
3	-11.9486	-9.7116	-8.7324		
CH3	$\mathrm{CH}_{3}\mathrm{NH}_{2}(\mathrm{H}_{2}\mathrm{O})_{2}(\mathrm{H}_{2}\mathrm{SO}_{4})_{n-1} + \mathrm{H}_{2}\mathrm{SO}_{4} \rightarrow \mathrm{CH}_{3}\mathrm{NH}_{2}(\mathrm{H}_{2}\mathrm{O})_{2}(\mathrm{H}_{2}\mathrm{SO}_{4})_{n}$				
1	-25.3774	-23.0963	-22.4171		
2	-18.4183	-16.1168	-15.1023		
3	-11.7854	-9.3885	-8.3435		
$\mathrm{CH}_{3}\mathrm{NH}_{2}(\mathrm{H}_{2}\mathrm{O})_{3}(\mathrm{H}_{2}\mathrm{SO}_{4})_{n-1} + \mathrm{H}_{2}\mathrm{SO}_{4} \rightarrow \mathrm{CH}_{3}\mathrm{NH}_{2}(\mathrm{H}_{2}\mathrm{O})_{3}(\mathrm{H}_{2}\mathrm{SO}_{4})_{n}$					
1	-26.9087	-24.7256	-23.7733		
2	-18.3629	-15.5194	-14.2609		

and third sulfuric acid molecules. This result indicates that, for the formation of $CH_3NH_2-H_2SO_4-H_2O$ clusters, the water molecules promote the addition of the first sulfuric acid molecule but prevent the addition of more molecules. For the clusters containing the same number of water molecules, with increasing size of the cluster, the growth of the clusters by addition of sulfuric acid molecules becomes more difficult. In addition, as the above analysis of hydration, the Gibbs free energies of adding sulfuric acid molecules decrease with a decrease in temperature, which indicates that the growth of $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 0-3 and n = 0-3) clusters occurs more easily in the high troposphere.

As shown above, the Gibbs free energies of formation associated with addition of a single water molecule and the additional addition of a sulfuric acid molecule are analyzed. However, we still could not identify whether adding a sulfuric acid or water molecule clearly occur at each step in the actual atmosphere. The process of cluster growth also depends on the relative concentrations of reactants in the gas phase, the stability of the forming clusters, and other conditions. For example, in comparison with the process of hydration the free energies of the addition of sulfuric acid are 13 kcal/mol smaller at least, whereas the concentration of water molecules in the atmosphere exceeds that of sulfuric acid gas by 8-10 orders of magnitude. Understanding the very first steps of electrically neutral cluster formation and subsequent growth is so difficult that the mechanism of NPF and growth is still an extremely important problem to be solved for the world. Our work can serve as a reference for further research.

D. Hydrate Distributions and Influence of Humidity and Temperature. From the cluster growth mechanism we discussed above, we can know clusters which may form more easily from a thermodynamics aspect but not information about which clusters are dominant in the atmosphere. To get this information, we studied the hydrate distributions in different atmosphere environments: i.e., at different relative humidities and temperatures.

We calculated the hydrate distributions for all of the studied clusters using the same method as Loukonen et al. did.³³ Detailed information about the functions and explanations for calculations is given in the Supporting Information. The sensitivities of the hydrate distributions to the relative humidity

are presented in Figures 4-6 at three relative humidities (20%, 50%, and 80%) with a constant temperature of 298.15 K.



Figure 4. Hydrate distributions of $CH_3NH_2(H_2SO_4)(H_2O)_n$ (n = 0-3) clusters at three different relative humidities. In all cases T = 298.15 K.



Figure 5. Hydrate distributions of $CH_3NH_2(H_2SO_4)_2(H_2O)_n$ (n = 0-3) clusters at three different relative humidities. In all cases T = 298.15 K.



Figure 6. Hydrate distributions of $CH_3NH_2(H_2SO_4)_3(H_2O)_n$ (n = 0-3) clusters at three different relative humidities. In all cases T = 298.15 K.

As shown in Figure 4, the clusters with one sulfuric acid molecule were most extensively hydrated. At most tropospheric relative humidities, the total concentrations of sulfuric acid in these clusters were dispersed mainly in the monohydrates and dihydrates. With the peak of the distribution, the cluster "core", $CH_3NH_2(H_2SO_4)$, is most likely to prefer combining two water molecules in the atmosphere. The reason for the low distribution of $CH_3NH_2(H_2SO_4)(H_2O)_3$ may be the dilution



Figure 7. Hydrate distributions of $CH_3NH_2(H_2SO_4)(H_2O)_n$ (n = 0-3) clusters (a) and $CH_3NH_2(H_2SO_4)_2(H_2O)_n$ (n = 0-3) clusters (b) at two different temperatures when RH = 50%.

effect of water molecules in the structures, which weakens the acid-base reaction and makes the cluster not very stable.

The hydration patterns of clusters containing two sulfuric acid and methylamine molecules are revealed in Figure 5. The hydrate distribution is virtually static with a change in relative humidity. The peak of the cluster distribution occurs for the unhydrated clusters with a share of nearly 100% at RH < 20%. The dihydrate and trihydrate may account for 10% at high values of relative humidity (RH > 80%). Structural reasons for this are compelling: methylamine can bind two acids together due to its ability to form two strong hydrogen bonds (as shown in Figure 2b). Adding water molecules to this complex means breaking these strong hydrogen bonds.

The hydrate distributions of the three-acid clusters with methylamine are shown in Figure 6. The clusters stay almost completely dry. The peak of the cluster distribution in this case occurs for the unhydrated clusters with a share of practically 100%. This would suggest that the clusters consisting of three sulfuric acid molecules and methylamine will never bond with water molecules regardless of how much water actually is available. From Figures 4-6, the general trend of hydration in all cases is more extensive with an increase in RH and the dominant clusters do not change with the relative humidity for all of the cases.

Figure 7 shows the hydrate distributions of $CH_3NH_2(H_2SO_4)(H_2O)_n$ (*n* = 0-3) (Figure 7a) and $CH_3NH_2(H_2SO_4)_2(H_2O)_n$ (n = 0-3) (Figure 7b) clusters at three different temperatures when RH = 50%. As shown in Figure 7, the differences of both hydrate distributions of the clusters containing one acid molecule and two acid molecules at three temperatures are much smaller than that at three different RHs. The temperature sensitivity of the hydrate distributions with constant relative humidity is relatively weak. This is most likely due to the opposeing influences of temperature on the free energy of formation and the absolute water concentration. Lowering the temperature shifts the Gibbs free energies into more negative values, which implies more hydration. However, decreasing the temperature also diminishes the absolute water concentration. To a large extent these two competing effects cancel out, leaving the hydrate distributions reasonably temperature independent.

E. Optical Properties. Figures 8-11 present the changes in the Rayleigh light scattering properties of the clusters containing different sulfuric acid molecules as a function of the number of water molecules, which include the Rayleigh light scattering intensities of natural light R_{n} , the depolarization



Article

Figure 8. Rayleigh light scattering intensities as a function of water molecules. MA, SA, and W denote CH_3NH_2 , H_2SO_4 , and H_2O , respectively.



Figure 9. Depolarization ratio as a function of water molecules. MA, SA, and W denote CH_3NH_2 , H_2SO_4 , and H_2O , respectively.



Figure 10. Isotropic mean polarizabilities as a function of water molecules. MA, SA, and W denote CH_3NH_2 , H_2SO_4 , and H_2O , respectively.

ratios σ_{n} , isotropic mean polarizabilities $\overline{\alpha}$, and anisotropic polarizabilities $\Delta \alpha$. As shown in Figures 8 and 10, for the



Figure 11. Anisotropic polarizabilities as a function of water molecules. MA, SA, and W denote CH_3NH_2 , H_2SO_4 , and H_2O , respectively.

clusters containing the same number of sulfuric acid molecules, the Rayleigh light scattering intensities R_n and isotropic mean polarizabilities $\overline{\alpha}$ increase nearly linearly as the number of water molecules increase, whereas the Rayleigh light scattering intensities increase rapidly near 400000 au in comparison to 20 au for isotropic mean polarizabilities. Because of the small number of water molecules in our study, it is not very clear whether the nonlinear dependence closely follows the trend of a second-order polynomial for scattering intensities R_n , which is observed in the clusters of sulfuric acid hydration and chloride hydration.^{43,72} The depolarization ratios $\overline{\alpha}$ and anisotropic polarizabilities $\Delta \alpha$ are very much size dependent, which is consistent with the study of sulfuric acid hydration systems.⁷²

The influence of different numbers of the sulfuric acid molecules on the Rayleigh light scattering can be observed from the different lines with different colors in Figures 8–11. The Rayleigh light scattering intensities R_n and isotropic mean polarizabilities $\overline{\alpha}$ increase with increasing numbers of sulfuric acid molecules, which is consistent with the influence of the water molecules. From Figure 8, the Rayleigh light scattering intensities increase 100000–400000 au by adding a sulfuric acid molecule, in comparison to 50000–100000 au by adding a water molecule. In addition, as shown in Figure 10, the isotropic mean polarizabilities increase nearly 40 au by adding a sulfuric acid molecule, in comparison to 10 au by adding a water molecule. These data indicate that the influence of adding a sulfuric acid molecule is larger than the influence of a water molecule.

Comparatively, it is observed that the depolarization ratios σ_n and the anisotropic polarizabilities $\Delta \alpha$ show patterns quite different from those of the other two parameters. When $n \ge 1$, the anisotropic polarizabilities vary slowly except for the $CH_3NH_2(H_2SO_4)_3(H_2O)_2$ cluster, and with an increasing number of water molecules, the calculated depolarization ratio is observed to decay rapidly from $CH_3NH_2(H_2SO_4)$ to $CH_3NH_2(H_2SO_4)(H_2O)$. In contrast, when $n \ge 1$, the depolarization ratios are nearly the same value regardless of the number of sulfuric acid molecules. As shown in eq 1, this difference is due to an increase in the mean isotropic polarizabilities $\overline{\alpha}$ with the number of water molecules in combination with relatively gentle variation of anisotropic polarizabilities $\Delta \alpha$. This result is consistent with what is to be expected as the cluster changes from a molecular cluster to a spherical isotropic particle.

CONCLUSIONS

In this paper, the BH algorithm coupled with the DFT method was employed to search for the global minima of Article

 $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (m = 0-3, n = 0-3). An analysis of structures and energetics showed that in some of the clusters the water molecules distribute in a relatively dispersed fashion. The stepwise Gibbs free energies of the formation of clusters show that H₂SO₄ plays a crucial role in the hydration of the cluster containing CH₃NH₂ molecules in certain cases, addition of a water molecule to CH₃NH₂ at 273.15 and 298.15 K; in comparison with the process of hydration the free energies of the addition of sulfuric acid are 13 kcal/mol smaller at least. The Gibbs free energies of growth at low temperatures are smaller, indicating that the growth of $CH_3NH_2(H_2SO_4)_m(H_2O)_n$ (*m* = 0-3, *n* = 0-3) clusters occurs more easily in the high troposphere. From the analysis of hydrate distributions, we found that $CH_3NH_2(H_2SO_4)$ -(H₂O)₂, CH₃NH₂(H₂SO₄)₂, and CH₃NH₂(H₂SO₄)₃ are most likely to exist in the atmosphere. The general trend of hydration in all cases is more extensive with an increase in RH, whereas the distributions do not significantly change with the temperature. In addition, the Rayleigh scattering properties were studied. It turns out that both the addition of H₂SO₄ and H₂O molecules result in increased Rayleigh scattering intensities and isotropic mean polarizabilities, and the influence of water molecules is not as large as that of sulfuric acid molecules. When $n \ge 1$, the anisotropic polarizabilities vary gently and the depolarization ratios are nearly the same low value regardless of the number of sulfuric acid molecules, implying that the clusters can grow from a molecular cluster to a spherical isotropic particle. Our work provides a reliable reference for further research on NPF containing methylamine in the atmosphere.

ASSOCIATED CONTENT

Supporting Information

Text, tables, and figures giving details about the PW91/6-311++G(3df,3pd) optimized Cartesian coordinates, DF-MP2-F12 single point energies, the harmonic frequencies and IR intensities of each cluster, differences between the PW91 and DF-MP2-F12 binding energies, benchmarks of the methods, the structural patterns of the clusters of the two bases (methylamine and dimethylamine), the method of calculating the hydrate distributions, and the calculated isotropic mean polarizabilities ($\overline{\alpha}$) of monomers using different DFT functionals and basis sets. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpca.5b03325.

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Notes

The authors declare no competing financial interest.

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