

Effect of ammonia on new particle formation: A kinetic H₂SO₄-H₂O-NH₃ nucleation model constrained by laboratory measurements

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[1] A clear understanding of the nucleation mechanisms is important to understand the lifecycle of atmospheric particles and to provide reliable predictions of climate change associated with aerosols. On the basis of the classical ternary homogeneous nucleation (THN) theory developed in recent years, the presence of ppt level NH₃ concentration significantly enhances nucleation rates. Here we compare the predicted NH₃ enhancement with that derived from several reported experiments. We find that the differences between results predicted and observed are very large. Compared to the binary homogeneous nucleation of H₂SO₄-H₂O (no NH₃), the classical THN theory predicts up to ~30 orders of magnitude enhancement in the nucleation rates in the presence of ppt level NH₃, while the laboratory measurements show only one to two orders of magnitude enhancement in the presence of several ppt to several ppm level of NH₃. Furthermore, the classical THN theory predicts a decrease in nucleation rates as RH increases, but the measurements indicate an opposite trend. Since experimental results are probably more reliable than the theoretical model, we developed a kinetic THN model so that the nucleation enhancement effect of NH₃ derived from these experimental results could be included. The kinetic model assumes that H₂SO₄ is the principal specie dominating the cluster growth and nucleation, while H₂O and NH₃ are secondary species influencing the cluster compositions and hence the evaporation coefficient of H₂SO₄ from the clusters. The kinetic model is a new approach to simulating THN, and it can take into account the thermodynamic data of molecular clusters derived from density functional theory study and prenucleation cluster measurements. The preliminary simulations using the kinetic THN model constrained by the experimental results indicate a negligible contribution of THN to new particle formation in the boundary atmosphere. Our analysis suggests that the kinetic THN model is unlikely to underpredict the real ternary nucleation rates by much as long as there is no significant error in the experimental results. The implication of this finding and areas for further investigations are discussed.

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1. Introduction

[2] The indirect effect of aerosols on climate provides the largest uncertainty in current climate change assessment. While the contribution of secondary particles to total particle mass is not significant, they usually dominate the number concentrations of atmospheric aerosols and those particles acting as cloud condensation nuclei (CCN) [Seinfeld and Pandis, 1998]. In order to provide reliable predictions of climate change associated with aerosols, the formation rates of new particles (secondary particles) in the atmosphere must be understood. Binary homogeneous nucleation (BHN) of sulfuric acid and water has generally been assumed to be the mechanism of new particle formation. However, it has been known in recent years that BHN theory cannot explain observed nucleation events in the

boundary troposphere [e.g., Weber *et al.*, 1996; Clarke *et al.*, 1998]. One alternative mechanism proposed is ternary homogeneous nucleation (THN) involving H₂SO₄-H₂O-NH₃. Another alternative mechanism is the ion-mediated nucleation of H₂SO₄-H₂O [Yu and Turco, 2000, 2001]. The focus of this paper is on the possible role of ammonia in stabilizing the critical embryo and thus enhancing the nucleation rate. The effect of NH₃ on H₂SO₄-H₂O homogeneous nucleation has been investigated theoretically and the classical THN model has been developed [e.g., Coffman and Hegg, 1995; Korhonen *et al.*, 1999; Napari *et al.*, 2002a, 2002b].

[3] In the classical THN model, the rate of H₂SO₄-H₂O-NH₃ nucleation is calculated as

$$J = C \exp(-\Delta G^*/kT), \quad (1)$$

where C is a kinetic factor and ΔG^* is the Gibbs free energy change to form a critical cluster. Here k is the Boltzmann's

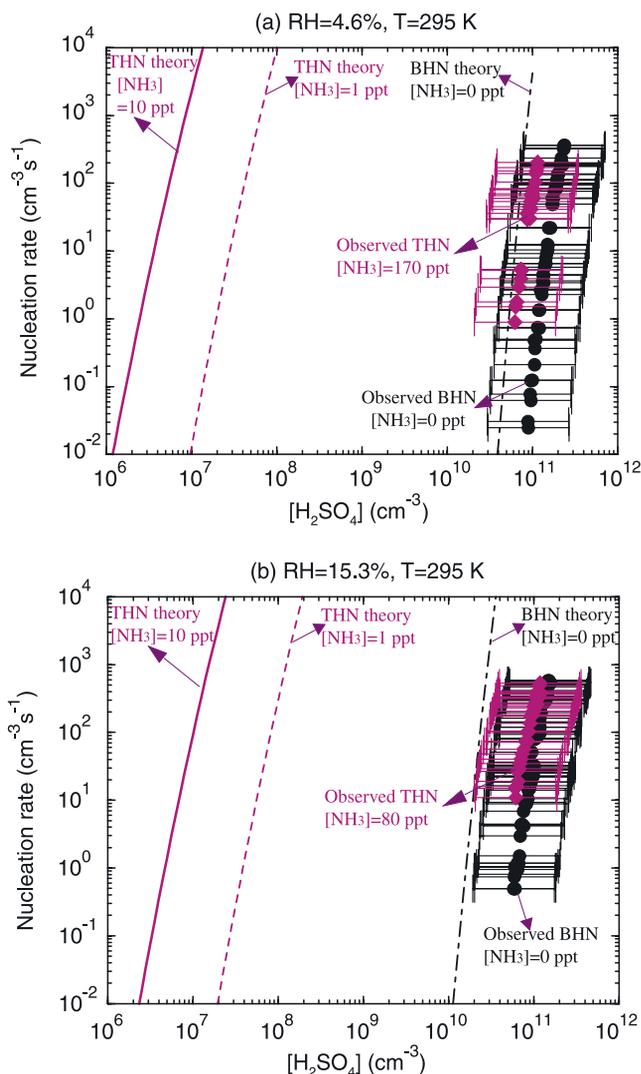


Figure 1. A comparison between predicted and observed nucleation rates as a function of [H₂SO₄] for both binary and ternary nucleation at (a) RH = 4.6%, and (b) RH = 15%. The observed nucleation rates for binary (filled circles) and ternary (diamonds) are from *Ball et al.* [1999]. Predicted nucleation rates for binary (dot-dashed lines) and ternary (dashed lines for [NH₃] = 1 ppt, solid lines for [NH₃] = 10 ppt) are based on the parameterization of classical binary [*Vehkamäki et al.*, 2002] and ternary [*Napari et al.*, 2002a, 2002b] nucleation models, respectively.

constant, while T is the temperature. The Gibbs free energy change to form a cluster containing m_1 H₂SO₄ molecule, m_2 H₂O molecules, and m_3 NH₃ molecules is

$$\Delta G = -m_1 kT \ln(p_1/p_{s,1}) - m_2 kT \ln(p_2/p_{s,2}) - m_3 kT \ln(p_3/p_{s,3}) + 4\pi r^2 \sigma, \quad (2)$$

where p_i ($i = 1, 2, 3$) is the ambient partial pressure of free molecules of species i and $p_{s,i}$ is the equilibrium vapor

pressure of species i above the surface of a flat solution with same composition. Here σ is the surface tension and r is the radius of the cluster or droplet.

[4] To calculate the nucleation rate based on equation (1), one must decide the composition and size of critical clusters which needs composition-dependent thermodynamic data including surface tension, solution density, and equilibrium vapor pressure of H₂SO₄, H₂O, and NH₃ over the surface of the flat ternary solution. Currently, the experimental information on these parameters is not available. The thermodynamic data needed in the classical THN model has been calculated using the thermodynamic multicomponent solution model via integrating various extrapolations, approximations, and assumptions [*Coffman and Hegg*, 1995; *Korhonen et al.*, 1999; *Napari et al.*, 2002a]. On the basis of the classical THN theory, NH₃ at ppt level can significantly enhance the H₂SO₄-H₂O nucleation and THN can lead to significant formation of new particles in the boundary atmosphere. THN rates are very sensitive to the thermodynamic data. As a result, the THN rates calculated based on the classical THN model are expected to have large uncertainties due to the uncertainties associated with the thermodynamic data.

[5] The exact role of NH₃ in enhancing nucleation and the validity (or uncertainties) of the classical THN theory must be assessed by comparing model predictions with experimental results. While there exist some experimental investigations on the possible role of NH₃ in enhancing H₂SO₄-H₂O homogeneous nucleation [e.g., *Ball et al.*, 1999; *Kim et al.*, 1998], the classical THN theory has never been assessed quantitatively against the experimental results. In this paper we compare the NH₃ enhancement derived from reported experiments with that predicted by the classical THN model. As we show in section 2, the differences between results observed and predicted are very large. With the understanding that experimental results are probably more reliable than the theoretical model, we develop a kinetic THN model with the NH₃ enhancement effect constrained by the experimental results (section 3). Using this kinetic THN model, we explore the possible contribution of ternary nucleation to the production of new particles in the boundary atmosphere. Summary and discussion are given in section 4.

2. Comparisons Between Classical THN Model Predictions and Experimental Results

[6] Sulfuric acid is the principal specie controlling the nucleation rates both in binary and ternary nucleation theories. Figure 1 shows a comparison between predicted and observed nucleation rates as a function of sulfuric acid vapor concentration ([H₂SO₄]) for binary and ternary nucleation at relative humidity (RH) = 4.6% (Figure 1a) and RH = 15% (Figure 1b). The temperature is 295 K. The symbols are the binary (filled circles) and ternary (diamonds) nucleation rates reported by *Ball et al.* [1999]. The error bars indicate possible range of [H₂SO₄] in the nucleation zone. The ammonia vapor concentration ([NH₃]) in the experimental THN study as indicated in the figure was calculated from the ratio of flows in the NH₃ dilution system and the total flow. The actual [NH₃] in nucleation zone may be substantially less but is expected to be larger

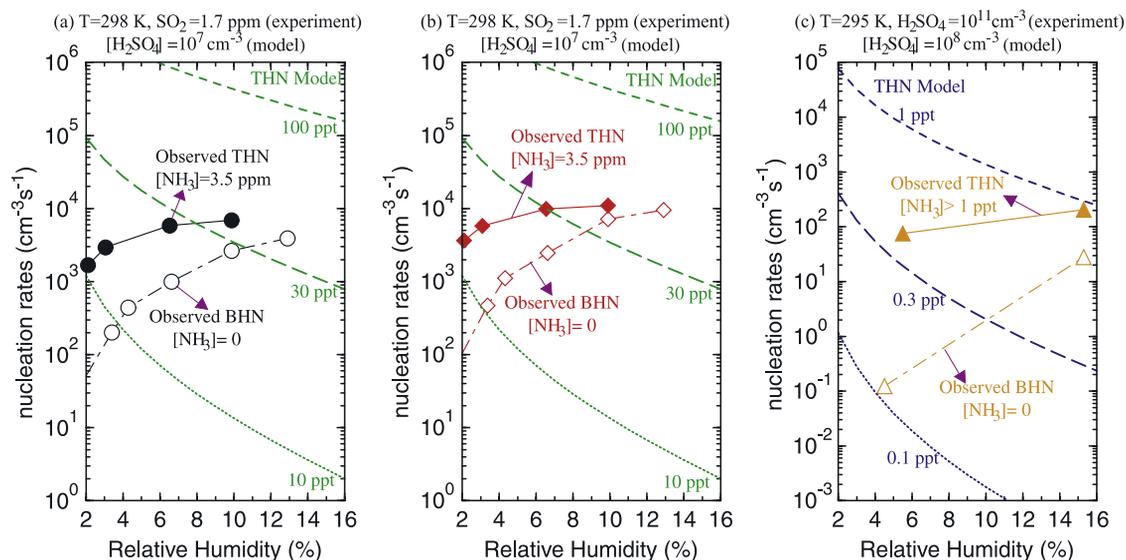


Figure 2. The dependence of nucleation rates on RH. The unfilled and filled symbols are the experimental results for binary and ternary nucleation, respectively. The lines are the ternary nucleation rates at three different $[\text{NH}_3]$ calculated based on the classical THN model of *Napari et al.* [2002b]. The data in Figures 2a and 2b are the experimental formation rates of neutral particles derived from the measurements of *Kim et al.* [1998]. The data in Figure 2c are from *Ball et al.* [1999] for $[\text{H}_2\text{SO}_4]$ of 10^{11} cm^{-3} . The experimental conditions (T, $[\text{SO}_2]$, and $[\text{NH}_3]$) and parameters used in the model calculations (T, $[\text{H}_2\text{SO}_4]$, and $[\text{NH}_3]$) are indicated in each panel.

than 1 ppt [*Ball et al.*, 1999]. Theoretical binary nucleation rates (dot-dashed lines) and ternary nucleation rates (dashed lines for $[\text{NH}_3] = 1$ ppt, solid lines for $[\text{NH}_3] = 10$ ppt) are calculated with the parameterization of the most recent version of classical binary [*Vehkamäki et al.*, 2002] and ternary [*Napari et al.*, 2002b] nucleation models, respectively. It is clear from Figure 1 that there exist huge differences between the observed and predicted enhancement in the nucleation rates due to the presence of NH_3 at ppt level. Within the ranges of T and RH considered in Figure 1, the experimental results indicate one to two orders of magnitude enhancement in the nucleation rates. However, classical THN theory predicts an enhancement of ~ 30 orders of magnitude. For $T = 295 \text{ K}$, $[\text{H}_2\text{SO}_4] = 10^8 \text{ cm}^{-3}$, and $\text{RH} < 15\%$, the nucleation rate calculated with binary homogeneous nucleation model is less than $10^{-30} \text{ cm}^{-3} \text{ s}^{-1}$ but with 1 ppt of $[\text{NH}_3]$ the classical THN model predicts a nucleation rate of $>10^2 \text{ cm}^{-3} \text{ s}^{-1}$.

[7] *Ball et al.*'s [1999] measurements are not the only measurements that indicate a rather modest enhancement in the nucleation rate by the addition of NH_3 to $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ or $\text{SO}_2\text{-H}_2\text{O}$ system. In their study of the nanoparticle formation from $\text{SO}_2/\text{H}_2\text{O}$ or $\text{SO}_2/\text{H}_2\text{O}/\text{NH}_3$ air mixtures by ionization irradiation, *Kim et al.* [1998] found that the presence of 0.71–3.6 ppm NH_3 increases the number concentration of neutral nucleated particles by a factor of less than 10. These neutral particles were believed to be mostly formed via binary or ternary homogeneous nucleation. *Diamond et al.* [1985] and *Christensen et al.* [1994] observed similar modest increases of particle number concentration in their experimental nucleation study when NH_3

was added to $\text{SO}_2/\text{H}_2\text{O}$ system. In his laboratory investigation of particle formation by photo-oxidation of SO_2 with OH radical, *Nolan* [1987] found that the difference in the values of nucleation rates for the cases without NH_3 and with the NH_3 (~ 50 ppb to 1 ppm) is less than a factor of 10. *Nolan* [1987] also observed no obvious change in the measured new particles when the added NH_3 mixing ratio increased from ~ 50 ppb to 1 ppm. All these experimental investigations on the effect of NH_3 on nucleation indicate that the presence of NH_3 (mixing ratio range from a few ppt to more than 100 ppm) only slightly enhances the nucleation rates, which is significantly different from the calculations based on the classical THN theory as shown in Figure 1.

[8] In addition to the large differences in the absolute values of nucleation enhancement due to the presence of NH_3 , classical THN theory and experimental observations also give quite different dependence of nucleation rates on RH. Figure 2 shows the dependence of nucleation rates on RH. The unfilled and filled symbols are the experimental results for binary nucleation and ternary nucleation, respectively. The lines are the ternary nucleation rates at three different $[\text{NH}_3]$ (10, 30, and 100 ppt for Figures 2a and 2b, and 0.1, 0.3, and 1 ppt for Figure 2c) calculated based on the classical THN model of *Napari et al.* [2002b]. In the model calculations, $[\text{H}_2\text{SO}_4]$ is assumed to be 10^7 cm^{-3} in Figures 2a and 2b and 10^8 cm^{-3} in Figures 2c. The data in Figures 2a and 2b are the experimental nucleation rates of neutral particles derived from the measurements of *Kim et al.* [1998]. Most of these neutral particles are believed to be formed via homoge-

neous nucleation [Kim *et al.*, 1998]. There is no direct measurement of $[\text{H}_2\text{SO}_4]$ in the work of Kim *et al.* The experimental data corresponding to $[\text{H}_2\text{SO}_4]$ of 10^{11} cm^{-3} from Ball *et al.* [1999] (see Figure 1) are shown in Figure 2c. The experimental conditions (T, SO_2 , and NH_3 concentration) are marked in each panel.

[9] It is clear from Figure 2 that the trend of ternary nucleation rates on RH predicted by the classical THN model is opposite to that observed in laboratory studies. THN theory predicts a decrease in nucleation rates as RH increases, but instead, the measured ternary nucleation rates increase with increasing RH. The theoretical THN rates are very sensitive to $[\text{NH}_3]$ and the overprediction of the effect of NH_3 on nucleation is obvious in Figure 2. To obtain nucleation rates in a similar range, the concentrations of H_2SO_4 and NH_3 needed in the classical THN theory are much lower than those used in the laboratory study. The observed decreasing effect of ammonia on nucleation with increasing RH may suggest that the effect of NH_3 on nucleation in the atmosphere is very limited because RH in the atmosphere is typically much larger than RH in these experiments ($\sim 15\%$).

[10] The extraordinarily large deviation of ternary nucleation rates predicted based on classical THN theory from those observed experimentally, as we show in Figures 1 and 2, might suggest that substantial improvement in the current classical THN theory is needed and care should be taken when using the theory to predict particle formation in the atmosphere. It should be pointed out that the measurements of Ball *et al.* [1999] have been cited as evidence supporting the THN theory on the effect of NH_3 in enhancing the nucleation [Napari *et al.*, 2002a]. As we shown here, Ball *et al.*'s [1999] measurements are actually against the classical THN theory with regard to the possible role of NH_3 in new particle formation in the boundary atmosphere.

3. A Kinetic Model of $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ Ternary Nucleation

[11] On the basis of the classical THN theory, NH_3 significantly stabilizes the prenucleation clusters and leads to the enhancement of nucleation rates by up to ~ 30 orders of magnitude. However, as we described in the previous section, experimental studies indicate a much smaller enhancement in nucleation rates. That may suggest that the effect of NH_3 in stabilizing the small clusters is much less than that calculated based on classical THN theory. The formation of new particles in both binary and ternary system is actually a kinetic process involving forward and backward flux of clusters due to colliding of H_2SO_4 molecules with clusters and evaporation of H_2SO_4 from clusters. H_2O and NH_3 participate in the nucleation through influencing the composition of clusters and hence stability and evaporation coefficient of H_2SO_4 molecules.

[12] Recently, Yu [2005a, 2006] showed that the binary homogeneous nucleation (BHN) of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ can be treated as quasi-unary nucleation of H_2SO_4 in equilibrium with H_2O vapor and developed a kinetic $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ nucleation model. In the kinetic model, the growth/shrinking of clusters through the uptake/evaporation of

H_2SO_4 molecules is simulated explicitly by solving the following equations:

$$\frac{dn_{i_a}}{dt} = \delta_{i_a-1,1}\beta_{i_a-1}n_{i_a-1} - \gamma_{i_a}n_{i_a} - \beta_{i_a}n_{i_a} + \gamma_{i_a+1}n_{i_a+1}, \quad i_a \geq 2 \quad (3)$$

$$\frac{dn_1}{dt} = P - \sum_{i_a=1}^{\infty} \beta_{i_a}n_{i_a} + 2\gamma_2n_2 + \sum_{i_a=3}^{\infty} \gamma_{i_a}n_{i_a}, \quad (4)$$

where n_{i_a} is the number concentration of clusters containing i_a H_2SO_4 molecules (i_a -mers) and n_1 is the total concentration of H_2SO_4 monomers. Here β_{i_a} is the average i_a -mer forward (or growth) rate coefficient which can be calculated from the kinetic collision rate of hydrated monomers with i_a -mers, and γ_{i_a} is the average reverse (or evaporation) rate coefficient or escape frequency of H_2SO_4 molecules from i_a -mers which can be calculated using the Kelvin equation [Yu, 2005a]. P is the production rate of H_2SO_4 molecules. $\delta_{i_a-1,1} = 1$, when $i_a > 2$ and $= 0.5$ when $i_a = 2$. It should be noted that the model described here is kinetic in a physical sense and is different from a chemical kinetic model.

[13] The nucleation rates based on the kinetic binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ nucleation model (J_{BHN}^{Kin}) can be calculated as

$$J_{BHN}^{Kin} = \beta_{i_a^*}n_{i_a^*} - \gamma_{i_a^*+1}n_{i_a^*+1}, \quad (5)$$

where i_a^* is the number of H_2SO_4 molecules in the critical clusters ($i_a = i_a^*$ when $\beta_{i_a} = \gamma_{i_a}$). The nucleation rates reach a steady state value after certain time at a given (constant) $[\text{H}_2\text{SO}_4]$ ($n_1 = [\text{H}_2\text{SO}_4]$).

[14] Capillarity approximation is implied in the kinetic model as the Kelvin equation is used to calculate the compositions and evaporation coefficients of small clusters. Capillarity approximation may be not valid for clusters containing a few molecules. Nevertheless, the appropriateness of treating binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ nucleation as quasi-unary nucleation and using Kelvin equation to calculate evaporation coefficient appears to be supported by the good agreement of the nucleation rates predicted based on the kinetic quasi-unary model with recent experimental results [Yu, 2005a, 2006].

[15] In the kinetic quasi-unary nucleation model, the contribution of H_2O to nucleation is through the hydration of H_2SO_4 clusters (or modification of the cluster compositions) that reduces the H_2SO_4 vapor pressure over the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ clusters and hence the evaporation coefficient of H_2SO_4 from clusters. Similarly, the role of NH_3 in nucleation is also to stabilize the cluster and reduce the evaporation coefficient of H_2SO_4 from clusters by changing the cluster compositions. Thus we can incorporate the effect of NH_3 on nucleation in the kinetic model by modifying the evaporation coefficient,

$$\gamma_{i_a}^{THN} = \frac{\gamma_{i_a}^{BHN}}{F_{\text{NH}_3}}, \quad (6)$$

where $\gamma_{i_a}^{BHN}$ and $\gamma_{i_a}^{THN}$ are the evaporation coefficient of H_2SO_4 molecules from binary $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ and ternary

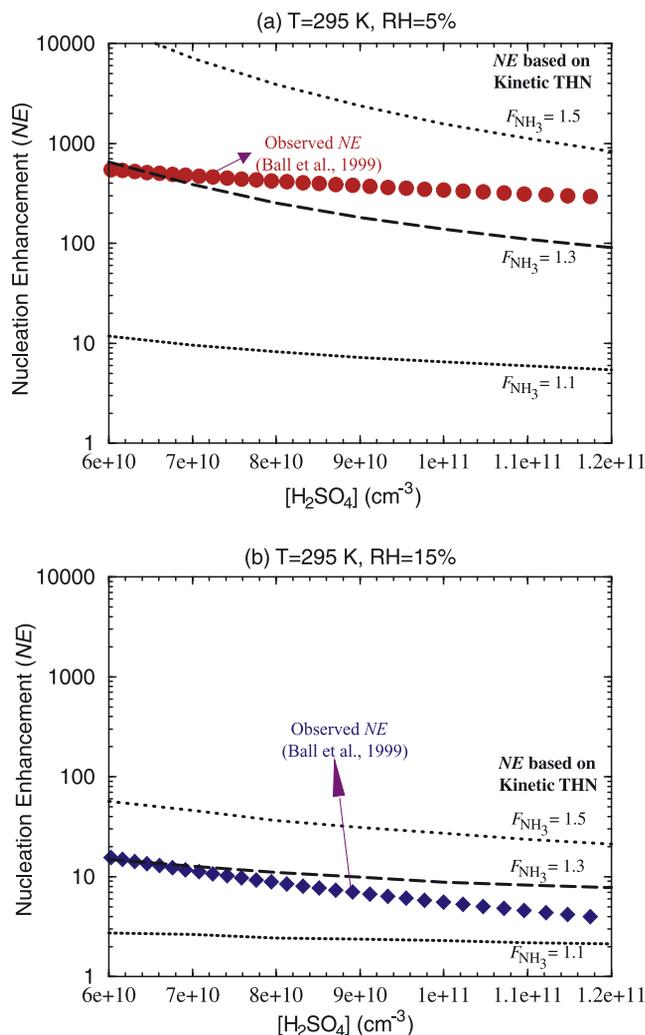


Figure 3. Nucleation Enhancement (NE) as a function of $[H_2SO_4]$ corresponding to the conditions in *Ball et al.*'s [1999] laboratory study ($T = 295$ K, $RH = 5\%$ and 15%). The symbols are NE values derived from experimental data of *Ball et al.* [1999]. The lines are NE calculated based on our kinetic ternary and binary models, representing three different values of ammonia stabilizing factor F_{NH_3} (1.1, 1.3, and 1.5).

H_2SO_4 - H_2O - NH_3 clusters, respectively. F_{NH_3} is the NH_3 stabilizing factor.

[16] With evaporation coefficient calculated based on equation (6), we develop a kinetic quasi-unary H_2SO_4 - H_2O - NH_3 nucleation model that simulates the ternary nucleation kinetically by solving equations (3)–(5). The kinetic model is a new approach to simulate THN, and it captures the main physics of the THN that H_2SO_4 is the principal nucleation specie dominating the cluster growth (condensation and evaporation), while H_2O and NH_3 serve as secondary species influencing the evaporation coefficient of H_2SO_4 from clusters.

[17] The difficult task of the kinetic model is to determine F_{NH_3} which is likely a function of cluster size (i_a), composition, T , RH , $[NH_3]$, etc. To properly define F_{NH_3} , one

needs to know the thermodynamic data regarding the ternary system and small molecular clusters.

[18] As a preliminary investigation, we derive the possible range of F_{NH_3} by constraining the model-simulated nucleation enhancement with those observed in the experimental studies. Here we define nucleation enhancement (NE) as the ratio of steady state nucleation rates (at a given fixed $[H_2SO_4]$) in the presence of NH_3 (ternary) to those in the absence of NH_3 (binary). Figure 3 shows the values of NE as a function of $[H_2SO_4]$ corresponding to the conditions in the laboratory study of *Ball et al.* [1999] ($T = 295$ K, $RH = 5\%$ and 15%). The symbols are NE values derived from experimental data of *Ball et al.* [1999]. The lines are NE calculated based on our kinetic ternary and binary models, representing three different values of F_{NH_3} (1.1, 1.3, and 1.5). It is clear from Figure 3 that F_{NH_3} value of ~ 1.3 gives nucleation enhancement close to the observed values. In other words, the experimental studies suggest that at the presence of NH_3 , the mean evaporation coefficient of sulfuric acid molecules from clusters is reduced only by a factor of around 1.3.

[19] With the NH_3 stabilizing effect derived from experimental studies, we can explore the nucleation rates in the presence of NH_3 in the boundary atmosphere. We should emphasize that F_{NH_3} in ambient atmosphere may be quite different from that derived via experiments as F_{NH_3} may depend on T , RH , and $[NH_3]$. To be conservative, we use $F_{NH_3} = 1.5$. Figure 4 is the kinetic quasi-unary H_2SO_4 - H_2O - NH_3 nucleation rate contours in the RH versus $[H_2SO_4]$ planes at $T = 280$ K and $T = 295$ K. In the boundary atmosphere, $[H_2SO_4]$ is generally lower than 10^8 cm^{-3} . It is clear from Figure 4 that the ternary nucleation rates with NH_3 stabilizing factor (F_{NH_3}) derived from experimental results are negligible in the boundary atmosphere.

[20] Obviously, there exist uncertainties in the calculated nucleation rates in Figure 4 as a result of uncertainties in F_{NH_3} . In the ambient atmosphere, $[NH_3]$ can range from sub-ppt level to ppt level. While the effect of $[NH_3]$ on F_{NH_3} remains to be investigated, existing experimental studies [*Nolan*, 1987; *Kim et al.*, 1998; *Ball et al.*, 1999] indicate that the nucleation enhancement is not very sensitive to $[NH_3]$. For example, there is no significant difference in the nucleation rate enhancement between the measurements of *Ball et al.* [1999] and *Kim et al.* [1998], though one used ppt level $[NH_3]$ while the other used ppm level $[NH_3]$ (see Figure 3). No obvious change in the measured new particles for NH_3 concentrations range from ~ 50 ppt to 1 ppm was observed in the laboratory investigation of *Nolan* [1987] of particle formation by photo-oxidation of SO_2 with OH radical in the presence of H_2O and NH_3 . In the ambient atmosphere, RH is generally higher and $[H_2SO_4]$ tends to be much lower than what used in the laboratory studies shown in Figure 3. The evaporation coefficient of H_2SO_4 molecules from ternary H_2SO_4 - H_2O - NH_3 clusters should be independent of $[H_2SO_4]$; thus the difference in $[H_2SO_4]$ should not cause change in F_{NH_3} . As to RH , both measurements of *Ball et al.* [1999] and *Kim et al.* [1998] indicate the effect of NH_3 is reduced as RH increases. Thus using the F_{NH_3} derived at lower RH may overpredict the NH_3 enhancement at higher RH . On the basis of these analyses about the possible difference between F_{NH_3} derived from experiments and in the real

Contours of nucleation rates ($\text{cm}^{-3}\text{s}^{-1}$) based on kinetic THN model

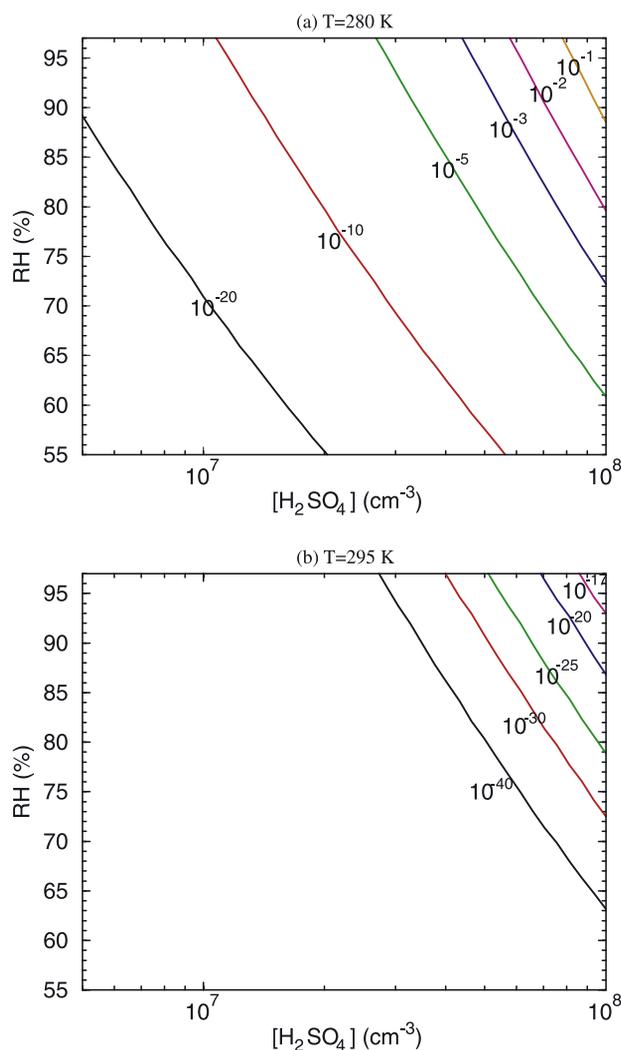


Figure 4. The contours of kinetic $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ nucleation rates in the RH versus $[\text{H}_2\text{SO}_4]$ planes at (a) $T = 280$ K and (b) $T = 295$ K. The nucleation rates are calculated with the kinetic quasi-unary $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ nucleation model with ammonia stabilizing factor constrained by experimental results.

atmosphere, we may conclude that the nucleation rates shown in Figure 4 are unlikely to underpredict too much the real ternary nucleation rates as long as there is no significant error in the experimental results which indicate less than two orders of magnitude enhancement in the nucleation rates and a smaller enhancement at larger RH .

[21] In the above, the possible value of F_{NH_3} is derived from the observed nucleation enhancement reported by *Ball et al.* [1999]. F_{NH_3} can also be estimated from measured H_2SO_4 vapor pressure over bulk ternary solution. *Marti et al.* [1997] observed that ammonia reduces H_2SO_4 vapor pressure over the ternary solution and the degree of reduction in the vapor pressure (i.e., F_{NH_3}) depends on ammonia to sulfate ionic mole ratio ($[\text{NH}_4^+]:[\text{SO}_4^{2-}]$) in the solution. Figure 5 shows the values of F_{NH_3} for bulk solution derived

from the data of *Marti et al.* [1997]. F_{NH_3} is ~ 3 when ionic ratio is less than 0.5 but increases to ~ 30 and ~ 300 when ionic ratio reaches 0.8 and 1.0, respectively. Figure 5 also indicate that F_{NH_3} tends to decrease as RH increases. It should be noted that F_{NH_3} shown in Figure 5 is for bulk solution and it is not clear if ammonia can neutralize and thus stabilize small sulfuric acid clusters in a similar way. The density functional theory (DFT) study of *Ianni and Bandy* [1999] suggests that NH_3 is not able to neutralize and stabilize H_2SO_4 dimers. As a sensitivity study, we simulate the effect of ammonia stabilization on nucleation for two different cases: Case 1 assumes that clusters of all sizes are stabilized by the same F_{NH_3} , while case 2 assumes that only clusters containing more than 10 H_2SO_4 molecules (i.e., $i_a > 10$) are stabilized (by F_{NH_3}).

[22] Figure 6 presents the simulated nucleation enhancement factor under different values of F_{NH_3} (3, 30, 300; corresponding to different degree of neutralization, see Figure 5) for the two cases at $RH = 5\%$ (Figure 6a) and $RH = 15\%$ (Figure 6b). The values observed by *Ball et al.* [1999] are also shown for comparison. It is obvious from Figure 6 that the nucleation should be enhanced significantly if the small clusters are neutralized and stabilized same as bulk solution (case 1). The nucleation enhancement is dramatically reduced if we assume that small clusters (in this case $i_a \leq 10$) are not neutralized and stabilized by ammonia (case 2). Comparison with the observation of *Ball et al.* [1999] (and those of *Kim et al.* [1998], *Christensen et al.*, [1994], and *Diamond et al.* [1985] as well) suggests that

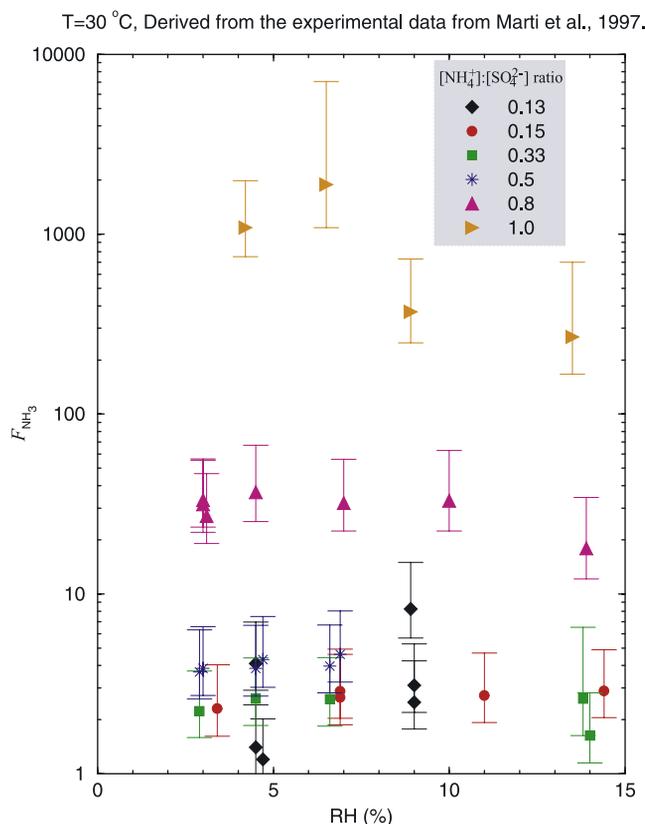


Figure 5. The values of F_{NH_3} for bulk ternary solution derived from the data of *Marti et al.* [1997].

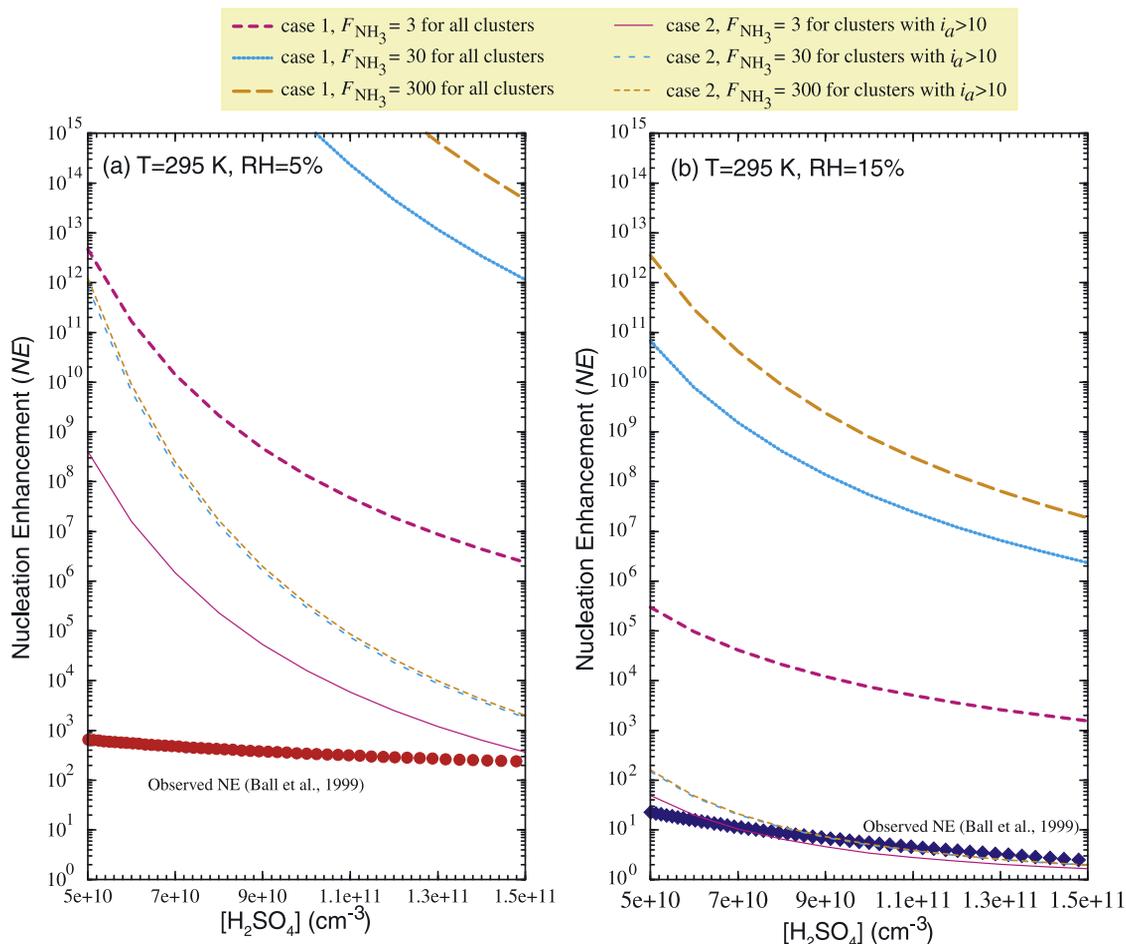


Figure 6. Simulated nucleation enhancement factor under different values of F_{NH_3} (3, 30, 300; corresponding to different degree of neutralization as shown in Figure 5) for two cases at (a) $RH = 5\%$ and (b) $RH = 15\%$. Case 1 assumes that clusters of all sizes are stabilized by the same F_{NH_3} while case 2 assumes that only clusters containing more than 10 H_2SO_4 molecules are stabilized (by F_{NH_3}).

the neutralization and stabilization of small prenucleation sulfuric acid clusters by ammonia are probably very limited. Otherwise, much more significant enhancement in nucleation rates at the presence of ammonia should be detected in the laboratory experiments.

4. Summary and Discussion

[23] On the basis of the classical THN theory, the presence of ppt level NH_3 concentration significantly enhances the nucleation rates. Several experimental investigations on the possible role of NH_3 in enhancing the H_2SO_4 - H_2O homogeneous nucleation were reported in the literature; however, the classical THN theory has never been assessed quantitatively against these experimental results. In this study we compare the NH_3 enhancement derived from reported experiments with that predicted based on the recent version of the classical THN model.

[24] We find that the differences between results observed and predicted are huge. The classical THN theory predicts up to around 30 order of magnitude enhancement in the nucleation rates when ppt level of ammonia is added to the

binary system. However, the existing laboratory measurements indicate only one to two orders of magnitude enhancement in the nucleation rates when NH_3 at concentrations ranging from several ppt to several ppm is added to H_2SO_4 - H_2O or SO_2 - H_2O system. To predict nucleation rates in similar range to those observed in the laboratory, the THN theory requires much lower concentrations of H_2SO_4 (about 3 orders of magnitude smaller than the corresponding $[H_2SO_4]$ used in the experiments). The other significant difference between the THN theory and measurements is the opposite dependence trends of ternary nucleation rates on RH. THN theory predicts a decrease in nucleation rates as RH increases but to the contrary, the measurements indicate an increase in nucleation rates with increasing RH.

[25] Since experimental results are probably more reliable than the theoretical model, we develop a kinetic THN model so that the NH_3 enhancement effect derived from the experimental results can be taken into account. Our preliminary investigations using the kinetic THN model constrained by the experimental results indicate a negligible contribution of THN to new particle formation in the

boundary atmosphere. While there exists uncertainty in the calculated nucleation rates based on the kinetic THN model, our analysis suggests that the kinetic nucleation rates are unlikely to underpredict too much the real ternary nucleation rates as long as there is no significant error in the experimental results which indicate less than about two orders of magnitude enhancement in the nucleation rates and a smaller enhancement at larger RH.

[26] Our conclusion about the negligible contribution of THN to new particle formation in the boundary atmosphere is consistent with the density functional theory (DFT) study of *Ianni and Bandy* [1999], who found that NH_3 is not able to stabilize H_2SO_4 dimers and concluded that NH_3 appears to have no role in the initialization of new particles in the atmosphere. On the other hand, equilibrium thermodynamic study based on liquid droplet model indicates that in the presence of small ammonia concentrations, H_2SO_4 vapor molecules in the lower atmosphere may be bound to stable ammonia-bisulfate clusters [*Vehkamäki et al.*, 2004]. It remains to be investigated whether H_2SO_4 molecules in the lower atmosphere are bound to stable ammonia-bisulfate clusters or not. Nevertheless, *Vehkamäki et al.* [2004] suggest that the formation of stable ammonia-bisulfate may actually inhibit the participation of H_2SO_4 in nucleation.

[27] The classical THN theory has been applied to interpret some observed nucleation events in the boundary atmosphere. For example, significant nucleation events were frequently observed during the 1999 New Particle Formation and Fate in the Coastal Environment (PARFORCE) coastal field campaign at Mace Head [*O'Dowd et al.*, 2002a], and *Kulmala et al.* [2002] concluded that all particle formation events observed at coastal sites can be initiated by ternary nucleation of $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$. More recently, frequent regional scale particle nucleation events were observed during the Pittsburgh Air Quality Study (PAQS) [*Stanier et al.*, 2004; *Zhang et al.*, 2004a], and *Gaydos et al.* [2005] argued that classical THN model gives excellent model-measurement agreement. However, our conclusion about the negligible contribution of THN to new particle formation in the boundary atmosphere, if confirmed, may suggest that mechanisms other than THN are responsible for these observed nucleation events. It appears that the new particle formation observed during PARFORCE is associated with the nucleation involving iodine-containing vapors [*O'Dowd et al.*, 2002b]. Using an updated version of ion-mediated nucleation (IMN) model, *Yu et al.* [2004] found that IMN mechanism appears to be able to explain the nucleation observed during PAQS. Our updated IMN model (F. Yu, manuscript in preparation, 2006) simulates explicitly the growth and evaporation of both charged and neutral clusters with size dependent growth and evaporation coefficient calculated with recently developed schemes [*Nadykto and Yu*, 2003; *Yu*, 2005a, 2005b, 2006]. In addition to ions, certain organic species may also enhance the nucleation rates [*Zhang et al.*, 2004b]. Further investigations are needed to determine the relative contributions of various nucleation mechanisms to new particle formation under different atmospheric conditions.

[28] With regard to the role of NH_3 in stabilizing $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ clusters, there is another experimental study reported

by *Hanson and Eisele* [2002] who found the enhancement in the formation of small clusters (clusters containing 2–6 H_2SO_4 molecules) at the presence NH_3 . Since the nucleated particles were not directly measured in the study of *Hanson and Eisele* [2002], and due to the limitation and uncertainties of the measurements, it is hard to determine to what degree the presence of NH_3 enhanced the nucleation rates. Nevertheless, a careful analysis of *Hanson and Eisele's* [2002] measurements may provide important information to constrain F_{NH_3} (especially the dependence of F_{NH_3} on the cluster sizes).

[29] The lack of reliable thermodynamic data is a problem for both classical and kinetic ternary nucleation model. The classical model uses the thermodynamic data of bulk solution calculated from thermodynamic multicomponent solution model. It is not clear how accurate the approximation to apply bulk properties to small ternary prenucleation clusters tends to be. Since the kinetic model explicitly simulates the evolution of clusters starting from monomers, it has the capability to take the advantage of bonding thermodynamic data of small clusters, which can be derived from density functional theory study [*Ianni and Bandy*, 1999] and prenucleation cluster measurements [*Hanson and Eisele*, 2002]. The kinetic model also enables us to make use of the experimental results to constrain the model. For example, instead of evaluating the Kelvin equation to calculate the evaporation coefficient for small molecular clusters, the thermodynamic data can be derived from DFT or other molecular level computations or experimental results [e.g., *D'Auria et al.*, 2004]. It will be difficult for the classical nucleation model to take into account such particular information about small cluster formation because the classical model assumes that the equilibrium concentrations of critical clusters are achieved instantaneously at given conditions, and it does not explicitly consider how these critical clusters are formed.

[30] While ammonia is known to be able to efficiently neutralize the acid solution, the efficiency of ammonia in stabilizing the small acid clusters and thus enhancing the nucleation rates remains to be investigated. As we illustrate in this paper, classical THN predictions conflict with experimental results. Comparison of our simulations based on the kinetic model with the observation of *Ball et al.* [1999] (and those of *Kim et al.* [1998], *Christensen et al.* [1994], *Diamond et al.* [1985] as well) suggests that the neutralization and stabilization of small prenucleation sulfuric acid clusters by ammonia are probably very limited. Obviously, more research is needed to quantify the real role of NH_3 in nucleation. Well-controlled laboratory experiments are the most useful tool to determine the magnitude of enhancement in nucleation rates when NH_3 is added to the binary system. Measurements of prenucleation clusters as well as DFT study of ternary clusters can provide important data to constrain F_{NH_3} and to improve the kinetic quasi-unary $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ nucleation model. It should also be noted that NH_3 molecule interacts strongly with ions due to its high dipole moment and is likely to be a key component of small ion clusters in the boundary atmosphere. Since NH_3 can stabilize small clusters, it could also enhance the ion-mediated nucleation. The possible role of NH_3 in nucleation via ion-mediated nucleation of $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$ remains to be investigated.

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