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Kinetic modeling of nucleation experiments involving SO_2 and OH: new insights into the underlying nucleation mechanisms

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Abstract. Nucleation is an important source of atmospheric aerosols which have significant climatic and health implications. Despite intensive theoretical and field studies over the past decades, the dominant nucleation mechanism in the lower troposphere remains to be mysterious. Several recent laboratory studies on atmospheric nucleation may shed light on this important problem. However, the most interesting finding from those studies was based on the derived H_2SO_4 concentration whose accuracy has not yet been evaluated by any other means. Moreover, the threshold H_2SO_4 concentration needed to reach the same degree of nucleation reported by two separate nucleation studies varies by about one order of magnitude. In this study, we apply a recently updated kinetic nucleation model to study the nucleation phenomena observed in those recent experiments. We show that the H_2SO_4 concentration can be estimated with a higher level of accuracy with the kinetic model by constraining the simulated particle size distributions with observed ones. We find that the required H_2SO_4 concentrations to achieve the best agreement between modeling and measurements are a factor of $\sim$2 to 4 higher than reported in those experiments. More importantly, by comparing the derived thermodynamic properties associated with the nucleation process, we conclude that different unknown species may participate in the two separate nucleation experimental studies, which may explain the large difference in the reported threshold H_2SO_4 concentration. Although the unknown species involved has yet to be identified, the derived values of thermodynamic properties can serve as a valuable guideline for the search of their chemical identities using advanced quantum-chemical approaches.

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1 Introduction

Atmospheric aerosols have been extensively investigated due to their climatic and health impacts (NRC, 2005; Alessandrini et al., 2006; Hoffmann et al., 2006; McConnell et al., 2006; IPCC, 2007; Rundell et al., 2007). Nucleation has been known as an important source of secondary aerosols in the troposphere. There exist three relatively well-developed theories: binary H_2SO_4-H_2O homogeneous nucleation (BHN) (Noppel et al., 2002; Vehkamaki et al., 2002; Yu, 2005, 2007), ternary NH_3-H_2SO_4-H_2O nucleation (THN) (Coffman and Hegg, 1995; Korhonen et al., 1999; Anttila et al., 2005; Yu, 2006a) and ion-mediated H_2SO_4-H_2O nucleation (Yu and Turco, 2000; Lovejoy et al., 2004; Yu, 2006b; Yu et al., 2008). In addition to BHN, THN is now also considered to be unimportant in the lower ambient troposphere (Merikanto et al., 2007; Yu and Turco, 2008). In contrast, Yu et al. (2008) suggests that ion-mediated H_2SO_4-H_2O nucleation may contribute substantially to new particle formation in the lower troposphere. It should be noted that the importance of ion-mediated nucleation in the atmosphere remains controversial. The possible reasons behind differences in the theories, interpretation and therefore conclusions have been discussed in detail in Yu et al. (2008) Yu and Turco (2008), and related online discussions. Besides BHN, THN, and IMN, other (yet to be identified) nucleation processes may also contribute to new particle formation in the atmosphere in some regions or under certain conditions.

Recent laboratory studies (Berndt et al., 2005, 2006, 2007, 2008; Svensmark et al., 2007; Benson et al., 2008; Young et al., 2008) reported new particle formation in the nucleation reactor/chamber under the conditions mimicking those in the lower ambient troposphere. The H_2SO_4 vapors in those experiments were produced in the same way as that in the real atmosphere (i.e., via the oxidation of SO_2 by OH), which sets them apart from earlier studies (Wyslouzil et al., 1991; Viisanen et al., 1997; Ball et al., 1999; Zhang et al., 2004)

in which H_2SO_4 vapors were obtained from the direct vaporization of the liquid H_2SO_4 reservoir. The most interesting finding in Berndt et al. (2005) is that only $\sim 10^7$ cm^{-3} of H_2SO_4 was needed to initiate the nucleation if H_2SO_4 vapors were produced *in situ* via the oxidation of SO_2 while $\sim 10^{10}$ cm^{-3} of H_2SO_4 was need if H_2SO_4 vapors were derived from the liquid H_2SO_4 reservoir. It has been suggested that the nucleation, starting via the oxidation of SO_2 which eventually leads to H_2SO_4 vapors, may be different from that starting directly from H_2SO_4 vapors. Similar laboratory experiments have been reported in more recent papers of Berndt et al. (2006, 2007, 2008) and in the work of Benson et al. (2008) and Young et al. (2008), although both Benson et al. (2008) and Young et al. (2008) found that the threshold H_2SO_4 vapor concentrations required to achieve nucleation rates of ~ 1 cm^{-3} s^{-1} are at least one order of magnitude higher than those derived in Berndt et al. (2006, 2007).

Given the importance of H_2SO_4 in observed atmospheric nucleation events (Kulmala et al., 2004), lower required threshold concentration of H_2SO_4 vapor *in-situ* produced via OH and SO_2 may indicate that a third specie facilitating the binary H_2SO_4-H_2O homogeneous nucleation may exist in those laboratory environments. Therefore, it is plausible to speculate that the ternary "unknown species"-H_2SO_4-H_2O nucleation may occur in those experiments. Berndt et al. (2007) suggested that the unknown species be produced during the conversion process of SO_2 into H_2SO_4. Since the temperature and concentrations of initial gases in those studies resemble those in the lower troposphere, the underlying "unknown species"-H_2SO_4-H_2O nucleation mechanism occurring in those experiments, if confirmed in the real atmosphere, may contribute to global new particle formation. In this regard, it is important to delineate the underlying process of nucleation observed in the abovementioned chamber studies. One critical question to be addressed is: is the large difference in the threshold H_2SO_4 concentration ($[H_2SO_4]$) between Berndt et al. (2008) and Benson et al. (2008)/Young et al. (2008) simply due to the errors/uncertainties in $[H_2SO_4]$ estimations or because of different nucleation mechanisms occurred? Since $[H_2SO_4]$ in the nucleation zone has never been directly measured and $[H_2SO_4]$ changes as air mass passed through the nucleation reactor/chamber, another related question is how $[H_2SO_4]$ variations (and uncertainties) may affect the interpretation of measurements obtained at the end of the reactor/chamber.

In this study, we attempt to address the above questions by kinetically simulating the time-dependent formation process of nanoparticles and their subsequent growth inside the nucleation reactors. We employed a size-resolved aerosol microphysical model with the most up-to-date kinetic quasi-unary nucleation (QUN) module (Yu, 2007). A number of sensitivity studies have been carried out to analyze the uncertainties and provide insights into the possible nucleation processes in those recently reported chamber studies.

2 Methods

A size-resolved aerosol microphysical model with the most up-to-date kinetic QUN module (Yu, 2007) has been employed and modified to study the possible nucleation processes in recently reported chamber studies. Since the H_2SO_4 concentration is changing along the axis of the reactor due to the competition between its production and loss, the kinetic aerosol model is better suited to study the aerosol formation and evolution in the concentration-changing environment. Yu (2007) substantially reduced the uncertainty in the H_2SO_4-H_2O binary homogeneous calculations by using two independent measurements to constrain monomer hydration in the H_2SO_4-H_2O system and incorporating recently determined energetics of small neutral H_2SO_4-H_2O clusters. In the past, we have applied this model to investigate the nanoparticle formation and evolution in the continuously diluting exhaust of diesel vehicles and it yields very good agreement with the measured particle size distributions (Du and Yu, 2006, 2008).

In this study, we modified the kinetic QUN model to derive $[H_2SO_4]$ needed to explain particle size distributions observed in laboratory studies, and to estimate quantitatively the level of stabilization of small sulfuric clusters by yet-to-be-identified specie(s) required to explain the nucleation rates observed in the recently reported nucleation chamber/reactor. Since H_2SO_4 vapors control the particle growth, the measured particle size distributions can be used to constrain $[H_2SO_4]$ inside the nucleation reactor. Because $[H_2SO_4]$ is an important parameter in any of the current nucleation theories, knowing correct $[H_2SO_4]$ in those recent laboratory measurements would give us more valuable insights into those studies. Another advantage of this aerosol microphysical model is that it can yield the values of stepwise Gibbs free energy changes associated with each of initial nucleation steps. This may give us a hint on the chemical identities of the unknown species involved in the nucleation, which may serves as a useful guideline for the species search using quantum-chemical calculations.

2.1 A modified kinetic H_2SO_4-H_2O quasi-unary nucleation model to treat ternary "unknown species"-H_2SO_4-H_2O nucleation

In essence, nucleation is a kinetic process determined by the cluster growth and decay (Yu, 2007). It can be simplified and illustrated by the following equation,

$$A + A_{i-1} \overset{\beta_{i-1}/\gamma_i}{\longleftrightarrow} A_i \tag{1}$$

where β_i and γ_i is the forward rate and evaporation rate of the cluster A_i (i.e., cluster containing i number of A ligand), respectively. Equation (1) only considers collisions between monomers and clusters while collisions among clusters are taken into account in the QUN as well. Similar to the role of NH_3 in the binary H_2SO_4-H_2O nucleation (Yu,

2006a), the unknown specie(s) may facilitate the binary homogeneous nucleation by reducing γ_i of binary clusters. In view of this, we incorporate the third "unknown" specie into the QUN model by modifying γ_i of binary clusters in a similar way as in Yu (2006a). This approach allows us to simulate the ternary "unknown species"-H_2SO_4-H_2O nucleation process without the need to know the chemical identity of the species. γ_i can be calculated by the stepwise Gibbs free energy change ($\Delta G_{i-1,i}$) associated with the above reaction by the following formula (Yu, 2007),

$$\frac{\beta_{i-1}}{\gamma_i} = \exp\left(-\frac{\Delta G_{i-1,i}}{kT}\right) \quad (2)$$

where k is the Boltzman constant and T is the temperature. In the QUN model, γ_i of a binary H_2SO_4-H_2O cluster is calculated with Eq. (2) after obtaining values of β_{i-1} and $\Delta G_{i-1,i}$ of binary clusters ($\Delta G^B_{i-1,i}$) (for details, please refer to Eqs. (14) and (15) in Yu, 2007). We assume that the difference in $\Delta G_{i-1,i}$ between ternary clusters and binary clusters is large for small clusters, and gradually approaches to zero as the size of cluster becomes bigger. In this study, theγ_i of ternary clusters ("unknown species"-H_2SO_4-H_2O clusters) is obtained using Eq. (2) with the $\Delta G_{i-1,i}$ of ternary cluster ($\Delta G^T_{i-1,i}$) calculated by the following equations,

$$\Delta G^T_{i-1,i} = \Delta G^B_{i-1,i} - dG\,(i) \quad (3)$$

$$dG\,(i) = a + \frac{b}{i^c} \quad (4)$$

$dG\,(i)$ is a term to account for the presence of the unknown species. It is a free parameter and assumed to be a function of cluster size. The values of $dG\,(i)$ can be varied to account for different degrees of stabilization to the binary H_2SO_4-H_2O clusters induced by the unknown species. It is chosen in such a way that the peak concentration of simulated particle size distribution matches that of measured one.

With the modified QUN module incorporated into the size-resolved aerosol microphysical model, we then apply it to simulate the nucleation process and the subsequent evolution of aerosol size distribution in the nucleation reactor. A discrete-sectional bin structure is used in the model to represent the size spectra of molecular clusters/particles ranging from sub-nanometers (the molecular size) to several micrometers and a set of differential equations are solved to simulate kinetically the formation and evolution of clusters/nanoparticles (Yu, 2006a).

β_i and γ_i are the two key parameters determining the evolution of the particle size distribution and thus nucleation rates (Yu, 2007). There exists one free parameter in each of them: [H_2SO_4] in calculating β_i and $dG\,(i)$ in obtaining γ_i. As we will show in Sect. 3, the median size of nucleated particles at the end of nucleation reactor is controlled by [H_2SO_4] while $dG\,(i)$ determines the peak concentrations and hence nucleation rates. Therefore, the measured median sizes of particle size distributions can be used to constrain H_2SO_4 concentrations. Once the H_2SO_4 concentration is fixed, the observed peak number concentration can then be used to constrain or derive $dG\,(i)$.

2.2 Calculations of [H_2SO_4] profiles in nucleation reactors

Due to different methods in producing H_2SO_4 vapors, [H_2SO_4] profiles are derived differently for Berndt et al. (2008) and Young et al. (2008). In calculating [H_2SO_4] profiles in Berndt et al. (2008), a chemical kinetic model was developed based on the following reactions,

$$OH + SO_2 \rightarrow ... \rightarrow H_2SO_4 \quad (5)$$

$$H_2SO_4 \rightarrow \text{wall} \quad (6)$$

Both Berndt et al. (2008) and Berndt et al. (2005) used the same method to produce H_2SO_4 and OH. OH concentration profile, explicitly given in Berndt et al. (2005), is adopted in our simulations. One can obtain different [H_2SO_4] profiles by modifying the OH concentration profile. With the same concentrations of initial gases and wall lost rate, we reproduced [H_2SO_4] given in Berndt et al. (2008). Different from Berndt et al. (2008) in which H_2SO_4 vapors were produced continuously in the nucleation chamber, H_2SO_4 vapors in Young et al. (2008) were produced before entering the fast flow nucleation reactor and subject mainly to the wall loss inside the reactor. The loss of H_2SO_4 vapors to nucleation and condensation processes is generally negligible compared to the wall loss due to the significant difference (several orders of magnitude) in the H_2SO_4 mass between the gas phase and the particle phase. [H_2SO_4] decreases exponentially inside the reactor in Young et al. (2008) due to the wall loss ([H_2SO_4]=[H_2SO_4]$_0$ exp($-Lt$), where L is the first order wall loss rate constant), while it first increases and then decreases in Berndt et al. (2008).

3 Results

3.1 A kinetic study of nucleation experiments reported in Young et al. (2008)

We first studied a case from Young et al. (2008) with 24 s of nucleation time and 4.9 ppm of initial SO_2 concentrations at T=288 K and RH=23%. The [H_2SO_4] profiles inside the nucleation reactor with three different initial values used in our simulations are presented in Fig. 1a. The [H_2SO_4] inside the reactor decreases exponentially with time due to the wall loss. The [H_2SO_4] at the end of the 24 s of nucleation time was constrained by the residual [H_2SO_4] measured at the end of the nucleation reactor which was assumed to be 2.4×10^9 cm^{-3} in this case (see Fig. 11 in Young et al., 2008).

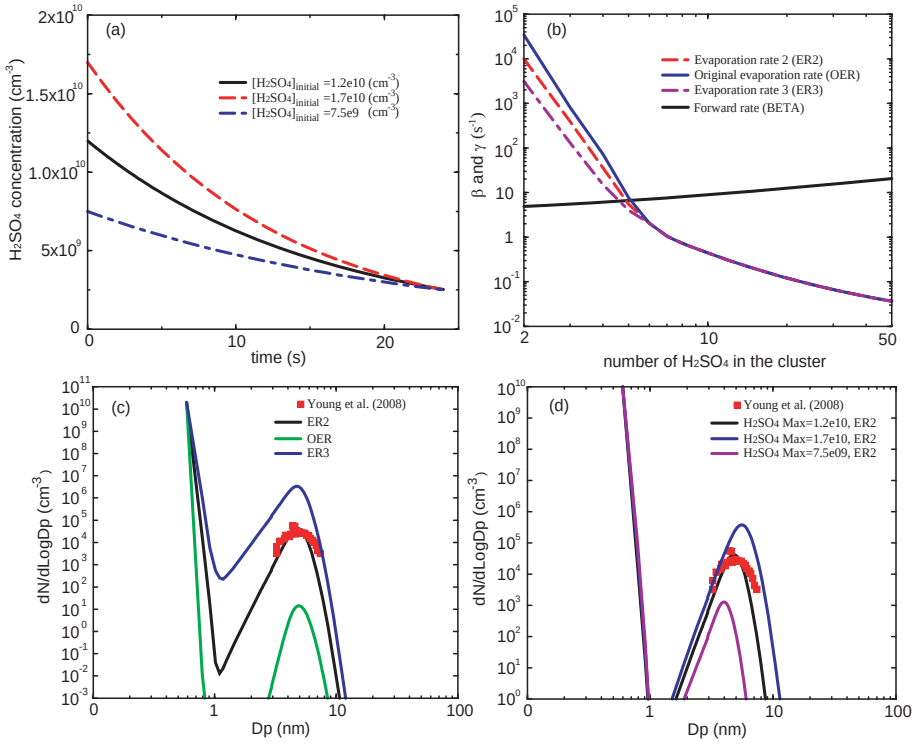

Fig. 1. **(a)** Evolution profiles of the H_2SO_4 concentration as function of time used in the simulations at three different initial [H_2SO_4] in the case of 24 s of nucleation time; **(b)** the assumed evaporation rates and forward rate used in the simulation of Young et al. (2008) at T=288 K and RH=23%; **(c)** effects of different cluster evaporation rates on the peak concentration of predicted particle size distribution with 1.2×10^{10} cm^{-3} of H_2SO_4; **(d)** effects of [H_2SO_4] on mean size of predicted particle size distribution with fixed cluster evaporation rate (ER2). The symbols in (c) and (d) are data from Young et al. (2008).

Due to the possible involvement of "unknown species" in the binary nucleation process, the evaporation rate profile of binary clusters/nanoparticles has to be modified to take into account the third species. $\Delta G^B_{i-1,i}$ (i.e., $\Delta G_{i-1,i}$ of binary H_2SO_4-H_2O clusters) are first calculated based on best available thermodynamics of sulfuric acid-water solution. Different profiles of $\Delta G^T_{i-1,i}$ are then derived with varied $dG\,(i)$ profiles (see Eq. 3). Finally, different profiles (i.e. ER2 and ER3) of evaporation rates of ternary clusters are obtained by Eq. (2). Figure 1b shows the evaporation rate and forward rate as a function of cluster/nanoparticle diameter at T=288 K and RH=23%. The solid curve represents the evaporate rate profile for binary H_2SO_4-H_2O clusters/nanoparticles predicted by QUN. The other two curves show the modified evaporate rate profiles for ternary "unknown species"-H_2SO_4-H_2O clusters/nanoparticles used in this case study. The cluster forward rate profile is calculated based on 1.2×10^{10} cm^{-3} of the initial [H_2SO_4].

With the [H_2SO_4] profile and cluster evaporation rates as illustrated in Fig. 1a–b, the particle size distribution can be obtained by solving a set of differential equations (Du and Yu, 2008). The calculated particle size distributions are then compared with measured ones to determine which [H_2SO_4] profile and cluster evaporation rates in Fig. 1a–b can best describe the observed nucleation phenomena. Figure 1c shows predicted particle size distributions with three different cluster evaporation rate profiles and a fixed [H_2SO_4] profile (i.e. black solid curve in Fig. 1a). It should be noted that mean sizes of calculated particle size distributions stay unchanged with the fixed [H_2SO_4] profile. They are insensitive to different evaporation rate profiles used in the simulation. With the same cluster evaporation rate profile, the mean size of calculated particle size distribution would change with different [H_2SO_4] profiles, as illustrated in Fig. 1d. This indicates that H_2SO_4 vapors dominate particle growth and its concentration determines particle mean size. This feature is then used to derive the initial concentration of H_2SO_4 vapors. In this way, the [H_2SO_4] profile, the free parameter in derivation of β_i, is determined. Based on the simulation, a 1.2×10^{10} cm^{-3} of initial [H_2SO_4] is needed to explain observed particle growth rate in this case.

Once the [H_2SO_4] profile inside the nucleation reactor is determined, $dG\,(i)$, the free parameter needed to derive evaporation rate profiles of ternary clusters/nanoparticles, is adjusted in such a way that the peak concentration of predicted particle size distribution matches that of measured one (see Fig. 1c). In this way, $dG\,(i)$ and the resultant ternary cluster evaporation rate profile (ER2 in this case) can be determined by comparisons with observation.

Figure 1 illustrated the approaches we used in this study as to obtain the accurate [H_2SO_4] profile and cluster evaporation rate profile based on measured particle size distributions. We showed that [H_2SO_4] profile can be obtained with a high degree of accuracy with this approach. In order to validate the derived cluster evaporation rate profile-ER2, we carried out two additional case studies with different nucleation times (t=37 s and 54 s) and initial SO_2 concentrations (4.6 ppm and 4.4 ppm) at the same ambient conditions. Since the T and RH in these two cases are the same as those of the first case study, the ER2 obtained is fixed in these two case studies with only one variable [H_2SO_4] in the simulation. Theoretically, the [H_2SO_4] not only determines the mean size of nucleation mode as mentioned above, but also controls the nucleation rate which can be reflected by the peak concentration of nucleation mode. Thus, the assumed [H_2SO_4] profile in the simulation has to yield a particle size distribution that matches not only the mean size but also the peak concentration of measured particle size distributions. Failure in matching both criteria may be a sign of poor evaporation rate profile (i.e. ER2 in this case) assumed.

The initial value [H_2SO_4] is selected to be 1.3×10^{10} and 1.4×10^{10} (cm^{-3}) for the t=37 s and 54 s case, respectively. The [H_2SO_4] at the end of residence time was also taken from the reported residual [H_2SO_4] (Young et al., 2008) which was 1.4×10^{9} cm^{-3} (t=37 s) and 1.5×10^{8} cm^{-3} (t=54 s), respectively. With the assumed ER2 and [H_2SO_4] profile, the evolution of particle size distributions inside the nucleation reactor has been simulated kinetically, as shown in Fig. 2. In both cases presented here, nucleation process inside the reactor starts as early as 0.1 s and continues as the peak concentration of nucleation mode increases until ~10 s. Since then, the H_2SO_4 condensational growth dominates the evolution of particle size distribution. The reason that the growth process outweighs the nucleation one in the evolution of particle size distributions after ~10 s is due to the rapid decrease in [H_2SO_4] resulting from the wall loss and the high sensitivity of nucleation rate to [H_2SO_4]. This also shows that nucleation happens only during a fraction of total residence time in the nucleation reactor.

As one can see, the predicted particle size distributions at the end of residence times in both cases are in an excellent agreement with the measurements. Good matches of predicted mean sizes of nucleation mode with measured ones indicate that the selected initial values and time profiles of [H_2SO_4] are appropriate and probably have a high level of accuracy. This also suggests that the ER2 may truly represent the cluster evaporation rates of nucleation occurred in the simulated experiment, given the good agreement of predicted peak concentrations of nucleation mode with measured ones.

Since the intersection of the cluster forward rate and evaporation rate locates the size of critical cluster (Yu, 2005), the predicted minimum number of H_2SO_4 molecules in the critical cluster is shown to be ~4 based on our simulation.

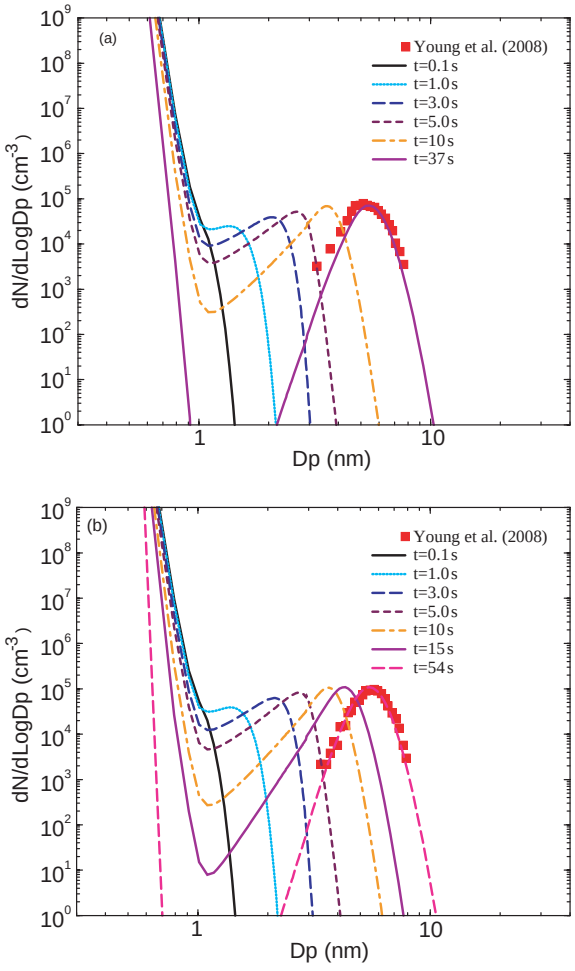

Fig. 2. Evolution of particle size distribution calculated based on the ER2 profile and given H_2SO_4 concentration profiles as shown in Fig. 1 at **(a)** t=37 s and **(b)** t=54 s. The symbols are measurements (taken at t=37 s and t=54 s, respectively) from Young et al. (2008).

This value in Young et al. (2008) was reported to be ~3, which was calculated from the slopes of nucleation rate vs. [H_2SO_4] plots. Considering the nature of the comparison and uncertainties associated with modeling and experiments, the agreement in the number of H_2SO_4 molecules in the critical cluster is reasonable.

In addition, an important parameter regarding the experiment, the wall loss factor (WLF), can be derived by dividing the obtained initial [H_2SO_4] by that measured at the exit of the reactor. The WLF based on the [H_2SO_4] profile in our study is calculated to be 5, 9 and 90 for the case with the nucleation time of 24 s, 37 s, and 54 s, respectively. The first two derived WLFs for cases with nucleation time of 24 s and 37 s are about a factor of 2 higher than those estimated in Young et al. (2008). However, for the case with nucleation time of 54 s, the difference in WLF estimation is as large as a factor of 7.6. Because the difference in the mean size of measured particle size distribution between 37 s case and 54 s

one is very small (i.e. ~0.25 nm, see Fig. 9 in Young et al., 2008), the [H_2SO_4] in these two cases should be very close since H_2SO_4 vapors dominate the particle growth. This suggests that the value of initial [H_2SO_4] used for the case with the nucleation time of 54 s is reasonably good. Thus, the significantly high WLF estimation for the 54 s case should be reasonable since the [H_2SO_4] at the end of the reactor is set to be the residual H_2SO_4 concentration reported in Young et al. (2008).

3.2 A kinetic study of nucleation experiments reported in Berndt et al. (2008)

We also carried out similar kinetic analysis of the work of Berndt et al. (2008). Both Young et al. (2008) and Berndt et al. (2008) focused on experimental investigations of nucleation starting via SO_2 and OH oxidation, although they had different experimental setups (especially on the method to produce OH). Here we adopted the same methodology used in the above case study and applied it to study the experiment of Berndt et al. (2008).

The [H_2SO_4] profile in the nucleation reactor first needs to be calculated by numerically solving the Eqs. (5) and (6) with an assumed OH concentration, as shown in Fig. 3a. The profile calculated by Berndt et al. (2008) was also included. Berndt et al. (2008) studied the effect of added background H_2SO_4 on nucleation (injected at t=0 s, and subject to wall loss). Figure 3a also gives three profiles of the background [H_2SO_4] with different initial values. The cluster evaporation rate profiles for both binary H_2SO_4-H_2O clusters and ternary "unknown species"-H_2SO_4-H_2O clusters are presented in Fig. 3b.

With the assumed [H_2SO_4] profile and the ternary cluster evaporation rate profile, the formation of nanoparticles and their evolution can be simulated kinetically and are presented in Fig. 4. No background [H_2SO_4] is assumed in this simulation. As one can see, the [H_2SO_4] profile with a maximum value of $\sim 8.5\times10^8$ (cm^{-3}) was needed in order to give a good agreement with the measured particle size distribution. Since the measured particle number concentration by CPC is 10 times higher than that integrated from the measured particle size distribution (Berndt et al., 2008), the peak concentration of simulated particle size distribution is higher than that of the measured one. Based on their chemical kinetic model, Berndt et al. (2008) predicted the maximum value for H_2SO_4 vapors to be $\sim 2.3\times10^8$ (cm^{-3}); however, this value clearly would yield a much smaller mean size of the particle size distribution (i.e. 1.2 nm in difference, see orange solid curve in Fig. 4). The underestimation of [H_2SO_4] in the study of Berndt et al. (2006) was pointed out in another work (Sorokin and Arnold, 2007), which is consistent with this study.

Figure 4 also shows that the nucleation inside the nucleation reactor started to become significant at t=~30 s due to the rapid increase of the [H_2SO_4] via OH and SO_2 reaction and continues until t=~100 s. Since then, H_2SO_4 condensational growth began to dominate the change of particle size distribution due to the absence of H_2SO_4 production (no UV illumination in the third section of the nucleation reactor) and the wall loss. In addition, for the case studied here, the minimum number of H_2SO_4 molecules in the critical cluster (corresponding to the time period with maximum nucleation rate) is predicted to be ~5 based on Fig. 4b and may increase as [H_2SO_4] decreases. This value was reported to be ~4 for the nucleation observed in Berndt et al. (2005). Again the agreement is reasonable.

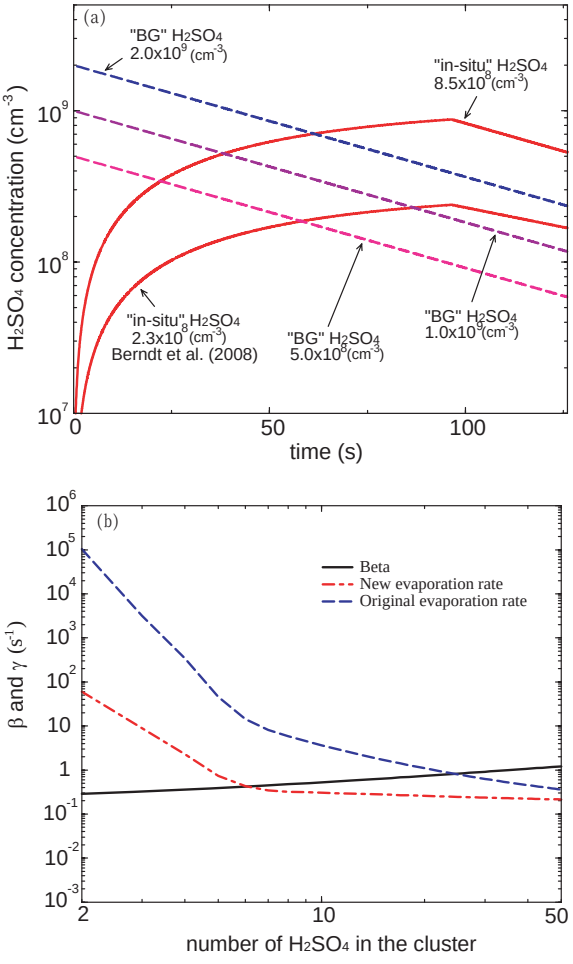

Fig. 3. (a) Simulated evolution profiles of *in-situ* produced H_2SO_4 concentration at two different maximum concentrations and background H_2SO_4 concentration at several initial concentrations, and **(b)** the comparison of the evaporation rate profile obtained based on the QUN model with that assumed in the present case study and the forward rate. T=288 K and RH=23%.

The most surprising conclusion made in the work of Berndt et al. (2008) is that H_2SO_4 vapors do not contribute to cluster/particle growth. They came to this conclusion based on an experiment in which the measured particle size distributions were not changed when they switched on and off the background H_2SO_4 source. In this study, we examined the same experiment and studied the sensitivity of particle size

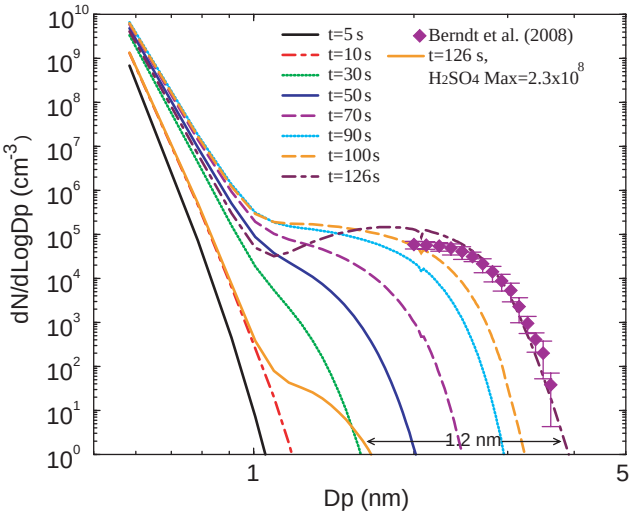

Fig. 4. Simulated evolution of the particle size distribution in the nucleation reactor with total residence time of 126 s at T=293 K and RH=23%. The measurement of particle size distribution with error bars by Berndt et al. (2008) was also included.

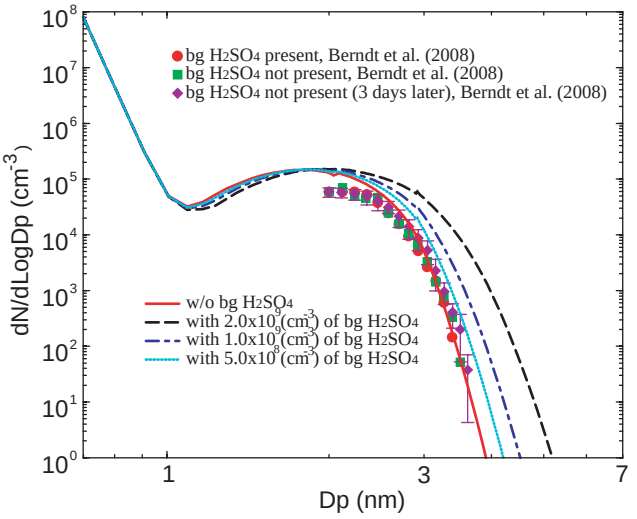

Fig. 5. Effects of background H_2SO_4 concentration on the particle size distribution at the end of nucleation chamber (t=126 s).

distribution to the background [H_2SO_4].

Figure 5 shows the particle size distributions at the end of the nucleation reactor (t=126 s) under several different initial background values of [H_2SO_4]. The background [H_2SO_4] profiles with different initial values are shown in Fig. 3a. It is assumed that wall loss is the major factor to change the background [H_2SO_4] profile inside the reactor. The wall loss coefficient is set to be 0.017 (s^{-1}) which is taken from Berndt et al. (2008). In the simulation, we assume that the background H_2SO_4 vapor only contributes to the particle growth and does not participate in the nucleation. This assumption allows us to focus on the role of background H_2SO_4 on particle growth alone.

We found through our simulation that, as expected, the effect of background [H_2SO_4] on particle growth depends on the relative abundance of background versus *in-situ* produced H_2SO_4. Compared to the measurements, the particle diameter can increase by as much as 1 nm if the background [H_2SO_4] with an initial value of 2.0×10^9 cm^{-3} was switched on. If the initial value decreases to 1.0×10^9 cm^{-3}, which is on the lower end of the reported initial [H_2SO_4], the increase in particle diameter decreases to ~0.5 nm. However, the gap in particle size distributions is still large enough to be discerned. We found that if the background [H_2SO_4] is less than 5.0×10^8 cm^{-3}, the difference in calculated particle size distributions between with and without background H_2SO_4 source cases are within measurement uncertainties due to instrument limitations. As a result, the particle size distribution would appear to be unchanged when the background H_2SO_4 source was switched on and off.

The H_2SO_4-like substance $HOSO_4$ was suggested in Berndt et al. (2008) to explain the particle growth; however, its concentration is much lower than that of H_2SO_4. In addition, the produced nanoparticles, which have the affinity to $HOSO_4$, should also have the similar affinity to H_2SO_4 since H_2SO_4 has similarities to $HOSO_4$ chemically and structurally. Although sulfur-containing species are very likely to be the particle growth contributor based on the chemical reactions taking place inside the nucleation reactor, the possibility of some species other than H_2SO_4 and $HOSO_4$ contributing to particle growth cannot be excluded. However, to our best knowledge, it remains unknown and needs further experimental investigations. Therefore, the statement that some unknown species, not the H_2SO_4 vapor, is responsible for the observed cluster/particle growth needs to be much more carefully examined experimentally, given the importance of H_2SO_4 in cluster/particle growth observed in numerous ambient nucleation measurements (Kulmala et al., 2004) and the fact that no actual background H_2SO_4 concentration measurements in nucleation zone was carried out in the work of Berndt et al. (2008).

3.3 Thermochemistry: implications for the underlying nucleation mechanisms

The above simulations of nucleation and evolution processes inside the nucleation reactor/chamber aimed at studying the nucleation experiments from a kinetic point of view; however, the underlying nucleation mechanisms remain mysterious. Identification of the "unknown species" requires the knowledge of thermochemistry associated with the nucleation process. One advantage of the kinetic QUN model used in this study is the output of $\Delta G_{i-1,i}$ associated with the simulated nucleation process, which may give us insights into the underlying nucleation mechanisms.

Figure 6 shows the $\Delta G_{i-1,i}$ of the binary H_2SO_4-H_2O homogeneous nucleation calculated based on the QUN and those of the ternary "unknown species"-H_2SO_4-H_2O nucleation derived from both case studies. Also included were $\Delta G_{i-1,i}$ of the hydrated H_2SO_4 dimer and trimer at the two temperatures derived based on the experimentally measured thermochemistries (Kazil et al., 2007). In theory, nucleation rate is determined by clusters smaller than the critical one. Therefore, we only need to focus on $\Delta G_{i-1,i}$ with $i \leq 5$ because the number of H_2SO_4 molecules in the critical cluster for both studies was reported to be less than 6. At T=288 K and RH=23%, the $\Delta G_{i-1,i}$ of the hydrated H_2SO_4 dimer and trimer based on QUN is -7.1 and -9.3 kcal/mol, respectively. These Gibbs free energies are not low enough to explain the observed nucleation in Young et al. (2008). As one can see, with the presence of the third unknown species, the $\Delta G_{i-1,i}$ of ternary clusters for the dimer and trimer needs to be reduced to -7.8 and -9.5 kcal/mol in order to explain the observed nucleation. In the case of Berndt et al. (2008), the formation energies of ternary clusters need to be even lower. The $\Delta G_{i-1,i}$ of the dimer and trimer ternary clusters is ~ -11 and -12.5 kcal/mol, respectively. Although the differences in $\Delta G_{i-1,i}$ between binary and ternary clusters are significant for smaller ones, they gradually approach to zero as the cluster size grows.

As mentioned earlier, both Young et al. (2008) and Berndt et al. (2008) initiated their nucleation experiments via SO_2 and OH oxidation. Nearly all the initial gases in their experiments are the same except that organics or CO were used in Berndt et al. (2008) for the OH titration. Organics have been shown not to affect nucleation by replacing them with CO. Thus it is reasonable to speculate that the underlying nucleation mechanism occurred in both studies should be the same. However, by comparing $\Delta G_{i-1,i}$ of the binary clusters with that of the ternary clusters for each case study and inter-comparing $\Delta G_{i-1,i}$ of ternary clusters derived from both case studies, we found out that the proposed "unknown species" may be different for the two independent studies. It implies that the underlying nucleation mechanisms happened in the two separate studies (after taking into account the difference in T, RH, and [H_2SO_4] profiles) may be different.

There exist several reasons leading us to conclude that the "unknown species" involved in both studies are different. Firstly, the $\Delta G_{i-1,i}$ profiles of ternary clusters derived from both studies behave in a different way. The $\Delta G_{i-1,i}$ profile of the ternary clusters in the case of Young et al. (2008) quickly approaches to that of binary clusters at i=6 while the difference in $\Delta G_{i-1,i}$ between the binary cluster and ternary cluster in the case of Berndt et al. (2008) is as large as -1.5 Kcal/mol even at i=10. Secondly, the largest difference in $\Delta G_{i-1,i}$ between binary and ternary clusters is ~ -1 Kcal/mol at i=2 for the case of Young et al. (2008); however, it is as large as ~ -4 Kcal/mol in the case of Berndt et al. (2008). Our calculation shows that the temperature variation cannot explain this large difference ($\sim$3 kcal/mole)

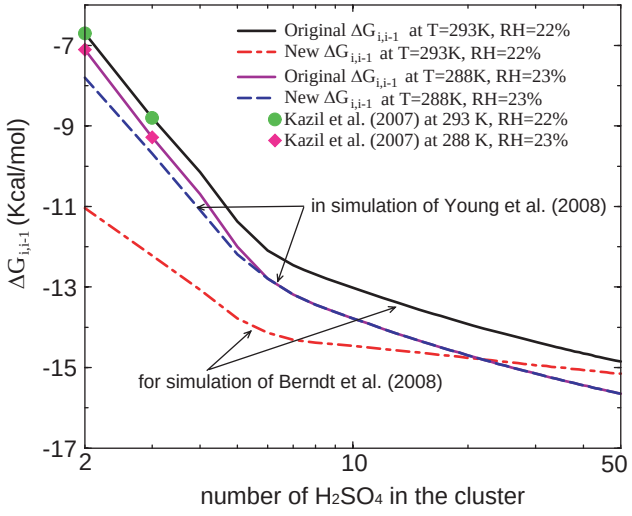

Fig. 6. Comparisons of the stepwise Gibbs free energy changes associated with the ternary "unknown species" H_2SO_4-H_2O nucleation derived kinetically from case studies of Young et al. (2008) and Berndt et al. (2008) with those from the binary H_2SO_4-H_2O homogeneous nucleation.

in $\Delta G_{i-1,i}$ between 293 K and 288 K. Thirdly, the derived pairs of ΔH and ΔS were abnormal. Based on the definition of Gibbs free energy change ($\Delta G = \Delta H - T\Delta S$), we also calculated ΔH and ΔS since ΔG of the ternary clusters at two different temperature are available. For example, at i=2, $\Delta G_{i-1,i}$ of ternary clusters is -7.8 Kcal/mol and -11 Kcal/mol for T=288 K and 293 K, respectively. The calculated ΔH is unrealistically as high as 176.53 Kcal/mol. All these evidences lead us to conclude that the two $\Delta G_{i-1,i}$ profiles of ternary clusters derived from two independent studies may represent two different "unknown species" involved in each experiment. Although both of experiments started via OH and SO_2 oxidation, two different species may participate in and enhance the binary H_2SO_4-H_2O homogeneous nucleation. The likely reasons for the different nucleation mechanisms in quite similar experiments, in which H_2SO_4 vapors were produced *in-situ* by SO_2 and OH oxidation and majority of the initial gas species are the same, need further investigations.

The possible candidates for the "unknown species" may be $HOSO_2$, $HOSO_4$ or even impurities. Currently, the chemical identity of the "unknown species" has not yet been resolved; however, the derived $\Delta G_{i-1,i}$ of the ternary clusters can serve as a useful guideline for the search of the "unknown species" using quantum-chemical methods. Berndt et al. (2008), on the basis of the lack of the changes in measured particle size distribution with and without background H_2SO_4, suggested that the mechanism for their observed nucleation phenomenon be the free radical nucleation and no role of H_2SO_4 in nucleation and growth. This is surprising because H_2SO_4 is known to be a key nucleation

and condensation precursor in the atmosphere. It should be pointed out that the previous study of Berndt et al. (2007) clearly shows the increase of total particle number concentration as the number concentration of the "*in-situ*" produced H_2SO_4 increases. This is a clear indication that H_2SO_4 molecules were involved in the observed nucleation. The sensitivity of particle size distribution to the H_2SO_4 concentration was also observed in Benson et al. (2007) and Young et al. (2008). It remains to be understood why adding background H_2SO_4 into nucleation chamber does not influence the measured particle size distributions in the study of Berndt et al. (2008) (also see Fig. 5).

4 Summary and discussion

Recent laboratory studies initiating nucleation via SO_2 and OH oxidation presented important information for the investigation of possible nucleation mechanisms in the lower troposphere. The purpose of this work is to study those experiments from a modeling perspective. We applied a size-resolved aerosol microphysical model with the most up-to-date kinetic quasi-unary nucleation module to simulate the nucleation and the subsequent growth of newly-formed particles inside the nucleation reactor. Since H_2SO_4 vapors dominate the particle growth, by matching the mean size of predicted nucleation mode with the measured one, the $[H_2SO_4]$ inside the nucleation reactor can be calculated with a higher degree of accuracy. In addition, the values of stepwise Gibbs free energy changes associated with initial steps of nucleation can also be obtained, which can provide valuable insights into the "unknown species".

Our simulations suggest that the $[H_2SO_4]$ in the two separate studies was underestimated. In the case study of Young et al. (2008), more than $\sim 10^{10}$ cm^{-3} of H_2SO_4 was needed at the inlet of the nucleation reactor in order for newly formed particles to grow to observed sizes under the given nucleation time. The WLFs calculated based on the derived initial $[H_2SO_4]$ is at least a factor of 2 higher than those reported in the experiment. In the simulation of Berndt et al. (2008), the $[H_2SO_4]$ profile with a maximum value of $\sim 8.5\times 10^8$ cm^{-3} was needed to give the best agreement with the measured particle size distribution. This is larger than the reported value by a factor of $\sim$4. We demonstrated that relatively unchanged particle size distributions can be achieved with and without background H_2SO_4 vapors if the background $[H_2SO_4]$ is smaller than $\sim 5.0\times 10^8$ cm^{-3}. It remains to be investigated why adding background H_2SO_4 into nucleation chamber does not influence the measured particle size distributions.

As for the number of H_2SO_4 molecules in the critical cluster, the value predicted in our study is a little higher but close to those calculated based on slope of nucleation rate vs. $[H_2SO_4]$ plots. We also studied the kinetics of particle evolution inside the nucleation reactor. We found that nucleation dominates only within a fraction of total residence time in the reactor and the H_2SO_4 condensational growth then takes over as the $[H_2SO_4]$ begins to decrease.

More importantly, although both Berndt et al. (2008) and Young et al. (2008) initiated nucleation via SO_2 and OH oxidation, comparisons of the derived values of stepwise Gibbs free energy changes related to initial steps of nucleation show that two different "unknown species" may participate in the nucleation observed in the experiments. It implies that nucleation mechanisms occurred in the two separate studies may be different. Although the chemical identity of the "unknown species" has not yet been resolved, the derived values of $\Delta G_{i-1,i}$ of the ternary clusters can provide an important direction for the future search of the "unknown species" with quantum-chemical methods.

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References

Alessandrini, F., Schulz, H., Takenaka, S., Lentner, B., Karg, E., Behrendt, H. and Jakob, T.: Effects of ultrafine carbon particle inhalation on allergic inflammation of the lung, J. Allergy Clin. Immun., 117, 824–830, 2006.

Anttila, T., Vehkamaki, H., Napari, I., and Kulmala, M.: Effect of ammonium bisulphate formation on atmospheric water-sulphuric acid-ammonia nucleation, Boreal Environ. Res., 10, 511–523, 2005.

Ball, S. M., Hanson, D. R., Eisele, F. L., and McMurry, P. H.: Laboratory studies of particle nucleation: Initial results for H_2SO_4, H_2O, and NH_3 vapors, J. Geophys. Res., 104, 23709–23718, 1999.

Benson, D. R., Young, L. H., Kameel, F. R., and Lee, S. H.: Laboratory-measured nucleation rates of sulfuric acid and water binary homogeneous nucleation from SO_2 + OH reaction, Geophys. Res. Lett., 35, L11801, doi:10.1029/2008GL033387, 2008.

Berndt, T., Boge, O., and Stratmann, F.: Formation of atmospheric H_2SO_4-H_2O particles in the absence of organics: A laboratory study, Geophys. Res. Lett., 33, L15817, doi:10.1029/2006GL026660, 2006.

Berndt, T., Boge, O., and Stratmann, F.: Atmospheric H_2SO_4/H_2O particle formation: Mechanistic investigations, Nucleation and Atmospheric Aerosols, Galway, Ireland, Springer, 2007.

Berndt, T., Boge, O., Stratmann, F., Heintzenberg, J., and Kulmala, M.: Rapid formation of sulfuric acid particles at near-atmospheric conditions, Science, 307, 698–700, 2005.

Berndt, T., Stratmann, F., Bräsel, S., Heintzenberg, J., Laaksonen, A., and Kulmala, M.: SO_2 oxidation products other than H_2SO_4 as a trigger of new particle formation. Part 1: Laboratory investigations, Atmos. Chem. Phys., 8, 6365–6374, 2008, http://www.atmos-chem-phys.net/8/6365/2008/.

Coffman, A. D. and Hegg, D. A.: A preliminary study of the effect of ammonia on particle nucleation in the marine boundary layer, J. Geophys. Res., 100(D4), 7147–7160, 1995.

Du, H. and Yu, F.: Role of the binary H_2SO_4-H_2O homogeneous nucleation in the formation of volatile nanoparticles in the vehicular exhaust, Atmos. Environ., 40, 7579–7588, 2006.

Du, H. and Yu, F.: Nanoparticle formation in the exhaust of vehicles running on ultra-low sulfur fuel, Atmos. Chem. Phys., 8, 4729–4739, 2008, http://www.atmos-chem-phys.net/8/4729/2008/.

Hoffmann, B., Moebus, S., Stang, A., Beck, E. M., Dragano, N., Mohlenkamp, S., Schmermund, A., Memmesheimer, M., Mann, K., Erbel, R., and Jockel, K. H.: Residence close to high traffic and prevalence of coronary heart disease, Eur. Heart J., 27, 2696–2702, 2006.

IPCC: Climate Change 2007, in: The Physical Scientific Basis, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., New York, Cambridge Univ. Press, 2007.

Kulmala, M., Vehkamaki, H., Petaja, T., Dal Maso, M., Lauri, A., Kerminen, V. M., Birmili, W., and McMurry, P. H.: Formation and growth rates of ultrafine atmospheric particles: a review of observations, J. Aerosol Sci., 35, 143–176, 2004.

Korhonen, P., Kulmala, M., Laaksonen, A., Viisanen, Y., McGraw, R., and Seinfeld, J. H.: Ternary nucleation of H_2SO_4, NH_3, and H_2O in the atmosphere, J. Geophys. Res., 104, 26349–26353, 1999.

Kazil, J., Lovejoy, E. R., Jensen, E. J., and Hanson, D. R.: Is aerosol formation in cirrus clouds possible?, Atmos. Chem. Phys., 7, 1407–1413, 2007, http://www.atmos-chem-phys.net/7/1407/2007/.

Lovejoy, E. R., Curtius, J., and Froyd, K. D.: Atmospheric ion-induced nucleation of sulfuric acid and water, J. Geophys. Res., 109, D08204, doi:10.1029/2003JD004460, 2004.

McConnell, R., Berhane, K., Yao, L., Jerrett, M., Lurmann, F., Gilliland, F., Kunzli, N., Gauderman, J., Avol, E., Thomas, D., and Peters, J.: Traffic, susceptibility, and childhood asthma, Environ. Health Persp., 114, 766–772, 2006.

Merikanto, J., Napari, I., Vehkamaki, H., Anttila, T. and Kulmala, M.: New parameterization of sulfuric acid-ammonia-water ternary nucleation rates at tropospheric conditions, J. Geophys. Res., 112, D15207, doi:10.1029/2006JD007977, 2007.

Noppel, M., Vehkamaki, H., and Kulmala, M.: An improved model for hydrate formation in sulfuric acid–water nucleation, J. Chem. Phys., 116, 218–228, 2002.

NRC: Radiative forcing of climate change: Expanding the concept and addressing uncertainties, National Academies Press, 2005.

Rundell, K. W., Hoffman, J. R., Caviston, R., Bulbulian, R., and Hollenbach, A. M.: Inhalation of ultrafine and fine particulate matter disrupts systemic vascular function, Inhal. Toxicol., 19, 133–140, 2007.

Sorokin, A. and Arnold, F.: Laboratory study of cluster ions formation in H_2SO_4-H_2O system: Implications for threshold concentration of gaseous H2SO4 and ion-induced nucleation kinetics, Atmos. Environ., 41, 3740–3747, 2007.

Svensmark, H., Pedersen, J. O. P., Marsh, N. D., Enghoff, M. B., and Uggerhøj, U. I.: Experimental evidence for the role of ions in particle nucleation under atmospheric conditions, Proc. R. Soc. A: Math., Phys. Eng. Sci., 463, 385–396, 2007.

Vehkamaki, H., Kulmala, M., Napari, I., Lehtinen, K. E. J., Timmreck, C., Noppel, M., and Laaksonen, A.: An improved parameterization for sulfuric acid-water nucleation rates for tropospheric and stratospheric conditions, J. Geophys. Res., 107(D22), 4622, doi:10.1029/2002JD002184, 2002.

Viisanen, Y., Kulmala, M., and Laaksonen, A.: Experiments on gas-liquid nucleation of sulfuric acid and water, J. Chem. Phys., 107, 920–926, 1997.

Wyslouzil, B. E., Seinfeld, J. H., Flagan, R. C., and Okuyama, K.: Binary nucleation in acid-water systems. II. Sulfuric acid-water and a comparion with methanesulfonic acid-water, J. Chem. Phys., 94, 6842–6850, 1991.

Young, L. H., Benson, D. R., Kameel, F. R., Pierce, J. R., Junninen, H., Kulmala, M., and Lee, S.-H.: Laboratory studies of H_2SO_4/H_2O binary homogeneous nucleation from the SO_2+OH reaction: evaluation of the experimental setup and preliminary results, Atmos. Chem. Phys., 8, 4997–5016, 2008, http://www.atmos-chem-phys.net/8/4997/2008/.

Yu, F.: Quasi-unary homogeneous nucleation of H_2SO_4-H_2O, J. Chem. Phys., 122, 074501, 1–8, 2005.

Yu, F.: Effect of ammonia on new particle formation: A kinetic H_2SO_4-H_2O-NH_3 nucleation model constrained by laboratory measurements, J.Geophys. Res., 111, D01204, doi:10.1029/2005JD005968, 2006a.

Yu, F.: From molecular clusters to nanoparticles: second-generation ion-mediated nucleation model, Atmos. Chem. Phys., 6, 5193–5211, 2006b, http://www.atmos-chem-phys.net/6/5193/2006/.

Yu, F.: Improved quasi-unary nucleation model for binary H_2SO_4-H_2O homogeneous nucleation, J. Chem. Phys., 127, 504301, 2007.

Yu, F. and Turco, R. P.: Ultrafine aerosol formation via ion-mediated nucleation, Geophys. Res. Lett., 27, 883–886, 2000.

Yu, F. and Turco, R.: Case studies of particle formation events observed in boreal forests: implications for nucleation mechanisms, Atmos. Chem. Phys., 8, 6085–6102, 2008, http://www.atmos-chem-phys.net/8/6085/2008/.

Yu, F., Wang, Z., Luo, G., and Turco, R.: Ion-mediated nucleation as an important global source of tropospheric aerosols, Atmos. Chem. Phys., 8, 2537–2554, 2008, http://www.atmos-chem-phys.net/8/2537/2008/.

Zhang, R., Suh, I., Zhao, J., Zhang, D., Fortner, E. C., Tie, X., Molina, L. T., and Molina, M. J.: Atmospheric new particle formation enhanced by organic acids, Science, 304, 1487–1490, 2004.