Quasi-unary homogeneous nucleation of H₂SO₄-H₂O

Fangqun Yu[a)]

Atmospheric Sciences Research Center, State University of New York at Albany, 251 Fuller Road, Albany, New York 12203

We show that the binary homogeneous nucleation (BHN) of H_2SO_4-H_2O can be treated as quasi-unary nucleation of H_2SO_4 in equilibrium with H_2O vapor. A scheme to calculate the evaporation coefficient of H_2SO_4 molecules from H_2SO_4-H_2O clusters is presented and a kinetic model to simulate the quasi-unary nucleation of H_2SO_4-H_2O is developed. In the kinetic model, the growth and evaporation of sulfuric acid clusters of various sizes are explicitly simulated. The kinetic quasi-unary nucleation model does not have two well-recognized problems associated with the classical BHN theory (violation of the mass action law and mismatch of the cluster distribution for monomers) and is appropriate for the situations where the assumption of equilibrium cluster distribution is invalid. The nucleation rates predicted with our quasi-unary kinetic model are consistent with recent experimental nucleation experiments in all the cases studied, while the most recent version of the classical BHN model systematically overpredicts the nucleation rates. The hydration of sulfuric acid clusters, which is not considered in the classical model but is accounted for implicitly in our kinetic quasi-unary model, is likely to be one of physical mechanisms that lead to lower nucleation rates. Further investigation is needed to understand exactly what cause the difference between the kinetic quasi-unary model and the classical BHN model. © 2005 American Institute of Physics. [DOI: 10.1063/1.1850472]

I. INTRODUCTION

Atmospheric aerosols impact climate indirectly by acting as cloud condensation nuclei and altering cloud formation, cloud properties, and precipitations.[1,2] The aerosol indirect radiative forcing is poorly constrained in climate models and this represents the single greatest uncertainty in assessing climate change.[3] To reduce the uncertainty in aerosol indirect radiative forcing and to improve the predictive understanding of the aerosol radiative forcing on Earth's climate, the mechanisms of atmospheric aerosol formation have to be identified and the uncertainties in the predicted nucleation rates have to be reduced.

Gaseous H_2SO_4 and H_2O are two well-recognized nucleation precursors in the atmosphere as they have very low vapor pressure over the binary H_2SO_4-H_2O solution. Binary homogeneous nucleation (BHN) of H_2SO_4 and H_2O has been extensively studied in the past half century, and the classical BHN theory has been widely used to predict the particle formation in the troposphere and stratosphere.[4–11] The first study of H_2SO_4-H_2O BHN rate was presented by Doyle[12] who applied the BHN theory which was first developed by Flood[13] and later significantly improved by Reiss.[14] In the classical BHN theory, the rate of nucleation J can is written as[13]

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

where C is a frequency factor and $\Delta G*$ is the free energy required to form a critical cluster. k is the Boltzmann's constant and T is the temperature. By assuming (as in the unary

nucleation theory) that each clusters grow or shrink by acquisition or loss of single molecules, Reiss[14] first derived an expression for the frequency factor C as the following:

$$C = \frac{\beta_a \beta_b}{\beta_a \sin^2 \theta + \beta_b \cos^2 \theta} 4\pi r^{*2}(n_a + n_b)Z, \qquad (2)$$

where β_a and β_b are the impingement rates (i.e., number of molecules colliding with the cluster per unit area per unit time) of species a and b. n_a and n_b are number densities of species a and b. θ is the angle between the n_a axis and direction of the pass through the saddle point. $r*$ is the radius of critical cluster and Z is the Zeldovich nonequilibrium factor. Equation (1) combined with Eq. (2), can be rearranged as

$$J = K_{act} n *, \qquad (3)$$

$$K_{act} = \frac{\beta_a \beta_b}{\beta_a \sin^2 \theta + \beta_b \cos^2 \theta} 4\pi r^{*2} Z, \qquad (4)$$

$$n * = (n_a + n_b)\exp(-\Delta G * /kT), \qquad (5)$$

where $n*$ is the equilibrium concentration of the critical embryos at the given condition and K_{act} can be considered as the flux coefficient around the critical size. It is noteworthy that the flux coefficient K_{act} takes into account both the forward and reverse flux around the critical size.[14]

The nucleation rate predicted by Eq. (3) is very sensitive to $\Delta G*$ and a small variation in $\Delta G*$ (as a result of uncertainties in surface tension, vapor pressures, etc.) can lead to significant uncertainty in the predicted J. Sulfuric acid vapor molecules tend to form hydrates which stabilize the vapor and hinder nucleation. The effect of hydration on nucleation

a)Electronic mail: yfq@asrc.cestm.albany.edu

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has been taken into account in the updated versions of classical BHN theory.[15,16] A recent version of H_2SO_4-H_2O hydration model with many improvements is described in Noppel et al.[17] The nucleation rates are reduced by a factor of 10^3–10^8 when the hydration effect is included.

The widely used cluster size distribution expressed by Eq. (5) is known to violate the mass action law and gives an inconsistent concentration of monomers.[18,19] Attempts to correct these inconsistencies have been made.[19,20] One form of the cluster size distribution that obeys the law of mass action and takes into account the effect of hydration is given below as[17]

$$n(i_a,i_b) = n_a^{free}\left(\frac{n_b^{free}}{n_0}\right)^2 K_1 K_2 \exp\left[-\frac{\Delta G(i_a,i_b) - \Delta G(1,2)}{kT}\right]$$

$$= n(1,2)\exp\left[-\frac{\Delta G(i_a,i_b) - \Delta G(1,2)}{kT}\right], \quad (6)$$

where $n(i_a,i_b)$ and $\Delta G(i_a,i_b)$ are the concentration and the formation energy of the cluster containing $i_a H_2SO_4$ molecules and i_b water molecules, respectively. n_a^{free} and n_b^{free} are the concentrations of free molecules of components $a(H_2SO_4)$ and $b(H_2O)$ in the vapor, respectively. n_0 is the reference vapor concentration (usually taken to be Loschmidt's number). K_i is the equilibrium constant for the addition of a water molecule to an existing hydrate $(H_2SO_4)(H_2O)_{i-1}$. In Eq. (6), the dihydrate $(i_a=1, i_b=2)$ is chosen as a reference point. Any other hydrates for which the equilibrium constant are known could alternatively be chosen as the reference point.[17]

Binary homogeneous nucleation of H_2SO_4-H_2O has also been investigated in the laboratory.[21,22] Vehkamäki et al.[23] showed that the nucleation rates predicted with the most recent version of the classical BHN theory[17] are generally some orders of magnitudes higher than the recent laboratory results reported by Viisanen et al.[21] and Ball et al.[22]

The widely used classical BHN theory not only has the issues of the mass action law violation and monomer concentration mismatch,[18,19] but also its assumption of instantaneously achieved equilibrium distribution of critical clusters [Eq. (5)] at given H_2SO_4 concentration and ambient conditions may be invalid when the concentrations of H_2SO_4 vapor, temperature, and relative humidity (RH) in the air mass change rapidly.[24] These problems of classical BHN model can be avoided if the cluster evolution during BHN of H_2SO_4-H_2O is simulated directly using a kinetic model. While the kinetic simulation of unary system is relatively simple and it has been shown that the classical expression of unary nucleation rates can be derived kinetically,[25] an explicit kinetic simulation of the binary collision and dissociation among H_2SO_4 and H_2O clusters/molecules is very complex. However, as we show in this study, the binary nucleation of H_2SO_4-H_2O can be reduced to the quasi-unary nucleation of H_2SO_4 in equilibrium with H_2O vapor and a kinetic model can be developed accordingly.

In Sec. II, we present in detail a kinetic model for simulating the quasi-unary nucleation of H_2SO_4-H_2O. In Sec. III, the nucleation rates predicted with the kinetic quasi-unary nucleation model are compared with those observed in recent laboratory nucleation measurements as well as those predicted by the most recently updated version of the classical BHN theory. The summary and discussion are provided in Sec. IV.

II. A KINETIC MODEL TO SIMULATE THE QUASI-UNARY NUCLEATION OF H_2SO_4-H_2O

A. Quasi-unary nucleation of H_2SO_4-H_2O

In the H_2SO_4-H_2O binary system that is of interest to us, the number concentration of water vapor molecules n_b is much larger than that of H_2SO_4 vapor molecules n_a but H_2SO_4-H_2O clusters are not diluted with respect to component H_2SO_4. n_b/n_a is generally larger than 10^8 in the ambient atmosphere. Even in the laboratory study of H_2SO_4-H_2O homogeneous nucleation, n_b/n_a is large than 10^5. After a single H_2SO_4 molecule collides with or evaporates from a $(H_2SO_4)_{i_a}(H_2O)_{i_b}$ cluster, many H_2O molecules impinge in a very short time such that the equilibrium of the cluster with respect to H_2O vapor is achieved quickly (compared to the time period that another H_2SO_4 molecule strikes or leaves the cluster). In such a case, the binary H_2SO_4-H_2O nucleation is actually controlled by the growth/shrink of clusters through the uptake/evaporation of H_2SO_4 molecules. In other words, the binary H_2SO_4-H_2O nucleation can be reduced to the unary nucleation of H_2SO_4 except that the H_2SO_4 clusters containing different numbers of H_2SO_4 molecules (i_a) also contain different but fixed number of H_2O molecules $[i_b(i_a)]$ at given T and RH. We name such a nucleation mechanism as quasi-unary nucleation. Now the two-dimensional cluster distribution $n(i_a,i_b)$ or n_{i_a,i_b} is simplified to one-dimensional cluster distribution $n[i_a,i_b(i_a)]$ or $n_{i_a,i_b(i_a)}$. For convenience, we write $n_{i_a,i_b(i_a)}$ as n_{i_a} and call the binary clusters containing $i_a H_2SO_4$ molecules i_a-mer with the understanding that each i_a-mer has $i_b(i_a)$ of water molecules associated with it.

The idea of sulfuric acid in equilibrium with water vapor is not new. Shugard, Heist, and Reiss[26] have pointed out that sulfuric acid–water clusters may always be regarded as being in equilibrium with water and they have shown for the first time that binary nucleation rates can be expressed in terms of two decoupled one-dimensional summations. The equilibrium of sulfuric acid clusters with water has also been assumed in our earlier kinetic simulation of new particle formation in aircraft exhaust[27] and in the ambient atmosphere.[28] In these studies, the evaporation of clusters is considered by adjusting the sticking coefficient but is not explicitly treated due to the lack of thermodynamic data. Evaporation of sulfuric acid clusters is explicitly treated in a recent study by Lovejoy et al.,[29] who calculate the evaporation coefficient using the liquid drop model. Lovejoy et al.[29] stated that arbitrary terms have to be added to liquid droplet Gibbs free energies to give nucleation rates consistent with the experimental results of Ball et al.[22] However, Lovejoy et al.[29] did not present the details of evaporation coefficient calculation and comparison with experimental results. One of the main objectives of this study is to describe in detail an approach to calculate the evaporation coefficient of H_2SO_4 molecules from neutral sulfuric acid clusters and to show that no arbi-
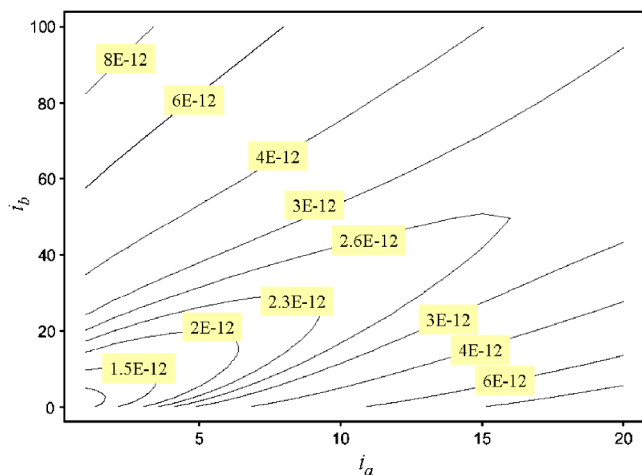
FIG. 1. The formation energy $\Delta G(i_a, i_b)$ of the cluster containing i_a H$_2$SO$_4$ molecules and i_b water molecules ($T=295$ K, RH$=50\%$, and $n_a=10^8$ cm^{-3}). The values marked in each curve are in ergs.

trary adjustments are needed to reproduce the experimental results reported by Viisanen et al.[21] and Ball et al.[22]

B. Properties of (H$_2$SO$_4$)$_{i_a}$(H$_2$O)$_{i_w}$ (i_a-mer)

The Gibbs free energy change to form a cluster containing i_a H$_2$SO$_4$ molecules and i_b water molecules (i.e., i_a-mer) $\Delta G(i_a, i_b)$ is

$$\Delta G(i_a, i_b) = -i_a kT \ln(n_a/n_{a,sol}^{\infty}) - i_b kT \ln(n_b/n_{b,sol}^{\infty}) + 4\pi r^2 \sigma, \tag{7}$$

where $n_{a,sol}^{\infty}$ and $n_{b,sol}^{\infty}$ are the concentrations of H$_2$SO$_4$ and H$_2$O vapor molecules in the equilibrium vapor above a flat surface of a solution having the same acid mole fraction as the i_a-mers. σ is the surface tension of the binary solution which depends on the composition of cluster and temperature. Values of the input parameters $n_{a,sol}^{\infty}$, $n_{b,sol}^{\infty}$, and σ are calculated using the approaches and parameterizations from Noppel et al.[17] and Vehkamki et al.[23] It should be noted that Eq. (7), which is used to decide the degree of cluster hydration (including monomers, see below) in our model, does not contain the hydration effect term that appears in the conventional hydration model.[16,17]

Figure 1 shows the values of $\Delta G(i_a, i_b)$ at $T=295$ K, RH$=50\%$, and $n_a=10^8$ cm^{-3}. At a given i_a, there exists a minimum point for $\Delta G(i_a, i_b)$. At this minimum point, the clusters are most stable and can be considered as in equilibrium with water vapor. Thus, the equilibrium number of H$_2$O molecules in i_a-mers [i.e., $i_b(i_a)$] can be decided by locating the minimum point of $\Delta G(i_a, i_b)$ at a given i_a. When i_b is known, the acid mole fraction of i_a-mers (x_{i_a}) can be readily calculated as

$$x_{i_a} = i_a/(i_a + i_b) \tag{8}$$

and the mass and radius of i_a-mers are
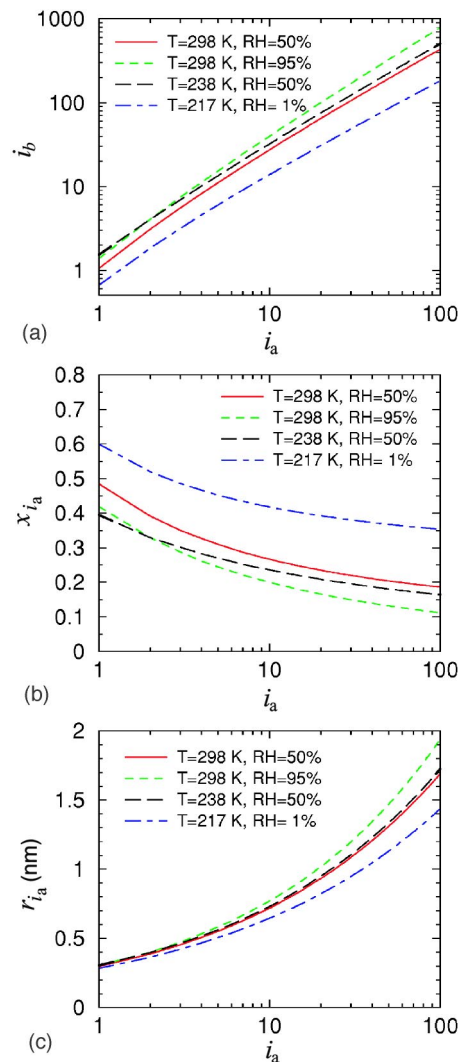
$$m_{i_a} = i_a M_a + i_b M_b, \tag{9}$$

FIG. 2. Properties of i_a-mers (clusters containing i_a H$_2$SO$_4$ molecules) at four different atmospheric conditions: (a) Number of H$_2$O molecules (i_b) associated with the i_a-mers, (b) sulfuric acid mole fraction of the i_a-mers (x_{i_a}), and (c) radius of the i_a-mers (r_{i_a}).

$$r_{i_a} = \left(\frac{3m_{i_a}}{4\pi\rho_{i_a}} \right)^{1/3}, \tag{10}$$

where M_a and M_b are the molecular mass of H$_2$SO$_4$ and H$_2$O, respectively. ρ_{i_a} is the density of i_a-mers, which is calculated according to the parametrization given in Vehkamäki et al.[23]

Figure 2 shows the values of (a) i_b, (b) x_{i_a}, and (c) r_{i_a} as functions of i_a at four different atmospheric conditions. Both T and RH affect the cluster properties. In the real situation, there exists a distribution of i_a-mers containing different number of H$_2$O molecules. The i_b values given in Fig. 2(a) are the numbers of H$_2$O molecules in the most stable and abundant clusters and can also be considered as the average number of H$_2$O molecules associated with i_a-mers. The average number of water molecules associated with acid monomers ($i_a=1$) is consistent with the hydration theory. It is noteworthy that i_b, x_{i_a}, and r_{i_a} are independent of H$_2$SO$_4$ vapor concentration n_a.
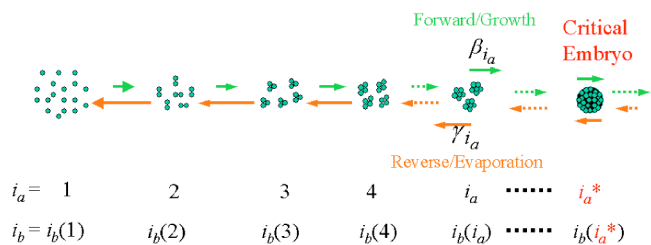
FIG. 3. A schematic showing the growth and evaporation of $(H_2SO_4)_{i_a}(H_2O)_{i_b}$ clusters (or i_a-mers) that lead to nucleation. $(H_2SO_4)_{i_a}(H_2O)_{i_b}$ clusters are always in equilibrium with water vapor and i_b is a function of i_a at given T and RH. The binary H_2SO_4-H_2O nucleation is actually a result of cluster growth/shrink through the uptake/evaporation of H_2SO_4 monomers followed by immediate equilibrium with water vapor. The binary H_2SO_4-H_2O nucleation can be simplified to the quasi-unary nucleation of H_2SO_4.

C. A kinetic approach to simulate the quasi-unary nucleation of H_2SO_4-H_2O

As we discussed in Sec. II A, the binary H_2SO_4-H_2O nucleation is controlled by the cluster growth/shrink through the uptake/evaporation of H_2SO_4 monomers and can be treated as quasi-unary nucleation of H_2SO_4. Figure 3 shows schematically the growth and evaporation of $(H_2SO_4)_{i_a}(H_2O)_{i_b}$ clusters (i_a-mers) that lead to the nucleation. Here β_{i_a} is the forward (or growth) rate coefficient for the collision of hydrated monomers with i_a-mers, and γ_{i_a} is the reverse (or evaporation) rate coefficient of H_2SO_4 molecules from i_a-mers. i_a^* is the number of H_2SO_4 molecules in the critical clusters.

The number concentration of i_a-mers is governed by the following kinetic balance equations:

$$\frac{dn_{i_a}}{dt} = \beta_{i_a-1}n_{i_a-1} - \gamma_{i_a}n_{i_a} - \beta_{i_a}n_{i_a} + \gamma_{i_a+1}n_{i_a+1}, \quad i_a \geqslant 2, \quad (11)$$

$$\frac{dn_1}{dt} = P - \sum_{i_a=1}^{\infty} \beta_{i_a}n_{i_a} + 2\gamma_2 n_2 + \sum_{i_a=3}^{\infty} \gamma_{i_a}n_{i_a}, \quad (12)$$

where P is the production rate of H_2SO_4 molecules. The coagulation among clusters is neglected in Eq. (11) which is a good approximation when $n_1 \gg n_{i_a}(i_a>1)$. The scavenging of clusters by preexisting particles is not considered in this study. The second term to the right of Eq. (12) refers to the condensation of hydrated monomers. Sulfuric acid molecules (unhydrated) are assumed to evaporate from clusters (reflected in the way γ_{i_a} are calculated, see below), but these sulfuric acid molecules can be considered to hydrate instantaneously after they evaporated from clusters. Thus, the third and fourth terms to the right of Eq. (12) represent the sources of hydrated monomers from evaporation. The forward rate coefficient β_{i_a} is the kinetic collision rate of hydrated monomers of the number concentration $n_1=n_a$ with i_a-mers,

$$\beta_{i_a} = \left(\frac{8\pi kT(m_1 + m_{i_a})}{m_1 m_{i_a}} \right)^{1/2} (r_1 + r_{i_a})^2 n_1. \quad (13)$$

The reverse (or evaporation) rate coefficient γ_{i_a} is the escape frequency of H_2SO_4 molecules from i_a-mers. When i_a-mers are in equilibrium with surrounding H_2SO_4 vapor, the escape
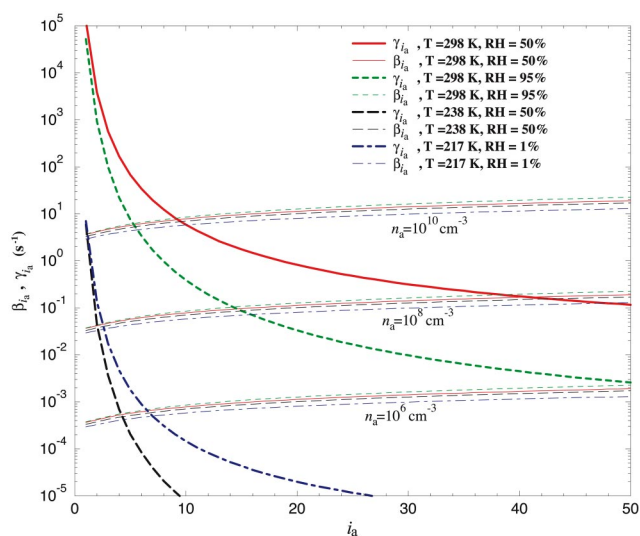

FIG. 4. β_{i_a} and γ_{i_a} as a function of i_a at four different atmospheric conditions. β_{i_a} are given at three H_2SO_4 vapor concentrations ($n_a=10^6$, 10^8, and 10^{10} cm^{-3}). β_{i_a} and γ_{i_a} are equal at the critical i_a values.

frequency of H_2SO_4 from i_a-mers equals the collision frequency of monomers with i_a-mers. γ_{i_a} can be calculated based on the saturation H_2SO_4 vapor concentration over the surface of i_a-mers with radius r_{i_a} and acid mole fraction of x_{i_a}. Here

$$\gamma_{i_a} = \left(\frac{8\pi kT(m_1 + m_{i_a})}{m_1 m_{i_a}} \right)^{1/2} (r_1 + r_{i_a})^2 n_{a,sol}^{\infty} \exp\left(\frac{2M_a\sigma}{\rho_{i_a}RTr_{i_a}} \right) \quad (14)$$

where $n_{a,sol}^{\infty}$ is the concentration of H_2SO_4 vapor molecules in the equilibrium vapor above a flat surface of a solution having the same acid mole fraction as the i_a-mers and R is the general gas constant. The exponential term in Eq. (14) takes into account the Kelvin effect. The Kelvin equation has long been used to calculate the evaporation rates of small clusters in the so-called Kelvin model of nucleation.[30–34] It has been found that the predictions of the Kelvin model are relatively close to those given by the self-consistent classical theory.[31]

Figure 4 shows β_{i_a} and γ_{i_a} as functions of i_a at four different atmospheric conditions. As may be seen from Fig. 4, γ_{i_a} is very sensitive to T and RH while the effects of T and RH on β_{i_a} are small. β_{i_a} is proportional to H_2SO_4 vapor concentrations n_a but γ_{i_a} is independent of n_a. The intersection points of β_{i_a} and γ_{i_a} are where the critical sizes i_a^* are located. Thus, the size and composition of the critical clusters can be decided in an easy and straightforward way in the kinetic quasi-unary nucleation model. The clusters larger than critical size ($i_a>i_a^*$) tend to grow since their collision frequency (with monomers) exceeds their evaporation frequency. On the other hand, subcritical clusters ($i_a<i_a^*$) tend to evaporate because their evaporation frequency is larger than their collision frequency. It is clear from Fig. 4 that i_a^* increases with decreasing n_a, decreasing RH, and increasing T.

With the values of β_{i_a} and γ_{i_a} calculated from Eqs. (13) and (14), the time-dependent concentrations of clusters of
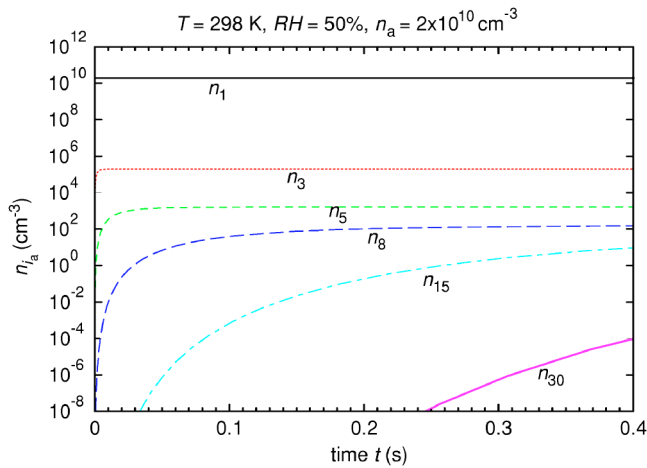
FIG. 5. Concentrations of n_1, n_3, n_5, n_8, n_{15}, and n_{30} as a function of time ($T=298$ K and RH$=50$%). $n_1 = 2 \times 10^{10}$ cm^{-3} at $t=0$ s.

various sizes can be obtained by solving the differential Eqs. (11) and (12) explicitly. Figure 5 shows the concentrations of n_1, n_3, n_5, n_8, n_{15}, and n_{30} as a function of time t at $T = 298$ K and RH$=50$%. The initial concentration of H$_2$SO$_4$ monomer $n_1 = 2 \times 10^{10}$ cm^{-3} and $P=0$ cm^{-3} s^{-1}. Under this condition, the critical size $i_a^* \approx 8$. The clustering process leads to the formation of clusters of various sizes. n_1 hardly changes in this case, which means that the clustering process consumes only very small fraction of monomers. $n_{i_a}(i_a > 1)$ first increases but reaches an equilibrium concentration after certain time period. The larger the size of cluster i_a, the longer it takes to reach its equilibrium concentration. The size distributions of clusters at six different times for the same case are shown in Fig. 6. The growth of clusters can be clearly seen. The concentrations of clusters smaller than critical sizes ($i_a^* \approx 8$) do not further change after about 0.4 s. In other words, the subcritical cluster distribution reach equilibrium (i.e., $dn_{i_a < i_a^*}/dt = 0$) after around 0.4 s.

As shown in Eqs. (3)–(5), the nucleation rate in the classical binary homogeneous nucleation theory ($J_{\text{BHN}}^{\text{CLA}}$) is de-
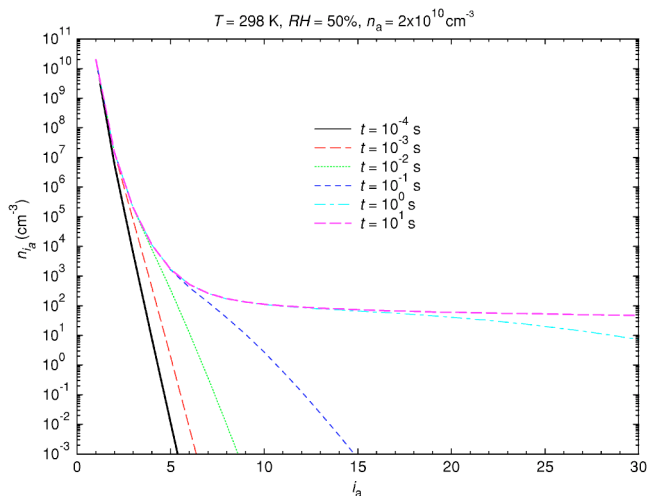

FIG. 6. The size distributions of clusters at six different times. $n_1 = 2 \times 10^{10}$ cm^{-3} at $t=0$ s and $T=298$ K, RH$=50$%. The number of sulfuric acid molecule in the critical clusters i_a^* is ~ 8.

fined as the net flux of critical clusters to bigger size. The quasi-unary nucleation rate in our kinetic model ($J_{\text{QUN}}^{\text{KIN}}$) is defined in a similar way,

$$J_{\text{QUN}}^{\text{KIN}} = \beta_{i_a^*} n_{i_a^*} - \gamma_{i_a^*+1} n_{i_a^*+1}. \qquad (15)$$

In the classical BHN theory, the concentration of critical clusters is estimated based on the equilibrium distribution of clusters, which is a function of free energy to form these clusters. In our kinetic model, the concentration of critical clusters is calculated explicitly and assumption of equilibrium distribution is not necessary. The kinetic approach is more appropriate when precursor gas concentrations T and RH change rapidly[24] such as, e.g., in the exhaust plumes from motor vehicles or aircraft engines. The equilibrium concentrations of clusters can be obtained by solving Eq. (15) iteratively:

$$n_{i_a^*} = \frac{\beta_{i_a^*-1}}{\gamma_{i_a^*}} n_{i_a^*-1} = \frac{\beta_{i_a^*-1}}{\gamma_{i_a^*}} \frac{\beta_{i_a^*-2}}{\gamma_{i_a^*-1}} n_{i_a^*-2}$$

$$= \cdots = \frac{\beta_{i_a^*-1}}{\gamma_{i_a^*}} \frac{\beta_{i_a^*-2}}{\gamma_{i_a^*-1}} \cdots \frac{\beta_2}{\gamma_3} \frac{\beta_1}{\gamma_2} n_1$$

$$= \frac{\beta_1}{\gamma_{i_a^*}} \left[\prod_{i_a=2}^{i_a^*-1} n_{a,sol}^\infty \exp\left(\frac{2 M_a \sigma}{\rho_{i_a} R T r_{i_a}} \right) \right]^{-1} n_1^{i_a^*-1} = C_{i_a^*} n_1^{i_a^*}, \qquad (16)$$

where the prefactor is given by the following equation:

$$C_{i_a^*} = \left(\frac{2 m_{i_a^*}}{m_1 + m_{i_a^*}} \right)^{1/2} \left(\frac{2 r_1}{r_1 + r_{i_a^*}} \right)^2$$

$$\times \left[\prod_{i_a=2}^{i_a^*} n_{a,sol}^\infty \exp\left(\frac{2 M_a \sigma}{\rho_{i_a} R T r_{i_a}} \right) \right]^{-1}. \qquad (17)$$

It is obvious from Eq. (16) that our model satisfies the law of mass action with respect to the sulfuric acid concentration. In our kinetic quasi-unary model, when a monomer collides with an i_a-mer, the resulting ($i_a + 1$)-mer instantaneously hydrates further to reach equilibrium with water [noting that $i_b(i_a + 1) > i_b(i_a) + i_b(1)$] (see Figs. 2 and 3). A cluster containing i_a sulfuric acid molecules (i.e., i_a-mer) is formed from i_a hydrated monomers [contain $i_b(1)$ water molecules] and $i_b(i_a) - i_a^* i_b(1)$ water molecules. The $i_b(i_a) - i_a^* i_b(1)$ water molecules are added to the clusters via cluster hydration process which is implicitly included in our model via their effect on the composition and thermodynamical properties of clusters (i.e., the prefactor C_{i_a}).

Figure 7 shows the kinetic quasi-unary nucleation rates of H$_2$SO$_4$-H$_2$O ($J_{\text{QUN}}^{\text{KIN}}$) as a function of time corresponding to the case shown in Figs. 5 and 6. For the comparison, the nucleation rates predicted with the most recent version of classical BHN theory[23] ($J_{\text{BHN}}^{\text{CLA}}$) are also shown. $J_{\text{QUN}}^{\text{KIN}}$ first increases with time but reaches a constant value after about 0.4 s. $J_{\text{BHN}}^{\text{CLA}}$ does not change with time as acid monomer concentration n_a hardly changes during the time period (see Fig. 5). It is clear that, at a given condition, a transient period of time is needed to establish steady-state nucleation.[35–37] $J_{\text{BHN}}^{\text{CLA}}$ is a factor of 60 higher than $J_{\text{QUN}}^{\text{KIN}}$ after the steady-state
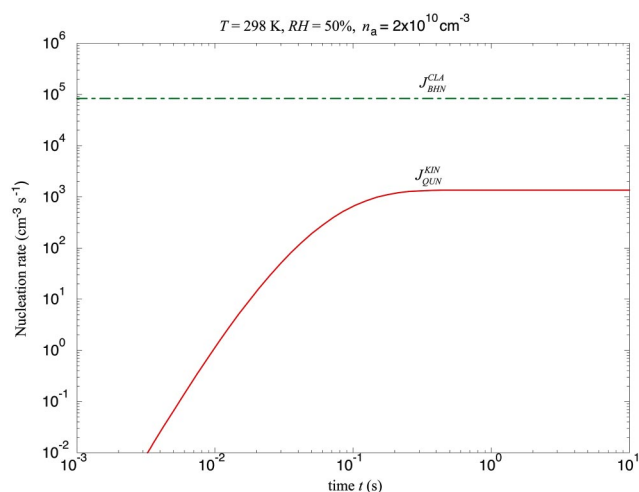
FIG. 7. The kinetic quasi-unary nucleation rates of H_2SO_4-H_2O (J_{QUN}^{KIN}) as a function of time corresponding to the case shown in Figs 5 and 6. The nucleation rates predicted with the classical binary homogeneous nucleation model (Ref. 23) (J_{BHN}^{CLA}) are also shown for comparison.

distribution of subcritical clusters is established ($t > 0.4$ s), and the differences are larger at $t < 0.4$ s. Since the thermodynamic data used in both models are the same, the difference between J_{BHN}^{CLA} and J_{QUN}^{KIN} is likely caused by the fundamental difference in the treatment of nucleation process. More comparisons are given in the following section.

III. COMPARISONS WITH LABORATORY MEASUREMENTS AND CLASSICAL MODEL

The appropriateness of simplifying the binary H_2SO_4-H_2O nucleation into quasi-unary nucleation of hydrated H_2SO_4 has to be judged by comparison with well-controlled laboratory nucleation experiments. In this section we compare nucleation rates obtained in two recent experimental nucleation studies[21,22] with those predicted with the kinetic quasi-unary nucleation model (J_{QUN}^{KIN}) as well as those predicted with the classical BHN model (J_{BHN}^{CLA}). The steady-state values of J_{QUN}^{KIN} are used for comparison. Figure 8 shows the nucleation rates as a function of sulfuric acid vapor concentration n_a at six different relative humidities (52.3%, 38.2%, 15.3%, 10%, 7.5%, and 4.6%) and two different temperatures (298 K and 295 K). The experimental data in Figs. 8(a) and 8(b) are from Vissanen et al.[21] and those in Figs. 8(c)–8(f) are from Ball et al.[22] The dashed lines (with symbols at the ends) in Figs. 8(a) and 8(b) represent the uncertainty in the experimental results associated with the uncertainty in sulfuric acid concentration and nucleation time: One end lies at the maximum sulfuric acid concentration and nucleation time (50 s) and the other end at the minimum sulfuric acid concentration (60% of the maximum) and nucleation time (1 s).[21] The error bars in Figs. 8(c)–8(f) represent the possible range of H_2SO_4 gas concentration in the nucleation zone.[22]

The solid lines in Fig. 8 are the nucleation rates predicted with our kinetic quasi-unary H_2SO_4-H_2O nucleation model (J_{QUN}^{KIN}). The dot-dashed lines are the nucleation rates predicted by the most recently updated version of classical BHN theory (J_{BHN}^{CLA}).[23] The nucleation rates predicted with

our kinetic quasi-unary nucleation model J_{QUN}^{KIN} are consistent with the experimental data within the range of uncertainties in all the cases studied, while the classical BHN theory systematically overpredicts the nucleation rates and J_{BHN}^{CLA} is beyond the possible ranges of experimental results for the cases with RH $\geqslant 10\%$. J_{BHN}^{CLA} is consistently higher than J_{QUN}^{KIN} which is likely caused by the fundamental difference in the treatment of the nucleation process. It should be noted that in our kinetic model, when a monomer collides with a cluster, the resulting larger cluster instantaneously hydrates further to reach equilibrium with water. Thus, our model implicitly takes into account the hydration of sulfuric acid clusters in addition to the monomer hydration. All existing hydration model only considers the hydration of monomers. Since the hydration is known to reduce the nucleation rates, the hydration of clusters that is implicitly considered in our kinetic quasi-unary model may have contributed to the lower nucleation rates. Nevertheless, further investigation is needed to understand exactly what cause the difference between our model and the classical binary model.

The ratio of J_{BHN}^{CLA} to J_{QUN}^{KIN} is larger at lower RH and reaches above 10^7 at RH$=10\%$. The consistently better agreement of J_{QUN}^{KIN} with the experimental results suggests that binary H_2SO_4-H_2O nucleation can be treated as quasi-unary. Since J_{QUN}^{KIN} is sensitive to the evaporation coefficient of small clusters, the nice agreement of J_{QUN}^{KIN} with experiment results indicates that the evaporation coefficients we calculate are in the right range.

IV. SUMMARY AND DISCUSSION

In the binary H_2SO_4-H_2O system that is of interest to us, the number concentration of H_2O vapor molecules is much larger than that of H_2SO_4 vapor molecules but H_2SO_4-H_2O clusters are not diluted with respect to component H_2SO_4. After one H_2SO_4 molecule strikes or leaves a H_2SO_4-H_2O cluster, many H_2O molecules collide with the cluster in a very short period of time (compared to the time period that another H_2SO_4 molecule strikes or leaves the cluster) and the binary H_2SO_4-H_2O cluster can be assumed to be in equilibrium with H_2O vapor. Thus, the binary homogeneous nucleation (BHN) of H_2SO_4-H_2O can be treated as quasi-unary nucleation of H_2SO_4 in equilibrium with H_2O vapor.

A kinetic quasi-unary nucleation model of H_2SO_4-H_2O, which simulates the growth and evaporation of sulfuric acid clusters of various sizes explicitly, has been developed and evaluated in this study. Schemes to calculate the composition and reverse (or evaporation) rate coefficient of H_2SO_4-H_2O clusters in equilibrium with water at given T and RH are presented. The forward (or growth) rate of H_2SO_4-H_2O cluster is calculated based on the kinetic collision rate of H_2SO_4 monomers with the cluster. The size of critical clusters is decided by locating the intersection point of evaporation rate coefficient curve and growth rate curve, and the kinetic quasi-unary nucleation rate is defined as the net flux of critical clusters to bigger sizes. Since the kinetic quasi-unary nucleation model simulates the cluster distribution kinetically, it does not have two well known problems associated with classical BHN theory (violation of mass action law and
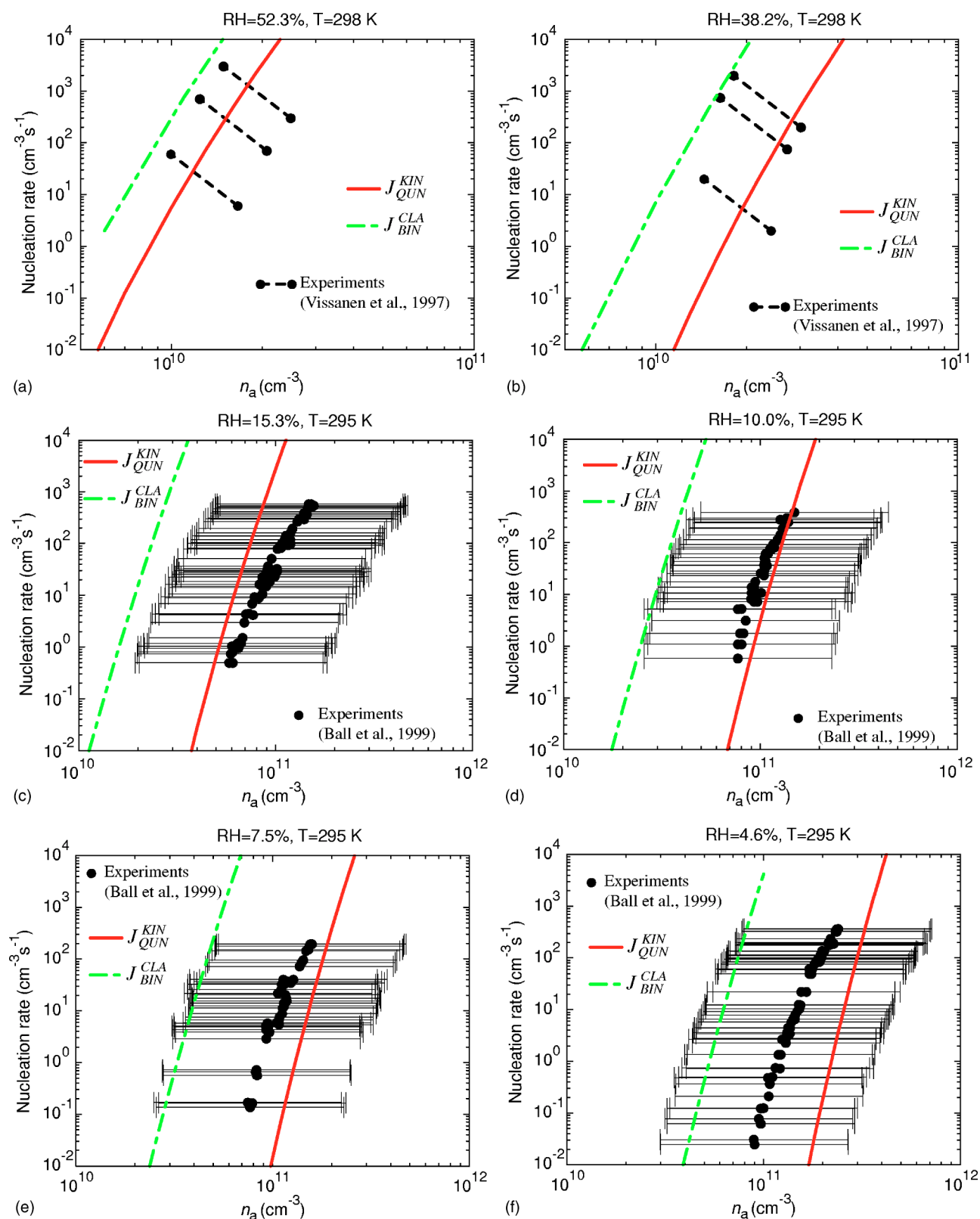
FIG. 8. Nucleation rates as a function of sulfuric acid vapor concentration n_a at (a) RH=52.3% , T=298 K; (b) RH=38.2% , T=298 K; (c) RH =15.3% , T=295 K; (d) RH=10.0% , T=295 K; (e) RH=7.5% , T=295 K; and (f) RH=4.6% , T=295 K. The solid lines are the nucleation rates predicted with our kinetic quasi-unary H₂SO₄-H₂O nucleation model (J_{QUN}^{KIN}). The dot-dashed lines are the nucleation rates predicted by the most recent version of classical binary homogeneous nucleation model (Ref. 23) (J_{BHN}^{CLA}). The experimental data in (a) and (b) are from the work of Vissanen *et al.* (Ref. 21) and in (c)–(f) are from the work of Ball *et al.* (Ref. 22).

incorrect monomer concentration given by cluster distributions) and is appropriate for the situations where the assumption of equilibrium cluster distribution is invalid.

The steady-state nucleation rates predicted with kinetic quasi-unary nucleation model (J_{QUN}^{KIN}) are compared to those observed in the recent laboratory nucleation experiments as

well as those predicted by the most recent version of classical BHN theory ($J_{\mathrm{BHN}}^{\mathrm{CLA}}$). $J_{\mathrm{QUN}}^{\mathrm{KIN}}$ are consistent with the recent experimental measurements within the range of uncertainties, while $J_{\mathrm{BHN}}^{\mathrm{CLA}}$ are beyond the possible ranges of experimental data when RH $\geq 10\%$. $J_{\mathrm{BHN}}^{\mathrm{CLA}}$ are consistently higher than $J_{\mathrm{QUN}}^{\mathrm{KIN}}$ and the ratio of $J_{\mathrm{BHN}}^{\mathrm{CLA}}$ to $J_{\mathrm{QUN}}^{\mathrm{KIN}}$ is larger at lower relative humidity. Since the same thermodynamic data are used in calculating $J_{\mathrm{BHN}}^{\mathrm{CLA}}$ and $J_{\mathrm{QUN}}^{\mathrm{KIN}}$, the difference between $J_{\mathrm{BHN}}^{\mathrm{CLA}}$ and $J_{\mathrm{QUN}}^{\mathrm{KIN}}$ is probably due to the fundamental difference in the treatment of nucleation process. We suggest that the hydration of sulfuric acid clusters, which is not considered in the classical model but is accounted for implicitly in our kinetic quasi-unary model, may lower the nucleation rates. The consistently better agreement of $J_{\mathrm{QUN}}^{\mathrm{KIN}}$ with the experimental data suggests that the treatment of binary H_2SO_4-H_2O homogeneous nucleation as quasi-unary nucleation should be appropriate. In the future, an analytical (or classical) version of quasi-unary nucleation theory will be developed and the reason why BHN theory overpredicts the nucleation rates will be explored. It may become necessary to consider the effect of sulfuric acid cluster hydration (in addition to monomer hydration) on nucleation rates.

$J_{\mathrm{QUN}}^{\mathrm{KIN}}$ are very sensitive to the evaporation coefficient of H_2SO_4 molecules from small sulfuric acid clusters. The evaporation coefficient depends on the cluster composition and size as well as ambient conditions. Uncertainties in the thermodynamic data lead to uncertainties in evaporation coefficient and hence $J_{\mathrm{QUN}}^{\mathrm{KIN}}$. In our kinetic quasi-unary nucleation model, the most recently available thermodynamic data are used and the consistently good agreement of $J_{\mathrm{QUN}}^{\mathrm{KIN}}$ with the experimental data suggests that the calculated evaporation coefficient of small H_2SO_4-H_2O clusters should be in the right range. In the atmosphere, neutral H_2SO_4-H_2O clusters are continuously generated by the recombination (or neutralization) of charged clusters. Proper treatment of evaporation process of neutral H_2SO_4-H_2O clusters is important in predicting the ion-mediated nucleation rates.[27] The schemes to calculate the evaporation coefficient which have been developed and verified in this study can be used to improve the ion-mediated nucleation model.

ACKNOWLEDGMENTS

[1] S. Twomey, J. Atmos. Sci. **34**, 1149 (1977).

[2] R. J. Charlson, S. E. Schwartz, I. M. Hales *et al.*, Science **255**, 423 (1992).

[3] J. E. Penner, M. Andreae, H. Annegran *et al.*, in *Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, edited by J. T. Houghton, Y. Ding, D. J. Griggs *et al.* (Cambridge University Press, U.K. and New York, 2001), Chap. 5, pp. 289–416.

[4] P. Mirabel and J. L. Katz, J. Chem. Phys. **60**, 1138 (1974).

[5] R. P. Turco, P. Hamill, O. B. Toon, R. C. Whitten, and C. S. Kiang, J. Atmos. Sci. **36**, 699 (1979).

[6] P. Hamill, R. P. Turco, C. S. Kiang, O. B. Toon, and R. C. Whitten, J. Aerosol Sci. **13**, 561 (1982).

[7] S. Kreidenweis and J. H. Seinfeld, Atmos. Environ. **22**, 283 (1988).

[8] C. Andronache, W. L. Chameides, D. D. Davis *et al.*, J. Geophys. Res. **102**, 28511 (1997).

[9] A. D. Clarke, V. N. Kapustin, F. L. Eisele, R. J. Weber, and P. H. McMurry, Geophys. Res. Lett. **26**, 2425 (1999).

[10] P. J. Adams and J. H. Seinfeld, J. Geophys. Res. **107**, 4370 (2002).

[11] B. Pun, Y. Zhang, S.-Y. Wu, K. Vijayaraghavan, and C. Seigneur, Models-3/Community Multiscale Air Quality Model (CMAQ). User's Guide to Alternative Particulate Matter and Cloud Modules (2003).

[12] G. J. Doyle, J. Chem. Phys. **35**, 795 (1961).

[13] H. Flood, Z. Phys. Chem. Abt. A **170**, 286 (1934).

[14] H. Reiss, J. Chem. Phys. **18**, 840 (1950).

[15] R. H. Heist and H. Reiss, J. Chem. Phys. **61**, 573 (1974)

[16] A. Jaecker-Voirol, P. Mirabel, and H. Reiss, J. Chem. Phys. **87**, 4849 (1987)

[17] M. Noppel, H. Vehkamäki, and M. Kulmala, J. Chem. Phys. **116**, 218 (2002)

[18] G. Wilemski, J. Chem. Phys. **62**, 3763 (1975)

[19] G. Wilemski and B. E. Wyslouzil, J. Chem. Phys. **103**, 1127 (1995).

[20] M. Kulmala, A. Laaksonen, and S. L. Gürshick, J. Aerosol Sci. **23**, 309 (1992).

[21] Y. Viisanen, M. Kulmala, and A. Laaksonen, J. Chem. Phys. **107**, 920 (1997).

[22] S. M. Ball, D. R. Hanson, F. L. Eisele, and P. H. McMurry, J. Geophys. Res. **104**, 23709 (1999).

[23] H. Vehkamäki, M. Kulmala, I. Napari, K. E. J. Lehtinen, C. Timmreck, M. Noppel, and A. Laaksonen, J. Geophys. Res. **107**, 4622 (2002).

[24] F. Yu, Geophys. Res. Lett. **30**, 1526 (2003).

[25] J. H. Seinfeld and S. N. Pandis, *Atmospheric Chemistry and Physics* (Wiley, Hoboken, NJ, 1998).

[26] W. J. Shugard, R. H. Heist, and H. Reiss, J. Chem. Phys. **61**, 5298 (1974).

[27] F. Yu and R. P. Turco, J. Geophys. Res. **103**, 25,915 (1998).

[28] F. Yu and R. P. Turco, J. Geophys. Res. **106**, 4797 (2001).

[29] E. R. Lovejoy, J. Curtius, and K. D. Froyd, J. Geophys. Res. **109**, D08204 (2004).

[30] B. N. Hale, Metall. Trans. A **23A**, 1863 (1992).

[31] J. L. Katz, Pure Appl. Chem. **64**, 1661 (1992).

[32] G. Wilemski, J. Chem. Phys. **103**, 1119 (1995).

[33] D. E. Temkin and V. V. Shevelev, J. Cryst. Growth **66**, 380 (1984).

[34] J. S. Li and G. Wilemski, J. Phys. Chem. B **105**, 11778 (2001).

[35] W. J. Shugard and H. Reiss, J. Chem. Phys. **65**, 2827 (1976).

[36] F. J. Schelling and H. Reiss, J. Chem. Phys. **74**, 3527 (1981)

[37] R. McGraw, J. Chem. Phys. **102**, 2098 (1995).