Improved quasi-unary nucleation model for binary H_2SO_4–H_2O homogeneous nucleation

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Aerosol nucleation events have been observed at a variety of locations worldwide, and may have significant climatic and health implications. Binary homogeneous nucleation (BHN) of H_2SO_4 and H_2O is the foundation of recently proposed nucleation mechanisms involving additional species such as ammonia, ions, and organic compounds, and it may dominate atmospheric nucleation under certain conditions. We have shown in previous work that H_2SO_4–H_2O BHN can be treated as a quasi-unary nucleation (QUN) process involving H_2SO_4 in equilibrium with H_2O vapor, and we have developed a self-consistent kinetic model for H_2SO_4–H_2O nucleation. Here, the QUN approach is improved, and an analytical expression yielding H_2SO_4–H_2O QUN rates is derived. Two independent measurements related to monomer hydration are used to constrain the equilibrium constants for this process, which reduces a major source of uncertainty. It is also shown that the capillarity approximation may lead to a large error in the calculated Gibbs free energy change for the evaporation of H_2SO_4 molecules from small H_2SO_4–H_2O clusters, which affects the accuracy of predicted BHN nucleation rates. The improved QUN model—taking into account the recently measured energetics of small clusters—is thermodynamically more robust. Moreover, predicted QUN nucleation rates are in better agreement with available experimental data than rates calculated using classical H_2SO_4–H_2O BHN theory. © *2007 American Institute of Physics.*
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I. INTRODUCTION

New particle formation, which is frequently observed throughout the lower troposphere,[1] is an important source of atmospheric aerosols. Observations indicate that the newly formed particles can grow to the size of typical cloud condensation nuclei within a day under favorable conditions.[2–4] A clear understanding of particle formation mechanisms is therefore critically important for quantitatively assessing the climate-related, health and environmental impacts of atmospheric particles. Although nucleation phenomena have been intensively studied in the past, there are still major uncertainties concerning the nucleation mechanisms occurring in the atmosphere.

Gaseous H_2SO_4 and H_2O are active nucleation agents because of their low vapor pressures over their binary solution. Field measurements indicate that H_2SO_4 and H_2O are clearly involved in many, if not most, nucleation events observed in the atmosphere.[5–8] In addition to H_2SO_4–H_2O binary homogeneous nucleation (BHN),[9,10] ternary nucleation (involving H_2SO_4–H_2O–NH_3),[11] ion-mediated nucleation (H_2SO_4–H_2O-ions),[12,13] and organic-enhanced nucleation (H_2SO_4–H_2O-organics)[14] have been proposed as possible alternative mechanisms leading to new particle formation in the atmosphere. Nevertheless, H_2SO_4–H_2O BHN is the foundation of all these nucleation theories, and it may dominate nucleation in certain atmospheric regions, or under certain favorable conditions.[15,16] BHN has in fact been inte-

grated into a generalized kinetic ion-mediated nucleation model, in which the stability of neutral clusters also is a factor affecting overall ion-mediated nucleation rates.[13] Laboratory experiments indicate that ammonia and specific organics species can enhance H_2SO_4–H_2O BHN rates by about one to two orders of magnitude,[11,14,17] although uncertainties in existing BHN predictions remain in the range of a few orders of magnitude or more. For a better understanding of particle formation mechanisms under atmosphere conditions, it is necessary to improve the existing theories for H_2SO_4–H_2O homogeneous nucleation. The extent of acid monomer hydration and the accuracy of the capillarity approximation are two major sources of uncertainties in calculated H_2SO_4–H_2O nucleation rates.

In the systems of interest, water vapor concentrations are high enough that binary homogeneous nucleation of H_2SO_4 and H_2O can be treated as quasi-unary nucleation (QUN) process for H_2SO_4 in equilibrium with water vapor.[18,19] Yu[10,19] developed a self-consistent kinetic homogeneous nucleation model for H_2SO_4–H_2O. To apply the QUN approximation in this case, the key assumptions include the following: (1) for given temperature (T) and relative humidity (RH), the sulfuric acid clusters of various sizes are in equilibrium with water vapor; (2) the average cluster composition (i.e., the number of H_2O molecules i_b in a cluster containing i_a H_2SO_4 molecules) can be approximated as the most stable compositions; and (3) binary H_2SO_4–H_2O nucleation is controlled by the condensation/evaporation of H_2SO_4 molecules from subcritical clusters. The QUN model effectively transforms the usual two-dimensional nucleation

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problem into a one-dimensional problem, and allows for the explicit representation of the time-dependent evolution of precritical size clusters.

The QUN model does not exhibit two well-known problems associated with the classical BHN theory, that is, violation of the law of mass action and an erroneous monomer concentration.[20] The QUN approach is appropriate for conditions like those occurring in the rapidly diluting engine exhaust,[16] where the assumption of a steady-state equilibrium cluster distribution is no longer valid. Further, as shown below, the QUN model can effectively compensate for the dearth of thermodynamic measurements for small clusters.

In our previous studies,[10,19] $H_2SO_4-H_2O$ nucleation rates based on the QUN model were calculated as a net flux of particles crossing the critical size barrier based on cluster size distributions determined from the cluster kinetic equations. For clusters smaller than the critical size, the distribution achieves a quasi-steady-state after a certain short time period, which in turn defines the steady-state nucleation rate. These previous QUN simulations, however, were subject to large uncertainties associated with the thermodynamics for monomer hydration and the limitations of the capillarity approximation.

In this work, an analytical expression for the $H_2SO_4-H_2O$ quasi-unary nucleation rate is first derived (Sec. II). Moreover, uncertainties in the QUN model are reduced here by incorporating relevant laboratory data not previously used (Sec. III). For example, we employ two independent measurements to constrain monomer hydration. Further, we apply H_2SO_4 clustering thermodynamic data obtained in recent experimental study to investigate the validity of the capillarity approximation, and use these data to fine-tune the QUN model. Finally, nucleation rates predicted with the improved version of the QUN model are compared with values measured in the laboratory, and predicted by classical BHN theory for similar conditions (Sec. IV).

II. QUASI-UNARY NUCLEATION—ANALYTICAL REPRESENTATION

For a given total H_2SO_4 monomer concentration (n_1), the time-dependent evolution of the local cluster size distribution can be obtained by solving the following set of the differential equations:

$$\frac{dn_{i_a+1}}{dt} = \delta_{i_a,1}\beta_{i_a}n_{i_a} - \gamma_{i_a+1}n_{i_a+1} - \beta_{i_a+1}n_{i_a+1}$$
$$+ \gamma_{i_a+2}n_{i_a+2}, \quad i_a \geqslant 1, \tag{1}$$

where n_{i_a} is the number concentration of clusters containing i_a H_2SO_4 molecules [and $i_b(i_a)$ H_2O molecules] (hereafter denoted as i_a-mers). β_{i_a} is the collision frequency defining the growth rate of i_a mers, and γ_{i_a} is the dissociation frequency related to the evaporation of H_2SO_4 molecules from i_a-mers. Equivalently, β_{i_a} is the forward reaction rate coefficient multiplied by the H_2SO_4 vapor concentration n_1. Note that $\delta_{i_a,1}=0.5$ if $i_a=1$, and $\delta_{i_a,1}=1$ if $i_a \neq 1$. Coagulation among clusters and scavenging of clusters by preexisting

particles are not considered in Eq. (1), but are readily incorporated if needed.[16]

To obtain the QUN nucleation rate (denoted as J_{QUN}), Yu[10,19] first solved Eq. (1) to obtain the cluster size distribution, and then applied the following relation:

$$J_{QUN} = \beta_{i_a^*}n_{i_a^*} - \gamma_{i_a^*+1}n_{i_a^*+1}, \tag{2}$$

where i_a^* is the number of sulfuric acid molecules in the critical cluster. Here, we show that an analytical expression for the steady-state value of J_{QUN} can also be deduced, following a procedure similar to that used to derive the unary nucleation rates.[21–23]

For a given (fixed) total monomer concentration (n_1), the cluster size distribution (below a certain sufficiently large size i_L) reaches quasi-steady-state, for which J_{QUN} is simply the net flux from i_a-mers to (i_a+1)-mers,

$$J_{QUN} = \delta_{i_a,1}\beta_{i_a}n_{i_a} - \gamma_{i_a+1}n_{i_a+1}. \tag{3}$$

If we define a quantity f_{i_a} as

$$\delta_{i_a,1}\beta_{i_d}f_{i_a} = \gamma_{i_a+1}f_{i_a+1}, \tag{4}$$

then

$$f_{i_a} = \frac{\beta_{i_a-1}}{\gamma_{i_a}}f_{i_a-1} = \frac{\beta_{i_a-1}}{\gamma_{i_a}}\frac{\beta_{i_a-2}}{\gamma_{i_a-1}}f_{i_a-2}$$
$$= \frac{\beta_{i_a-1}}{\gamma_{i_a}}\frac{\beta_{i_a-2}}{\gamma_{i_a-1}}\cdots\frac{\beta_1 f_1}{\gamma_2 2} = \frac{f_1}{2}\prod_{j=1}^{i_a-1}\frac{\beta_j}{\gamma_{j+1}}. \tag{5}$$

By combining Eqs. (3) and (4), we find

$$J_{QUN}\frac{1}{\delta_{i_a,1}\beta_{i_d}f_{i_a}} = \frac{n_{i_a}}{f_{i_a}} - \frac{n_{i_a+1}}{f_{i_a+1}}. \tag{6}$$

Summing Eq. (6) from $i_a=1$ to i_L, we obtain

$$J_{QUN}\sum_{i_a=1}^{i_L}\frac{1}{\delta_{i_a,1}\beta_{i_d}f_{i_a}} = \frac{n_1}{f_1} - \frac{n_{i_L+1}}{f_{i_L+1}}. \tag{7}$$

Under nucleating conditions, n_i/f_i decreases rapidly with increasing i, and for a sufficiently large i_L, $n_{i_L+1}/f_{i_L+1} \ll n_1/f_1$. Thus, Eq. (7) becomes

$$J_{QUN} = n_1\left(\sum_{i_a=1}^{i_L}\frac{f_1}{\delta_{i_a,1}\beta_{i_d}f_{i_a}}\right)^{-1}$$
$$= 0.5n_1\left(\sum_{i_a=1}^{i_L}\frac{1}{\beta_{i_a}\prod_{j=1}^{i_a-1}(\beta_j/\gamma_{j+1})}\right)^{-1}. \tag{8}$$

Equation (8) is an analytical expression for the quasi-unary $H_2SO_4-H_2O$ homogeneous nucleation rate. This expression is kinetically self-consistent, and more straightforward than the result based on classical binary nucleation theory.[9] It should also be noted that the expression for unary systems often quoted in the literature[21–23] does not take into account the factor of 0.5 associated with $\delta_{i_a,1}$, thus overestimating the nucleation rate by a factor of 2.

J_{QUN} can be calculated using Eq. (8) if β_{i_a} and γ_{i_a} are known. The forward rate parameter β_{i_a} is effectively defined

by the kinetic collision coefficient for hydrated monomers with i_a-mers, which can be accurately calculated using the standard collision theory.[19] It is more difficult to determine the reverse frequency γ_{i_a} which describes the rate at which H_2SO_4 molecules escape from i_a-mers.

Since the ratio $\beta_{i_a-1}/\gamma_{i_a}$ in Eqs. (5) and (8) is the equilibrium constant for the reaction "(i_a-1)-mer+monomer $\leftrightarrow i_a$-mer" for a given H_2SO_4 partial vapor pressure (or monomer concentration n_1) and temperature, it can be expressed in terms of stepwise Gibbs free energy changes $(\Delta G_{i_a-1,i_a})$ as

$$\frac{\beta_{i_a-1}}{\gamma_{i_a}} = \exp\left(-\frac{\Delta G_{i_a-1,i_a}}{RT}\right), \tag{9}$$

where R is the molar gas constant and T is the temperature.

$\Delta G_{i_a-1,i_a}$ relates to the reference Gibbs free energy change $(\Delta G^0_{i_a-1,i_a})$ at the reference vapor concentration $\rho^0 = p^0/k_B T$ (p^0 is generally taken to be 1 atm, with k_B the Bottzmann constant) as

$$\Delta G_{i_a-1,i_a} = -RT\ln(n_1/\rho^0) + \Delta G^0_{i_a-1,i_a}. \tag{10}$$

By rearranging Eq. (9) and taking into account Eq. (10), we find

$$\gamma_{i_a} = \frac{\beta_{i_a-1}}{n_1}\rho^0 \exp\left(\frac{\Delta G^0_{i_a-1,i_a}}{RT}\right). \tag{11}$$

It should be noted that n_1 in the denominator of Eq. (11) cancels the factor of n_1 in the expression for β_{i_a-1}, so that γ_{i_a} is independent of n_1.

The typical approach in nucleation modeling is to derive $\Delta G^0_{i_a-1,i_a}$ by treating clusters as spherical droplets having the same macroscopic properties as the bulk liquid (capillarity approximation). With the capillarity approximation, $\Delta G^0_{i_a-1,i_a}$ can be calculated using a revised Kelvin equation that takes into account surface enrichment or adsorption,[10]

$$\Delta G^0_{i_a-1,i_a} = -RT\ln\left(\frac{\rho^0_{\text{free}}}{n^s_{1,\text{free}}}\right) + \frac{2\sigma v_a}{r_{i_a}} = -RT\ln\left(\frac{\rho^0/F_{\text{hy}}}{n^s_{1,\text{free}}}\right)$$
$$+ \frac{2\sigma v_a}{r_{i_a}} = -RT\ln\left(\frac{\rho^0}{n^s_{1,\text{total}}}\right) + \frac{2\sigma v_a}{r_{i_a}}, \tag{12}$$

where

$$F_{\text{hy}} = 1 + K_1\left(\frac{\rho_{w,\text{free}}}{\rho^0}\right) + K_1 K_2\left(\frac{\rho_{w,\text{free}}}{\rho^0}\right)^2 + \cdots$$
$$+ K_1 K_2 \ldots K_h\left(\frac{\rho_{w,\text{free}}}{\rho^0}\right)^h \tag{13}$$

is the ratio of the total concentration of sulfuric acid molecules (free+hydrates) to the number concentration of free (nonhydrated) sulfuric acid molecules when the concentration of free water molecules is $\rho_{w,\text{free}}$. In Eq. (12), $n^s_{1,\text{free}}$ and $n^s_{1,\text{total}}$ are, respectively, the concentrations of free and total sulfuric acid molecules in the saturated vapor above a flat surface of a solution having the same bulk composition as the i_a-mer. ρ^0_{free} is the concentration of free sulfuric acid molecules when the total concentration of sulfuric acid mol-

ecules is ρ^0 (or 1 atm). σ is the surface tension of the binary solution, v_a is the partial molecular volume of sulfuric acid, and r_{i_a} is the equivalent radius of i_a-mer. In Eq. (13), K_h represents the equilibrium constants for the successive addition of water molecules to a sulfuric acid monomer, calculated at the reference water vapor concentration ρ^0.

By combining Eqs. (11) and (12) we finally obtain

$$\gamma_{i_a} = \frac{\beta_{i_a-1}}{n_1}n^s_{1,\text{total}}\exp\left(\frac{2\sigma v_a}{RTr_{i_a}}\right)$$
$$= \frac{\beta_{i_a-1}}{n_1}F_{\text{hy}}n^s_{1,\text{free}}\exp\left(\frac{2\sigma v_a}{RTr_{i_a}}\right). \tag{14}$$

In our application of this model, $n^s_{1,\text{free}}$ is calculated using the parameterization of Taleb *et al.*[24] with the pure acid saturation vapor pressure given by Noppel *et al.*[9] The bulk cluster density and surface tension are calculated using parameterizations of Vehkamäki *et al.*[25] The forward frequency β_{i_a} is determined via

$$\beta_{i_a} = \left(\frac{8\pi k_B T(m_1 + m_{i_a})}{m_1 m_{i_a}}\right)^{1/2}(r_1 + r_{i_a})^2 n_1, \tag{15}$$

where m_{i_a} is the mass of i_a-mer.

Consideration of Eqs. (8) and (14) reveals that there are three major sources of the uncertainty in J_{QUN}: (1) the monomer hydration factor (F_{hy}), (2) the capillarity approximation (Kelvin effect), and (3) the sulfuric acid vapor pressure ($n^s_{1,\text{free}}$). The focus of this study is to address the first two sources of error. In the next section, we show that experimental data can be effectively incorporated into the QUN model to improve the accuracy of the J_{QUN} calculation.

III. CONSTRAINTS ON KEY PARAMETERS BASED ON LABORATORY OBSERVATIONS

A. Monomer hydration

Predicted $H_2SO_4-H_2O$ homogeneous nucleation rates are sensitive to the degree of monomer hydration. Indeed, γ_{i_a} is proportional to F_{hy} [Eq. (14)], and J_{QUN} is roughly proportional to $(F_{\text{hy}})^{i^*_a}$. The equilibrium constants K_h for the successive addition of water molecules to a sulfuric acid monomer can be calculated as

$$K_h = \exp\left(\frac{-\Delta G_h}{RT}\right) = \exp\left(\frac{-\Delta H_h + T\Delta S_h}{RT}\right), \tag{16}$$

where ΔG_h, ΔH_h, and ΔS_h are the molar Gibbs free energy, enthalpy, and entropy changes, respectively, as a result of the addition of one water molecule to a monomer hydrate containing h-1 water molecules.

There are large uncertainties in the values of K_h that are used to calculate F_{hy}. Noppel *et al.*[9] compiled K_h values computed using different methods, such as the liquid droplet hydration model, *ab initio* calculations, and the parameterization of experimental data, and showed that the divergence in K_h values is quite large. More recently, the hydration thermodynamics of sulfuric acid monomers has been studied us-
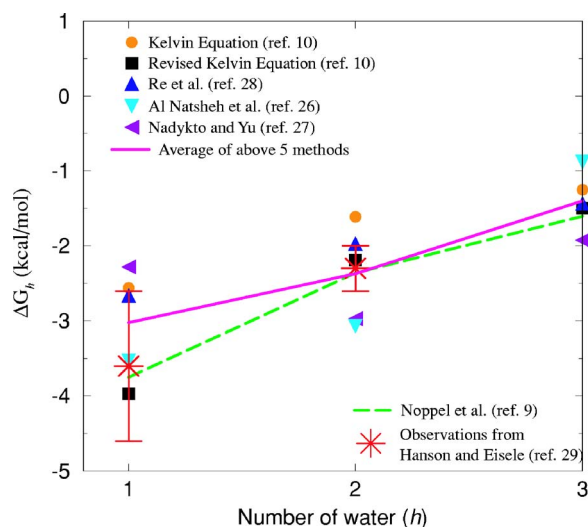
FIG. 1. (Color online) Gibbs free energy change for sulfuric acid monomer hydration (ΔG_h, $h = 1, 2, 3$) determined by five different methods for standard conditions ($T = 298.15$ K, $\rho^0 = 1$ atm). ΔG_h averaged over the five values and fitted results given by Noppel et al. (Ref. 9) are also shown. The star symbols with error bars are from the observations of Hanson and Eisele. (Ref. 29)

ing density functional theory (DFT) with several different methods and basis sets.[26,27]

Figure 1 shows the values of ΔG_h ($h = 1, 2, 3$) under standard conditions ($T = 298.15$ K, $\rho^0 = 1$ atm) calculated using five different methods: two liquid droplet models (Kelvin and revised Kelvin equations[10]) and three[26–28] DFT simulations. Compared are derived ΔG_h values, an average over the five results, a data fit given by Noppel et al.,[9] and observed values for ΔG_1 and ΔG_2 from Hanson and Eisele.[29] It is clear that the different methods yield quite different values of ΔG_h. The ΔG_1, ΔG_2, and ΔG_3 based on different assessments differ by up to 1.7, 1.5, and 1.0 kcal/mol, respectively. The only available observed value for ΔG_1 has an uncertainty of ~2 kcal/mol. The averaged ΔG_h given in this study is close to the fitted value given by Noppel et al.[9] for dihydration and trihydration, but is about 0.75 kcal/mol less negative for monohydration. Due to the limited observational data, and inherent experimental uncertainty, it is not possible to fix the values of ΔG_h more accurately at this time. Nevertheless, another independent set of relevant laboratory measurements reported by Marti et al.[30] can be used to further constrain ΔG_h and K_h.

Figure 2 compares the total sulfuric acid vapor concentrations (i.e., $n_{1,\text{total}}^s = F_{\text{hy}} n_{1,\text{free}}^s$) over solutions of varying H_2SO_4 mass fraction (wt %) at three different temperatures, as observed by Marti et al.[30] using a chemical ionization mass spectrometer (symbols), with those calculated using K_h given by Noppel et al.[9] (dot-dashed lines), and averaged K_h values from this study (solid lines). The dashed lines indicate the calculated concentration of free (unhydrated) sulfuric acid molecules over the solution (i.e., $n_{1,\text{free}}^s$). As has been pointed out previously,[30] the hydration of H_2SO_4 monomers (especially at high RH or low H_2SO_4 wt %) is obvious. McGraw and Weber[31] showed that the calculated $n_{1,\text{total}}^s$ based on the liquid droplet hydration model overestimates
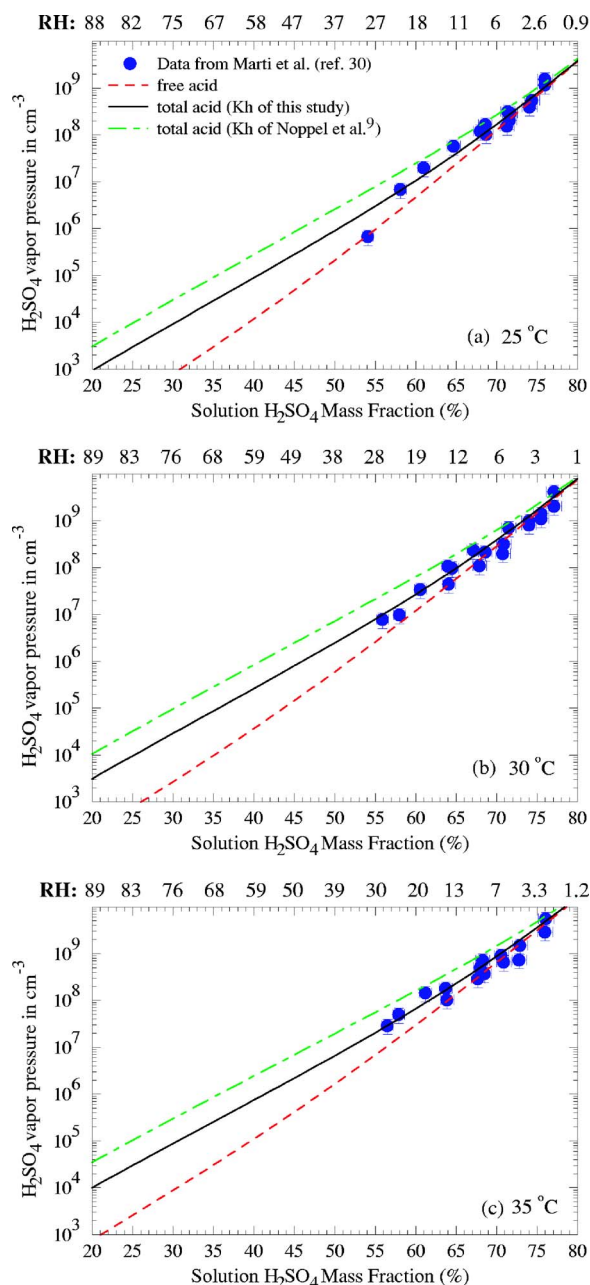

FIG. 2. (Color online) Total and free sulfuric acid vapor concentration over solutions of varying H_2SO_4 mass fraction (wt%) at three different temperatures. The equilibrium RH values corresponding to each wt% are given along the top scale of each panel. The filled circles represent the total sulfuric acid vapor concentrations measured by Marti et al. (Ref. 30) using a chemical ionization mass spectrometer.

the extent of hydration, which results in a substantial underprediction of H_2SO_4–H_2O binary homogeneous nucleation rates. Figure 2 also indicates that the hydration parameters given by Noppel et al.,[9] while apparently consistent with the experimental data of Hanson and Eisele,[29] overestimate the degree of hydration, especially at low H_2SO_4 wt % (or high RH). By contrast, the average results of this study (solid curve, Fig. 1), which lie within the uncertainty range of the measurements of Hanson and Eisele,[29] offer more reasonable agreement with the measurements of Marti et al.[30] For RH > ~20%, $n_{1,\text{total}}^s$ calculated based on K_h's of Noppel et al.[9] is a factor of ~3 higher than that based on the average K_h's
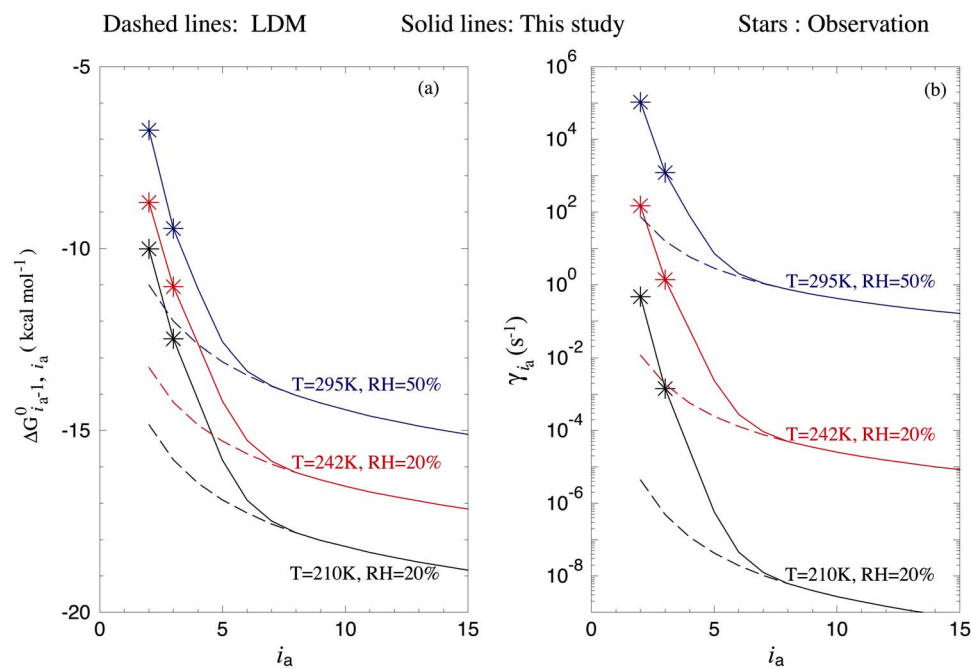
FIG. 3. (Color online) A comparison of $\Delta G^0_{i_a-1,i_a}$ and γ_{i_a} calculated with the liquid droplet model (LDM) (dashed lines) with those based on enthalpy and entropy changes fitted to laboratory measurements (Refs. [32] and [33]) (indicated by star symbols, for $i_a=2, 3$ only) under three sets of atmospheric conditions. The solid lines are extrapolated curves with $\Delta G^0_{i_a-1,i_a}$ and γ_{i_a} for $i_a=2$ and 3 constrained by laboratory measurements (Refs. [32] and [33]) and for $i_a \geq 4$ parameterized based on Eq. (17) in the text.

derived in this study. Such overestimation in K_h will lead to the reduction of BHN rates by two to four orders of magnitude when i_a^* lies between ~ 4 and ~ 9.

The averaged ΔH_h and ΔS_h (and hence ΔG_h and K_h) derived here using the five different approaches illustrated in Fig. 1, which seem to give results that are consistent with measurements by Hanson and Eisele[29] and Marti *et al.*,[30] are used in the present QUN model. The averaged ΔH_h are -12.96, -12.15, and -11.10 kcal mol^{-1}, and the average ΔS_h are -33.34, -32.79, and -32.53 cal mol^{-1} K^{-1}, for $h=1,2,3$, respectively.

B. Capillary approximation for energetics of small H_2SO_4–H_2O clusters

The liquid droplet (or capillary) approximation is assumed when we use Eq. (12) to calculate $\Delta G^0_{i_a-1,i_a}$. In the past, the validity of capillary approximation for small nucleating clusters has been questioned, but never adequately addressed.[22,23] Recently, laboratory measurements of the equilibrium constants (and thermodynamics) for water-mediated clustering of two and three sulfuric acid molecules under different conditions of T and RH have become available.[32,33] Figure 3 compares the $\Delta G^0_{i_a-1,i_a}$ and γ_{i_a} values calculated using the liquid droplet model (LDM) (dashed lines) with those based on measurements (stars, for $i_a=2, 3$ only) for three atmospheric states. Figure 3(a) indicates that LDM overestimates $\Delta G^0_{i_a-1,i_a}$ by ~ 4–5 kcal/mol for $i_a=2$, and ~ 2–3 kcal/mol for $i_a=3$. Such an overestimation will cause a significant underestimation of γ_{i_a}—about three to five orders of magnitude for γ_2 and one to three orders of magnitude for γ_3 [Fig. 3(b)]. It is clear from this comparison that LDM is invalid for small sulfuric acid clusters, and the application of the capillarity approximation to sulfuric acid dimers and trimers alone could lead to an overestimation of nucleation rates by four to eight orders of magnitude.

It is anticipated that $\Delta G^0_{i_a-1,i_a}$ approaches the bulk (or LDM) values as cluster size increases.[34,35] Indeed, it is already obvious in Fig. 3(a) that the difference between bulk and observed $\Delta G^0_{i_a-1,i_a}$ ($d\Delta G^0_{i_a-1,i_a}$) decreases by about 2 kcal/mol ($\sim 50\%$) as i_a increases from 2 to 3. Nevertheless, we do not have measurements at this point to define how quickly $\Delta G^0_{i_a-1,i_a}$ approaches bulk values beyond $i_a=3$. In this study, we parameterize $d\Delta G^0_{i_a-1,i_a}$ for $i_a \geq 4$ as

$$d\Delta G^0_{i_a-1,i_a} = d\Delta G^0_{i_a-2,i_a-1} \left(\frac{d\Delta G^0_{2,3}}{d\Delta G^0_{1,2}} \right)^{i_a-3}, \quad i_a \geq 4. \quad (17)$$

The solid lines in Fig. 3 are the extrapolated curves with $\Delta G^0_{i_a-1,i_a}$ and γ_{i_a} for $i_a=2$ and 3 calculated directly based on enthalpy and entropy changes fitted to the laboratory measurements,[33] and for $i_a \geq 4$ parameterized according to Eq. (17). Based on this model, $d\Delta G^0_{i_a-1,i_a}$ decreases rapidly as i_a increases, and $\Delta G^0_{i_a-1,i_a}$ (and hence γ_{i_a}) approaches bulk properties at $i_a=\sim 7$–8.

Figure 3 shows that the capillarity approximation (or Kelvin equation based on liquid droplet model) can lead to large errors in predicted cluster thermodynamic parameters at small cluster sizes, and hence nucleation rates. The extrapolated values for $\Delta G^0_{i_a-1,i_a}$ as shown in Fig. 3, while subject to additional uncertainty, are more constrained than previous representations, and provide a reasonable basis for the advanced QUN model proposed here. Also, as demonstrated above, the QUN model can effectively employ even limited thermodynamic measurements for small clusters in calculating nucleation rates.

IV. COMPARISON WITH MEASUREMENTS AND CLASSICAL BHN PREDICTIONS

Figure 4 compares predicted nucleation rates as a function of total sulfuric acid vapor concentration (n_1) with values measured for eight different atmospheric states covering
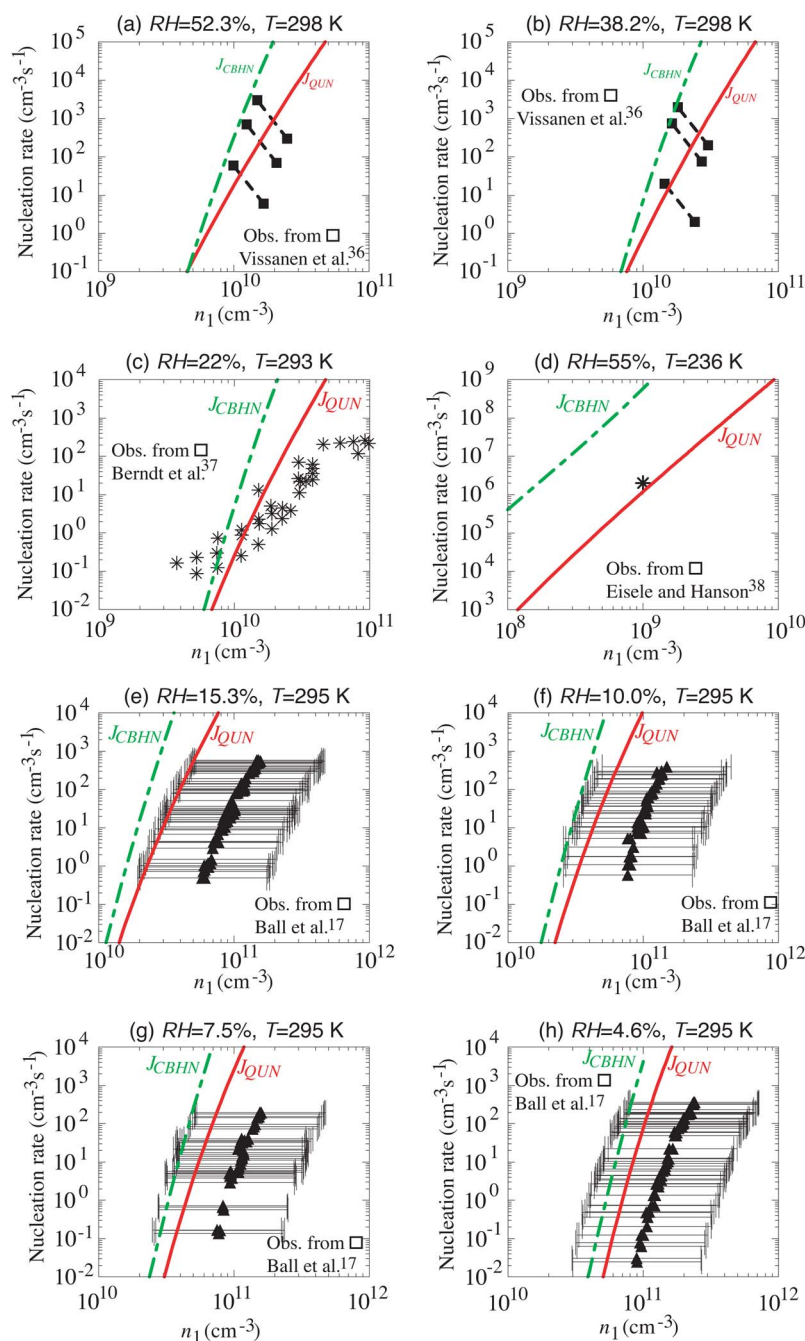
FIG. 4. (Color online) Nucleation rates as a function of total sulfuric acid vapor concentration (n_1) at eight different relative humidities and four different temperatures. The solid lines and dot-dashed lines are, respectively, the nucleation rates predicted by the classical BHN theory (J_{CBHN})[2] Ref. [25] and the improved $H_2SO_4-H_2O$ quasi-unary nucleation model discussed in this paper (J_{QUN}). The experimental data are as follow [(a) and (b)] Viisanen *et al.* (Ref. [36]) (c) Berdnt *et al.* (Ref. [37]) (d) Eisele and Hanson (Ref. [38]), and [(e)–(h)] Ball *et al.* (Ref. [17]).

a range of conditions of n_1, T, and RH. The solid lines and dot-dashed lines are, respectively, the nucleation rates predicted by the classical BHN theory (J_{CBHN})[25] and the improved $H_2SO_4-H_2O$ quasi-unary nucleation model discussed in this paper [J_{QUN}, Eq. (8)]. As can be seen in the figure, under all conditions shown, J_{QUN} consistently falls within the range of experimental uncertainty, and in every case provides a more accurate representation of the data than the classical BHN theory which tends to overestimate nucleation rates. The QUN approach is clearly superior in these comparisons.

The differences between J_{CBHN} and J_{QUN} amount to several orders of magnitude. If the CBHN approach was to adopt the same K_h's (monomer hydration equilibrium constants) as those derived here for the revised QUN model, J_{CBHN} in Fig. 4 would be an additional two to four orders of

magnitude larger (as described in a previous section), increasing the overall difference to as much as five to seven orders of magnitude. CBHN is based on the capillarity approximation that, as shown in Fig. 3, significantly underpredicts γ_{i_a} for small clusters and thus overpredicts nucleation rates.

The J_{QUN} has other advantages. For example, Fig. 4 indicates that the improved QUN model gives better agreement with the measurements of the power dependence of nucleation rates on the sulfuric acid monomer concentration (n_1) by Ball *et al.*[17] (i.e., the slope of $\log_{10} J$-$\log_{10} n_1$ curves). Figure 5 illustrates the dependence of J_{CBHN} and J_{QUN} on T and RH. Again, it shows that J_{CBHN} is consistently several orders of magnitude larger than J_{QUN}, except when the nucleation rates are very low ($<10^{-5}$ cm^{-3} s^{-1}, and therefore irrel-
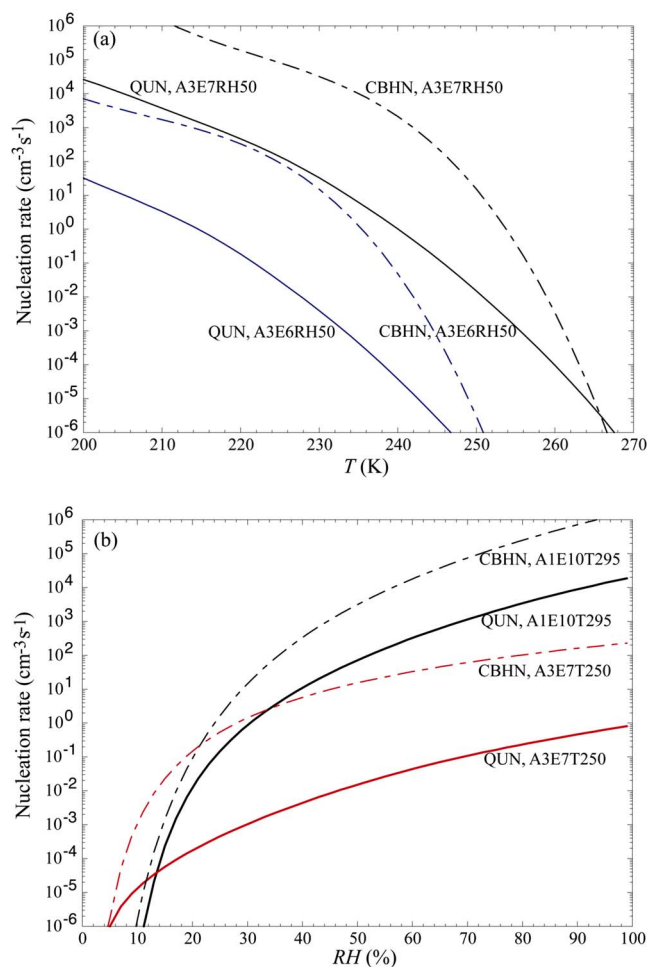
FIG. 5. (Color online) The dependence of predicted nucleation rates on T (a) and RH (b) based on the CBHN and QUN models. Read A3E7RH50 as $n_1 = 3 \times 10^7$ cm^{-3} and RH=50%. Read A3E7T250 as $n_1 = 3 \times 10^7$ cm^{-3} and T=250 K.

evant). Similarly, CBHN predicts a steeper increase in nucleation rates as T decreases or RH increases in the region where nucleation rates transit from negligible values to significant ones. This difference is largely associated with the capillarity approximation used in the CBHN model as opposed to use of new observational constraints in the QUN approach (see Fig. 3). While the QUN model appears to provide greater fidelity with regard to the dependence of the nucleation rate on n_1, there is currently insufficient data to test more accurately the dependence of nucleation rates on T and RH.

V. SUMMARY

H_2SO_4 and H_2O are clearly involved in many of the nucleation events observed in the atmosphere. $H_2SO_4-H_2O$ binary homogeneous nucleation (BHN) rates are generally considered to be insignificant in the ambient lower atmosphere. However, $H_2SO_4-H_2O$ BHN is the foundation for recently proposed nucleation mechanisms involving ammonia, ions, and organics, and BHN may dominate nucleation under certain conditions (for example, in engine exhaust plumes or in the upper troposphere).

$H_2SO_4-H_2O$ BHN can be treated as quasi-unary nucleation (QUN) process involving H_2SO_4 in equilibrium with water vapor. In this study, an analytical expression was derived for $H_2SO_4-H_2O$ quasi-unary nucleation rates, and the QUN model was improved by constraining model parameters using laboratory measurements. Based on two independent observations related to monomer hydration, it was found that the hydration equilibrium constants used in the most recent version of classical BHN model significantly overestimate the extent of monomer hydration. Equilibrium constants for monomer hydration that are consistent with the two independent measurements were derived and incorporated into the QUN model. It was also demonstrated that the capillarity approximation may lead to a large errors in the equivalent thermodynamic parameters estimated for small $H_2SO_4-H_2O$ clusters, and hence in BHN nucleation rates. To further advance the QUN model, a parameterized formula was developed for the Gibbs free energy change related to the condensation and evaporation of H_2SO_4 molecules from small $H_2SO_4-H_2O$ clusters that takes into account recently measured thermodynamic factors for small clusters.

The predicted nucleation rates based on our extended QUN model are consistent with experimental data within the stated ranges of uncertainty. Even with a fortuitous cancellation of errors in the classical BHN model associated with specific degrees of hydration and with the capillarity approximation, the differences between nucleation rates predicted with BHN and QUN models are several orders of magnitude. Further, the dependence of nucleation rates on key parameters is quite different between the models. Additional laboratory measurements are needed to resolve the remaining differences, and improve our understanding of $H_2SO_4-H_2O$ nucleation processes sufficiently for reliable application. In this latter respect, the QUN model can effectively exploit new measurements of the thermodynamics of small clusters to constrain nucleation theory and reduce the overall uncertainty in calculated nucleation rates.

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