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Effect of ammonium bisulphate formation on atmospheric water-sulphuric acid-ammonia nucleation

Tatu Anttila[1)2)], Hanna Vehkamäki[3)], Ismo Napari[3)] and Markku Kulmala[3)]

[1)] *Institut für Chemie und Dynamik der Geosphäre, Forschungszentrum Juelich, D-52425 Juelich, Germany*
[2)] *Finnish Meteorological Institute, Research and Development, Erik Palmenin Aukio 1, P.O. Box 503, FI-00101 Helsinki, Finland*
[3)] *Department of Physical Sciences, P.O. Box 64, FI-00014 University of Helsinki, Finland*

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The effect of formation of stable ammonium bisulphate clusters on the ternary water-sulphuric acid-ammonia nucleation was investigated by means of the classical thermodynamics. The performed calculations show that most of the sulphuric acid in the atmosphere is likely to be bound to stable ammonium bisulphate clusters. Consequently the nucleation rates calculated with the new model are orders, sometimes even tens of orders, of magnitude lower than the rates produced by the previous ternary model which neglected the formation of these clusters. The new nucleation rates compare favourably with the available experimental results, unlike the old ones, which are far too high. In contrast to the old ternary model, the revised model does not predict significant nucleation rates that would explain new particle formation events every time they are observed, and we have to look for other nucleation mechanisms like multi-component nucleation involving organics or ion induced nucleation to understand atmospheric new particle formation.

Introduction

Nucleation of tiny, thermodynamically stable clusters from gaseous precursors is a first step in atmospheric aerosol formation, and it constitutes an active research topic due to its possible health effects and impacts on the radiation balance of the Earth (Kulmala *et al*. 2004). Different nucleation routes have been investigated, and a ternary nucleation mechanism involving water, sulphuric acid and ammonia has been widely used to explain particle formation taking place under different atmospheric conditions. The ternary model developed by Korhonen *et al*. (1999) and Napari *et al*. (2002) has been applied hitherto to explain particle formation occurring in a boreal forest site in southern Finland (Kulmala *et al*. 2001), in the Pittsburgh region of the eastern United States (Gaydos *et al*. 2005) and in a coastal site at Mace Head, Ireland (Kulmala *et al*. 2002).

In spite of its explanatory power, the ternary nucleation model has some questionable features which deserve closer investigation. Above all, the model tends to predict extremely high nucleation rates and critical clusters consisting only of a few molecules under conditions relevant to the troposphere, in particular for air masses containing elevated ammonia concentrations. The analysis of *in situ* measurements of gaseous

sulphuric acid and ammonia, for example during the QUEST field measurement campaign (Boy *et al.* 2005), demonstrated that the model may give even unphysical results: using the measurement data as an input for the ternary model, the resulting nucleation rates were so high that they often exceeded the kinetic limit, i.e. the rate at which two molecules collide in the nucleating vapour. No consistently calculated nucleation rate, however, should be higher than the kinetic collision rate.

The reason for the undesired behaviour of the ternary model of the Napari *et al.* (2002) is that it does not take into account formation of stable ammonium bisulphate clusters which have a similar effect than that of hydrate formation: sulphuric acid bounded into ammonium bisulphate clusters has a smaller nucleation potential than that of free sulphuric acid (Vehkamäki *et al.* 2004) and consequently the nucleation rates are reduced. Vehkamäki *et al.* (2004) predicted the formation of stable ammonium sulphate clusters using the classical thermodynamics, but the resulting nucleation rates and critical cluster compositions have not been investigated so far.

We investigate to what extent gaseous ammonia and sulphuric acid is bound to ammonium bisulphate clusters according to the developed theory and present a revised version of the ternary nucleation theory that accounts for the formation of stable ammonium bisulphate clusters. We show the resulting nucleation rates and critical cluster compositions for various conditions and compare the results with available experimental data. Finally we discuss the implications of the revised ternary nucleation mechanism to the atmospheric new particle formation.

Theory

The dimensionless equilibrium constant for addition of i water, j sulphuric acid, and k ammonia molecules to a sulphuric acid molecule is

$$\hat{K}(i,j,k) = \exp\left\{-\left[\Delta G(i,j,k) - \Delta G(0,1,0)\right]/k_B T\right\} \quad (1)$$

where $\Delta G(i,j,k)$ is the formation work of a cluster with i water, j sulphuric acid, and k ammonia molecules. In the classical droplet model, the work of formation is given by (Laaksonen *et al.* 1999)

$$\begin{aligned}\Delta G(i,j,k) = &-ik_B T \ln\frac{\rho_w^f}{\rho_{ws}^f(x_a,x_b)} \\ &-jk_B T \ln\frac{\rho_a^f}{\rho_{as}^f(x_a,x_b)} \\ &-kk_B T \ln\frac{\rho_b^f}{\rho_{bs}^f(x_a,x_b)} + 4\pi r^2\sigma(x_a,x_b)\end{aligned} \quad (2)$$

where ρ_l^f is the vapour number density of free molecules in the ambient air and ρ_{ls}^f is the equilibrium number density in the vapour corresponding to a liquid phase with composition (x_a,x_b). Subscripts l = w, a, b refer to water (w), acid (a) and ammonia (b, base). The classical radius and surface tension of the droplet are given by r and $\sigma(x_a,x_b)$, respectively. The molecular numbers i, j and k here are the total number of molecules (core + surface excess) as described in Napari *et al.* (2002b).

The vapour densities are obtained from ideal gas law as

$$\rho_l^f = P_l^f / k_B T \quad (3)$$

where P_l^f is the vapour pressure of component l, and the equilibrium vapour density is given by

$$\rho_{ls}(x_a,x_b) = P_{ls}^f(x_a,x_b)/k_B T = P_{ls}^0 A_l(x_a,x_b)/k_B T \quad (4)$$

where $A_l(x_a,x_b)$ is the activity of component l in the solution. $P_{ls}^f(x_a,x_b)$ and P_{ls}^0 are the equilibrium vapour pressures (of free molecules) for component l above the solution and pure liquid, respectively.

When Eqs. 2, 3, and 4 are used in Eq. 1, one obtains

$$\begin{aligned}\hat{K}(i,j,k) = &\left(\rho_w^f\right)^i\left(\rho_a^f\right)^{j-1}\left(\rho_b^f\right)^k \\ &\times\left(\frac{k_B T}{P_{ws}^0 A_w}\right)^i\left(\frac{k_B T}{P_{as}^0 A_a}\right)^j\left(\frac{k_B T}{P_{bs}^0 A_b}\right)^k \\ &\times\frac{P_{as}^0}{k_B T}\exp\left[-\frac{4\pi(r^2\sigma - r_a^2\sigma_a)}{k_B T}\right]\end{aligned} \quad (5)$$

where the arguments referring to liquid compositions are dropped off for shortness. Here r_a and σ_a are the radius and the surface tension, respectively, of an acid molecule. The first row of Eq. 5 shows how the equilibrium constant depends on

the ambient vapour densities. Now we separate this vapour concentration dependence by defining a dimensional equilibrium constant $K(i,j,k)$ by

$$\hat{K}(i,j,k) = \left(\rho_{\mathrm{w}}^{\mathrm{f}}\right)^{i}\left(\rho_{\mathrm{a}}^{\mathrm{f}}\right)^{j-1}\left(\rho_{\mathrm{b}}^{\mathrm{f}}\right)^{k} K(i,j,k) \quad (6)$$

which allows the number density of a cluster containing i water, j sulphuric acid, and k ammonia molecules to be expressed as

$$\rho(i,j,k) = K(i,j,k)\left(\rho_{\mathrm{w}}^{\mathrm{f}}\right)^{i}\left(\rho_{\mathrm{a}}^{\mathrm{f}}\right)^{j-1}\left(\rho_{\mathrm{b}}^{\mathrm{f}}\right)^{k} \quad (7)$$

where $K(i,j,k)$ depends only on the number of various molecules in the cluster i, j, k and temperature, but is independent of ambient vapour densities. The partial pressures needed to calculate the liquid phase activities A_{l} are obtained from the thermodynamic model of Clegg *et al*. (1998) (*see* also http://www.hpc1.uea.ac.uk/e770/aim.html). More details on how the surface tension and liquid density are calculated are presented in Korhonen *et al*. (1999) and Napari *et al*. (2002b).

Because the total number of molecules of species l in the vapour is equal to the sum of the free molecules l and those attached to clusters of various sizes, we can write for each component

$$\rho_{\mathrm{l}}^{\mathrm{tot}} - \sum_{i,j,k}\rho(i,j,k) = 0 \quad (8)$$

where $\rho^{\mathrm{tot}}{}_{\mathrm{l}}$ is the total number density of component l. Now applying Eq. 7 to Eq. 8 and writing $\rho(1,0,0) = \rho_{\mathrm{w}}$, $\rho(0,1,0) = \rho_{\mathrm{a}}$, and $\rho(0,0,1) = \rho_{\mathrm{b}}$, we obtain for water

$$\begin{aligned}\rho_{\mathrm{w}}^{\mathrm{tot}} - \rho_{\mathrm{w}}^{\mathrm{f}}\Big[1 + K(1,1,0)\rho_{\mathrm{a}}^{\mathrm{f}} + K(1,1,1)\rho_{\mathrm{a}}^{\mathrm{f}}\rho_{\mathrm{b}}^{\mathrm{f}} \\ + K(1,1,2)\rho_{\mathrm{a}}^{\mathrm{f}}\left(\rho_{\mathrm{b}}^{\mathrm{f}}\right)^{2}\Big] - 2\left(\rho_{\mathrm{w}}^{\mathrm{f}}\right)^{2}\Big[K(2,1,0)\rho_{\mathrm{a}}^{\mathrm{f}} \\ + K(2,1,1)\rho_{\mathrm{a}}^{\mathrm{f}}\rho_{\mathrm{b}}^{\mathrm{f}} + K(2,1,2)\rho_{\mathrm{a}}^{\mathrm{f}}\left(\rho_{\mathrm{b}}^{\mathrm{f}}\right)^{2}\Big] = 0\end{aligned} \quad (9)$$

for sulphuric acid

$$\begin{aligned}\rho_{\mathrm{a}}^{\mathrm{tot}} - \rho_{\mathrm{a}}^{\mathrm{f}}\Big[1 + K(1,1,0)\rho_{\mathrm{w}}^{\mathrm{f}} + K(2,1,1)\left(\rho_{\mathrm{w}}^{\mathrm{f}}\right)^{2} \\ + K(0,1,1)\rho_{\mathrm{b}}^{\mathrm{f}} + K(1,1,1)\rho_{\mathrm{w}}^{\mathrm{f}}\rho_{\mathrm{b}}^{\mathrm{f}} + K(2,1,2)\left(\rho_{\mathrm{w}}^{\mathrm{f}}\right)^{2}\rho_{\mathrm{b}}^{\mathrm{f}} \\ + K(0,1,2)\left(\rho_{\mathrm{b}}^{\mathrm{f}}\right)^{2} + K(1,1,2)\rho_{\mathrm{w}}^{\mathrm{f}}\left(\rho_{\mathrm{b}}^{\mathrm{f}}\right)^{2} \\ + K(2,1,2)\left(\rho_{\mathrm{w}}^{\mathrm{f}}\right)^{2}\left(\rho_{\mathrm{b}}^{\mathrm{f}}\right)^{2}\Big] - 2\left(\rho_{\mathrm{a}}^{\mathrm{f}}\right)^{2}\Big[K(0,2,2)\left(\rho_{\mathrm{b}}^{\mathrm{f}}\right)^{2} \\ + K(0,2,1)\rho_{\mathrm{b}}^{\mathrm{f}}\Big] = 0\end{aligned} \quad (10)$$

and for ammonia

$$\begin{aligned}\rho_{\mathrm{b}}^{\mathrm{tot}} - \rho_{\mathrm{b}}^{\mathrm{f}}\Big[1 + K(0,1,1)\rho_{\mathrm{a}}^{\mathrm{f}} + K(1,1,1)\rho_{\mathrm{w}}^{\mathrm{f}}\rho_{\mathrm{a}}^{\mathrm{f}} \\ + K(2,1,1)\left(\rho_{\mathrm{w}}^{\mathrm{f}}\right)^{2}\rho_{\mathrm{a}}^{\mathrm{f}} + K(0,2,1)\left(\rho_{\mathrm{a}}^{\mathrm{f}}\right)^{2}\Big] \\ - 2\left(\rho_{\mathrm{b}}^{\mathrm{f}}\right)^{2}\Big[K(0,1,2)\rho_{\mathrm{a}}^{\mathrm{f}} + K(1,1,2)\rho_{\mathrm{w}}^{\mathrm{f}}\rho_{\mathrm{a}}^{\mathrm{f}} \\ + K(2,1,2)\left(\rho_{\mathrm{w}}^{\mathrm{f}}\right)^{2}\rho_{\mathrm{a}}^{\mathrm{f}} + K(0,2,2)\left(\rho_{\mathrm{a}}^{\mathrm{f}}\right)^{2}\Big] = 0\end{aligned} \quad (11)$$

Here we have only taken into account those cases where the cluster contains two molecules of each species at most and the number of ammonia molecules does not exceed twice the amount of sulphuric acid molecules. The latter constraint is due to Clegg activity model (Clegg *et al*. 1998) being restricted to non-alkaline solutions. However, the calculations performed with another thermodynamic model (Korhonen *et al*. 1999) have shown that amounts of alkaline clusters are negligible and therefore this constraint has no practical significance. It should be noted that the Clegg model is based on molalities, and can not be used for totally waterless clusters. Here the waterless limit was treated using $n_{\mathrm{W}} = 10^{-10}$ and we also checked that the choice of this value did not affect the results.

Both in atmospheric and laboratory measurements only the total number of vapour molecules (*see* Eq. 8) is usually known. Thus, for the nucleating vapour we have to solve Eqs. 9–11 to obtain the concentrations of free molecules $\rho^{\mathrm{f}}_{\mathrm{l}}$ needed in the formation free energy in Eq. 2. In the equilibrium vapour activities (or chemical potentials) give directly the concentrations of free molecules $\rho^{\mathrm{f}}_{\mathrm{ls}}$ (Noppel 2000, Noppel *et al*. 2002). Figure 1 illustrates how the formation free energy curve (for simplicity in one dimension only) changes if some of these molecules are bound to stable clusters instead of being free. The stable pre-critical clusters lie in a minimum of the free energy curve, and the maximum corresponding to the critical clusters size moves toward larger sizes and the maximum becomes higher. The effective nucleation barrier is the energy difference between the stable clusters at the minimum and the critical clusters at the maximum of the free energy curve.

The composition of the critical nuclei and the nucleation rate can be calculated once the concentrations of free molecules have been determined from Eqs. 9–11. By minimising the

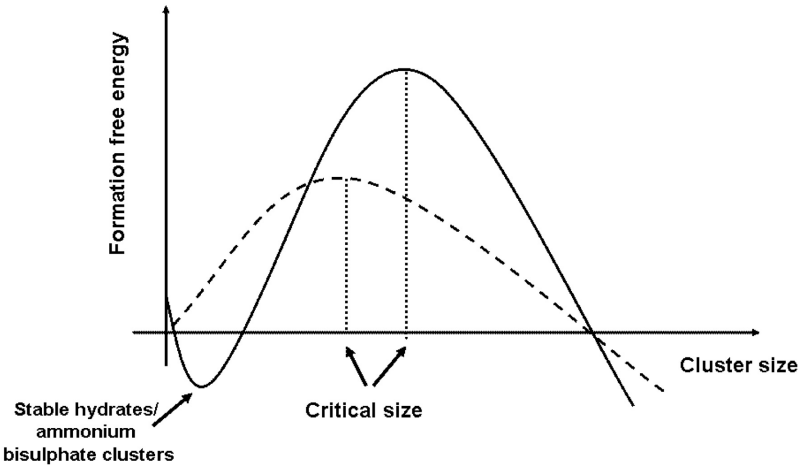

Fig. 1. Schematic figure of the formation free energy curves in the cases when sulphuric acid molecules are bound to stable ammonium bisulphate clusters or hydrates (solid line) and when the sulphuric acid molecules are free (dashed curve).

formation energy of Eq. 2 with respect to the particle numbers i, j, k, the following two equations are obtained

$$v_a(x_a^*, x_b^*) \ln \frac{\rho_w^f}{\rho_{ws}^f(x_a^*, x_b^*)} = v_w(x_a^*, x_b^*) \ln \frac{\rho_a^f}{\rho_{as}^f(x_a^*, x_b^*)} \quad (12)$$

$$v_a(x_a^*, x_b^*) \ln \frac{\rho_b^f}{\rho_{bs}^f(x_a^*, x_b^*)} = v_b(x_a^*, x_b^*) \ln \frac{\rho_a^f}{\rho_{as}^f(x_a^*, x_b^*)} \quad (13)$$

where v_l are the partial molecular volumes and the asterisk refers to the critical cluster. The composition of the critical cluster is obtained by solving simultaneously Eqs. 12 and 13. The radius of the critical cluster is then

$$r^* = \frac{2\sigma(x_a^*, x_b^*) v_l(x_a^*, x_b^*)}{k_B T \ln\left[\rho_l^f / \rho_{ls}^f(x_a^*, x_b^*)\right]} \quad (14)$$

and the work of formation

$$\Delta G^* = \frac{4}{3}\pi (r^*)^2 \sigma(x_a^*, x_b^*). \quad (15)$$

Nucleation rate is calculated from

$$J = \frac{|\lambda|/\pi}{\sqrt{-\det(\mathbf{D})/\pi}} F^e \exp\left(\frac{-\Delta G^*}{k_B T}\right) \quad (16)$$

where **D** is a matrix obtained from the second derivatives of formation energy (Eq. 2). The parameter λ is the negative eigenvalue of the matrix **KD**, where **K** is the condensation matrix. For the normalisation factor F^e we have used the value $F^e = \rho_a^f \exp[\Delta G(0,1,0)/(kT)]$ which ensures that the cluster distribution written in the form $\rho(i,j,k) = F^e \exp[-\Delta G(i,j,k)/(kT)]$ gives correct value for the free sulphuric acid concentration. Further details can be found in Napari *et al*. (2002b) and Noppel (2002).

Results

Figure 2 shows the distribution of sulphuric acid molecules bound into different pre-critical clusters according to Eq. 7 with the equilibrium constants given by Eq. 5, and all the liquid properties are taken from the Clegg *et al*. (1998) model. Classical theory predicts that almost all the sulphuric acid is bound to ammonium bisulphate cluster (A_1B_1). Depending on the ammonia mixing ratio some sulphuric acid is also in hydrates or clusters where one or two water molecules have joined ammonium bisulphate, or ammonium sulphate clusters, but none of it is free. In contrast, according to the equilibrium constants obtained from quantum chemical calculations of Bandy and Ianni (1998) and Ianni and Bandy (1999) most sulphuric acid molecules are free. For binary water-sulphuric acid system the classical predictions agree qualitatively with experiments of Hanson and Eisele (2000) at 298 K (Vehkamäki *et al*. 2004), and the reasons for

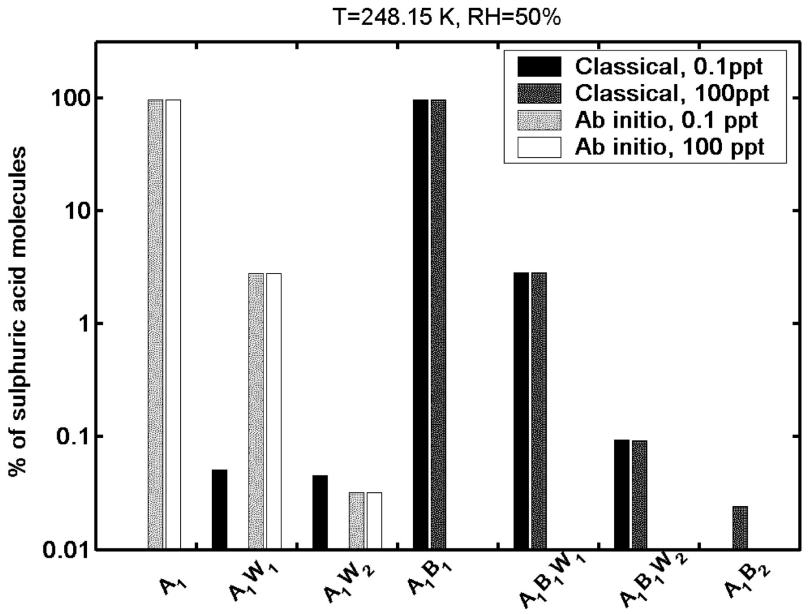

Fig. 2. Percentage of sulphuric acid molecules bound into clusters containing different amounts of water (W), sulphuric acid (A) and ammonia (B). The subscripts indicate how many molecules of each molecular type are in the cluster. Cluster distributions according to classical thermodynamics and quantum chemistry results of Bandy and Ianni (1998), Ianni and Bandy (1999) are shown. Note that the vertical axis is logarithmic.

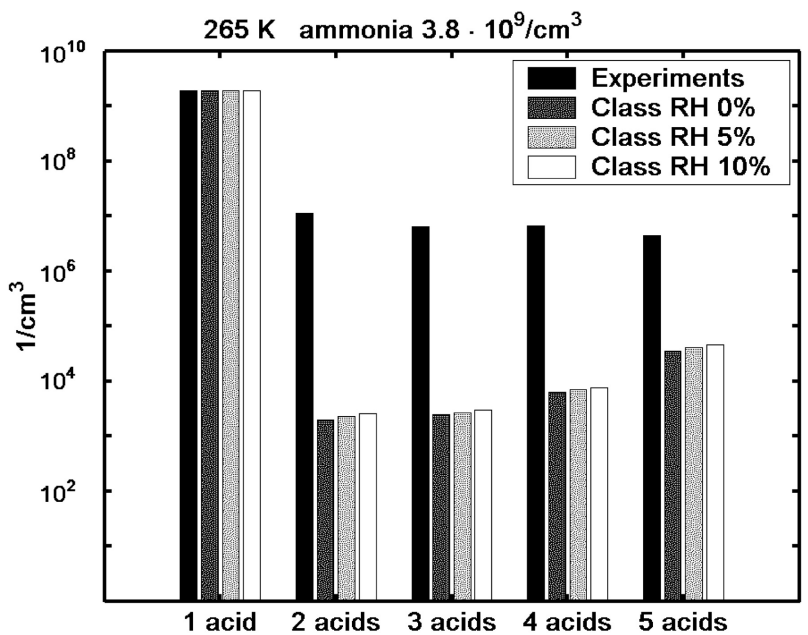

Fig. 3. Distribution of clusters identified by their sulphuric acid content. Experimental results by Hanson and Eisele (2002) are compared with classical theory predictions at different relative humidities. The theoretical number of clusters containing one sulphuric acid molecule has been set to match the experimental value.

the failure of quantum chemical results to do so are currently under investigation. In this paper we use the equilibrium constants given by the classical theory.

Figure 3 shows a comparison of classical theory with the cluster distribution measurements of Hanson and Eisele (2002). Their experimental technique is such that an unknown number of water molecules originally bounded to clusters are lost before the mass on the cluster is measured. Probably also some ammonia molecules are lost in the same way. Thus we have characterised the clusters by the number of sulphuric acid molecules (j) in them, and calculated the sum $\rho_j = \sum k\rho(i,j,k)$ with number of waters $i = 0,\ldots, 10$ and number of ammonia molecules $k = 0 \ldots (j - 1)$.

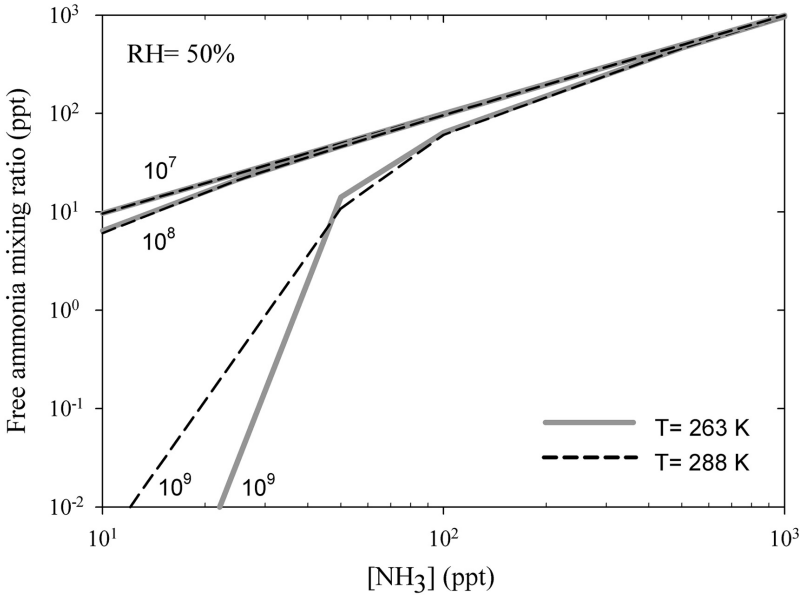

Fig. 4. Mixing ratio of free ammonia molecules as a function of the total mixing ratio of ammonia for temperatures of T = 263 K and T = 288 K. Relative humidity is 50%. The sulphuric acid concentration (in cm^{-3}) is indicated in the figure.

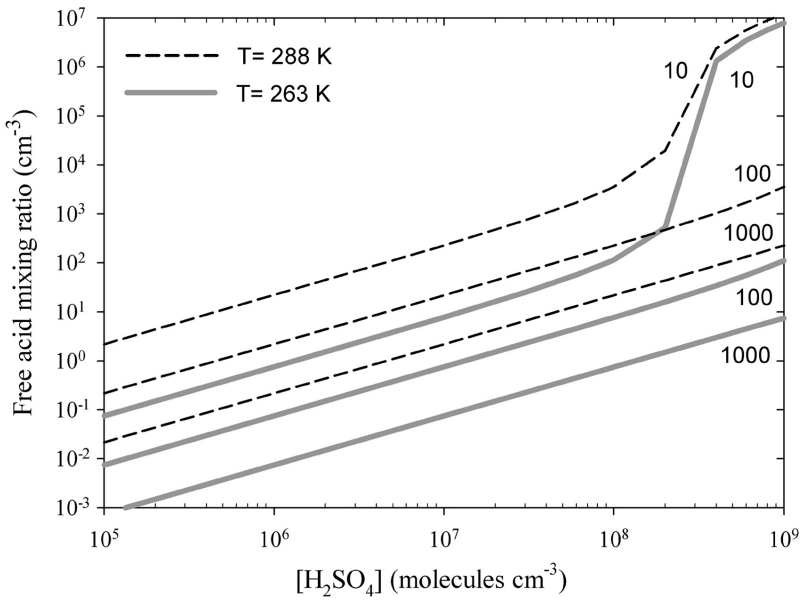

Fig. 5. Concentration of free sulphuric acid molecules as a function of total concentration of sulphuric acid for temperatures of T = 263 K and T = 288 K. Relative humidity is 50%. Ammonia mixing ratio (in ppt) is indicated in the figure.

The experimental sulphuric acid concentration 1.9 × 10^9 cm^{-3} is taken to be the sum of all clusters containing one sulphuric acid molecule, from which the number of free sulphuric acid molecules is calculated. Due to uncertainties in the relative humidity value we have calculated the distribution for dry conditions and for relative humidities 5% and 10%. The amount of water does not affect the cluster distribution significantly. Figure 3 indicates that classical theory might underestimate the number of clusters containing more than one sulphuric acid molecule. Clusters with a single sulphuric acid molecule dominate the cluster distribution, and in essence their formation probabilities decide the value of the nucleation rate. Taking into account clusters with more acid molecules results in minor corrections. Unfortunately the experimental results of Hanson and Eisele (2002) cannot be used to obtain information about how the one-acid clusters are distributed to free

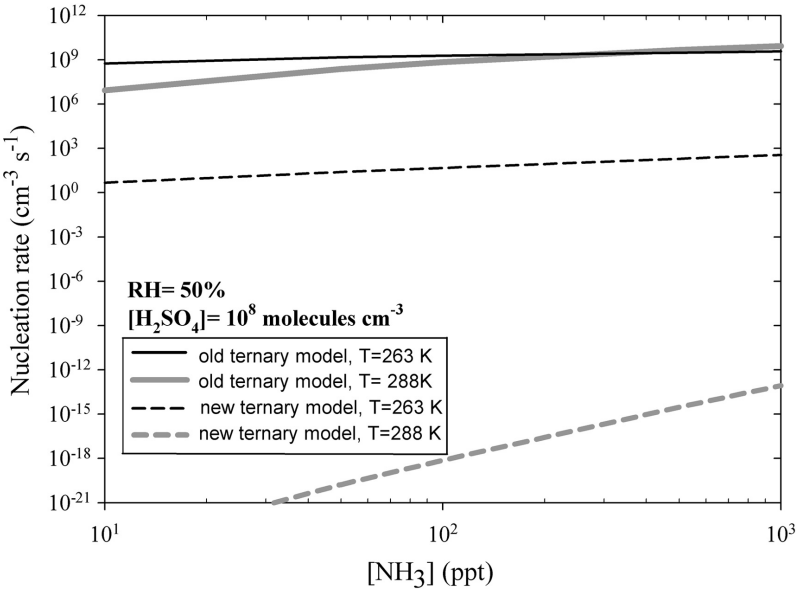

Fig. 6. Nucleation rate as a function of ammonia mixing ratio when relative humidity is 50% and sulphuric acid concentration 10^8 cm^{-3}. The old and new ternary models are compared at T = 263 K and T = 288 K.

acids, hydrates, and ammonium bisulphate clusters. Due to a lack of any other experimental data for water–sulphuric-acid–ammonia clusters the results in Fig. 3 are presented here to show that the classical predictions shown in Fig. 2 are reasonable, if not exactly correct, and that they are preferred over the *ab initio* predictions due to better agreement with experimental data.

Figures 4 and 5 show the concentration of free molecules as a function of the total concentration of molecules for ammonia and sulphuric acid, respectively. Ammonium bisulphate formation lowers significantly the number of free ammonia molecules as compared with the total concentration of ammonia only when sulphuric acid concentration is of the order of 10^9 cm^{-3} with ammonia mixing ratios between 10 and 1000 ppt. This occurs when the concentration of sulphuric acid approaches the concentration of ammonia. The free acid concentration depends nearly linearly on the total acid concentration. At low ammonia concentrations (10 ppt) and high sulphuric acid concentrations we see a transition to the region where all added sulphuric acid remains free since there is no unbound ammonia available. Cluster formation does not cause the free water concentration to deviate from the total concentration of water molecules in any of the cases studied since the concentration of water vapour is much higher than that of sulphuric acid or ammonia.

Figures 6, 7 and 8 show the nucleation rate as a function of ammonia mixing ratio, relative humidity and sulphuric acid concentration, respectively. The present theory is compared with the old ternary theory of Napari *et al*. (2002). Ammonium bisulphate formation reduces the nucleation rate by several orders of magnitude in all cases. The nucleation rate is a rather weak function of relative humidity and ammonia concentration under atmospheric conditions and sulphuric acid is clearly the limiting substance for new particle formation. Nucleation rate depends strongly also on the temperature (Fig. 9).

The ammonia-to-sulphate ratio in the critical cluster varies between 0.8 and 1.5 in typical conditions where the concentration of sulphuric acid is greater than 1 cm^{-3}. Only under conditions with very high ammonia and very low sulphuric acid concentration does the ratio approach two, corresponding to ammonium sulphate. Figure 10 shows the temperature dependence of the molecular content of the critical cluster for rather high sulpuric acid concentration and medium ammonia mixing ratio. With these vapour concentrations clusters contain almost an equal amount of ammonia and sulphuric acid, corresponding to ammonium bisulphate composition, and very little water. With constant gas concentrations higher temperatures naturally lead to larger critical clusters, because the vapour becomes less

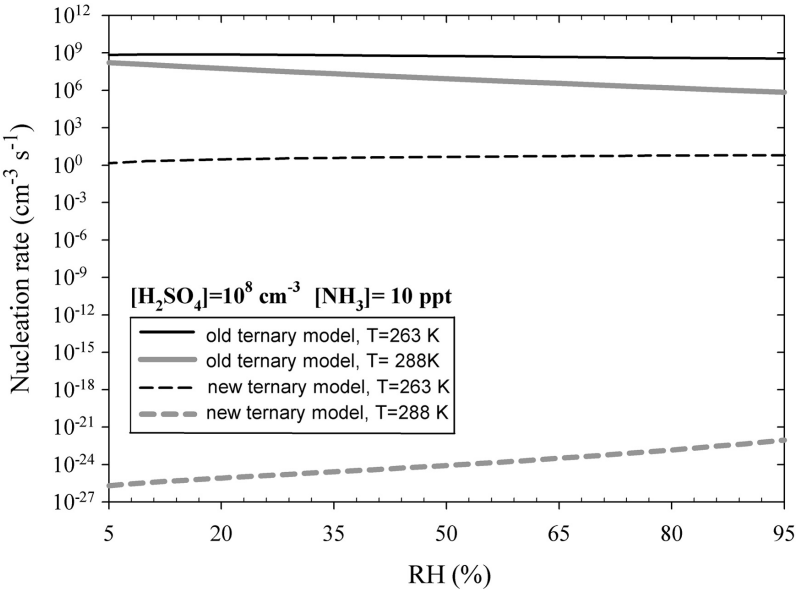

Fig. 7. Nucleation rate as a function of relative humidity when sulphuric acid concentration is 10^8 cm^{-3} and ammonia mixing ratio 10 ppt. The old and new ternary models are compared at T = 263 K and T = 288 K.

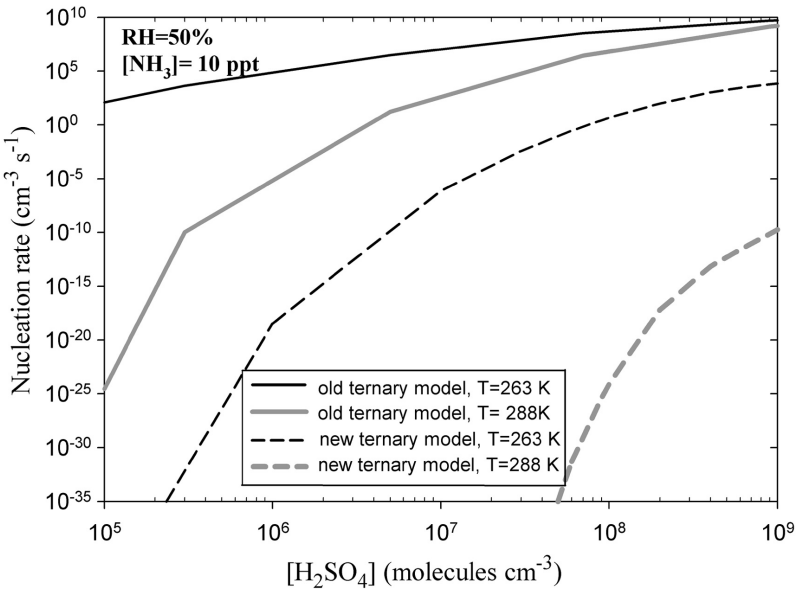

Fig. 8. Nucleation rate as a function of sulphuric acid concentration when relative humidity is 50% and ammonia mixing ratio 10 ppt. The old and new ternary models are compared at T = 263 K and T = 288 K.

supersaturated when the temperature increases.

The conditions for achieving nucleation rate 1 cm^{-3} s^{-1} are shown in Fig. 11 for both the old and new ternary models. The sulphuric acid concentrations required for producing this nucleation rate in binary water sulphuric acid nucleation (Vehkamäki *et al*. 2002) are also indicated. It is noteworthy that at low ammonia but high sulphuric acid concentrations ternary nucleation requires more sulphuric acid than binary nucleation. This is due to the fact that available ammonia binds sulphuric acid molecules to stable clusters, which have lower nucleation potential than free acid molecules, while ammonia concentrations are still too low to make the ternary nucleation channel effective. We were not able to continue the ternary curves to lower ammonia concentrations than shown in Fig. 11 because of numerical difficulties: if the ammonia concentration is very low, some of the elements of the **KD**

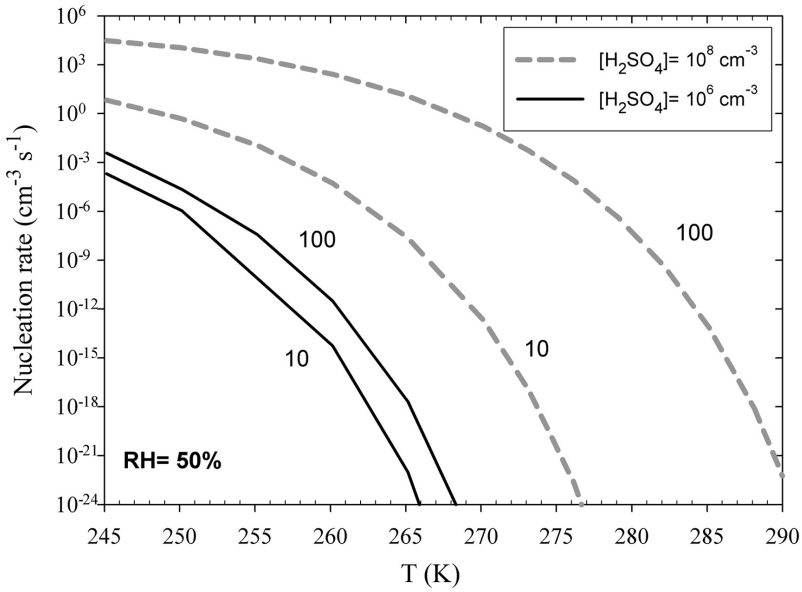

Fig. 9. Nucleation rate as a function of temperature at RH = 50% when sulphuric acid concentration is 10^6 and 10^8 cm^{-3}. Ammonia mixing ratio is indicated in the figure.

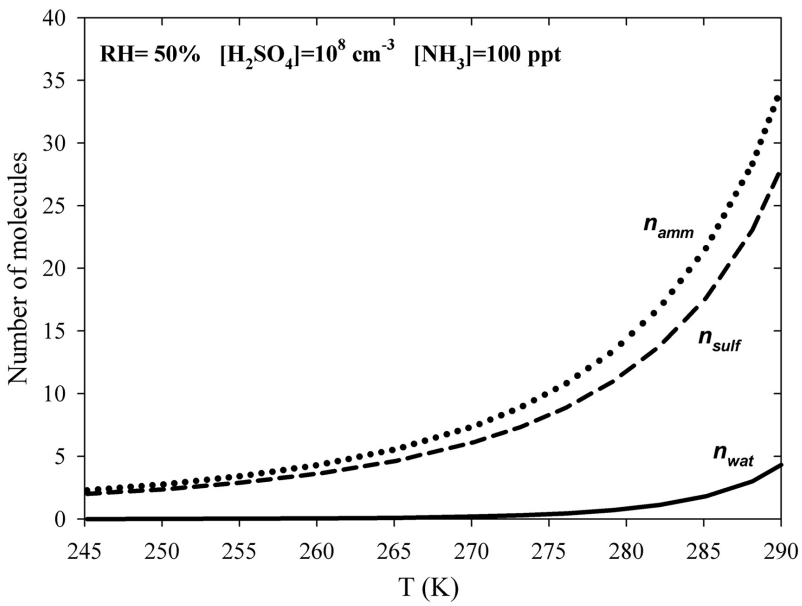

Fig. 10. Temperature dependence of the molecular content of critical clusters.

matrix tend to zero, and the numerical extraction of the eigenvalues becomes impossible in practice. Nevertheless, in some cases we did see indication that the curves start to approach the binary limit. On the other hand, the ternary model is not expected to reduce the binary model, because in the binary model the normalisation factor F^e gives the correct cluster concentration for hydrates with one acid and two water molecules, while in the ternary model F^e is set to give the correct value for free sulphuric acid.

Figure 12 shows the experimental nucleation rates of Ball *et al.* (1999) and theoretical predictions for the same conditions. The old ternary nucleation model, where stable ammonium bisulphate formation is not taken into account, gives extremely high nucleation rates, but the difference between experimental results and predictions of the revised ternary model stays below four orders of magnitude.

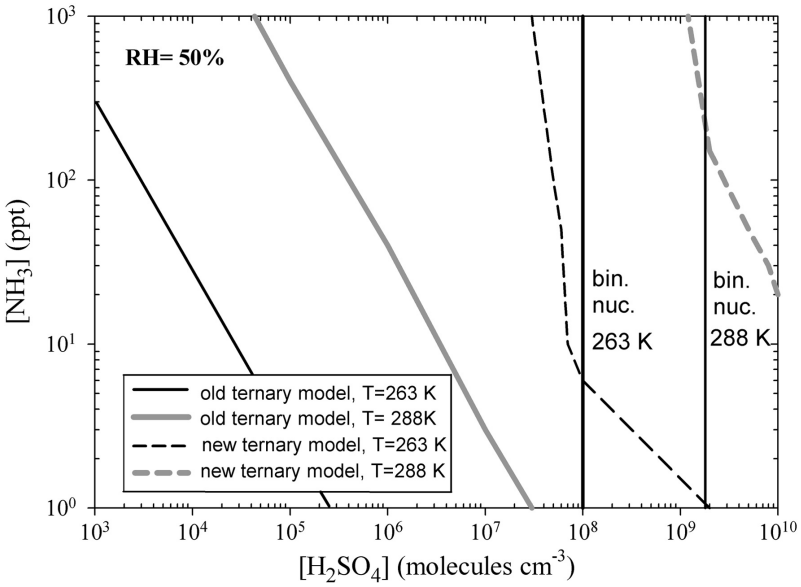

Fig. 11. The sulphuric acid and ammonia concentrations needed to reach the nucleation rate of 1 cm^{-3} s^{-1}. The old and new ternary models are compared at T = 263 K and T = 288 K. The required sulphuric acid concentration for binary water-sulphuric acid nucleation is shown as vertical lines.

The critical clusters predicted by the revised ternary model are typically dry clusters with ammonia to sulphate ratio between one and two. Accordingly we have calculated the nucleation rate also considering the system as unary, i.e. one component, ammonium bisulphate nucleation. In conditions like those of Ball *et al*. (1999) experiments, where the concentration of ammonia is much higher than that of sulphuric acid, it is reasonable to assume that the concentration of ammonium bisulphate clusters is the same as the sulphuric acid concentration. We used the thermodynamic model of Clegg at the limit of dry ammonium bisulphate to estimate the surface tension (0.0883 Nm^{-1}), density (1719 kg m^{-3}) and saturation vapour pressure (7.5×10^{-10} Pa) for pure ammonium bisulphate at 295.15 K. A similar value for saturation vapour pressure was also obtained using critical point and boiling point data. Nucleation rates predicted for unary ammonium bisulphate system agree very well with the experimental results (Fig. 12).

Conclusions

The previously-developed model for ternary sulphuric acid-ammonia-water nucleation took into account the fact that sulphuric acid forms hydrates with water molecules. However, it neglected the ammonium bisulphate formation which has a stronger effect and, in fact, it governs the ternary nucleation process according to the classical theory. In the revised ternary nucleation model the total number of sulphuric acid, ammonia and water molecules per volume unit are used as an input, because they are obtained from atmospheric/laboratory measurements. Free acid and ammonia concentrations are then calculated using the cluster size distribution given by the classical thermodynamic theory. Both the hydrate and ammonium bisulphate formation are taken into account.

Nucleation rates calculated with the new model are orders, sometimes even tens of orders, of magnitude lower than the rates produced by the previous model. The new nucleation rates compare favourably with the available experimental results, unlike the old ones, which are far too high. The best agreement with experimental nucleation rates is obtained by treating the water-sulphuric acid-ammonia nucleation as formation of dry ammonium bisulphate clusters which nucleate as a one component system.

The old model of classical ternary nucleation predicted ternary nucleation to occur almost everywhere in the lower atmosphere at all times. Thus the fact that particle formation bursts are not observed all the time was accounted for the difficulty of nucleated particles to grow to

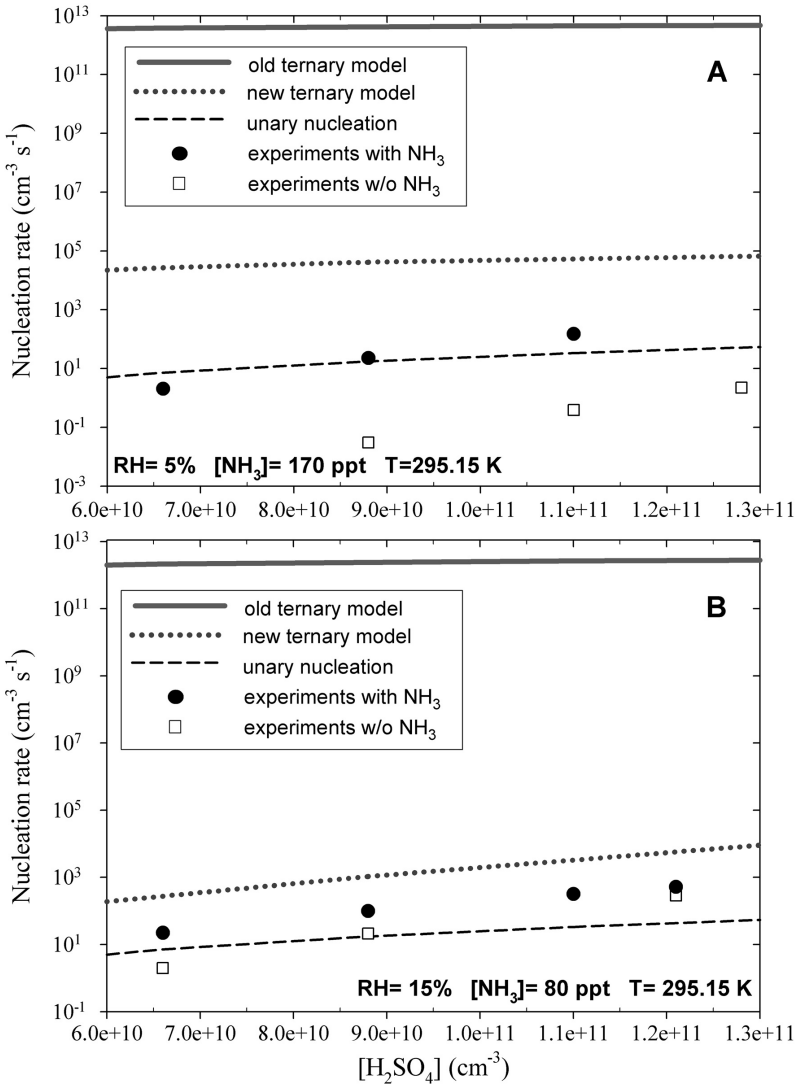

Fig. 12. Nucleation rate as a function of sulphuric acid concentration. Relative humidity and ammonia mixing ratio are (**A**) RH = 50% and ξ = 170 ppt, and (**B**) RH = 15% and ξ = 80 ppt. The model data is compared to the old ternary model, the unary model, and the experiments of Ball *et al.* (1999).

observable sizes (Kulmala *et al*. 2004). The new model, also based on classical nucleation theory, reverses the situation (Fig. 13): it does not predict high enough nucleation rates to explain all observed new particle formation events. This means that either we need a completely new theory of ternary nucleation or we have to look for other nucleation mechanisms like multi-component nucleation involving organics or ion-induced nucleation.

The classical theory, applied also in this study, treats the nucleating clusters using properties of macroscopic liquid, and is not well suited to conditions where the critical clusters are very small. Models based on classical thermodynamics (*see* also Yu 2005) are at present the only practical tool to estimate nucleation processes of real substances in the atmosphere, and when used, great care should be taken to apply it in a consistent manner. Improving molecular methods and increasing computer power will enable us to attack the problem of atmospheric nucleation from a microscopic point of view in the future.

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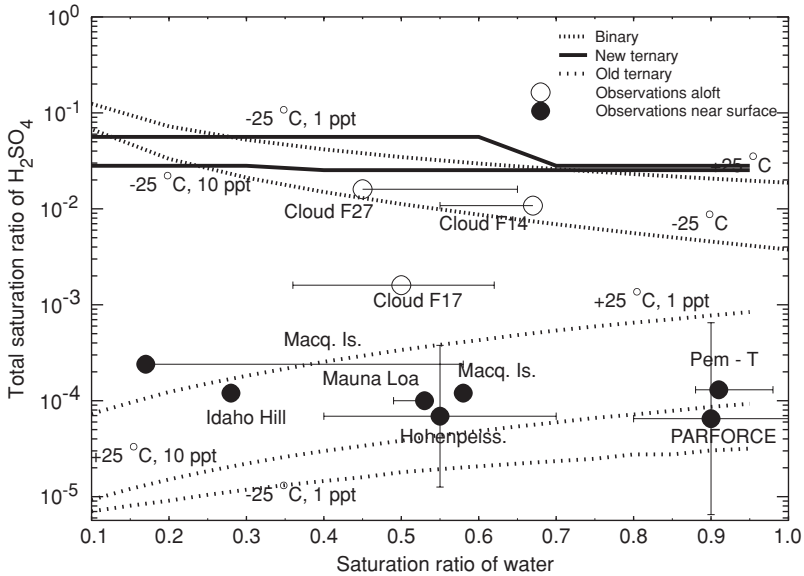

Fig. 13. Sulphuric acid relative acidity versus relative humidity during new particle formation events in various locations. The relative acidities required to produce a nucleation rate of 1 cm^{-3} s^{-1} according to the binary nucleation model as well as according to both old and new ternary models are also shown. *See* also Weber *et al.* (1999) and Kulmala *et al.* (2004).

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