Stable Ammonium Bisulfate Clusters in the Atmosphere

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Liquid drop model based equilibrium thermodynamics predicts that in the presence of even small ammonia concentrations practically all the atmospheric sulfuric acid molecules are bound to tiny, stable ammonium-bisulfate clusters. Hitherto sulfuric acid has been believed to form hydrates with water. Thermodynamic theory predicts correctly the hydrate formation observed experimentally. Results from *ab initio* computer simulations contradict the thermodynamic results and also the experimental findings for cluster formation in both sulfuric acid-water and ammonia-sulfuric acid-water mixtures.

Atmospheric aerosol particles have a central role in processes affecting global radiation balance and human health [1,2]. To assess the impact of natural anthropogenic vapor and particle emissions to the atmospheric system and air quality, we need to understand the gas-to-particle conversion mechanisms. While new particle formation is observed everywhere in the Earth's atmosphere [3], the actual birth mechanism of the particles has remained elusive. On the one hand the measurement methods have not been able to provide us with sufficient information on the formation rate and chemical composition of the smallest particles; on the other hand the results from theoretical developments have proved inconclusive. Atmospheric aerosol particles are assumed to form by homogeneous nucleation, however, the particles can be observed only after activation and subsequent growth by condensation and coagulation [4]. The current level of measurement expertise allows us to detect neutral particles with diameter around 3 nm (containing approximately 3000 molecules) [5], and it is only possible to directly determine their composition when they are around 30 nm (3×10^6 molecules) [6]. The freshly nucleated particles have less than 100 molecules, which means they have diameters less than 1 nm, and thus are well below the detection limit. Theoretical tools are therefore required to obtain information on the initial stages of particle formation and the factors affecting when, where, and what kind of particles are formed.

Pure water alone is not able to form droplets in atmospheric conditions. Calculations indicate that sulfuric acid (H_2SO_4) is the principal substance participating in the atmospheric nucleation [7], and simultaneous observations of gas concentrations and particle formation events support this idea [3]. Binary water-sulfuric acid nucleation seems to be able to explain the particle formation in the free troposphere [3] but in the atmospheric boundary layer a more efficient mechanism is needed. Ternary nucleation of water, sulfuric acid, and ammonia (NH_3) has been suggested by theory as a competing route [8], and the effectiveness of this mechanism is supported by laboratory experiments [9]. Ion-induced nucleation of water and sulfuric acid [10] relies on the observed reservoir of positive and negative ions in the atmosphere below the 1.6 nm limit. It has been suggested that a similar reservoir of stable neutral particles might also be maintained by nucleation [11], although it cannot be detected with current instrumentation. In this Letter we show, within the framework of classical nucleation theory, that such a reservoir is likely to exist and ammonia participates in the nucleation by forming stable ammonium-bisulfate particles.

In classical nucleation theory the formation free energy of a cluster containing n_W water molecules, n_A sulfuric acid molecules, and n_B ammonia molecules is calculated from [12]

$$\Delta G(n_W, n_A, n_B, S_W, S_A, S_B, T) = A(n_W, n_A, n_B, T)\sigma(x_A, x_B, T) - n_W kT \ln[S_W/\Gamma_W] - n_A kT \ln[S_A/\Gamma_A] - n_B kT \ln[S_B/\Gamma_B], \tag{1}$$

where T is the temperature, the mole fractions of sulfuric acid and ammonia in the bulk liquid are x_A and x_B, respectively, and the saturation ratios of water, acid, and ammonia are S_W, S_A, and S_B, respectively. We use the model of Clegg and Brimblecombe [13] for liquid phase activities $\Gamma_W(x_A, x_B, T)$, $\Gamma_A(x_A, x_B, T)$, and $\Gamma_B(x_A, x_B, T)$

[14], and the model presented by Korhonen *et al.* [15] for surface tension σ and liquid density needed to calculate the cluster surface area A.

Figures 1(a) and 1(b) show the predictions of classical theory for formation energy with respect to a free sulfuric acid molecule, $\Delta G_a = \Delta G(n_1, n_2, n_3) - \Delta G(0, 1, 0)$,
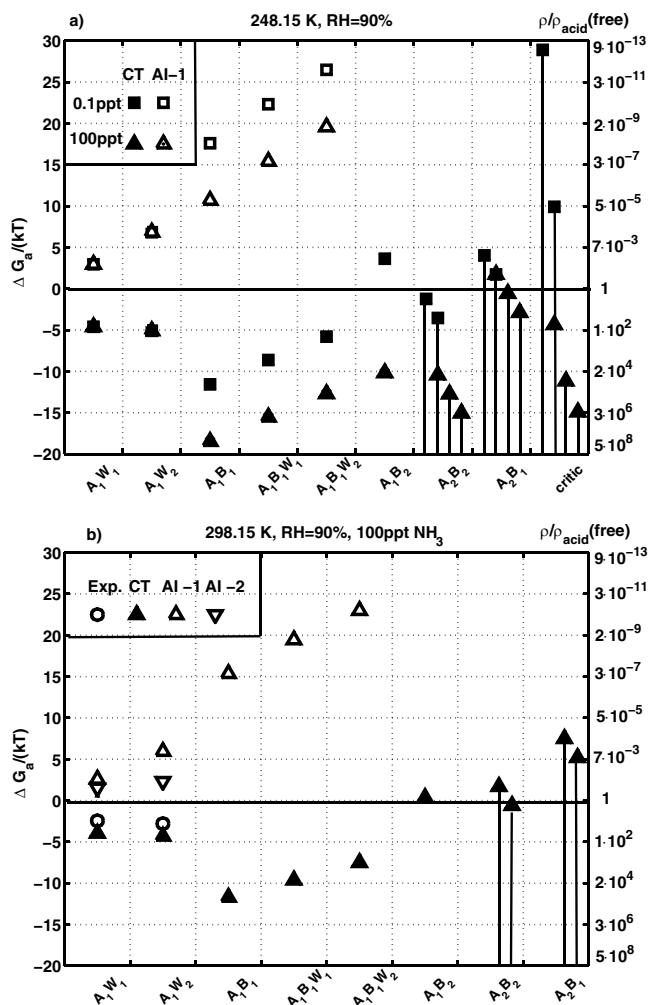
FIG. 1.   Formation free energies and equilibrium concentrations of small sulfuric acid (A), ammonia (B), and water (W) clusters compared to a free sulfuric acid molecule according to the classical theory (CT). Sulfuric acid concentration (see text for the values) is indicated by horizontal displacement of the data points with stems. Also the formation energies of critical clusters at corresponding conditions are shown. We also show corresponding values derived from *ab initio* calculations of Bandy and Ianni [21,23] (AI-1). At 298.15 K we show experimental results for sulfuric acid monohydrate and dihydrate [20] and *ab initio* values by Re *et al.* [22] (AI-2).

in typical atmospheric conditions. Particles are likely to be formed at cold temperatures represented by the 248.15 K case, and 298.15 K is the only temperature where laboratory experiments have been reported. The clusters studied are sulfuric acid mono- (A_1W_1) and dihydrate (A_1W_2), smallest ammonium-bisulfate (A_1B_1 and A_2B_2) and ammonium sulfate (A_1B_2) clusters, and the possible growth products of $1 + 1$ ammonium-bisulfate by addition of 1–2 water molecules or one sulfuric acid molecule. Note that ammonia concentration does not affect the formation energies of clusters with no ammonia, and sulfuric acid concentration only affects the data

points for clusters with more than one sulfuric acid molecules, since the reference level was taken to be a free sulfuric acid molecule. Changing relative humidity from 90% to 50% increases the formation energies of the clusters only slightly (change $\leq 1.2kT$ in all the cases shown).

The right vertical axis shows the equilibrium cluster distribution compared to free acid molecule concentration [16]

$$\frac{\rho}{\rho_{\text{acid}}^{\text{free}}} = \exp\left(\frac{-\Delta G_a}{kT}\right). \tag{2}$$

The classical nucleation theory used for atmospheric particle formation predictions usually assumes that sulfuric acid is bound to hydrates in the atmosphere. However, Figs. 1(a) and 1(b) indicate that the formation energy of the smallest $1 + 1$ ammonium-bisulfate cluster is always clearly lower than that of the hydrates even for ammonia mixing ratio 0.1 ppt. This means that practically all the sulfuric acid in the atmosphere would be bound to ammonium-bisulfate clusters. The effect of these stable clusters has not been taken into account in any of the present models predicting atmospheric particle formation. Stable cluster formation has a drastic impact on the formation free energy: The saturation ratios in Eq. (1) are defined as the pressure corresponding to the free molecules divided by the pressure of the saturated pure vapor. As seen from Fig. 1 for sulfuric acid the free and total (including acid molecules bound to hydrates and small ammonia containing clusters) number concentration can differ by a factor of 10^5. The vapor concentrations, measured by mass-spectrometric instruments, indicate the total number of sulfuric acid or ammonia molecules, including also molecules bound in small stable clusters, which are the part of the vapor phase, or at least some of them. In the collisional-dissociation chamber of a mass spectrometer cluster ions, depending on the pressure of the chamber, are stripped from ligands, like water. At higher temperatures also cluster ions made up of sulfuric acid and ammonia molecules may be broken into pieces [19]. In the model calculations presented in this Letter we use free sulfuric acid concentrations between 10^{-2}–10^3/cm^3 producing total atmospheric concentrations in the range 10^5–10^8/cm^3. The total acid concentration (molecules/cm^3) corresponding to the stems (from left to right) in Fig. 1 are (a) (248.15 K) 1×10^5, 1×10^6, 1×10^7, 1×10^8 and (b) (298.15 K) 1×10^7 and 1×10^8. For simplicity, we only report cases where the free and total ammonia concentrations differ less than 10% (thus the 0.1 ppt points for 298.15 K are left out). Figure 1 shows also that the $1 + 1$ bisulfate clusters are precritical and not activated to grow. Addition of a molecule of water, sulfuric acid, or ammonia all lead uphill on the energy surface. Growth by addition of water molecule is most favorable, but the addition of the next water

requires energy again. Since the concentrations of water molecules is much higher than ammonia molecules in the atmosphere, it is likely that free sulfuric acid molecules meet water first and form hydrates. When these clusters collide with ammonia, it is likely that water leaves the cluster since $A_1B_1W_{1-2}$ cluster are higher in formation free energy than A_1B_1.

The classical theory is known to be erroneous in that it uses bulk liquid properties to describe small molecular clusters. However, it has succeeded in predicting experimentally observed hydrate formation qualitatively, and even the order of magnitude of hydrate to free acid ratios is correct [7]. This can be seen in Fig. 1(b) where experimental results [20] for hydrates (available only for 298.15 K) are shown. Somewhat puzzling is the fact that formation free energies derived from quantum mechanical electron structure studies (*ab initio*) of small sulfuric acid clusters [21,22] are positive. The reaction free energies are obtained using $\Delta G_0 = \Delta H_0 - T\Delta S_0$, where the subscript 0 stands for a standard state (typically vapor pressure of all the reactants and products set as $p_0 = 1$ atm). The formation enthalpy ΔH_0 and the entropy contribution ΔS_0 are calculated from the minimum energy configurations and related vibration frequencies and moments of inertia, and they are often reported in the *ab initio* studies. To compare these values with classical theory predictions, we have to make use of the fact that the reaction free energy gives the equilibrium constant of the reaction $K_0 = \exp[-\Delta G_0/(kT)]$. Thus, the equilibrium concentration of the reaction $1 + 2 \leftrightarrow 3$ product ρ_3 in terms of the concentrations of the reactants ρ_1 and ρ_2 is given by

$$\rho_3 = \frac{\rho_1\rho_2}{\rho_0} \exp\left(\frac{-\Delta G_0}{kT}\right), \qquad (3)$$

where $\rho_0 = p_0/(kT)$, and we have assumed that the vapor behaves like an ideal gas. To get the concentration of clusters (ρ) with more than two molecules in terms of the free molecule concentrations, Eq. (3) has to be applied several times in a row. The *ab initio* value corresponding to the classical formation free energy ΔG_a is then calculated from Eq. (2).

In Fig. 1 we show the formation energies calculated from the *ab initio* results of Ianni and Bandy [21,23] for ammonium-bisulfate and ammonium-bisulfate-water clusters. These all have positive formation free energies, which led Ianni and Bandy to the conclusion that ammonia does not play any role in atmospheric sulfuric acid-water nucleation. Experimental evidence speaks against this deduction: the presence of ammonia significantly increases H_2O-H_2SO_4 nucleation rates [9] and small clusters containing ammonia and sulfuric acid have been observed to form [19]. A possible explanation for the discrepancy of observations and experiments may be the insufficient accuracy of *ab initio* calculations. If we take

the differences between results by Ianni and Bandy [21] and Re *et al.* [22] for vibrational frequencies, moments of inertia, and electronic energies as a rough estimate of the theoretical error, then the experimental value for the free energy ΔG_0 of acid monohydrate lies within the range of theory. It may also be that the experiments showing hydrate formation and enhancement of particle formation in the presence of ammonia are affected by some unknown factor, for example, impurity, which is not described by the quantum mechanical model.

We have seen that classical nucleation theory predicts formation of stable, precritical clusters which have not yet been activated to grow. We also used the classical theory to study the properties of critical clusters which are the smallest clusters that have overcome the nucleation barrier and are likely to grow. We show the critical cluster formation free energies in Fig. 1(a). At 298.15 K critical clusters were large and their energies were so high that they are left out of Fig. 1(b). Critical cluster size is the saddle point of the free-energy surface in the (n_W, n_A, n_B) space or the solution of simultaneous Kelvin equations [24]. At 248.15 K the critical clusters are waterless and their size varies between 5 and 27 molecules with ammonia to sulfuric acid ratio always 1.2. At 298.15 K the critical clusters are large, consisting of 142–2114 molecules, the water mole fraction is between 0.1 and 0.6, and ammonia to sulfate ratio is again always close to 1.2. The growth mechanism of critical clusters is given by the favored direction of the nucleation flow in the classical nucleation theory [25]. According to this theory the dry critical clusters grow by addition of entities consisting of one acid molecule and 1.2–1.4 ammonia molecules. Figure 2 shows the energetics of the growth path with the addition of one molecule of sulfuric acid and ammonia in turns. Only results for temperature 248.15 K with waterless critical clusters which have a negative formation energy are shown in this figure. The first addition of sulfuric acid is sometimes difficult, but after that the path (a) where sulfuric acid molecule joins the cluster first and ammonia then stabilizes the composition leads to nearly effortless growth. Path (b) with ammonia joining first is significantly less likely. The growth is easiest if it occurs via addition of stable $1 + 1$ ammonium-bisulfate clusters: the energetic path for this growth process is the line connecting every second point (the lower ones) in the zigzag curves seen in Fig. 2.

The thermodynamic nucleation theory indicates that practically all the vapor phase sulfuric acid in the lower atmosphere is bound to stable ammonium-bisulfate clusters. Formation of these clusters would reduce the potential of sulfuric acid to participate in the formation and growth of cloud condensation nuclei. The thermodynamic theory is known to be approximate and, probably, the amount of bound acid is somewhat overestimated. Nevertheless we think that the theory can be used to
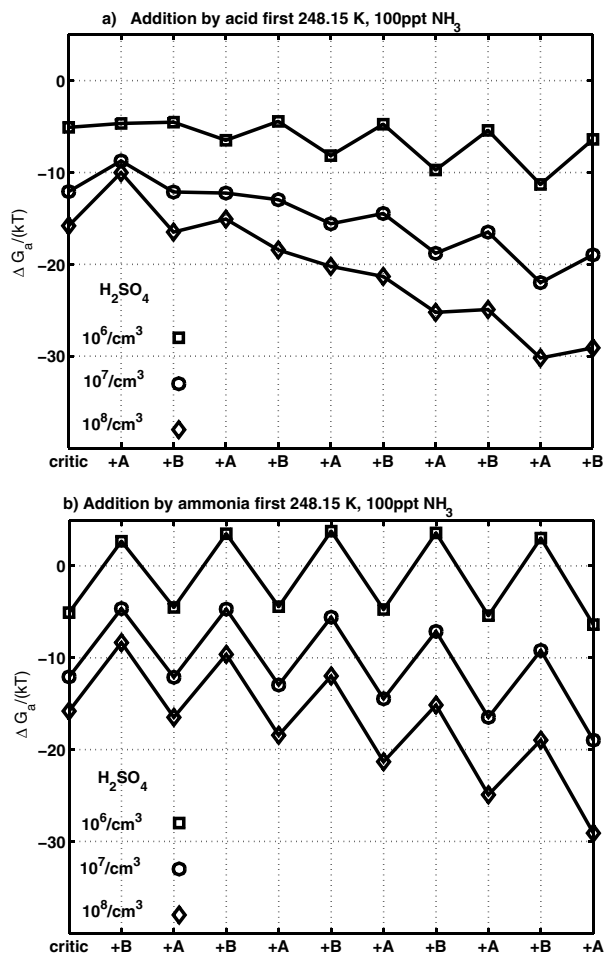
FIG. 2. The formation free energies along the critical cluster growth paths of addition of a sulfuric acid molecule (*A*) and an ammonia molecule (*B*) alternately. (a) shows the growth path where acid always arrives first; (b) ammonia always arrives first. Shown are only the cases where critical cluster is dry ammonium-bisulfate and has a negative formation energy.

point to the topics where more sophisticate theoretical tools should be applied and improved experiments made.

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