

## EARTH SCIENCES

# The missing base molecules in atmospheric acid–base nucleation

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## ABSTRACT

Transformation of low-volatility gaseous precursors to new particles affects aerosol number concentration, cloud formation and hence the climate. The clustering of acid and base molecules is a major mechanism driving fast nucleation and initial growth of new particles in the atmosphere. However, the acid–base cluster composition, measured using state-of-the-art mass spectrometers, cannot explain the measured high formation rate of new particles. Here we present strong evidence for the existence of base molecules such as amines in the smallest atmospheric sulfuric acid clusters prior to their detection by mass spectrometers. We demonstrate that forming  $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$  is the rate-limiting step in atmospheric  $\text{H}_2\text{SO}_4$ -amine nucleation and the uptake of  $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$  is a major pathway for the initial growth of  $\text{H}_2\text{SO}_4$  clusters. The proposed mechanism is very consistent with measured new particle formation in urban Beijing, in which dimethylamine is the key base for  $\text{H}_2\text{SO}_4$  nucleation while other bases such as ammonia may contribute to the growth of larger clusters. Our findings further underline the fact that strong amines, even at low concentrations and when undetected in the smallest clusters, can be crucial to particle formation in the planetary boundary layer.

**Keywords:** new particle formation, acid-base nucleation, aerosol, polluted urban environment

## INTRODUCTION

New particle formation (NPF) events occur frequently in various atmospheric environments [1,2]. These newly formed particles, after subsequent growth, constitute a major source of cloud condensation nuclei [3,4]. To assess the influences of NPF on radiative forcing [5], it is of fundamental importance to understand the NPF mechanisms. The first and key step of NPF is nucleation, during which gaseous precursors form the smallest stable clusters that are more likely to grow into large particles than to evaporate [6,7]. Among the reported nucleation mechanisms for atmospheric environments [8–17], acid–base nucleation is unique for its effectiveness

in forming neutral clusters at ambient temperatures and typical precursor concentrations in the planetary boundary layer. Laboratory experiments [8,18–20] and theoretical studies [21,22] have shown that many bases can stabilize  $\text{H}_2\text{SO}_4$  clusters and drive fast NPF. The atmosphere is a complex system containing various bases such as amines and ammonia. Identifying key base molecules in the small  $\text{H}_2\text{SO}_4$  clusters from a large pool of candidate base vapors [23] is pivotal to understanding atmospheric  $\text{H}_2\text{SO}_4$ -base nucleation.

Measurements of cluster composition via chemical ionization mass spectrometry can provide evidence for bases involved in NPF [8,20,24,25]; however, some base molecules are missing from the

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observed cluster signals obtained from these instruments. For instance, theoretical calculations based on quantum chemistry indicate that the acid–base ratio of most  $\text{H}_2\text{SO}_4$ -base clusters is 1:1 [21,26,27], as also hypothesized in some laboratory studies [18,20,24,28]. In contrast, signals from ambient  $\text{H}_2\text{SO}_4$  clusters contain fewer base molecules with many containing no base molecules at all [10,29]. This is likely a measurement artifact.

Due to the missing base molecules, the detected cluster signals cannot be used to exclusively identify the key bases. To be measured in a mass spectrometer, clusters must either be charged via chemical ionization or be naturally charged in the atmosphere. In either case, a cluster, especially a key cluster formed in the rate-limiting steps of  $\text{H}_2\text{SO}_4$  nucleation, may lose base molecules upon charging. This is because acid and base molecules nucleate effectively by forming strong hydrogen bonds (as well as other intermolecular forces). For instance, charging a neutral  $(\text{H}_2\text{SO}_4)_1(\text{base})_1$  cluster by deprotonation converts the acid–base pair to an unstable base–base pair, with  $\text{HSO}_4^-$  as a very strong base. The unstable  $(\text{HSO}_4^-)_1(\text{base})_1$  cluster subsequently loses the base molecule and hence is detected as a bare  $\text{HSO}_4^-$  ion. Charging by clustering with a reagent ion also affects cluster stability and may cause base evaporation [27]. Additionally, charged clusters may also lose base molecules inside the mass spectrometer due to collisions between cluster and carrier gas molecules [30].

For much the same reason, matching the composition of large atmospheric  $\text{H}_2\text{SO}_4$  clusters to those measured in laboratory experiments cannot exclusively identify the key base. With many candidate bases in the atmosphere, the bases measured in large clusters may not be the key bases for forming the smallest clusters.

Comparing  $\text{H}_2\text{SO}_4$  concentrations and particle formation rates [9,10,19,31] also cannot exclusively identify the key base. The same particle formation rate may be driven by either weak bases with high concentrations or strong bases with concentrations even lower than the instrumental detection limit [22].

Understanding nucleation mechanisms at the molecular level is also substantially challenged by the missing bases from detected atmospheric  $\text{H}_2\text{SO}_4$  cluster signals. As previously mentioned, nucleation pathways and the most relevant stable clusters can be predicted with cluster kinetics and quantum calculations [7,32]. It has been suggested that  $\text{H}_2\text{SO}_4$  and the key base form  $(\text{H}_2\text{SO}_4)_1(\text{base})_1$  during nucleation [21,26,27]. Considering the uncertainties of quantum chemistry results, theoretical predictions require experimental verification; this verification of

cluster composition and rate-limiting steps has been largely precluded by the missing bases in those measurements. Well-controlled laboratory experiments [18,20] have demonstrated that a small cluster containing two  $\text{H}_2\text{SO}_4$  and one or two strong bases can already be stable against evaporation. However, the stability of various  $(\text{H}_2\text{SO}_4)_1(\text{base})_1$  clusters remains uncertain. Because  $(\text{H}_2\text{SO}_4)_1(\text{base})_1$  clusters have not been detected in the atmosphere, a previous study proposed that stabilization of  $(\text{H}_2\text{SO}_4)_2$  by adding a strong base to it may be the rate-limiting step for atmospheric nucleation [9].

To summarize, the missing bases in the smallest  $\text{H}_2\text{SO}_4$  clusters are key to a better understanding of atmospheric  $\text{H}_2\text{SO}_4$ -base nucleation. In this study, we provide strong evidence for the existence and importance of the missing bases in atmospheric  $\text{H}_2\text{SO}_4$  clusters using data from atmospheric measurements and laboratory experiments as well as process model simulations. We demonstrate that the first and rate-limiting step of neutral  $\text{H}_2\text{SO}_4$ -base nucleation, which is often referred to as the step in which the ‘critical cluster’ is formed in classical nucleation theory [33], is to form  $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$ , instead of the formation and subsequent stabilization of  $(\text{H}_2\text{SO}_4)_2$ . In polluted urban environments such as Beijing and Shanghai, a considerable fraction (up to 70%) of the  $\text{H}_2\text{SO}_4$  molecules is clustered with amines, with dimethylamine (DMA) as the key base. Depending on vapor concentrations and temperature, formation of  $(\text{H}_2\text{SO}_4)_1(\text{DMA})_1$  is either a major rate-limiting step or nucleation occurs close to the  $\text{H}_2\text{SO}_4 + \text{DMA}$  amine-saturation limit without a free energy barrier. Right after nucleation, the dominant cluster growth mechanism depends on the available DMA and other bases. At a high DMA concentration, cluster growth is mainly driven by the addition of  $(\text{H}_2\text{SO}_4)_1(\text{DMA})_1$ . At a low DMA concentration, synergy with other weaker but more abundant bases, e.g. ammonia or other amines, may enhance  $\text{H}_2\text{SO}_4$  cluster growth and hence increase the particle formation rate.

## RESULTS

To identify the key base(s) for nucleation in polluted atmospheres, we first focus on  $\text{H}_2\text{SO}_4$ -DMA nucleation and demonstrate that the key step is the formation of the undetected  $(\text{H}_2\text{SO}_4)_1(\text{DMA})_1$ . After that, we discuss  $\text{H}_2\text{SO}_4$ -base nucleation in the complex atmosphere with various candidate bases including DMA, ammonia and other amines. Following convention [8,9,34], we refer to the measured  $\text{H}_2\text{SO}_4$  clusters as n-mers according to the number of constituent  $\text{H}_2\text{SO}_4$  molecules. For

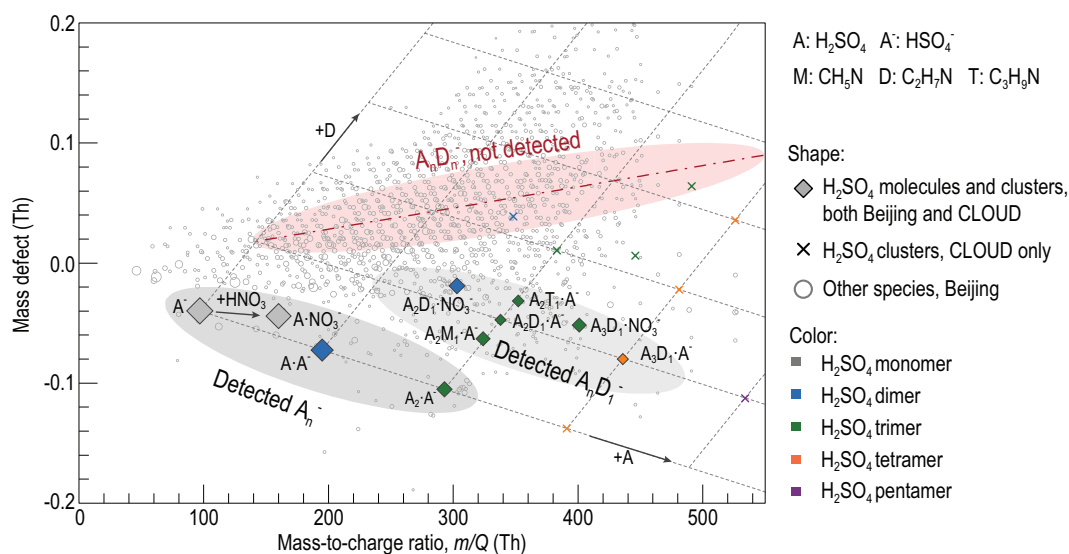
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**Figure 1.** Molecules and clusters measured during atmospheric acid–base NPF events from  $H_2SO_4$  and amines. Neutral molecules and clusters were negatively charged by  $NO_3^-$  and  $HN_2O_6^-$  during the detection using chemical ionization mass spectrometry. The detected  $H_2SO_4$  clusters in urban Beijing contained 0–1 amine molecules. The detected amine molecules in  $H_2SO_4$  clusters were mainly dimethylamine (DMA, D) and trimethylamine (T). Deprotonated or  $NO_3^-$  clustered  $A_nD_n$  clusters were not detected in urban Beijing. Clusters composed of more than five  $H_2SO_4$  or two DMA molecules have been reported for laboratory experiments [20,24,35] with high DMA concentrations, such as the CLOUD chamber experiments. All the  $H_2SO_4$ -DMA clusters detected in urban Beijing were also detected in these laboratory experiments. The colors of markers for  $H_2SO_4$  clusters indicate the number of  $H_2SO_4$  molecules contained in each cluster. The sizes of  $H_2SO_4$  clusters and other species measured in urban Beijing indicate their signal intensities, yet they follow a different size scale in order to emphasize the  $H_2SO_4$  clusters. The dashed grid indicates the numbers of  $H_2SO_4$  and DMA molecules contained in each deprotonated  $H_2SO_4$ -DMA cluster. The dash-dotted line indicates the deprotonated  $A_nD_n$  clusters, which were not detected. The shaded ellipses are drawn to guide the eye.

instance, all clusters containing two  $H_2SO_4$  molecules and any number of bases are referred to as  $H_2SO_4$  dimers. The acid–base cluster composition is written as  $A_mB_n$ , where A represents  $H_2SO_4$ , B represents a certain base and the subscripts indicate the numbers of molecules contained in a given cluster.

### Measured cluster composition

We observed neutral  $H_2SO_4$  clusters in urban Beijing during NPF events using advanced on-line chemical ionization mass spectrometers. As shown in Fig. 1, the signals of atmospheric  $H_2SO_4$  monomers and dimers contain no base molecules, while trimers and tetramers contain up to one amine molecule. The detected dominant species of monomers, dimers and trimers are  $A_1^-$ ,  $A_2^-$  and  $A_3^-$ , respectively, and tetramers were mainly detected as  $A_4D_1^-$  (D for DMA). In urban Beijing, we have not identified larger neutral cluster signals containing more than four  $H_2SO_4$  molecules or more than one amine molecule. The naturally charged  $H_2SO_4$  clusters, detected using an atmospheric pressure interface time-of-flight mass spectrometer, show much the same pattern, with no base

molecules present in  $H_2SO_4$  monomers and dimers (Fig. S1 in Supplementary Data online). The  $H_2SO_4$  clusters measured in urban Beijing have also been observed in laboratory experiments [20,24,35]. Due to the more abundant  $H_2SO_4$  and DMA vapors in these laboratory experiments, large clusters containing more  $H_2SO_4$  and DMA molecules were detected. Despite these, the  $H_2SO_4$  monomers therein were also observed only in the form of bare  $H_2SO_4$  molecules,  $A_1$ , i.e. the base molecule was missing.

The directly measured  $H_2SO_4$  monomer signals could be misinterpreted as an indication that most  $H_2SO_4$  monomers are bare molecules (or perhaps hydrated clusters with undetected water). This would suggest that  $H_2SO_4$ -DMA nucleation is initialized by the clustering between two bare  $H_2SO_4$  molecules and the addition of a DMA to an  $A_2$  [9], or that  $A_3$  is the rate-limiting step in stabilizing clusters against evaporation. However, such interpretations based on the directly observed signals from  $H_2SO_4$  clusters are very likely flawed. As discussed in the introduction, base molecules are missing from clusters measured under atmospheric conditions. This is mainly because a neutral cluster has to be charged during detection. The additional charge or reagent ion converts a stable  $H_2SO_4$ -DMA

cluster into a potentially unstable cluster. As the base strength of  $\text{HSO}_4^-$  is higher than DMA, the unstable cluster tends to become stable by evaporating DMA molecules [27]. The collision between a cluster and carrier gases in the mass spectrometer may also cause DMA evaporation [30]. In particular, the ubiquitous, large fractions of bare  $\text{A}_1^-$ ,  $\text{A}_2^-$  and  $\text{A}_3^-$  are artifacts of the detection process. The evidence is given below.

### Evidence for the existence of $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$

In this section, we show experimental evidence that a large fraction of  $\text{A}_1\text{D}_1$  clusters contributes to the signal of ambient  $\text{H}_2\text{SO}_4$  monomers using the measured  $\text{H}_2\text{SO}_4$  dimer concentration and its variation with DMA concentration and temperature. The measured dimer concentration and its variation can only be well explained by the existence of a large fraction of  $\text{A}_1\text{D}_1$  clusters in ambient  $\text{H}_2\text{SO}_4$  monomers, with  $\text{A}_1 + \text{D}_1 \rightarrow \text{A}_1\text{D}_1$  being the rate-limiting step for nucleation.

In order to show the influence of DMA concentration and temperature, we eliminate the strong dependence of dimer concentration on monomer concentration by comparing dimer concentration to its amine-saturation limit. The amine-saturation limit is herein referred to as the dimer concentration calculated with the assumption that each collision between two  $\text{H}_2\text{SO}_4$  monomers generates a stable  $\text{H}_2\text{SO}_4$  dimer, i.e. base concentration is not a rate-limiting factor. Hence, dimer concentration at the amine-saturation limit is approximately the theoretical maximum for a given monomer concentration and cluster scavenging rate.

$\text{H}_2\text{SO}_4$  dimers are mainly formed via



and



The latter two reactions should be efficient as  $\text{A}_2\text{D}_1$  and  $\text{A}_2\text{D}_2$  are stable against evaporation [20,22,36]. However, an  $\text{A}_2$  cluster needs to be further stabilized by adding one base molecule [9]; hence, the effectiveness of dimer formation via  $\text{A}_1 + \text{A}_1$  is governed by the stability of  $\text{A}_2$  against evaporation and its association rate with stabilizing bases.

The measured high concentrations of atmospheric  $\text{H}_2\text{SO}_4$  clusters provide indirect but strong experimental evidence for the existence of  $\text{A}_1\text{D}_1$  rather than only  $\text{A}_1$ . As shown in Fig. 2, if all the  $\text{H}_2\text{SO}_4$  monomers existed in the form of  $\text{A}_1$  but not  $\text{A}_1\text{D}_1$ ,  $\text{H}_2\text{SO}_4$  dimer, trimer and tetramer concen-

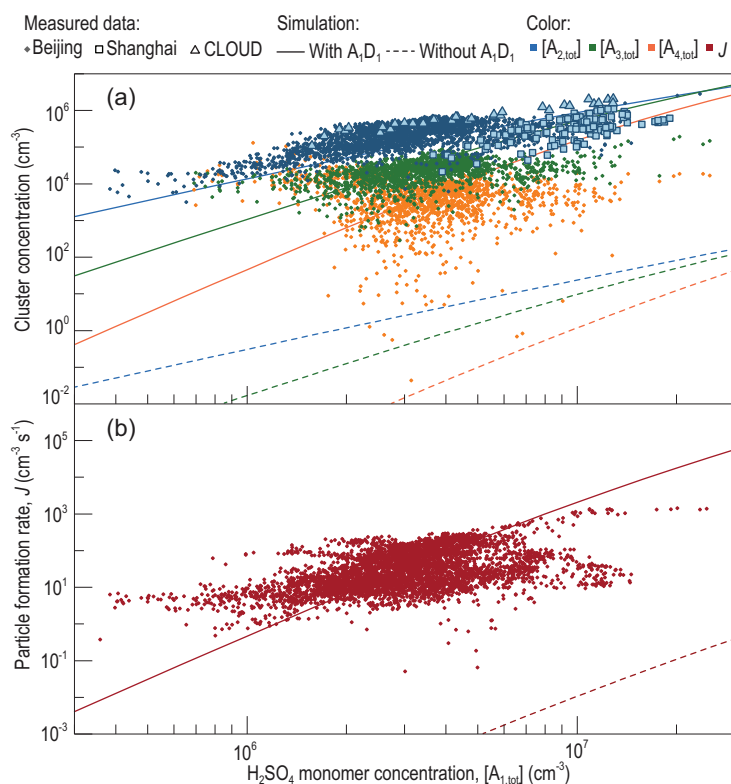
trations would be orders of magnitude lower than the measured values. This shows that the mechanism with dimer stabilization via  $\text{A}_2 + \text{D}_1$  [9] as the rate-limiting step is not effective for nucleation due to the instability of  $\text{A}_2$  [22]. This inefficiency is also supported by chamber experiments with  $\text{H}_2\text{SO}_4$  and ammonia [8], which have shown that despite the stability of ammonia-stabilized  $\text{A}_2$  [22] and a high ammonia concentration, the dimer stabilization mechanism is insufficient to explain the measured cluster concentrations (see Fig. S2). In contrast, if  $\text{A}_1\text{D}_1$  constituted a large fraction of  $\text{H}_2\text{SO}_4$  monomers and nucleation is rate-limited by forming  $\text{A}_1\text{D}_1$ , this could explain the cluster concentrations in Beijing [37,38], Shanghai [10] and also in Cosmics Leaving OUtdoor Droplets (CLOUD) chamber experiments [28].

The measured dependence of  $\text{H}_2\text{SO}_4$  dimer concentration on DMA concentration provides further strong support for the existence of  $\text{A}_1\text{D}_1$  as well as its importance. As shown in Fig. 3, the measured  $\text{H}_2\text{SO}_4$  dimer concentration increases with an increasing DMA concentration, which can be well explained by an increasing  $\text{A}_1\text{D}_1$  fraction in the  $\text{H}_2\text{SO}_4$  monomers. That is, with the same  $\text{H}_2\text{SO}_4$  monomer concentration, there are more  $\text{A}_1\text{D}_1$  clusters at a higher DMA concentration, driving more efficient  $\text{H}_2\text{SO}_4$  dimer formation towards its amine-saturation limit.

The measured temperature dependence of the  $\text{H}_2\text{SO}_4$  dimer concentration gives further evidence for the existence of  $\text{A}_1\text{D}_1$  and its significant fraction in ambient  $\text{H}_2\text{SO}_4$  monomers. Figure 4b shows that  $\text{H}_2\text{SO}_4$  dimer concentrations decrease with increasing temperature [39] for the measured NPF events in Beijing and Shanghai [10] (see also Fig. S3). This temperature dependence is consistent with the existence of  $\text{A}_1\text{D}_1$ . The evaporation rate of  $\text{A}_1\text{D}_1$  increases with an increasing temperature, and the  $\text{A}_1\text{D}_1$  fraction in monomers thus decreases significantly (Fig. 4a), causing the decreasing  $\text{H}_2\text{SO}_4$  dimer concentration (Fig. 4b).

The DMA-dependent  $\text{A}_1\text{D}_1$  fraction in  $\text{H}_2\text{SO}_4$  monomers is also very consistent with the CLOUD experiments [20]. During those experiments, high DMA concentrations (>5 ppt) and a low temperature (278 K) forced a high  $\text{A}_1\text{D}_1$  fraction that drove dimer formation close to its amine-saturation limit, and hence nucleation was found to be insensitive to DMA concentration in the (DMA-saturated) experimental conditions.

The experimental evidence above confirms the existence of  $\text{A}_1\text{D}_1$  and its importance in  $\text{H}_2\text{SO}_4$ -DMA nucleation. For the observed NPF events in urban Beijing, the median DMA concentration was 1.8 ppt and the  $\text{A}_1\text{D}_1$  fraction  $\text{H}_2\text{SO}_4$



**Figure 2.** (a)  $\text{H}_2\text{SO}_4$  cluster concentrations and (b) particle formation rates as a function of  $\text{H}_2\text{SO}_4$  monomer concentration. The measured  $\text{H}_2\text{SO}_4$  cluster concentrations and NPF rate were consistent with the simulation results for which forming an  $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$  cluster is the first and critical step of NPF. The amine molecule is mainly dimethylamine (D) for the moderate stability of  $\text{A}_1\text{D}_1$  against evaporation. The simulation without forming  $\text{A}_1\text{D}_1$  yields  $\text{H}_2\text{SO}_4$  cluster concentrations and a particle formation rate that are orders of magnitude lower than those measured in urban Beijing. The measured data in urban Beijing were collected during daytime (9:00–16:00 local time) NPF events with a 5-min temporal resolution. The  $\text{H}_2\text{SO}_4$  dimer concentrations for Shanghai [10] and CLOUD experiments [28] were previously reported. The concentrations of clusters containing the same number of  $\text{H}_2\text{SO}_4$  molecules were summed up, e.g.  $[\text{A}_{2,\text{tot}}]$  is the total concentration of measured or simulated  $\text{H}_2\text{SO}_4$  dimers containing any number of base molecules. The influencing factors, such as the cluster loss rate characterized by the condensation sink (CS), amine concentrations and temperature ( $T$ ), affect cluster concentrations and formation rate, and their slope versus  $[\text{A}_{1,\text{tot}}]$  [54, 68]. These influences are not corrected in this figure because they are minor compared to the differences between the simulation results with and without forming  $\text{A}_1\text{D}_1$ . The curves were simulated for  $[\text{DMA}] = 1.8 \text{ ppt}$  ( $\sim 4.7 \times 10^7 \text{ cm}^{-3}$ ),  $\text{CS} = 0.011 \text{ s}^{-1}$  and  $T = 281 \text{ K}$ , which are the medians of the measured data.

in monomers could be as high as 70% with 4-ppt DMA.

The existence of ambient  $\text{A}_1\text{D}_1$  clusters indicates moderate evaporation of  $\text{A}_1\text{D}_1$ , which is consistent with the evaporation rate obtained from quantum chemistry and laboratory experiments. We use cluster kinetics to derive the temperature-dependent evaporation rates of  $\text{A}_1\text{D}_1$  from atmospheric measurements (see Methods). These rates are consistent with reported quantum chemical results [22,36] (Fig. S4). Laboratory experiments have also estimated upper limits for the evaporation rate of  $\text{A}_1\text{D}_1$

clusters using high DMA concentrations ( $>5 \text{ ppt}$  at 278 K) [28,35], yet our atmospheric measurements provide consistent but lower evaporation rates at lower atmospheric DMA concentrations.

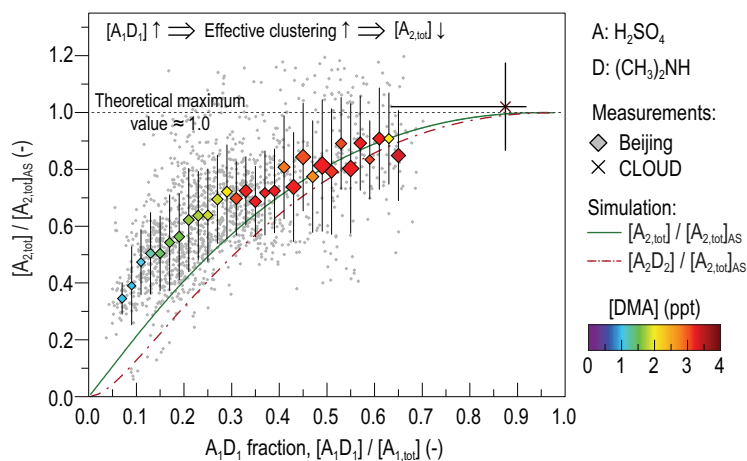
The measured NPF rate provides support for the above experimental evidence. The rapid formation of stable  $\text{H}_2\text{SO}_4$  dimers from  $\text{A}_1\text{D}_1$  enables a rapid formation of new particles. As shown in Fig. 2, the simulated NPF rate with a large  $\text{A}_1\text{D}_1$  fraction in  $\text{H}_2\text{SO}_4$  monomers is consistent with the measured formation rate in Beijing; otherwise, the simulated formation rate would be orders of magnitude lower. In Fig. 4c, NPF rates in Beijing and Shanghai decrease with increasing temperature, which can be explained by the decreasing stability of  $\text{A}_1\text{D}_1$  against evaporation as a function of increasing temperature. Besides, the existence of  $\text{A}_1\text{D}_1$  is also consistent with the positive correlation between NPF rate and DMA concentration for NPF in urban Beijing [37].

## Atmospheric nucleation with various bases

The above results also demonstrate that forming  $\text{A}_1\text{D}_1$  is the key rate-limiting step for atmospheric  $\text{H}_2\text{SO}_4$ -DMA nucleation. The key role of  $\text{A}_1\text{D}_1$  for  $\text{H}_2\text{SO}_4$ -DMA nucleation can be generalized to  $\text{H}_2\text{SO}_4$  nucleation with other bases: forming  $\text{A}_1\text{B}_1$  is often the rate-limiting step.  $\text{H}_2\text{SO}_4$  can nucleate close to its amine-saturation limit only when a considerable fraction of  $\text{H}_2\text{SO}_4$  monomers exist in the form of  $\text{A}_1\text{B}_1$  clusters. We use this criterion below to show that DMA is the missing key base from various candidates for nucleation in urban Beijing.

In addition to  $\text{C}_2$ -amine (probably DMA), we detected gas-phase methylamine (MA),  $\text{C}_3$ -amine (probably trimethylamine, TMA),  $\text{C}_4$ -amine and ammonia in urban Beijing [29] using mass spectrometry. The measured neutral  $\text{H}_2\text{SO}_4$  clusters also contain TMA (T) in the form of  $\text{A}_4\text{T}_1$  (Fig. 1).  $\text{C}_4$ -amine and ammonia were detected in the naturally charged  $\text{H}_2\text{SO}_4$  clusters (Fig. S1). The measured cluster signals are consistent with the measured gas-phase bases. Other candidate bases for  $\text{H}_2\text{SO}_4$ -base nucleation, such as ethylene diamine [19], were not detected in the gas-phase or  $\text{H}_2\text{SO}_4$  clusters.

The free energy barrier of  $\text{H}_2\text{SO}_4$  monomers and dimers containing different bases shows that despite the contributions from other amines, forming  $\text{A}_1\text{D}_1$  is still the key rate-limiting step for fast  $\text{H}_2\text{SO}_4$ -base nucleation in this complex urban atmosphere. An increasing value of free energy upon adding one molecule corresponds to a significant evaporation rate, and a decreasing value indicates that the growth of the cluster is faster than its



**Figure 3.**  $\text{H}_2\text{SO}_4$  dimer concentration as a function of theoretical  $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$  concentration. The measured  $\text{H}_2\text{SO}_4$  dimer concentration ( $[\text{A}_{2,\text{tot}}]$ ) is consistent with the simulated  $\text{A}_1\text{D}_1$  concentration, where D represents DMA. With a given  $\text{H}_2\text{SO}_4$  monomer concentration ( $[\text{A}_{1,\text{tot}}]$ ), increasing  $[\text{A}_1\text{D}_1]$  improves the effectiveness of clustering between  $\text{H}_2\text{SO}_4$  monomers in terms of forming stable  $\text{H}_2\text{SO}_4$  dimers.  $[\text{A}_{2,\text{tot}}]$  approaches its maximum, characterized by the amine-saturation limit ( $[\text{A}_{2,\text{tot}}]_{\text{AS}}$ ), as the simulated ratio of  $[\text{A}_1\text{D}_1]$  to  $[\text{A}_{1,\text{tot}}]$  increases. The simulation also shows that  $[\text{A}_{2\text{D}2}]$  comprises a major fraction in  $[\text{A}_{2,\text{tot}}]$ . Hence,  $[\text{A}_{2,\text{tot}}]$  can be used as an agent for the missing  $\text{A}_1\text{D}_1$  (see Methods). The Beijing data are shown in edged markers that represent the mean value of the measured 5-min resolution data group by  $[\text{A}_1\text{D}_1]/[\text{A}_{1,\text{tot}}]$ , with  $[\text{A}_1\text{D}_1]$  calculated using Equation (2). The marker size indicates the mean CS of each group. The variation bars indicate the standard deviation for each group. The data from CLOUD chamber studies were reported in ref. [20]. The  $[\text{A}_1\text{D}_1]/[\text{A}_{1,\text{tot}}]$  shown by the crossed marker and horizontal variation bar was estimated for  $[\text{DMA}] = 20$  ppt and 5–32 ppt, respectively. In this figure,  $[\text{A}_{1,\text{tot}}]$  and the  $[\text{A}_{2,\text{tot}}]$  shown in markers are measured data.  $[\text{A}_1\text{D}_1]$  and the  $[\text{A}_{2,\text{tot}}]$  shown in curves are simulation results.  $[\text{A}_{2,\text{tot}}]_{\text{AS}}$  is calculated using the measured  $[\text{A}_{1,\text{tot}}]$  and coagulation sink.

evaporation. As shown in Fig. 5, DMA governs the formation of stable  $\text{H}_2\text{SO}_4$  dimers because the free energy of  $\text{A}_1\text{D}_1$  is the lowest among the  $\text{H}_2\text{SO}_4$  monomers stabilized with other measured bases. For the typical conditions in urban Beijing, an  $\text{H}_2\text{SO}_4$  molecule needs to overcome a low free energy barrier to become an  $\text{A}_1\text{D}_1$  cluster. After that, the  $\text{A}_1\text{D}_1$  cluster grows into a particle via pathways with consecutively descending free energy.

In addition to DMA, TMA may have a secondary contribution to nucleation in urban Beijing. Considering the free energy of  $\text{A}_1\text{D}_1$  and  $\text{A}_1\text{T}_1$  [21] (Fig. 5), TMA is comparable to DMA in forming stabilized  $\text{H}_2\text{SO}_4$  dimers [18]. After accounting for the base concentrations, however, we find that the contribution of TMA does not affect the key role of DMA in nucleation in urban Beijing.

Weak bases, such as MA and ammonia (N), are thermodynamically unfavorable for atmospheric nucleation. Figure 5 shows the high free energy of  $\text{A}_1\text{M}_1$  and  $\text{A}_1\text{N}_1$ , despite the high ammonia concentration ( $\sim 1$  ppb during the observed NPF events in urban Beijing). As a result, the unstable  $\text{A}_1\text{M}_1$  or  $\text{A}_1\text{N}_1$  clusters with low concentrations significantly

limit  $\text{H}_2\text{SO}_4$ -MA and  $\text{H}_2\text{SO}_4$ -ammonia nucleation and they cannot explain the measured high  $\text{H}_2\text{SO}_4$  dimer concentration and particle formation rate.

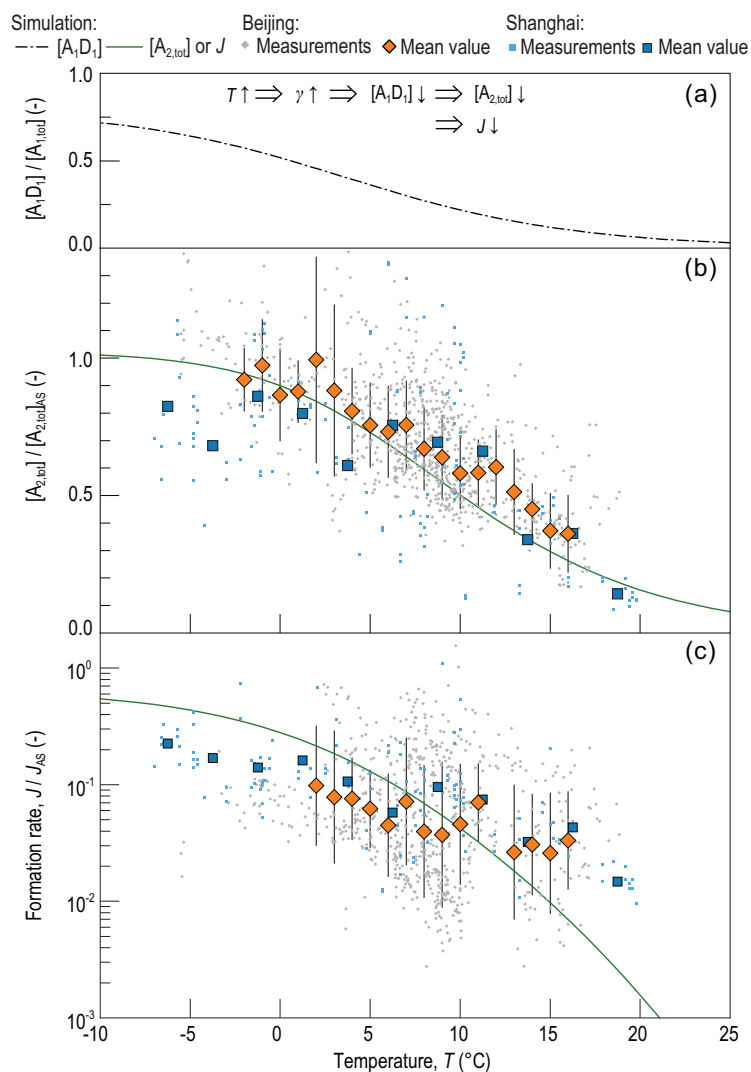
Strong bases with low concentrations are kinetically unfavorable for atmospheric nucleation despite their ability to form very stable clusters. We did not detect bases stronger than DMA (except  $\text{HSO}_4^-$ ), such as diamines [19], in the measured neutral and naturally charged  $\text{H}_2\text{SO}_4$  clusters or the gas phase, indicating their concentrations are below the instrumental detection limit. A low base concentration, especially when it is lower than the  $\text{H}_2\text{SO}_4$  concentration, may kinetically limit the fraction of  $\text{A}_1\text{B}_1$  in  $\text{H}_2\text{SO}_4$  monomers [19] even though  $\text{A}_1\text{B}_1$  might be thermodynamically favorable for nucleation. For instance, taking  $\text{HSO}_4^-$  as a base, the free energy of  $\text{A}_2^-$  is extremely low [27,40], yet forming  $\text{A}_2^-$  in the atmosphere is kinetically limited by the low ambient  $\text{HSO}_4^-$  concentration (typically  $< 10$  ions/ $\text{cm}^3$  for urban Beijing). In other words, ion-induced nucleation even at the ion-pair formation rate of a few particles  $\text{cm}^{-3} \text{s}^{-1}$  is simply not competitive with the high nucleation rates we observe ( $J \gg 10 \text{ cm}^{-3} \text{s}^{-1}$ ).

The temperature dependence of the  $\text{H}_2\text{SO}_4$  dimer concentration also provides evidence that DMA, rather than some unidentified strong base, is the missing key base for  $\text{H}_2\text{SO}_4$  nucleation in urban Beijing. Although the dimer concentration could reach the same value with a low concentration of an unidentified strong base [19,22], it is unlikely that this strong base would cause the similar temperature dependence of the dimer concentration (see Fig. S5).

## DISCUSSION

We have presented strong evidence that DMA is the missing key base for  $\text{H}_2\text{SO}_4$ -base nucleation in polluted urban environments, and the formation of  $\text{A}_1\text{D}_1$  up to a considerable fraction (70% for urban Beijing) in  $\text{H}_2\text{SO}_4$  monomers is the rate-limiting step. The existence of  $\text{A}_1\text{D}_1$  is robust despite the fast formation and depletion of  $\text{H}_2\text{SO}_4$  monomers. We find that ambient  $\text{A}_1\text{D}_1$  reaches its pseudo-steady-state concentration within minutes due to its short overall lifetime, and this pseudo-steady-state is not sensitive to a rapid change in the production rate of  $\text{A}_1$  molecules (see Fig. S6).

Although DMA is found to dominate nucleation in urban Beijing, other bases, particularly strong bases, may also contribute to nucleation at conditions such as low DMA concentrations and high temperatures. As shown in Fig. 3, the formation of  $\text{A}_1\text{D}_1$  cannot fully explain the measured dimer concentration at a low  $\text{A}_1\text{D}_1$  fraction ( $< 0.1$ ) in



**Figure 4.**  $H_2SO_4$  dimer concentration and particle formation rate as a function of temperature. (a) The simulated fraction of  $A_1D_1$  in  $H_2SO_4$  monomers, where D is dimethylamine; (b) normalized  $H_2SO_4$  dimer concentration ( $[A_{2,tot}]$ ) as a function of temperature; (c) normalized formation rate ( $J$ ) of 1.4 nm particles as a function of temperature. The evaporation rate of  $A_1D_1$  ( $\gamma$ ) increases with an increasing temperature, which decreases  $A_1D_1$  concentration. As a result,  $[A_{2,tot}]$  and  $J$  decrease with an increasing temperature. The temperature dependence of  $[A_1D_1]$  is consistent with the measured data in urban Beijing and Shanghai.  $[A_{2,tot}]_{AS}$  and  $J_{AS}$  are the total  $H_2SO_4$  dimer concentration and particle formation rate, respectively, at the amine-saturation limit (see Fig. 3 and Methods). The curves were simulated at the median CS ( $0.011\text{ s}^{-1}$ ) and the median amine concentration for the Beijing data set. The big markers are the median values of measured raw data grouped by temperature. The variation bars indicate the lower and upper quartiles for each group. The formation rate was calculated for 1.4 nm particles. The measured  $[A_{2,tot}]$  for urban Shanghai, shown in (b), was scaled with a multiplicative factor of 3 (see Methods) but this scaling does not affect the measured temperature dependence of  $[A_{2,tot}]$ .

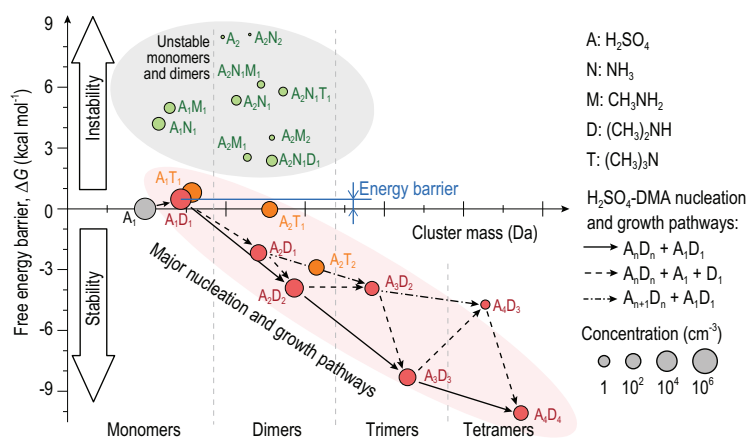
$H_2SO_4$  monomers. Further, with proper environmental conditions, other strong bases such as TMA and diamines may play important roles if they are more abundant than DMA [18,19].

Despite their minor roles in nucleation, ammonia and abundant weak amines may have synergistic effects on the initial growth of  $H_2SO_4$ -DMA clusters. Especially at relatively low DMA concentrations, a large fraction of  $H_2SO_4$  monomers are bare (or hydrated)  $H_2SO_4$  molecules (Figs 3 and 5). This bare  $H_2SO_4$  may not effectively contribute to the initial growth of  $H_2SO_4$ -DMA clusters due to the potential high evaporation rates of  $A_{n+1}D_n$  clusters ( $n \geq 2$ ). For instance, some quantum chemical results [22] have suggested that  $A_4D_3$  might be more likely to evaporate back into  $A_3D_3$  than to grow into  $A_4D_4$ . That is,  $H_2SO_4$  might not contribute effectively to the growth of ambient  $A_3D_3$ . However, with a high concentration of ammonia, a potentially unstable  $A_4D_3$  cluster can be rapidly stabilized by ammonia and form  $A_4D_3N_1$  (N stands for ammonia) [41]. This synergy enhances cluster growth via the condensation of  $A_1$  molecules and also increases the particle formation rate (see Fig. S7), which is consistent with laboratory results [42].

However, the synergy of weak bases should not boost particle formation when DMA is sufficient. When most  $H_2SO_4$  monomers exist in the form of  $A_1D_1$  at a high DMA concentration,  $A_nD_n + A_1D_1$  is the governing pathway for cluster growth [21,43] (Fig. S8) and the particle formation rate is limited by the other losses (e.g. coagulation loss) rather than cluster evaporation. In this case, adding weak bases such as ammonia should not significantly increase the formation rate of sub-2 nm particles [8]. Note that base substitution [41,44] is still possible via the fast formation and evaporation of unstable clusters such as  $A_3D_3N_1$ . Since these unstable clusters are more likely to evaporate than grow, observing a minor fraction of ammonia molecules in large  $H_2SO_4$  clusters [20,24] does not necessarily indicate a contribution of ammonia to the growth rate of the  $H_2SO_4$ -DMA clusters.

In addition to bases, water molecules may contribute to stabilizing  $H_2SO_4$  clusters and they are also missing from the detected cluster signals [45]. However, no significant dependence of  $H_2SO_4$  dimer concentration and particle formation rate on water vapor concentration was observed after accounting for the influences of other factors. This insignificant effect of hydration on  $H_2SO_4$ -DMA nucleation is consistent with quantum chemical calculations [21].

Although the nucleation rate of  $H_2SO_4$  and base is close to the amine-saturation limit (Fig. 3), sub-2 nm particle growth is mainly driven by the measured  $H_2SO_4$  monomers with only a minor contribution from dimers and larger  $H_2SO_4$  clusters. This is because the high coagulation sink in polluted urban environments suppresses the cluster



**Figure 5.** Gibbs free energy barrier of  $\text{H}_2\text{SO}_4$  clusters with various base molecules. Forming stable clusters against evaporation corresponds to a low free energy barrier ( $\Delta G$ ). Nucleation and cluster growth mainly follow the pathways with low  $\Delta G$ . A positive  $\Delta G$  corresponds to a free energy barrier that limits the nucleation rate and cluster concentrations. With typical concentrations of gaseous precursors in urban Beijing, forming  $\text{A}_1\text{D}_1$  and  $\text{A}_1\text{T}_1$  is more effective than forming  $\text{A}_2$ ,  $\text{A}_1\text{M}_1$  and  $\text{A}_1\text{N}_1$ , yet the moderate evaporation rates of  $\text{A}_1\text{D}_1$  and  $\text{A}_1\text{T}_1$  clusters (indicated by their  $\Delta G$ ) still limits NPF. Because of the considerable  $\text{A}_1\text{D}_1$  concentration and low  $\Delta G$  of  $\text{A}_n\text{D}_n$  clusters ( $n > 1$ ), the coagulation between  $\text{A}_1\text{D}_1$  and  $\text{A}_n\text{D}_n$  clusters is a major growth pathway. The results for this figure were simulated for the following conditions:  $[\text{A}_{1,\text{tot}}] = 3.4 \times 10^6 \text{ cm}^{-3}$ ,  $[\text{N}] = 1.1 \text{ ppb} (\sim 2.9 \times 10^{10} \text{ cm}^{-3})$ ,  $[\text{M}] = 0.2 \text{ ppt} (\sim 5.2 \times 10^6 \text{ cm}^{-3})$ ,  $[\text{D}] = 1.8 \text{ ppt} (\sim 4.7 \times 10^7 \text{ cm}^{-3})$ ,  $[\text{T}] = 0.5 \text{ ppt} (\sim 1.3 \times 10^7 \text{ cm}^{-3})$ ,  $\text{CS} = 0.011 \text{ s}^{-1}$  and  $T = 281 \text{ K}$ . These values are the medians for the Beijing data set during daytime (9:00–16:00) NPF events. The growth pathway from A to  $\text{A}_2\text{D}_1$  is not shown because it is identical to the pathway from  $\text{A}_1\text{D}_1$  to  $\text{A}_2\text{D}_1$ . The shaded ellipses and hollow arrows are drawn to guide the eye.

concentrations (Fig. 2), which is different from low-sink conditions such as in chamber experiments [46].

To summarize, the key cluster for ambient  $\text{H}_2\text{SO}_4$ -base nucleation is missing from the cluster signals detected using state-of-the-art instruments. Using consistent evidence from atmospheric measurements, laboratory experiments and a process model based on cluster kinetics and quantum chemistry, we demonstrate that  $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$  must be the missing key cluster for the polluted atmosphere, with DMA as the key base and forming  $(\text{H}_2\text{SO}_4)_1(\text{DMA})_1$  as the rate-limiting step. During  $\text{H}_2\text{SO}_4$ -amine nucleation, a substantial fraction of  $\text{H}_2\text{SO}_4$  monomers exist in the form of  $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$  and the uptake of  $(\text{H}_2\text{SO}_4)_1(\text{amine})_1$  is a major mechanism for the initial growth of clusters. Other abundant weak bases may have synergistic effects on the growth of  $\text{H}_2\text{SO}_4$ -DMA clusters by stabilizing larger  $\text{H}_2\text{SO}_4$ -DMA clusters before their evaporation and thus enhance the particle formation rate.

Further, we argue that atmospheric nucleation should be characterized using the rate-limiting factors and steps, instead of only the concept of the

‘critical cluster’. According to the definition of classical nucleation theory [7], the undetected key  $(\text{H}_2\text{SO}_4)_1(\text{DMA})_1$  cluster is the ‘critical cluster’ at typical atmospheric conditions for urban Beijing. It is worth clarifying that the ‘critical cluster’ depends on the vapor concentrations. For  $\text{H}_2\text{SO}_4$ -DMA nucleation with a high DMA concentration (20 ppt), as shown in Fig. S8, nucleation occurs without a free energy barrier and the particle formation rate is mainly limited by the coagulation sink. Conversely, in conditions with very low  $\text{H}_2\text{SO}_4$  and DMA concentrations, the ‘critical cluster’ can be  $\text{H}_2\text{SO}_4$  dimers or larger clusters, despite the extremely low evaporation rates of  $\text{A}_2\text{D}_1$  and  $\text{A}_2\text{D}_2$  [20,22,36]. As a result, it is crucial for both laboratory and theoretical studies to better represent atmospheric conditions or properly apply the results to atmospheric conditions.

## MATERIALS AND METHODS

### Atmospheric measurements

The data used in this study were obtained from atmospheric measurements in urban Beijing and urban Shanghai. The NPF process from gaseous precursors to particles was measured at both sites. The Beijing site is located at the west campus of the Beijing University of Chemical Technology ( $39^\circ 56' \text{ N}$ ,  $116^\circ 17' \text{ E}$ ),  $\sim 500 \text{ m}$  away from the west 3rd Ring Road. The data set used for this study was from 16 January 2018 to 13 March 2019, with gaseous amines and ammonia measurements available after 20 October 2018. Neutral gaseous  $\text{H}_2\text{SO}_4$  molecules and clusters,  $\text{C}_1$ – $\text{C}_3$  amines, ammonia, and aerosol size distributions were measured.  $\text{H}_2\text{SO}_4$  molecules and clusters were measured using high-resolution chemical ionization time-of-flight mass spectrometers (HToF-CIMS, Aerodyne Research, Inc.) with  $\text{NO}_3^-$  and  $\text{HN}_2\text{O}_6^-$  as the reagent ions [47]. Amines and ammonia were measured using a modified HToF-CIMS with  $\text{H}_3\text{O}^+$  or its hydrated clusters as the reagent ions [48]. Since isomers cannot be differentiated by an HToF-CIMS, the  $\text{C}_2$ -amines and  $\text{C}_3$ -amines were taken as DMA and TMA, respectively. Therefore, the measured DMA and TMA concentrations might be overestimated. However, since ethylamine is less effective than DMA in forming  $\text{A}_1\text{B}_1$  clusters [49], a major fraction of the measured  $\text{C}_2$ -amines are likely to be DMA. Other bases such as ethylene diamine were not identified. Aerosol size distributions were measured using a diethylene glycol scanning mobility particle spectrometer (DEG-SMPS) for sub-5 nm aerosols [50–52] and a particle size distribution system for 3 nm–10  $\mu\text{m}$  aerosols [53]. Ambient temperature was monitored using



a weather station (AWS310, Vaisala Inc.). Details of the measurement site, instruments and measurement uncertainties have been reported previously [37,38,54,55].

The Shanghai data set was reported in a previous study [10]. The Shanghai site is located at the campus of Fudan University (31°18' N, 121°30' E), ~100 m from the Middle Ring Road. Neutral gaseous H<sub>2</sub>SO<sub>4</sub> and aerosol size distributions were measured simultaneously from 4 December 2015 to 10 February 2016. H<sub>2</sub>SO<sub>4</sub> molecules and clusters were measured using an HTToF-CIMS with NO<sub>3</sub><sup>-</sup> and HN<sub>2</sub>O<sub>6</sub><sup>-</sup> as the reagent ions. Aerosol size distributions were measured using a particle size magnifier [56] (Airmodus Inc.) for 1–3 nm aerosols, and two scanning mobility particle spectrometers (SMPSs) (TSI Inc.) for 3–65 nm aerosols and 14–736 nm aerosols. No measured C<sub>2</sub>-amine concentration was available during this period, yet it was measured at the same site in August 2015 using an HTToF-CIMS with protonated ethanol as reagent ions [57]. Ambient temperature was recorded at a site ~5 km away.

The concentrations of H<sub>2</sub>SO<sub>4</sub> dimers, trimers and tetramers were evaluated using the same calibration factor for H<sub>2</sub>SO<sub>4</sub> monomers. The mass-dependent transmission efficiency of HTToF-CIMS was calibrated and corrected [58]. Due to the fragmentation of H<sub>2</sub>SO<sub>4</sub> clusters within HTToF-CIMS [30], the H<sub>2</sub>SO<sub>4</sub> dimer, trimer and tetramer concentrations might be underestimated. For the Beijing data set, the underestimation of H<sub>2</sub>SO<sub>4</sub> dimer concentration was estimated to be ~30%, which is close to the estimated values in a laboratory experiment [20]. This value is within the uncertainty range of H<sub>2</sub>SO<sub>4</sub> measurements and it does not affect the conclusions based on both the absolute value of H<sub>2</sub>SO<sub>4</sub> dimers and its dependence on amine concentration and temperature. The measured H<sub>2</sub>SO<sub>4</sub> dimer concentration in Shanghai was multiplied by three, yet only its temperature dependence is used for discussion in this analysis.

The formation rate of 1.4 nm particles (*J*<sub>1.4</sub>) in urban Beijing was retrieved from measured aerosol size distributions using a population balance formula [59] improved for intensive NPF events in polluted atmospheric environments. The *J*<sub>1.4</sub> in urban Shanghai was calculated from the reported *J*<sub>1.7</sub> using particle growth rate and the coagulation sink [60].

## Theory

Here we present a theory with reasonable approximations to illustrate the importance of (H<sub>2</sub>SO<sub>4</sub>)<sub>1</sub>(amine)<sub>1</sub> to the formation of clusters

containing two or more H<sub>2</sub>SO<sub>4</sub> molecules, though the figures in the main text are obtained using numerical simulation without these approximations. A dimensionless parameter,  $\eta$ , is defined to characterize the ratio of (H<sub>2</sub>SO<sub>4</sub>)<sub>1</sub>(base)<sub>1</sub> to H<sub>2</sub>SO<sub>4</sub> monomers. For a simplified system containing only H<sub>2</sub>SO<sub>4</sub> (A), a certain species of base (B), and aerosols, the population balance equation for A<sub>1</sub>B<sub>1</sub> is

$$\frac{d[A_1B_1]}{dt} = \beta_{AB} [A_1] [B_1] - (\gamma(T) + CS) [A_1B_1], \quad (1)$$

where [A<sub>1</sub>B<sub>1</sub>], [A<sub>1</sub>] and [B<sub>1</sub>] are the concentrations (cm<sup>-3</sup>) of A<sub>1</sub>B<sub>1</sub> clusters, bare A<sub>1</sub> molecules and B<sub>1</sub> molecules, respectively; *t* is time (s);  $\beta_{AB}$  is the coagulation coefficient (cm<sup>3</sup> s<sup>-1</sup>) between an A<sub>1</sub> molecule and a B<sub>1</sub> molecule;  $\gamma$  is the evaporation rate (s<sup>-1</sup>) of A<sub>1</sub>B<sub>1</sub> as a function of temperature *T* (K); and CS is the condensation sink (s<sup>-1</sup>) of A<sub>1</sub>B<sub>1</sub> contributed by aerosols and H<sub>2</sub>SO<sub>4</sub>-amine clusters. The growth of A<sub>1</sub>B<sub>1</sub>, e.g. the clustering between two A<sub>1</sub>B<sub>1</sub> molecules, is herein accounted for in CS. In urban Beijing and Shanghai, background aerosols contribute majorly to this CS term [37,61].

The overall lifetime of A<sub>1</sub>B<sub>1</sub>,  $\tau$  (s), can be estimated using Equation (1).  $\tau$  characterizes the typical time A<sub>1</sub>B<sub>1</sub> concentration takes to reach its pseudo-steady-state value and it is equal to 1/( $\gamma(T) + CS$ ). For instance, by setting the source term in Equation (1) to zero at the moment *t*<sub>0</sub> and keeping  $\gamma(T) + CS$  constant, [A<sub>1</sub>B<sub>1</sub>] at *t*<sub>0</sub> +  $\tau$  will reduce to 1/e of its concentration at *t*<sub>0</sub>. Considering the high CS for polluted environments,  $\tau$  is usually <10 min. Hence, A<sub>1</sub>B<sub>1</sub> is close to its pseudo-steady-state concentration regardless of a fast variation of atmospheric H<sub>2</sub>SO<sub>4</sub> production rate or H<sub>2</sub>SO<sub>4</sub> monomer concentration (Fig. S6).

Setting d[A<sub>1</sub>B<sub>1</sub>]/*dt* in Equation (1) to zero yields the formula for the pseudo-steady-state value of  $\eta$  [62]:

$$\begin{aligned} \eta &= \frac{[A_1B_1]}{[A_{1,tot}]} \\ &= \frac{[A_1B_1]}{[A_1] + [A_1B_1]} = \frac{\beta_{AB} [B_1]}{\beta_{AB} [B_1] + \gamma(T) + CS}. \end{aligned} \quad (2)$$

The amine-saturation limit is the formation rate of clusters or particles with no evaporation and a unity coagulation efficiency. In this study, we refer to the amine-saturation limit as that for H<sub>2</sub>SO<sub>4</sub> monomers corresponding to a sufficient base concentration. Accordingly, the H<sub>2</sub>SO<sub>4</sub> dimer concentration at

the amine-saturation limit can be calculated using Equation (3),

$$[A_{2,\text{tot}}]_{\text{AS}} = \frac{\beta_{11}[A_{1,\text{tot}}]^2}{2\text{CS}}, \quad (3)$$

where  $[A_{1,\text{tot}}]$  and  $[A_{2,\text{tot}}]$  are  $\text{H}_2\text{SO}_4$  monomer and dimer concentrations ( $\text{cm}^{-3}$ ), respectively; the subscript AS stands for amine-saturation limit;  $[A_{1,\text{tot}}] = [A_1] + [A_1B_1]$ ;  $\beta_{11}$  is the coagulation coefficient ( $\text{cm}^3 \text{s}^{-1}$ ) between two  $\text{H}_2\text{SO}_4$  monomers; and CS is the condensation sink ( $\text{s}^{-1}$ ) for  $\text{H}_2\text{SO}_4$  monomers.

The amine-saturation limit of  $[A_{2,\text{tot}}]$  is reached at an infinite  $[B_1]$ , with which  $\eta$  is equal to 1.0 according to Equation (2). Similarly, the amine-saturation limit of the particle formation rate is also reached at an infinite  $[B_1]$ . In this study, the amine-saturation limits of  $[A_{2,\text{tot}}]$  and the particle formation rate were obtained by setting the DMA concentration at  $10^6$  ppt so that nucleation was not limited by DMA concentration.

The  $[A_{2,\text{tot}}]$  and particle formation rates in Figs 3 and 4 were compared to their corresponding amine-saturation limits. With DMA as the base, and considering the high evaporation rate of neutral  $A_2$  and the negligible evaporation rates of  $A_2D_{1-2}$  [22,36], it can be approximated that only monomer collisions involving at least one  $A_1D_1$  (i.e.  $A_1D_1 + A_1$  or  $A_1D_1 + A_1D_1$ ) form a stable dimer. Hence, the  $[A_{2,\text{tot}}]$  for  $\text{H}_2\text{SO}_4$ -DMA nucleation can be approximated with  $\eta$  using Equation (4):

$$\begin{aligned} [A_{2,\text{tot}}] &= [\eta^2 + 2\eta(1 - \eta)][A_{2,\text{tot}}]_{\text{AS}} \\ &= \eta(2 - \eta)[A_{2,\text{tot}}]_{\text{AS}}. \end{aligned} \quad (4)$$

Equation (4) shows that  $[A_{2,\text{tot}}]$  increases monotonically with  $\eta$  within the domain of  $\eta$ , and  $[A_{2,\text{tot}}] = [A_{2,\text{tot}}]_{\text{AS}}$  at  $\eta = 1$ . Hence, the measured  $[A_{2,\text{tot}}]/[A_{2,\text{tot}}]_{\text{AS}}$  can be used to indicate  $\eta$ . Note that to obtain better accuracy, we calculated the results in Figs 3 and 4 numerically instead of using Equation (4). Considering these minor differences,  $[A_{2,\text{tot}}]$  may slightly exceed  $[A_{2,\text{tot}}]_{\text{AS}}$  because the amine-saturation limit in Equation (3) is calculated using  $A_1D_1$  and the thermal velocity of  $A_1$  is slightly higher than that of  $A_1D_1$ .

A process model is used to simulate the growth of  $\text{H}_2\text{SO}_4$  clusters. The simulated bases, B, include ammonia, MA, DMA and TMA. The outputs of this model are the cluster concentrations and formation rate. This model has been reported previously [37] and similar models can be found in the literature [18,32]. Only the neutral nucleation mechanism is accounted for in this model because the ion production rate is not comparable to the high NPF rate in

urban Beijing and Shanghai. The formation rate of  $\text{H}_2\text{SO}_4$  tetramers was taken as the simulated NPF rate [18] because the electrical mobility diameter of  $\text{H}_2\text{SO}_4$  tetramers was estimated to be 1.4 nm according to previous studies [63,64]. There are potential uncertainties caused by the difference between diameters for the measured and simulated particle formation rates, yet these uncertainties do not influence the conclusions in this analysis based on the temperature dependence of the particle formation rate.

The temperature-dependent evaporation rates of  $A_1D_1$  were estimated by fitting Equations (2) and (4) to the data set of urban Beijing. We fitted the evaporation rate (corresponding to standard Gibbs free energy) at 298 K to minimize the residue of  $[A_{2,\text{tot}}]/[A_{2,\text{tot}}]_{\text{AS}}$  as shown in Fig. 2, whereas the temperature dependence of standard Gibbs free energy (corresponding to evaporation rate) was calculated using enthalpy given by quantum chemical calculations [22]. That is, we fitted the absolute value of the evaporation rate but not its temperature dependence. The evaporation rates of other clusters used in this process model were calculated using the standard Gibbs free energy given by quantum chemical calculations [21,22]. As shown in Fig. S4, the experimentally determined evaporation rates of  $A_1D_1$  are within the uncertainty range of quantum chemical results and this uncertainty does not affect the findings. A coagulation enhancement factor due to Van der Waals force [65–67] was accounted for in the calculation of coagulation coefficients and evaporation rates. The species included in the process model were determined according to the evaporation rates. For instance,  $A_nD_{n+1}$  clusters were reported to be unstable against evaporation in various quantum chemical results [22,36] and hence they are not included in the model.

The free energy barrier shown in Fig. 5 was calculated using standard Gibbs free energy and the measured concentrations of acid and base vapors [7]. For an  $A_mB_n$  cluster, the formula for its free energy is given in Equation (5),

$$\begin{aligned} \Delta G(A_mB_n, T) &= \Delta G^\theta(A_mB_n, T) \\ &\quad - (m - 1)RT \ln \frac{P_A}{P_{\text{ref}}} \\ &\quad - nRT \ln \frac{P_B}{P_{\text{ref}}}, \end{aligned} \quad (5)$$

where  $\Delta G$  is the free energy barrier (also named formation free energy in some nucleation studies);  $\Delta G^\theta$  ( $\text{kcal mol}^{-1}$ ) is the standard formation free energy (also named binding energy in some nucleation studies);  $T$  (K) is temperature;  $R$  is the ideal gas constant;  $P_A$  and  $P_B$  are the partial pressures of

$A_1$  and  $B_1$ , respectively; and  $P_{\text{ref}}$  is the reference pressure used for calculating  $\Delta_f G^\theta$ .  $\Delta_f G$  characterizes the energy barrier for a bare sulfuric acid molecule  $A_1$  to form a certain cluster. The free energy of  $A_1$  is accordingly equal to zero. A positive free energy of  $A_1 B_1$  indicates that the association between  $A_1$  and  $B_1$  needs to overcome an energy barrier.

## DATA AVAILABILITY

Data can be found at <https://doi.org/10.5281/zenodo.6801940>. The Julia programming codes for the kinetic model in this study are available from the corresponding author upon request.

## SUPPLEMENTARY DATA

Supplementary data are available at [NSR](#) online.

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## AUTHOR CONTRIBUTIONS

R.C., D.R.W., M.K. and J.J. designed the research; R.C. and J.J. wrote the paper with input from other co-authors; R.C., R.Y., C.Y., D.Y. and C.D. contributed to data collection; R.C., R.Y. and J.J. analyzed data with help from D.Y., C.D., L.D., J. Kangasluoma, J. Kontkanen, R.H., Y.M., P.P., T.P., V.-M.K., F.B., J.Z., L.W., J.H., J.N.S., N.M.D., M.K. and D.R.W.

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